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Polymer Nanocomposites Based on Silver Nanoparticles

Synthesis, Characterization and Applications

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Contents

Fundamentals of Silver Nanoparticles and Their Toxicological Aspects

Arya Uthaman, Hiran Mayookh Lal, and Sabu Thomas

Abstract The silver nanoparticles have their unique optical, thermal, electrical and biological properties and are being used in various consumer products that range from photovoltaics to chemical sensors and biological health-care products owing to their strong antimicrobial properties. This chapter documents the updates information on various aspects silver nanoparticles. The historical background and brief description on their evolution from the ancient history to present era are elaborated herein. The basic techniques of synthesis of silver nanoparticles including their pros and cons are also given in this chapter. A brief account on various properties of silver nanoparticles, especially their biological properties owing to the strong antimicrobial activity, are discussed in detail. In this chapter, special emphasis is given to the potential environmental threats due to the increasing use of silver nanoparticles in modern materials and ensures large amount of silver release into ecosystem. This chapter also focuses the various toxicity effects of silver nanoparticles in different organism and human beings based on the updated studies. Furthermore, the toxicity effects of silver nanoparticles on various part of the body, illustrating gaps in current knowledge.

1 Historical Background of Silver Nanoparticles

Silver has been widely utilized in various fields of science and engineering. The history of this inorganic metal begins with its use from ancient civilizations, a rare, lustrous, resilient, antibacterial, and conductive metal made it valuable to ancient peoples. It was also used as precious material in jewellery, ornaments, currencies, conducting metals, photography, etc. among early people. Metals that including

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bulk silver were also used on the surface for the brilliant color variation. This drastic change in color occurred as the dimensions of the metals decreased. This has occurred when metal chloride mixed with molten glass, the metal nanoparticle was formed of different sizes and shapes, and the physical forms of metal nanoparticles interestingly interact with light and produced beautiful colors on the glass surface. The metal chlorides materialized in the molten glass before cooling and formed nanoparticles. Even though the craftsmen in that period did not know about nanoparticle, it was considered one of the first applications for nanotechnology. In the old days over 100 years, the AgNPs have been commercially utilized in different fields without understanding the nomenclature of nanotechnology. In 1989, citrate-stabilized silver colloidal particles with a size range of 7–9 nm were reported from Carey Lea (1889). From ancient times AgNPs in the form of colloidal particles has been routinely used in medical fields. The stabilized nanoscale sliver for the medical applications was commercialized since 1897 and with the trade name "Collargol." The gelatine stabilized silver particles with size ranges from 2 to 20 nm was introduced (Moudry 1960). Colloidal silver was applied as biocidal material since 1954 in America. Interestingly, the first silver-based biocidal product was first reported under the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) of the US under the trade name of Algaedyn that was derived from Moundry's patent, which is also currently used as an algaecide in swimming pools. The growing demand for silver, even in the present era, is due to many attributes such as its outstanding physical, chemical, conductive, antibacterial, optical, and catalytic properties. It is estimated that about 320 tones/year of AgNPs are produced presently and utilized worldwide. The long history of fabrication and use of colloidal nanosilver has resulted in plenty of research over the last 100 years, even if those researches were not reported under the nomenclature nanotechnology. The commercial sale of medicinal nanosilver colloids began in the earlier part of the 20th century and was widely utilized over 50 years under different trade names such as Collaragol, Argyrol, Pratrogol, etc. Over the last decades, the AgNPs incorporated polymer nanocomposites to achieve applications in various engineered products in the biomedical field, such as in antibacterial sprays and detergents, clothing, water filters, respirators, contraceptives soaps as well as in a large number of other household products.

2 Synthesis of Silver Nanoparticles

Generally, AgNPs are synthesized using different techniques resulting in different sizes and shapes for various applications. The synthesis techniques for nanoparticles are categorized into top–down and bottom–up approaches (Hamdy et al. 2006). The top–down-technique for the synthesis of AgNPs uses silver (Ag) metal in its bulk form and then reduces its size to nanoscale utilizing controlled and specialized methodologies such as laser ablation and lithography (Aryal et al. 2019). The bottom–up approach (also known as the self-assembly process) involves the usage of a solvent and subsequent reducing agent. The steps involved the dissolution of silver salt with the addition of reducing agents, to prevent the agglomeration of AgNPs stabilizing agents are added if wanted. Thus the physical and morphological characteristics of produced AgNPs are affected by the selection of solvent and reducing agents in this process (Gubarev et al. 2019).

2.1 Raw Materials for Synthesis of Silver Nanoparticles

In general, to synthesis AgNPs through a top–down approach, two different types of raw materials are required, while the bottom–up approach requires three different types of raw materials. The raw materials essential for the manufacturing AgNPs includes silver precursors to supply silver elements and a stabilizing (capping) agent to stabilize the thermodynamically unstable AgNPs. In the case of the bottom–up approach, a reducing agent is necessary to transform silver ions into nanoscale AgNPs. Various inorganic-organometallic compounds such as silver nitrate, silver bromide, silver chlorate, silver chloride, silver acetate, silver oxide, silver carbonate, silver sulfate, etc. are used bulk precursors to extract AgNPs from their ions (Zielińska et al. 2009). Besides precursors, the reducing agents are also an essential reagent for manufacturing AgNPs. Commonly, the reducing agents, such as sodium citrate, sodium boroxide, sodium borohydride, Tollen's reagent, ammonium formate, *N*-*N*-dimethyl formamide, analyne, etc. are commonly used chemical reagents. Phytochemical reducing agents such as chrysoeriol, luteolin, flavanol taxifolin, apigenin, quercetin, Flavones salvigenin, oleanolic acid, 2,3-dihydroxyoleanolic acid, tormentic acid, ursolic acid, triterpenic acid, etc. are also used. While considering the reagents, the stabilizing agents are relevant to mention, as AgNPs are thermodynamically unstable also the high surface energy may cause the aggregation of nanoparticles (Oswald ripening), unless they are stabilized. Different polymers are used as a stabilizing agent such as polyacrylamide, poly(vinyl alcohol), poly(vinyl pyrrolidone), polyester, polyurethane, etc. and also for the synthesis of AgNPs the surfactants like Triton-X 100, dodecyl sulfate SDS), lignin sulfonates, linear alkylbenzene sulfonates, cetyl triethyl ammonium bromide (CTAB), fatty alcohol ethoxylates, etc. are essential. The synthesis methods of AgNPs are clearly mentioned in the second chapter and hence are not specified again.

3 Properties of Silver Nanoparticles

AgNPs have tremendous properties in neat and composites. AgNPs in the nanocomposites are transparent and emit light by plasma absorption. In addition, exhibit different physical and chemical properties. Most of their properties depends on their aspect ratio, size, and shape.

3.1 *Physical Properties*

The bulk silver metal has a higher melting point than the AgNPs since the more atoms are situated at the surface of the AgNPs. The increase in surface tension of the particles by the compressive force leads to a reduction in the lattice parameter of the AgNps (Yeshchenko et al. 2010). Besides, the hardness and density in the polymer silver nanocomposites have only a minute increment than the neat polymers (Karak et al. 2010). The mechanical properties such as tensile strength, modulus, and elongation at break values of the AgNPs embedded polymer nanocomposites got a slight improvement but the increase in these properties is not so significant.

3.2 *Optical Properties*

By the electromagnetic radiation and electrons near to the nanoparticles shows an individual surface plasmon resonance (SPR). The concentration, size, distribution of AgNPs can strongly influence the SPR spectrum, and the transparency, saturation can be detected in the AgNPs. The transparent property of AgNPs is because the wavelength of visible light is much bigger than the particle sizes so, the scattering light of the particle size becomes negligible (Karak et al. 2010).

3.3 *Catalytic Properties*

In organic synthesis, the AgNPs based catalyst has a significant role due to their unique stability, reactivity, recyclability, and availability for green synthetic conditions for mass production of such catalysts (Yan et al. 2010). The catalytic containing AgNPs are highly photocatalytic at the ambient conditions having visible light illumination to degrade organic dyes. The AgNPs having chitosan can act as an adequate catalyst by the presence of molecular iodine in C–C coupling reactions of phenolic compounds (Murugadoss et al. 2009). The usage of bimetallic Rh/AgNPs catalyst in asymmetric conjugate addition of arylboronic acids to enones (Yasukawa et al. 2012). The enantioselectivity of the catalyst and the catalytic activity of AgNPs strongly depends on the hiral ligands. Compared with the homogenous chiral catalyst, the heterogeneous chiral catalyst has more benefits on its environment-friendly advantages.

3.4 *Electrical Properties*

The AgNPs are electrically conductive materials that depend on their shape, size, crystallinity, composition, and structure. The AgNPs can use in electronic devices as a conductive material with conductive electronic adhesives, thereby increase the contact resistance and current density of adhesives in electronic devices (Li et al. 2004). At high temperature, the electrical conductivity of AgNPs is similar to the bulk silver metal since the Kubo gap of the spherical 3 nm sized AgNPs is 5–10 meV (Rao et al. 2000).

3.5 Biological Properties

AgNPs have good medicinal properties because of their excellent antimicrobial effects. AgNPs have large surface area and can easily interact with the biomolecules such as fungi and bacteria thus they can exhibit better antibacterial, antifungal and antiviral properties. There are various kinds of active agents such as ligands, antibodies, drugs were chemically mixed together into the AgNPs to form chemically functionalized AgNPs. Thus, it can be applied in the biomedical fields like targeted drug delivery and as carriers for genes, wound treatment, etc. The AgNPs have a wide range of antimicrobial activities in contrast to fungi, Gramnegative bacteria, and certain viruses. The antibacterial effects of AgNPs is supposed because of the formation of the reactive oxygen species however, the mechanism behind antimicrobial activity of AgNPs is still unknown. It is also explained that the silver ions oxidised and forms biocide and in addition, with the penetration of bacterial cell membranes the biochemical process may damage. Xiu et al. (2012) reported, the AgNPs can pass through the bacteria cell via diffusion, and thereby causes endocytosis through the cell wall to the cytoplasm. Thus, the toxicity occurred to the bacterial cell that also causes the mitochondria damage. Hence, ATP is reduced and formed ROS. Nakkala et al. (2014) reported that Acorus calamus interfered AgNPs exhibit antioxidant, antimicrobial properties. The plant extract-based AgNPs synthesized from Boerhaavia diffusa plant extract have outstanding antibacterial properties against Pseudomonas fluorescens, Aeromonas hydrophila, and Flavobacterium branchiophilum. According to Gopinath et al. (2012), the AgNPs having *T. Terrestris* L. plants extract from the dried fruit body evince antibacterial properties against the multidrug-resistant bacteria like *E. coli*, B, *Pseudomonas aeruginosa*, *Staphylococcus aureus*, subtilis, and *Streptococcus pyogenes*. Besides, Pal et al. (2007) described that various crystal surfaces of AgNPs showed distinct prolonged antibacterial activities. Also, the authors compared the AgNPs surface to other surfaces. The crystal surface of the AgNPs has higher atom density and reactivity. So it may adhere more to the cell membranes. Lukman et al. (2011) discovered the antibacterial properties of AgNPs in contrast to Shigella, Proteus, and Salmonella. Gaikwad et al. (2013) reported that the antiviral effect depends on the size of the nanoparticle since the fungi biomass-based AgNPs with 20–40 nm showed a better antiviral effect. Titanium silver nanocomposites have a micro-galvanic effect, thus antibacterial activity opposed to *E. coli* and *S. aureus* besides, outstanding compatibility having less surface toxicity and increase proliferation of osteoblast cells (Cao et al. 2011). Chiang et al. (2009) discovered that silver-palladium nanohybrid exhibit biofilm-inhibiting property to kill the bacteria via producing micro-electric fields as well as electrochemical redox processes. Prucek et al. (2011) explained that iron oxide-based silver nanohybrids provides excellent antifungal and antibacterial properties. Amin et al. (2009) compared AgNPs with the gold nanoparticles, the AgNPs can highly obstruct the growth of *E. coli* and *S. aureus* bacteria. Chitosan-based silver nanocomposites are widely applied on the cotton surface to enhance the antibacterial property (Thomas et al. 2011). Li et al. (2013) utilized the electrospun nanofibers of the polyvinyl alcohol/chitosan/Ag-nanocomposites as the wound dressing material. The AgNPs synthesized using the chemical reduction technique. The prepared nanocomposite in this study provides excellent antimicrobial activity against Gram-negative bacterial strains. Thermally reduced AgNPs can exhibit higher active against Gram-positive bacteria.

Nylon6/silver nanofiber composites showed outstanding antibacterial properties and inhibited 99.9% to the *E. coli* bacterial strain having a 0.5 wt% dose level. However, at 1.25 wt% there is 100% inhibition and also the pristine polymers nevertheless have this kind of properties. For the purpose of antimicrobial implants, scaffolds, implant coatings; the silver nanocomposites having high performing biocompatible with antimicrobial surfaces and multifaceted properties. According to Latif et al. (2015) chitosan containing silver nanocomposites are widely used as in the stabilization and as a primary matrix in the dispersion also, excellent antimicrobial activities. In another study, the silver nanocomposites synthesized with the natural rubber as the matrix. Jain and Pradeep (2005) and Lv et al. (2009) discovered that the antibacterial activity of silver nanocomposite by incorporating AgNPs by mixing into the polyurethane foams, ceramic composites, etc.

3.6 Fundamentals of Antimicrobial Effect of Silver Nanoparticles

The AgNPs can produce a layer of water molecules from its surface; aids to release silver or its ions. Fabrega et al. (2009) reported that no toxicity is the main advantage of the antibacterial effects of AgNPs in the presence of organic substances. Marambio-Jones and Hoek (2010) explained that the antimicrobial activity of AgNPs is correlated with several factors such as the concentration of the nanoparticle, pH, type of microorganism, and temperature. In relation to gram-positive bacteria, the gram-negative bacteria showed better antimicrobial activity of AgNPs. Geoprincy et al. (2013) suggested that because of the structural differences in the cell wall-associated to the peptidoglycan layer thickness and beta-barrel proteins. According to Galdiero et al. (2011) the AgNPs can suppress viruses like hepatitis B virus and herpes simplex virus. The details on biomedical applications of silver nanoparticles and their polymer nanocomposites, based on their antimicrobial activity are discussed in chapter "An Overview of Applications of Silver-based Polymer Nano Composite as Biomaterials", hence it is not repeated here.

3.7 Mechanism Behind Antimicrobial Activity

The silver ions can highly bind with the sulfur-containing amino acid. Hence the bactericidal effect of silver ions significantly occurred. Many studies are undertaking the antimicrobial activity of nanoparticles regarding the antimicrobial effect of AgNPs, but the mechanism is still unknown. Many researchers have described the various mechanisms that shows the interaction of AgNPs with the cells of various bacteria. These theories include the accumulation of AgNPs in the cell, disruption of cell membranes by AgNPs due to the formation of reactive radicals, anchoring of cell membranes with AgNPs, the dephosphorylating of tyrosine by silver ions, interaction of AgNPs with the respiratory enzymes of microbes, and interaction of AgNPs with the DNA of microbes, etc. (Prabhu and Poulose 2012a). Primarily, the AgNPs are attached to the cell membrane and after that penetrate into the cell wall by changing the membrane structure. Because of the smaller size of the AgNps, can simply diffuse into the microbial cell membrane. Consequently, cell organelles are subjected to the extracellular environment and normal functions of the cell may be interrupted. It is also said that the diffusion of oxidized products AgNPs to bacterial cells interact with the enzymes and destroys the normal function of cells and hence results in cell death. The AgNPs can generally interact with the thiol group of DNA, nucleic acids, respiratory enzymes, and components of cytoplasm in microbes, etc. (Kim et al. 2011). Sintubin et al. (2011) reported that mainly three types of mechanisms are observed for the antibacterial activities of the silver nanoparticles, such as by the generation of ROS, the release of the silver ions, or by the direct contact.

It is well known about the basic differences between viruses and bacteria. The size of bacteria is much bigger than viruses. Instead of cellular structure in bacteria the viruses comprise of a protein coating or lipid envelope that surrounds the coating. Unlike bacteria the viruses do not have metabolism. Thus, the mechanism of AgNPs on viruses are different from those of bacteria. The anti-HIV effect of AgNPs at its early stage is reported by Lara et al. (2010). The AgNPs can inhibit the viral entry and resist the HIV-1 proteins at the post-entry stages of HIV life cycle. In another study by Xiang et al. (2013) indicate a damage of gene and capsid of H3N2 influenza virus as well as the destruction adenovirus occurred due the interaction of these virus with AgNPs. The morphology of viruses obtained from the TEM images proved the damages occurred in the virus structures. More details on silver nanoparticles as a potential antiviral agent is discussed in chapter "Silver Nanoparticle as an Effective Antiviral Agent", hence not repeated here.

3.8 Factors Affecting Antimicrobial Activity

Swathy (2014) investigated, the AgNPs on electric field application purposes, the silver ions may highly release and thereby improve the antibacterial activities.

Gupta et al. (1998) discovered that the antimicrobial activity of AgNPs got enhanced by the electric current across silver ions. In addition, antimicrobial activity may impact the pH of the medium. The antibacterial activity is also affected by the pH of the medium. Observed 90 and 10% inhibition of bacteria at pH 9 and pH 6 (Fabrega et al. 2009). It is also reported that the usage of capping agents while the chemical reduction of AgNPs can also affect the antimicrobial activity of AgNPs (Chen et al. 2013).

4 Toxicity Aspects of Silver Nanoparticles

The AgNPs is a widely utilized inorganic metal for various medical applications due to its excellent anti-bacterial properties. The outstanding performance of AgNPs in various fields of the application results in its immense production of AgNPs and its vast utilization. While considering the nanoparticles in different application fields, it is necessary to have knowledge of the toxicity of AgNPs in various aspects. The chemically synthesized AgNPs are more toxic than biosynthesized AgNPs. Several researchers have discovered that silver nanoparticles have toxicity in contrast to many cell lines and aquatic organisms. The study and determine the toxicological effects of AgNPs are still challenging.

AgNPs are potentially toxic to humans at their high doses. The silver ions and AgNPs can accumulate in a wide range of human external and internal body organs. The AgNPs deposited in the human skin and resulted in the blue-grey discoloration is identified during argyria. Besides the exposure of silver on human skin, AgNPs can accumulate in numerous organs including eyes, muscles, kidney liver, small intestine, brain, plet, spleen, muscles, blood, stomach, lungs, prostate, bladder, tong, salivary glands, teeth, thyroid, parathyroid, pancreas, duodenum, and heart. The AgNPs generally demonstrates toxicity via oxidative stress, generating reactive oxygen species, because of the redox reaction produced in the reactive surface of nanoparticles or the interaction of nanoparticles with mitochondria. The AgNPs can cause ill effects on human beings as well as cause toxicity in the environment mainly from the industrial wastes that include tones of silver. Free silver ions can cause harmful effects on humans and other living beings that including discoloration to permanent bluish-grey of skin (argyria) or eyes (argurosis). The exposure to silver compound solutions may cause toxic effects like damages in liver and kidney, skin, eye, irritation in the respiratory and intestinal tract, and inappropriate change in the cells. Before the application of AgNPs in humans or animals, it is essential to know about their harmful effects. Although there have been many studies on different aspects of AgNPs, there are comparatively limited studies that have performed to evaluate the toxic effects of AgNPs. The rat liver on in vitro toxicity assay of AgNPs on a low level of exposure evokes oxidative stress and impair mitochondrial function. By damaging the mitochondrial function and causing leakage through the cell membrane due to the presence of AgNPs in vitro mouse germ-line stem cells. On the male reproductive system, the AgNPs adversely affect the sperm cells by crossing the blood-testis barrier. The in vivo studies on target organs for AgNPs as liver revealed oral toxicity on rats. The higher formation of bile duct hyperplasia, with/without pigmentation, fibrosis, and necrosis found in the animal study. Thus suggested that when the storage of AgNPs for a long time, silver let out of old AgNPs is more toxic than that of new AgNPs (Prabhu and Poulose 2012b).

The over usage of metal nanoparticles may also seriously affect the environment and also it can cause harmful effect to the organisms with repeated exposure to nanoparticles (León-Silva et al. 2016; Abramenko et al. 2018). Tons of nanosilver is dumped into the aquatic environment annually from agricultural lands, wastewater plants, septic tanks, etc. The Ag^+ ions released from AgNPs has considered as the most toxic form of silver in water (Lekamge et al. 2018). The nanosilver induce a toxic effect on aquatic animals and obstruct osmoregulation for aquatic-animals especially in fish by interacting with gills of fish and hinders basolateral Na+ /K+-ATPase (Prabhu and Poulose 2012b). The Environmental Protection Agency (EPA) (the United States Environmental Protection Agency; USEPA) suggested the maximum permissible level (MPL) for silver in drinking water (0.1 mg/L) within few flushes. The environmental impacts and toxicity of AgNPs that includes its effect on various organs are still unknown. However, a large number of researches are available based on the various toxicity aspects of Ag NPs. A few of such research studies are summarized and discussed in following section of this chapter.

4.1 Oral Toxicity

The orally administrated silver for mammals and humans are absorbed in a range of 0.4–18%, and for humans at 18%, respectively. East et al. (1980) investigated orally administrated silver retention in a 47 years old woman who was already suffering from argyria. With the help of radioactive tracer, the retention percentage of silver at a level of 18% for an orally administrated dosage was observed. After the oral administration, the nanoparticulate silver shown to be less bioavailable based on higher fecal excretion and lower absolute levels in organs when comparing with ionic silver, based on head to head investigations (Van Der Zande et al. 2012). All the organs of the animal seem to have absorbed the silver, with the maximum amount of silver being absorbed in the stomach and intestines. Absorption of silver during oral administration was observed to first pass through the liver resulting in excretion into the bile (Kim et al. 2010a). The study was based on oral toxicity to F344 rats (male and female) for 90 days exposure to AgNPs (56 nm) revealed, the notable reduction in body weight for male rats observed after exposure of 28 days. The higher exposure to AgNPs for male and female rats results in significant liver damage. The accumulation of silver in all tissues was observed, and it increased according to the exposure dosage. The gender-related variation with the increase in the amount of silver was observed in the female kidneys compared to that of males.

The oral administration in animals such as mice, rats, and dogs has been described by Furchner et al. (1968). In this study, the authors analysed silver excretion of orally administrated 110 silver radionuclides in study animals. The faecal excretion values are 99.6, 98, 90, and 94% for mice, rats, dogs, and monkeys. Indicated the amount of silver absorbed range from 0.4 to 10% depending on the species, with 10% for dogs and 6% for monkeys.

The orally administrated silver has deposited in a wide range of organs such as in human skin, brain, liver, kidney, eyes, spleen, pelt, muscles, stomach, small intestine, urinary bladder, prostate, teeth, tongue, salivary glands, parathyroid, thyroid, pancreas, duodenum, and heart. Regarding the persistence of silver in the body, the amount of orally administrated silver retention in a 47 years old-woman who already suffered argyria found to remain at a constant level for up to 30 weeks (East et al. 1980). The orally administrated silver deposited caused by silver nitrate persisted in the eyes as granules over 12 months after administration (Matuk et al. 1981). Van Der Zande et al. (2012) found the silver ions or AgNPs were still persistent for eight weeks in the brain of the rat after oral administration.

4.2 Neuro Toxicity

The neurotoxic effect of silver occurred via secondary molecules released from the periphery, even without the presence of silver in the brain extracellular fluid (Mathur et al. 2018). The AgNPs can produce intercellular calcium rise and oxidative stress in the primary neural cells extracted from the frontal cortex of the mouse (Haase et al. 2012). Xu et al. (2013) reported, AgNPs could induce toxicity followed by neuronal cell death in rat cortinal cells. Change in cytoskeleton components, perturbation of postsynaptic and presynaptic proteins, and mitochondrial dysfunction are the reasons for the neuronal cell death. The commonly reported effects on silver involve the formation of reactive oxygen species and inflammation. The generation of oxidative stress for neural cells is a particular risk due to the reason it was involved in the pathogenesis of numerous neurodegenerative diseases, such as Huntington disease, Parkinson's disease, Alzheimer's disease, etc. Repar et al. (2018) investigated the neurotoxicity effects of citric coated AgNPs (AgSCs) in human beings using neurons and astrocytes derived from human embryonic stem cells. The study revealed that the higher concentration exposure to AgSCs exhibited a notable neurotoxic effect compared to lower concentration exposure of AgSCs. However, the lower concentration exposure increased the astrocyte/neuron ratio but not induced any morphological changes to neurons. The astrocytes could exert neuroprotective effects during lower concentration exposure to AgSCs suggested that the astrocytes protect neurons from oxidative stress and limit the neuronal death induced by oxidants. The higher exposure concentration of AgSCs reduces the astrocyte number that consequently causes neural death. The neurotoxicity effects from AgNPs and Ag ions exhibit the toxic effects in different specific ways of inducing their toxicities (Yin et al. 2018).

These differences in toxicity effect may depend on the charge/particle effects and differences in the up-take of two different forms of silver by the cells. Yin et al. (2018) investigated the development of neurotoxicity of AgNPs and ionic silver. The authors used the mouse embryonic stem cell (mESC) as a toxicology model. Exposure to AgNPs and Ag ions at a lower concentration below 1 µg/mL indicated no accumulation of reactive oxygen species or mESC viability. However, it affected the expressions of neural ectoderm marker genes such as *Sox1* and *Sox3*, *Nestin, Pax 6*, *Map 2*, and *NeuroD*. *Where Sox1 and Sox3* are in neural stem cells and neural epithelial stem. *Pax6* are equivalent in rats and human in the central nervous system. *Map2* are neural dendritic marker genes, and *NeuroD* is the master controller of the development of the brain. The exposure of AgNPs and Ag ions to a lower concentration below 1 µg/mL affected the expressions of all aforementioned neural ectoderm markers, indicating the evolution of neurotoxicity effect.

4.3 Environmental Toxicity

The growing demand in application of AgNPs enhanced products may cause a rise in toxic levels of environmental silver. Due to the inadequate assessment of the toxicological aspects of AgNPs and the rate at which they are released to the environment, control over the use of such products is lagging. There are several pathways of AgNPs that are involved in their unintended moving into the ecosystem, rising concerns over the bioaccumulation of AgNPs in the environment, and a higher risk of human exposure. The release of AgNPs to the ecosystem involves misuse or improper disposal of products such as Ag^+ biocides in household products, drinking water filter, and appliances, biomedical instruments, industrial waste, antibacterial textile products, etc. (Stensberg et al. 2011). The recent studies revels that environmental Ag^+ and AgNPs contains approximately 15% of the biocidal compounds released from plastic products and textile industries (Blaser et al. 2008a). The discharge of AgNPs into environment as a point source pollutant and consequently it may be collected in municipal waste water treatment plants (WWTPs). Those AgNPs entering WWTPs is approximately 7% accumulated in sledges that are later utilized as agricultural fertilizers (Blaser et al. 2008b). The AgNPs in the sludge may remain at the top layer of the soil and can enter potentially to surface water via ground tables or runoff (Hu et al. 2003). In addition to the adverse effect of environmental toxicity of AgNPs, there is another risk that exists as a higher release of AgNPs into the ecosystem may stimulate growth in bacterial strains with intensified resistance to silver (Silver 2003). It is reported that the silver can induce toxicity in the aquatic environment to a range of different organisms such as bacteria, invertebrates and algae, and fish. Kleiven et al. (2019) investigated the toxicity of silver (meso-silver and AgNO3) in algae living in the aquatic environment. The exposure to silver inhibits the growth of test algae. For the low concentration, exposure of AgNO3 and meso-silver, the remarkable changes observed in the early exposure period and these changes diminishes over time. In this case, a low concentration exposure of the silver to algae in the aquatic environment may recover after a short exposure. Bao et al. (2020) studied the silver toxicity effects on adult male and female zebrafish. All the fishes then exposed to 100 μg/L of AgNPs of two different size range at 20 and 80 nm for an exposure period of 14 days. The consequence of AgNPs on the livers and intestines of male and female zebrafishes investigated utilizing biomarkers.

The results indicated the intestinal Na/K-ATPase activity and superoxide-dismutase activity in male fish vary with the size of the AgNPs. The oxidative/anti-oxidative status, hepatic lipid metabolism, and neural signaling are more sensitive for male zebrafish than female ones. The AgNPs negatively affected the intestine than the liver by disruption of the antioxidant system and Na/K-ATPase. The 20 nm AgNPs showed higher toxicity comparatively than 80 nm AgNPs.

4.4 Reproductive Toxicity

The nanoparticles can directly penetrate the cell by going through biological membranes that results negatively by affecting the physiology of cell in the body due to their small size. The nanoparticles including AgNPs or any chemicals, when entered into the biological system, is a matter of great concern to the people regarding reproductive and developmental toxicity, due to the complex-biological process involved in reproductive physiology that could be disrupted by the exposure to such environmental contaminants. The living things at its early growth stages are more sensitive to the adverse influence of such environments. The effects of AgNPs on reproduction and development in two models, Drosophila and CD-1 mouse were investigated by Philbrook et al. (2011). The oral administration of AgNPs resulted in the mortality of fetal mice. The feeding of AgNPs negatively affected the developmental success in fecundity. Utilizing transmission electron microscopy presence of AgNPs in the fetal livers and kidneys of the mouse was identified. In another study (Austin et al. 2012), observed the distribution of AgNPs in pregnant mice and their growing embryos. The authors injected AgNPs with a size of 50 nm into mice on gestation days (GDs). In addition, the authors investigated the rate of silver ions released from AgNPs by a similar dosage of AgNO3 into another group of mice. The silver content in the maternal tissues of mice was analyzed utilizing inductively-coupled plasma mass spectroscopy (ICPMS). The authors observed that silver distributed in the material organs such as spleen, liver, lung, visceral yolk sac (VYS) and extraembryonic tissues, and a lesser extend inside embryos. The pattern of distribution was observed similarly for AgNPs and AgNO3. The increased accumulation of silver in the VYS and endometrium. The localization of AgNPs was observed from TEM and energy dispersive X-ray spectroscopy (EDS) in vesicles in endodermal cells of the VYS. Miresmaeili et al. (2013) studied the effect of AgNPs with size 70 nm on acrosome spermatozoa of male rats and the number of spermatogenic cells. The study involved oral administration of AgNPs every 12 h in one spermatogenesis period for the experimental group of male rats employing different gavages varying from 25, 50, 100, and 200 mg/kg concentration. The other group of rats treated as control fed with distilled water. The authors found, AgNPs influenced the percentage of spermatogonia cells and significantly affects spermatogenesis. Besides, it also affects the acrosome reaction in sperm cells in which those effects are prominent on a higher concentration of graves. The effects of AgNPs exposure on the ovary of female adult rats were studied by El-Nouri et al. (2013). The experimental rats were exposed at a high dose (300 mg/kg) and a low dose (30 mg/kg) of AgNPs via oral administration every day for two weeks and four weeks. At the same time and same way, the control rats were fed by giving physiological saline for 2 and 4 weeks. The effects of AgNPs was observed higher for higher concentrations of exposures. The results indicated the AgNPs showed evidence of bleeding, congestion, apoptosis, and fibrosis in cells of the ovary of rats in all doses and test durations. The possible effects of AgNPs influence on are given in Fig. 1. The exposure to AgNPs at 0.015–200 mg/kg/day negatively influenced spermatogenesis, Leydig cells, sperm quality, and histopathology of the testis. The influence of AgNPs affected more on female fertility comparatively than male fertility. Gromadzka-Ostrowska et al. (2012) reported, the intravenous administration of AgNPs effects in females by decreasing the number of follicles and altered ovarian histopathology through oral administration of AgNPs. The AgNPs can affect the embryonic survival and growth

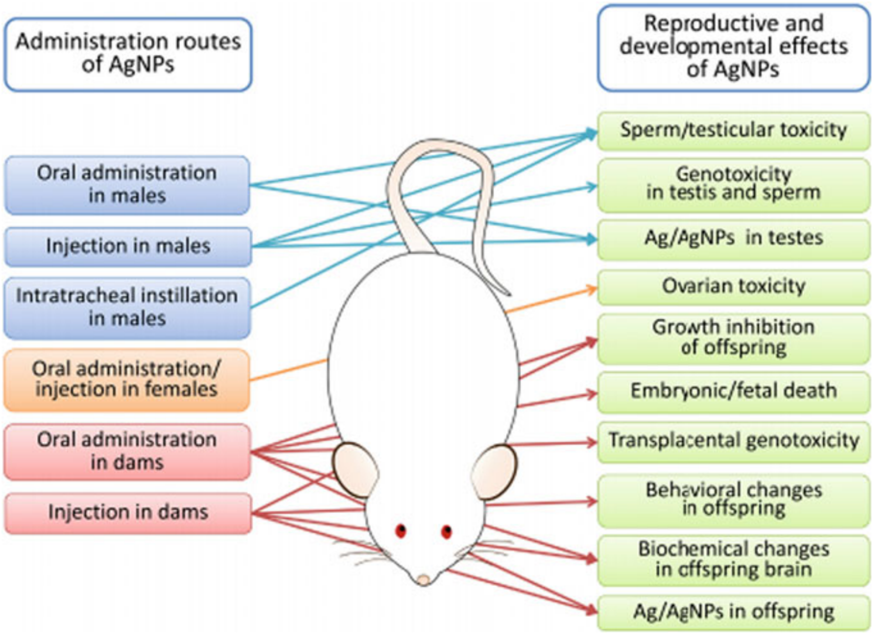

Fig. 1 Administration routes of AgNPs and its influence on reproductive and developmental studied in different animals reported in various literatures (Ema et al. 2017). Reproduced with permission

(Hong et al. 2014). However, the exposure to AgNPs did not affect negatively the morphological growth of offspring (Gromadzka-Ostrowska et al. 2012). The administration of AgNPs or silver ions during the pregnancy, there is a potential risk for induction of transplacental genotocixity.

4.5 Immunotoxicity

The continuous exposure of nanosilver or intravenous repeated-dose for 28 days of toxicity study revealed that the exposure to AgNPs affected several immunity parameters: increased spleen cell number and spleen weight, reduced thymus weight, reduced IFN-γ production and put down the NK cell activity (De Jong et al. 2013). The exposure to AgNPs 25 nm size effects on gene expression of the mouse brain was studied by Rahman et al. (2009), the results indicated dysfunction and impairment of the brain cells and immunotoxicity. After feeding the higher dose of AgNPs with size 13 nm for three days, the liver exhibited lymphocyte infiltration (Cha et al. 2008). Silver can induce anti-fibrillarin autoantibodies in genetically susceptible strains. Havarinasab et al. (2009) reported systematic autoimmune condition in genetically susceptible H-2s mouse strains following treatment 0.5 g/l silver in the drinking water for ten weeks. In another study (Park et al. 2010) the oral administration of 42 nm AgNPs for 28 days in doss of 0.25, 0.5, and 1 mg/kg of body weight per day. The authors observed an increase in plasma concentration of interleukin-1 and interleukin 4 in high dosage exposure, interleukin 6, 10 and 12 in middle and high dosage exposure, and immunoglobin E in the higher dose exposure. At a higher dose of silver, an increase in cell infiltration in the kidney cortex. A lowering of thymus weight, and increased level of allantoin in rat urine following a 28-day exposure of oral administration of silver ions at a dose up to 9 mg/kg of body weight per day (Hadrup et al. 2012a, b).

4.6 Effects of Silver on Body Weight

The exposure to silver reduces the body weight and retarded the growth in rats was reported by Matuk et al. (1981). The rats were administrated with 0.25% $AgNO3$ mixed in drinking water for 8 months with the corresponding dose to 81 mg/jk of bodyweight per day. The body weight became normal after the silver withdrawn from the body over a course of 10 weeks. In another study done by Hadrup et al. (2012a, b) reported a decreased body weight gain during the oral administration of silver acetate with a dose of 9 mg of silver per kilogram of body weight per day. Kim et al. (2010b) found the oral exposure of AgNPs resulted in a decreased bodyweight for male rats. The rats fed with 500 mg of 60 nm AgNPs/kg of body weight per day for 13 weeks. Shahare et al. (2013) also found a decrease in body weight followed by the oral administration of AgNPs (5-20 nm) with a dose of 5 mg/kg of body weight per day for 21 days.

4.7 Effects on Gastrointestinal Tract

The higher amount of silver deposition displayed in the gastrointestinal tract in the oral toxicity experiment was done by Loeschner et al. (2011). Throughout the test (28-day oral toxicity study), the AgNPs (14 ± 4 nm) remain stable inside the rat. The higher amount of silver deposited in the intestinal system with an indication of a higher amount of silver in faecal excretion following oral administration of AgNPs. Shahare et al. (2013) found the AgNPs with 5–20 nm size at a dose of 20 mg/kg of body weight for 21 days of administration to the mice and observed damages in the epithelial cell microvilli and intestinal glands. Jeong et al. (2010) found the AgNPs (60 nm) can induce the discharge of mucus granules and distorted mucus composition in the intestine following the oral administration of 30 mg/kg of body weight per day for 28 days. The higher dose increased the accumulation of AgNPs in the lamina propria in both the large and small intestine. Kim et al. (2010b) studied the effect of oral toxicity of AgNPs (56 nm) for 90 days. The study revealed a higher occurrence of bile-duct hyperplasia with or without fibrosis, necrosis, and pigmentation.

4.8 Effects of Silver Nanoparticle on Liver and Bile Duct

Silver toxicity has been widely reported in many enzymes that affect the function of the liver and bile ducts. Kim et al. (2008) investigated oral administration of AgNPs (60 nm) for 28 days and observed increased plasma alkaline phosphate at doss of 300 mg/kg of body weight per day in male rats and 1000 mg/kg of body weight per day for both male and female rats, and cholesterol doses at 1000 mg/kg of body weight per day only in female rats. Besides, (Kim et al. 2010a, b) also reported bile duct hyperplasia that included eosinophil infiltration of the portal tracks and hepatic lobules. Hadrup et al. (2012a, b) studied the oral administration of silver ions in the form of silver acetate at a dose of 9 mg of Ag/kg of body weight per day and nanoparticulate silver at a dose of 9 mg of 14 nm AgNPs/kg of body weight per day. Following oral administration of silver ions resulted in increased plasma alkaline phosphate and reduced plasma urea. Besides, the silver ions and AgNPs exposure resulted in increased urinary excretion of uric acid and increased metabolite allantoin. From another study reported by Van Der Zande et al. (2012) of 28-day oral exposure of AgNPs (<20/<15 nm, PVP coated) at doses 90 mg/kg body weight, and AgNO3 at silver doses 9 mg/kg body weight. The presence of silver in all organs and at the highest level in the liver and spleen. The increase in silver concentration in various organs attributed to the Ag+ in AgNPs suspension. However, the authors did not find any effects of hepatotoxicity in the tested animals. The liver inflammation in rats was reported by Sardari (2012) following the oral administration of AgNPs at doses 1 or 2 mg/kg of body weight per day for 30 days. The increased alanine aminotransfer and alkaline phosphate followed the oral exposure of AgNPs (42 nm) in doses up to 1 mg/kg body weight per day for 28 days.

4.9 Effects of Silver Nanoparticles on Cardiovascular System

The ionic silver in the form of silver chloride or silver nitrate concentrations of one part per thousand in drinking water with a dose of 57 and 68 mg of silver/kg of body weight per day, can induce cardiac alterations like left ventricular hypertrophy in rats (Olcott 1950). The effects of silver on the heart in turkeys was investigated by Peterson et al. (1973). The turkey fed with a diet that included 900 ppm of $AgNO_3$ for four weeks. For the silver administrated turkeys, observed enlarged heart and increased aortic elastin content. After the silver withdrawal from the body, the abnormality caused by the administration of silver was reverted to normal by 22 weeks of age. However, for the heart was found not reverted. In another study conducted by Jensen et al. (1974), 900 ppm of silver nitrate or silver acetate added to the diets of white turkey. The silver affected negatively by the depressed growth rate, sight decrease in hemoglobin level, and abnormality in the heart by cardiac enlargement. The authors noted a high-level percentage of the enlarged heart similar to that seen in round hearted disease in turkeys. The hemoglobin concentrations, red blood cell counts, and hematocrit found increased following the oral exposure of 60 nm AgNPs at doses of 300 mg/kg body weight per day in female rats for 28 days (Kim et al. 2008). The exposure to AgNPs (14 nm) stabilized with PVP and exposure to silver ions in the form of silver acetate was used study the toxicity effect in 4 weeks old Wister rats at doses 9 mg/kg body weight per day or silver acetate 9 mg silver/kg body weight per day for 28-day by Hadrup et al. (2012a, b). The equimolar dose of AgNPs resulted in increased silver plasma and organ concentrations. The results also indicated the increased hematocrit following the exposure to AgNPs. Espinosa-Cristobal et al. (2013) studied the distribution, accumulation, and toxicity of AgNPs in various organs of Wistar rats. In this study, the rats were exposed to AgNPs (14 and 36 nm) at a concentration of 535 mg/L (corresponding to a dose of 65 mg/kg body weight per day) in drinking water for 25 days. The silver concentration was observed higher in the liver, brain, and kidney. The blood urea nitrogen values were altered to a higher level, increases hematocrit and hemoglobin concentration in the female rats. The altering or increase in these blood-related parameters suggests the need for excessive oxygen transport in these animals. Ones the AgNPs entered the circulatory system; it can interact with the numerous proteins circulating in the bloodstream. Proteins in the bloodstream can come across and can bind to AgNPs in the blood. The interaction of AgNPs with the blood proteins can reduce its effect on antimicrobial properties (Gnanadhas et al. 2013). For instance, the smaller size of nanoparticles has stronger interaction for human serum albumin than the bigger size of nanoparticles, suggesting that the bioavailability depends on the size of nanoparticles (Zhang et al. 2015). Thus concluded, the size of AgNPs play a key role in their toxicity, the smaller particle size of AgNPs is more toxic than larger particles in addition to its chemical coating and biological effects.

5 Toxicological Effect of AgNPs Related to Human Exposure and Its Persistence in the Body

Although the continues evolution of Ag NPs in the various biomedical application, there is a lack of knowledge concerning the impact of AgNPs in the human health. The particle size of AgNPs possess a key role in increased toxicity due to their different mode of cellular uptake and further proceeding that leads to the adverse biological effects in living cells that would not be possible with the silver in their larger form. In fact, as the size of AgNPs decreases show the increased toxicity, even if the silver is inert in its bulk form. Apart from the size of any metal nanoparticles, the biological toxicity in living cells also depend on their chemical composition, agglomeration, shape and solubility. A commonly employed strategy for reducing the toxicity of Ag NPs is the use of capping agents that prevent the direct contact between cells and nanoparticles (Galdiero et al. 2011).

The Ag NPs were found to be cytotoxic to the mammalian cells based on their interaction and assessment of mitochondrial function, membrane leakage of lactate dehydrogenase, and atypical cell morphologies (Hussain et al. 2005). The AgNPs can interact with mammalian cells to the biological molecules at cellular level and can interfere with the antioxidant defence mechanism resulting in the formation of reactive oxygen species (ROS) (Aillon et al. 2009). The excess formation of ROS can cause damages in the biological components via oxidation of proteins, DNA and lipids (Wang et al. 2019). The higher exposure of living cells to AgNPs has been showed the formation of ROS in the human glioblastoma, human lung fibroblast, and resulted in cell cycle abnormalities and DNA damages (Asharani et al. 2009).

The exposure to higher concentration/dose of silver induces stronger cellular toxicity. The accidental exposure to AgNPs with a higher concentration of silver commonly happen. Several researchers have reported that the human utilization level of silver ranges to 0.4–27 μg/day. These values corresponds to 0.007–0.5 μg/kg of body weight per day. From the research reports, it is clear that the lowest effect level of exposure to AgNPs from animal studies is 0.5 mg/kg of body weight per day (Park et al. 2010), this study was based on increased plasma concentration on rats. In addition, from all these research observations, this level to be considered the Lowest Observed Adverse Effect Level (LOAEL). Then the No Observed Adverse Effect Level (NOAEL) would be the next level of lower dose at 0.25 mg/kg of body weight per day. If we divide the NOAEL with a toxicological uncertainty factor of 100, we can get a tolerable daily intake (TDI) of 2.5 μg/kg of body weight per day. So the reported dietary level is still under the margin of safety of approximately with a factor of 5 before the level of concern to reach the general population (Hadrup and Lam 2014). East et al. (1980) investigated silver retention in 47-year-old women who have already infected with argyria following the exposure of silver via oral administration. With the help of a radioactive tracer, the amount of silver found to persist without change for 30 weeks. In another study by Matuk et al. (1981) orally administrated silver deposited in the eyes as granules found persisted in the eyes for 12 months.

6 Conclusions

The extending application of silver nanoparticles can act as an essential material in nanoscience fields. From this, we can conclude that compared with the synthetic routes, the green synthesized silver nanoparticles are more beneficial. There are so many demerits for synthetically derived, such as expensive, stability problems, etc. The next chapter discuss about the eco-friendly and innocuous approaches for synthesis routes of silver nanoparticles avoiding the use of toxic chemicals.

The silver nanoparticles are consumed more due to their excellent antibacterial and anti-inflammatory properties. The higher concentration and higher utilization of silver nanoparticles can cause various toxic effects on living things and can cause ecological problems if excess silver is released to the environment. So environmental safety is required to be more investigated. The Environmental Protection Agency (EPA) (the United States Environmental Protection Agency; USEPA) suggested the maximum permissible level (MPL) for silver in drinking water (0.1 mg/L) within few flushes. From the observations, we can concluded that tolerable daily intake of AgNPs at 2.5 μg/kg of body weight per day. However, the reported dietary level is still under the margin of human safety of approximately with a factor of 5 before the level of concern to reach the general population. Further investigations on different physicochemical characteristics of silver nanoparticles are required to understand the exact mechanism of interaction of silver nanoparticles with organisms and their various toxicity aspects.

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Synthesis and Green Synthesis of Silver Nanoparticles

Aarti Sharma and Sarita Kumar

Abstract Nanoparticles, ranging in the size from 1 to 100 nm possess novel or enhanced properties compared with larger particles of bulk materials, based on their specific characteristics such as size, distribution and morphology. Noble metal nanoparticles are widely used in the nano-medicinal application; especially silver nanoparticles, which exhibit antifungal, antibacterial, anti-plasmodial and anti-mosquito properties due to the unique properties such as chemical stability, good conductivity and catalytic activity. Nanoparticles are largely synthesized by a variety of chemical and physical approaches. These techniques being expensive and potentially hazardous to the environment, can pose various biological risks. This has necessitated for the alternate eco-friendly and innocuous approaches. In recent years, the convergence between the two fields; nanotechnology and biology; has evolved a new field of nanobiotechnology that encompasses a number of biochemical and biophysical processes employing biological entities such as algae, bacteria, fungi, viruses, yeasts, and plants. Focus on green synthesis of nanoparticles without employing toxic and expensive chemicals frequently used in conventional chemical and physical processes, has augmented their applications and safe usage. This chapter describes the different methods to synthesize silver nanoparticles with a major focus on synthesizing nanoparticles via green route i.e., by utilizing biological entities for the facile, eco-friendly and cost-effective synthesis.

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1 Introduction

Nanotechnology is a rapidly growing field dealing with the synthesis, stratagem and manipulation of particle's structure ranging in a nanoscale from approximately 1 to 100 nm in size. It is predominantly the nanoparticles' smaller size, shape, large surface area to volume ratio, distribution, aggregation state, solubility, structure, and chemical composition that leads to completely new or enhanced properties with significant transformations. The nanoscale transformations of material enhance their biological, catalytic activity, mechanical properties, melting point optical absorption, thermal and electrical conductivity that are not seen in the same material at larger scales in their bulk form.

Noble metal nanoparticles such as silver, gold, titanium, and platinum are commonly used in the nano-medicinal application. In particular, the silver nanoparticle; an arch product from the field of nanotechnology; has gained infinite interest because of its unique properties such as chemical stability, good conductivity, catalytic activity, etc. Due to the excellent anti-bacterial, anti-viral, anti-fungal, and anti-inflammatory activities of silver nanoparticles, they are widely applied as a biomaterial. These nanoparticles incorporated with polymeric matrices are commonly used in composite fibers, cryogenic superconducting materials, biomedical fields, cosmetic products, the food industry, and electronic components (Klaus-Joerger et al. 2001; Ahmad et al. 2003). Silver displays a broad biocidal effect against microorganisms through the disruption of their unicellular membrane thus disturbing their enzymatic activities (Ahmed et al. 2016). The reports reveal that silver nanoparticles possess higher efficacy against the mosquito larvae as compared to gold nanoparticles (Song and Kim 2009).

2 Synthesis of Silver Nanoparticles

2.1 Different Approaches for Synthesis of Nanoparticles

Nanoparticles are largely synthesized by a variety of chemical and physical approaches. These techniques are quite expensive and potentially hazardous to the environment as these involve utilization of toxic and harmful chemicals which can pose various biological risks. In order to cope up with these interruptions; there is a dire need for alternate approaches which are eco-friendly and do not involve any toxic chemicals. Consequently, various biologically-inspired experimental approaches have been developed for the synthesis of nanoparticles which involves biological agents; such as microorganisms and plants. The focus on green synthesis of nanoparticles has resulted in the progress of an important branch of nanotechnology; called nano-biotechnology.

The synthesis of silver nanoparticles involves primarily two approaches; "top to bottom" approach and "bottom to up" approach (Fig. 1).

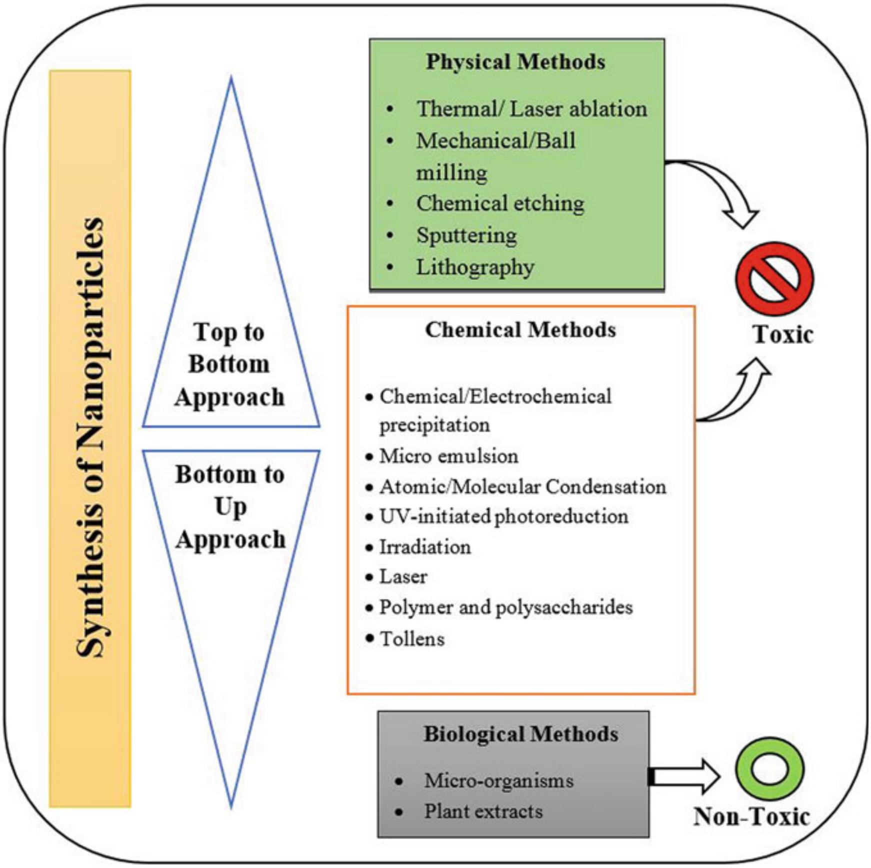

Fig. 1 Different approaches for the synthesis of silver nanoparticles [Self-Created]

The bottom to top approach includes chemical and biological methods for the formulation of nanoparticles by self-assembly of atoms to form new nuclei, which grow into a particle of nanoscale size (Fig. 2a) (Ahmed et al. 2016). On the other hand, in top to bottom approach, various lithographic techniques such as grinding, milling, sputtering and thermal/laser ablation are used in which an appropriate bulk material is broken down into fine particles by size reduction method (Fig. 2b). Limitations of this method are requirement of a large space, energy, temperature and a lot of time to succeed thermal stability.

The foremost aim of this chapter is to deliver guidance when selecting a synthetic method to synthesize silver nanoparticles for a desired application. Mechanistic insights to understand the role of certain factors, which could affect the synthetic outcome, are also discussed.

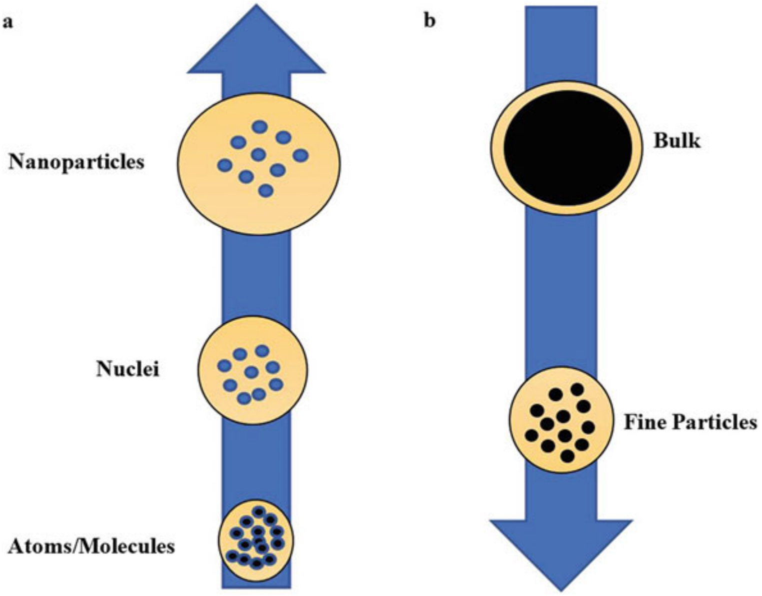

Fig. 2 Protocols employed for the synthesis of nanoparticles. **a** Bottom to top approach. **b** Top to bottom approach [Self-Created]

3 Chemical Synthesis of Silver Nanoparticles

3.1 Chemical Reduction

Chemical reduction technique is the most commonly used method for synthesis of silver nanoparticles due to its simplicity. This technique is carried out in a solution with the resultant product possessing colloidal characteristics. It uses different organic and inorganic reducing agents such as; ascorbic acid, sodium borohydride ($NaBH_4$), sodium citrate, elemental hydrogen, Tollens reagent, N, N-dimethylformamide (DMF), and polyethylene glycol-block copolymers for reduction of silver ions (Ag^+) in aqueous or non-aqueous solutions (Iravani et al. 2014). The reducing agents reduce silver ions (Ag^+) to the metallic silver (Ag^0) and agglomerate them into oligomeric aggregates. These aggregates, gradually lead to the formation of metallic colloidal silver nanoparticles.

The chemical reduction method also utilizes certain protective agents; surfactants for capping and stabilization of aggregating silver colloidal particles in the reaction mixture, so that the dispersive nanoparticles are unable to absorb or bind onto the nanoparticle surfaces, avoiding their agglomeration (Oliveira et al. 2005). Particle growth is stabilized by the interactions between surface of NPs and surfactants containing different functional groups (acids, alcohols, amines and thiols). It also protects NPs from sedimentation, particle agglomeration and from losing their surface properties. A few such effective agents which lead to stabilization of nanoparticles include polymeric compounds such as poly vinylpyrrolidone (PVP), poly vinyl alcohol (PVA), poly ethylene glycol (PEG), poly methacrylic acid (PMA), and poly methyl methacrylate (PMM).

The synthesis of nanoparticles using one reduction agent can limit their size. Formulation of both large-sized NPs and small-sized NPs possessing a well-defined shape and desired mono-dispersity is difficult with one reduction agent. Use of co-reduction method employing two different reductants can result in better control on nucleation and growth of nanoparticles. For example, sodium borohydride-mediated reduction technique could produce stable, monodispersed and uniform-sized silver colloidal nanoparticles of the size less than 10 nm due to instant nuclei generation (Agnihotri et al. 2014). While, large-sized silver nanoparticles with varied shapes; i.e., spherical, rods, cubes, and triangles could be formulated by addition of trisodium citrate, a weak reducing agent (Fig. 3). Thus, employing co-reduction method could result in formulation of both small-sized and large-sized nanoparticles. Reduction of silver salt using sodium borohydride ($NaBH_4$) and trisodium citrate ($C_6H_5Na_3O_7{\cdot}2H_2O$) had been conducted to form silver nanoparticles of different sizes and shapes (Rashid et al. 2013).

The reduction technique is considered useful as it enables the formulation of AgNPs with controlled particle size, shape and distribution by inducing variation in the molar concentration of the reactant and dispersant, feed rate of reactant, concentration of reducing agents, stabilizing agents, injection rate, temperature, etc. A minute change in these factors can lead to dramatic modifications in the average size, distribution, structure, stability and self-assembly patterns of nanoparticles. Let

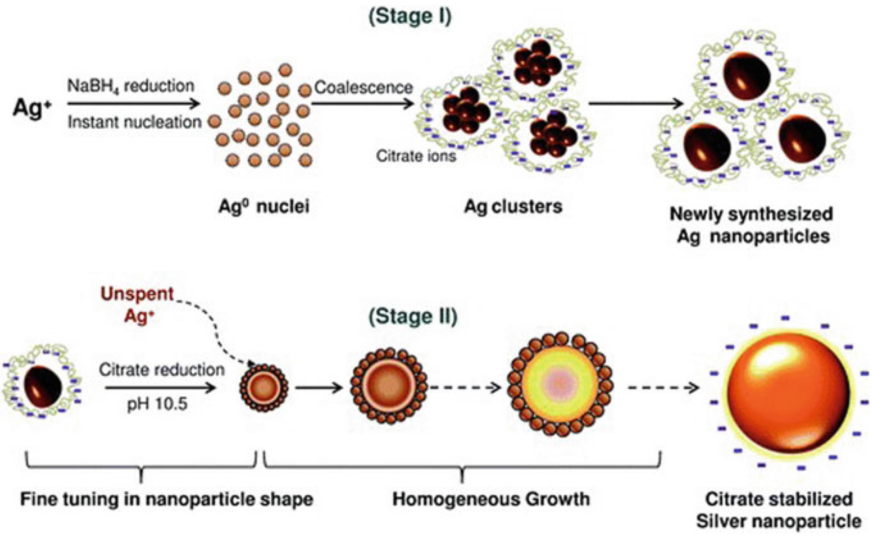

Fig. 3 Schematic representation of size-controlled silver nanoparticles synthesized employing the co-reduction approach. [Reproduced from Agnihotri et al. (2014) under the license (CC-BY3.0)]

us understand by taking the example of one characteristic feature—size of the nanoparticles. The size of colloidal silver NPs can be regulated by causing variations in the heating temperature, growing time, and by optimizing the reducing agent-silver precursor ratio. Thus, one of the important determinants of the size of NPs is the selection of an appropriate reducing agent, as its nature decides the particle size, shape and distribution. It should be noted here that the agent can reduce the metal precursor only if the reactivity of the reducing agent is attuned to the redox potential of the metal. Another crucial factor that decides the size of particles is the growing time of NPs dependent on the speed of reaction rate. The growing time of NPs is much less in case of fast reaction as compared to the slow reactions. During fast reactions, large amount of metal nuclei is formed rapidly resulting in small-sized particles. On the other hand, slow rate of reaction results in agglomeration of particles. In addition, selection of the surfactant is crucial because it not only governs the reactivity, stability, solubility and dispersibility of NPs but also the size and shape of the nanoparticles. The presence of surfactants including functionalities for interactions with particle surfaces can help in the stabilization of particle growth and their protection from agglomeration, sedimentation or losing their surface properties. Some protective agents found effective in stabilizing NPs are polymeric compounds, such as poly (vinyl alcohol), poly (vinylpyrrolidone), poly (ethylene glycol), poly (methacrylic acid), and polymethylmethacrylate (Iravani et al. 2014).

This method is the most common, rapid and facile. The only disadvantage is the mandatory use of few chemicals like reducing agent, stabilizer, catalysts and protective agents. Reduction technique for the synthesis of nanoparticles had been explored by Suriati et al. (2014). They synthesized silver nanoparticles *via* reduction of $AgNO_3$ by trisodium citrate and ascorbic acid as a surfactant and obtained AgNPs with size ranging from 35 to 80 nm, and an average of 50 nm. They also reported that the concentration of trisodium citrate was negatively correlated with the size of silver nanoparticles; increased concentration reducing the size of AgNPs. On the other hand, increasing the concentration of ascorbic acid resulted in the opposite effect. Moreover, with an increase in the concentration of ascorbic acid, the shape of nanoparticles changed from quasi-spherical to polygonal.

3.2 Microemulsion Techniques

Microemulsions are transparent, isotropic, thermally stable and homogenous liquid dispersions of at least three components. These three components comprise; non-polar phase (oil or mixture of hydrocarbons and olefins), polar phase (water which may contain salts and other components), and ionic surfactant. The term ‘microemulsion’ was suggested by Schulman et al. (1959). They suggested that addition of aliphatic alcohol (co-surfactant) in the mixture could synthesize stable NPs. According to them, surfactant and co-surfactant molecules separate the aqueous and organic phases; and decrease the interfacial tension by increasing the interfacial pressure. Further, the surfactants also act as a steric barrier and inhibit the amalgamation of droplets resulting in the stabilization of dispersion which is less viscous, transparent, isotropic and highly stable. The spherical droplets constituting the microemulsion system range from 600 to 8000 nm in diameter.

Nanoparticles can be synthesized by two kinds of microemulsion methods—One microemulsion method and two microemulsion method.

1. One microemulsion method includes ‘energy triggering method’ and ‘one microemulsion plus reactant’ method. In the energy triggering method, a triggering agent is introduced into the single microemulsion containing the reactant precursor. The triggering agent initiates the reaction leading to the formation of NPs. In one microemulsion plus reactant method, microemulsion already contains a reactant into which another reactant (liquid or gaseous phase) is added directly. Whether nanoparticles are formulated by energy triggering or microemulsion plus reactant method; the trigger/second reactant added to the microemulsion needs to diffuse through the interfacial wall of the microemulsion in order to encapsulate the reactant already present in the mixture and form NPs (Fig. 4).
2. Two microemulsion method involves the mixing of two microemulsions, each containing the different reactant. The microemulsions are mixed in a particular ration to obtain the NPs. The intermicellar collisions result in the proper mixing of the micelles and the reaction starts. As soon as the critical number of molecules is produced, the nuclei are formed and NPs are formulated. It is significant to note that the reaction requires a large number of intermicellar collisions for the exchange of reactants and adequate mixing.

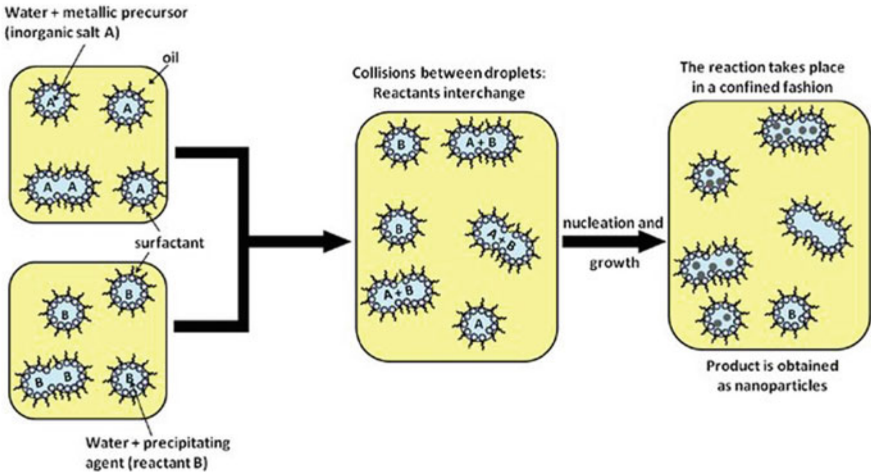

Fig. 4 Microemulsion reaction method for the synthesis of nanoparticles. [Reproduced from Sanchez-Dominguez et al. (2012) under the license (CC-BY 3.0)]

Microemulsion technique was used most commonly for the synthesis of metal NPs employing the reduction strategy. The factors which regulate the synthesis of NPs include type and type of surfactant, water/surfactant ratio (ω), the concentration of metal ion, type and concentration of reducing agent, etc. One of the major disadvantages of this process is the utilization of highly deleterious organic solvents. Therefore, huge amounts of surfactant and organic solvent must be parted and removed from the final product. Zhang et al. (2006) evidenced that as the water/surfactant ratio decreased from 15 to 2.5, the size of AgNPs reduced from ~5 to ~1.5 nm. They also observed that change in the amount of reducing agent affected the stability of colloid and delayed the process of synthesis. Similarly, with an increase in surfactant concentration (sodium *bis* (2-ethylhexyl) sulfosuccinate; AOT), the particle size of AgNPs was reduced.

Similarly, with an increase in the water/sodium *bis* (2-ethylhexyl) sulfosuccinate (AOT) molar ratio (ω) to 25, a morphology transition from a sphere-like nanocrystal to a wire-like structure was observed (Fig. 5) (Feng et al. 2018).

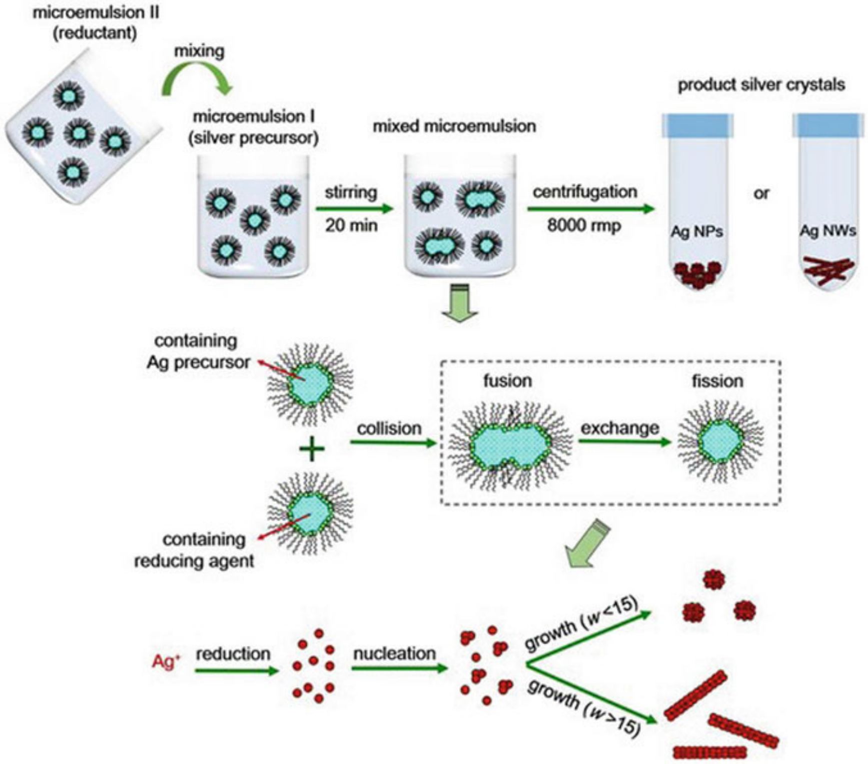

Fig. 5 Microemulsion process of NP formation and effect of water/surfactant molar ratio on the structure of NPs. [Reproduced from Feng et al. (2018) under the license (CC-BY 4.0)]

3.3 Sol-Gel Technique

The sol-gel technique is a wet chemical technique. It employs a colloidal solution (sol) made of solid particles with a diameter of a few hundred nanometres, while the gel is a solid macromolecule immersed in a solvent. Sol acts as the precursor for an integrated or discrete particle network (or gel) or network polymers; and thus, there is a chemical transformation of a sol into a gel state. The process involves two prime steps; hydrolysis and condensation. During hydrolysis, bonds of the precursor are broken down resulting in the initiation of the gel phase. Thereafter, the process of condensation results in the formation of NPs and excess water is removed to obtain the final product. Using sol-gel technique, silver nanoparticles have been formulated in an aqueous medium at room temperature in the presence of CH_3COONa (Sodium acetate) and hydrazine as a reducing agent (Shahjahan et al. 2017). They obtained mono-dispersive, spherical and highly crystalline silver nanoparticles.

The sol-gel technique has several advantages such as high purity and ultra-homogeneity achievable at low temperature and most significantly the possibility of making new compositions. However, the technique is also considered disadvantageous, as the cost of the raw materials used (the chemicals) is very high. In addition, often the occurrence of agglomeration and, a large volume shrinkage and cracking during processing and drying causes complications which need to be addressed.

3.4 UV-Initiated Photoreduction

UV-initiated photoreduction is an effective technique attempted by the researchers for the synthesis of silver nanoparticles. The technique requires certain stabilizing agents, such as citrate, polyvinylpyrrolidone (PVP), polyacrylic acid (PAA) and collagen. Different shapes of silver nanoparticles; nanosphere, nanowire, and dendrite; can be synthesized by UV-initiated photoreduction technique carried out at room temperature using stabilizers.

The properties of nanoparticles synthesized can be estimated as a function of UV irradiation time. Studies have reported that approximately 3 h of UV irradiation results in bimodal-sized distribution and relatively large-sized silver nanoparticles (Huang and Yang 2008). Further UV irradiation could disintegrate the silver nanoparticles into smaller size until a relatively stable size distribution and particle size is obtained.

PMA (Poly Methacrylic Acid) stabilized silver nanoparticles have been synthesized by chemical reduction process using a two-step UV irradiation (Spadaro et al. 2010). In the first step, 10:1 ratio of silver nitrate (Ag precursor salt) and PMA (capping polymer) ($AgNO_3$/PMA) mixture was exposed to a radiation density of 470 nW/cm^2 from a 6 W UV lamp for a maximum time of 1 h. The irradiation promoted the silver reduction due to the polymer which coordinated the Ag^+ ions through the COO^- groups. Consequently, the reduction of silver ions by PMA induced a colour change in the solution from colourless to yellow. The particle nucleation began and proceeded without any significant change in the polymer structure. In the second step, the mixture was again exposed to a 378 mW/cm^2 irradiation from a 25WUV lamp for 5 h during which the solution colour turned to dark orange. The UV power density applied about a thousand times larger than in the first step, tremendously increased the polymer reticulation kinetics, causing freezing of the NPs distribution already produced during the first step hence improving the control over NPs size distribution.

3.5 Electrochemical Method

Silver nanoparticles can also be synthesized electrochemically. The technique was first devised by Reetz and Helbig who anodically dissolved a metal sheet and reduced the intermediate metal salt formed at the cathode, obtaining metallic particles which were then stabilised by tetraalkylammonium salts (Fig. 6) (Reetz and Helbig 1994). Using a similar approach, several researchers formulated AgNPs by adopting modified techniques. Moreover, by regulating electrolysis parameters and composition of electrolytic solutions, the particle size can be controlled and the homogeneity of silver NPs can be improved.

Several chemicals, such as acetonitrile containing tetrabutylammonium salts (TBA bromide or TBA acetate), polyphenylpyrrole and Poly(N-vinyl-2-pyrrolidone) (PVP), etc. have been used by researchers for electrochemical synthesis of nanoparticles. Johans et al. (2002) synthesized silver nanospheroids of 3–20 nm diameter coated with polyphenylpyrrole by electrochemical reduction at the liquid/liquid interface which transferred the silver ion from aqueous phase to organic phase, where it reacted with pyrrole monomer. Ma et al. (2004) also adopted the electrochemical method for synthesizing spherical silver NPs of 10–20 nm diameter with narrow size distributions by selecting poly N-vinylpyrrolidone as the stabilizer for the silver clusters. They advocated that poly N-vinylpyrrolidone not only protects NPs from agglomeration, but also diminishes the rate of silver deposition significantly, while promotes the rate of silver nucleation and silver particle formation. In (2009), Khaydarov et al. devised a novel electrochemical method which does not involve any chemical stabiliser. They prepared spherical silver nanoparticles suspended in aqueous solutions, with an average size of 7.3 ± 3.1 nm, and which were sufficiently stable for at least 7 years even under ambient conditions.

The electrochemical methods can formulate nanoparticles of desired size and characteristics if the chemical agents are rightly selected and the process conditions are maintained appropriately. The electrochemical method is advantageous as it results in nanoparticles of high purity and the size of the nanoparticles can be controlled by adjusting the current density. Also, it does not require any expensive equipment or vacuum. However, during the electrochemical process, deposition of

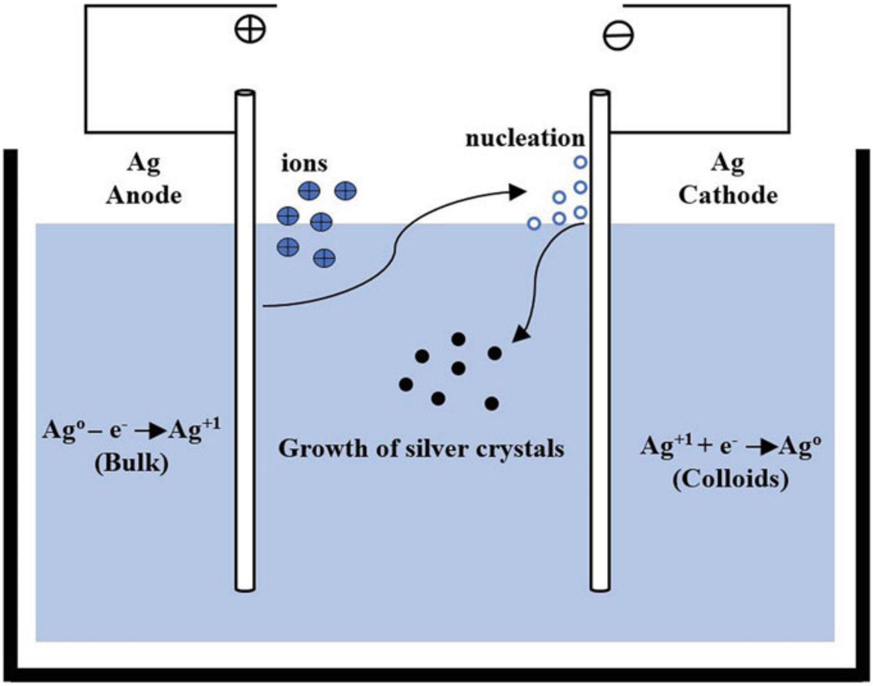

Fig. 6 Synthesis of silver nanoparticles by the electrochemical method [Self-Created]

silver on the cathode reduces the effective surface available for particle production and the particle production can stop completely.

3.6 Polysaccharides-Based Biosynthesis

Silver nanoparticles can also be synthesized with the addition of polysaccharides in aqueous media; such as starch, heparin, polyethylene glycol etc. which act as both capping and reducing agents. Silver nitrate (precursor), glucose (reducing agent), sodium hydroxide (accelerator), and starch (stabilizer) can be used for the reduction synthesis of silver nitrate. For example, silver nanoparticles of the size 5–20 nm can be synthesized using starch as a capping agent and β-D-glucose as a reducing agent (Raveendran et al. 2003). During the synthesis, starch coats the surface of nanoparticles and stabilizes them. It has been shown that on the addition of sodium hydroxide along with starch and glucose, small-sized silver nanoparticles (≤ 10 nm) can be synthesized (Tai et al. 2008). It has been shown that sulphated polysaccharides (obtained from marine red algae; *Porphyra vietnamensis* can reduce silver nitrate due to the presence of sulphate moiety and leads to the synthesis of silver nanoparticles of $\sim 13 \pm 3$ nm diameter.

Another polysaccharide, heparin; which acts as reducing/stabilizing agent as well as nucleation controller; has also been used to synthesize highly stable silver nanoparticles at 70 °C (Huang and Yang 2004). They also reported that with an increase in the concentration of silver nitrate-heparin mixture, the particle size of silver NPs also increases. Thus, optimization of the concentration of reaction mixture can provide the desired size of nanoparticles.

Polysaccharides are usually more stable than proteins thus nullifying the risk of irreversible denaturation. In addition, the cost-effective isolation and recovery of polysaccharides; and the occurrence of wide variations in physicochemical properties of carbohydrates make them advantageous and safe in the fabrication of nanoparticles.

3.7 Polymer-Based Biosynthesis

Polymeric compounds used for the biosynthesis of nanoparticles such as, poly (vinyl alcohol), poly (vinylpyrrolidone), poly (ethylene glycol), poly (methacrylic acid), and poly (methyl methacrylate) have been reported to be the effective protective agents used to stabilize NPs. The only shortcoming of this process is the use of different chemicals for reduction, stabilization, capping etc.

Polymers with ion-exchange capacity, containing phosphonic acid groups and possessing a low molecular weight can be used for the synthesis of nanoparticles. Co-polymers like beta-cyclodextrin, grafted onto graphene oxide or poly acrylic acid, which reduce and stabilize the silver ions can be used to formulate silver NPs using potassium per sulphate as the initiator. During the synthesis, the concentration of the alkali, silver nitrate, the co-polymer, temperature as well as the method of heating played an important role as deciding factors for the size of produced NPs. The polymer frequently used confined phosphonic acid groups and had low molecular weight. Co-polymers like cyclodextrin, grafted with poly acrylic acid, can be used to yield silver NPs using potassium per sulfate as the initiator.

Another polymer; poly (methyl vinyl etherco-maleic anhydride), was investigated to synthesize stable, spherical (10.2–13.7 nm), non-aggregating, face-centered cubic (FCC) nanoparticles with 5–8 nm polymer coating (Maity et al. 2011). The structure and size of NPs can be altered using different reducing and capping agents. For example, after heating at 70 °C for 30 min; Shervani et al. (2008) obtained large-sized (15–43 nm) spherical NPs; while at room temperature, they formulated small-sized particles of 8–24 nm diameter.

3.8 Tollens Method

Tollens method is a simple one-step technique for the synthesis of silver nanoparticles in which Tollens reagent ($Ag(NH_3)^{2+}$) is reduced by an aldehyde (Yin et al. 2002) or by saccharides. The reduction of Ag^+ by saccharides in the presence of ammonia can formulate diverse shapes of nanoparticles, such as hydrosols (20–50 nm) and films (50–200 nm). The size and morphology of NPs can be controlled by optimizing the concentration of ammonia and nature of reducing agent (glucose, galactose, maltose, and lactose etc.). Increase in the concentration of ammonia (0.005 M to 0.2 M) thus, generally results in a simultaneous and proportional augmentation in the particle size and polydispersity of nanoparticles (Kvítek et al. 2005). Thereafter, the synthesized nanoparticles can be stabilized and protected by various chemical agents; such as Poly Vinyl Pyrrolidone (PVP), Sodium Dodecyl Sulphate (SDS) and poly oxyethylene sorbitane monooleate (Tween 80).

4 Physical Methods of Synthesis of Silver Nanoparticles

4.1 Irradiation Method

Various irradiation methods are used to synthesize silver nanoparticles. Irradiating an aqueous solution of silver salt mixed with surfactant, with the help of laser and mercury lamp, can fabricate silver nanoparticles of a definite shape and size distribution (Eutis et al. 2005). Laser irradiation has also been used in photo-sensitization process of synthesizing silver nanoparticles using benzophenone or thiophene. The time of irradiation could control the size of the nanoparticles; resulting in silver NPs of about 20 nm when irradiated for a short duration; whereas the increased duration of irradiation produces nanoparticles of about 5 nm.

Silver nanoparticles have been synthesized by γ-ray irradiation of acetic water solutions containing $AgNO_3$ and chitosan (Chen et al. 2007). They showed that chitosan, an amino polysaccharide obtained from chitin, degrades into fragments when irradiated with γ-rays. The silver particles interact with NH_2 groups of the chitosan chain and get enveloped by the chitosan fragments. They synthesized particles with an average diameter of 4–5 nm which were densely dispersed in the solution; the size distribution of nanoparticles was affected by the irradiation dose.

4.2 Laser Ablation Method

Laser Ablation Synthesis in Solution (LASiS) is considered one of the best approaches to synthesize silver nanoparticles as compared to wet-chemical synthesis (Sportelli et al. 2018). They showed the preparation of stable Ag colloids in pure solvents without using either capping and stabilizing agents or reductants (Fig. 7). Moreover, the technique could achieve nanoparticles with different properties influencing their efficacy. On the other hand, LASiS can formulate low concentrations of AgNP colloids and cannot be used on an industrial scale. Nevertheless, Tsuji et al. (2017) synthesized silver nanoparticles using laser ablation of silver plates in the acetone–water mixed solution. They observed that after reducing the size of NPs by laser irradiation, spherical Ag nanoparticles spontaneously morphed into nanocubes after 1–14 days (Fig. 8).

Laser ablation can vaporize metallic bulk materials that cannot readily be evaporated in a liquid medium. The nature of produced silver nanoparticles is dependent on several factors; such as the wavelength of the laser, duration of the

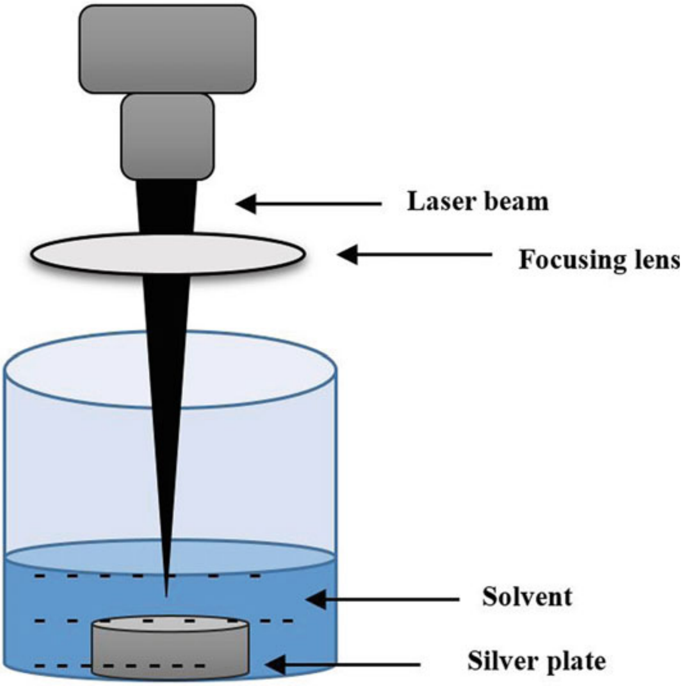

Fig. 7 Schematic representation of silver nanoparticles production with laser ablation in liquid medium [Self-Created]

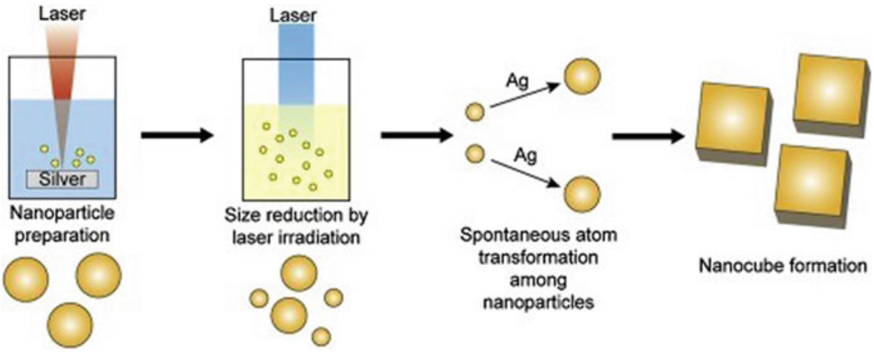

Fig. 8 Morphological changes from spherical silver nanoparticles to cubes after laser irradiation in acetone–water solutions. [Reproduced from Tsuji et al. (2017) with permission]

laser pulses (femtosecond, picosecond or nanosecond regime), ablation time duration, liquid medium and the presence of surfactant. Moreover, this technique is advantageous as it does not require chemical reducing agents and facilitates the production of pure and uncontaminated metal colloids.

4.3 Microwave-Assisted Synthesis

Microwave-assisted synthesis is a convenient and rapid method for the synthesis of silver nanoparticles. This technique is advantageous over others as a microwave can provide better and consistent heating yielding stable, uniformly dispersed and small-sized nanostructures, narrow size distribution and a high degree of crystallinity. Furthermore, microwave-assisted synthesis exhibits shorter reaction time, reduced consumption of energy and better yield preventing aggregation of particles (Nadagouda et al. 2011).

The size of the nanoparticles obtained by microwave-assisted method is regulated by the concentration of reducing agent and silver salt. The size and structure of NPs can also be controlled by varying concentration of solvents, surfactant polymers and temperature. Several reducing and stabilizing agents have been used to synthesize nanoparticles. The microwave irradiation of silver nitrate solution in ethanolic medium (ethanol acted as a reducing agent) using polyvinylpyrrolidone (PVP) as a stabilizer has formulated highly monodispersed, stable, polycrystalline, spherical with 10 ± 5 nm diameter silver nanoparticles within 5 s of microwave irradiation (Pal et al. 2009). Sodium alginate has been used as a stabilizer and reducer to obtain uniform and stable NPs which could be stored at room temperature for at least 6 months (Zhao et al. 2014). Starch has also been used as a template and reducing agent for the synthesis of silver NPs with an average size of 12 nm, using microwave-assisted synthetic method (Sreeram et al. 2008). Likewise, ethylene glycol and poly N-vinylpyrrolidone have been employed as respective reducing and stabilizing agents for synthesis of NPs resulting in NPs ranging from 62 to 78 nm in diameter (Katouki and Komarneni 2003).

4.4 High Energy Ball Milling Method

It is the simplest method to form nanoparticles in the powder form. Millers are of various shapes like planetary, rod, tumbler or vibratory. The ball mill system consists of one turn disc and two-four bowls. The turn disc rotates in one direction while the bowls rotate in the opposite direction. The centrifugal forces, created by the rotation of the bowl around its own axis along with the rotation of the turn disc, are applied to the powder mixture and milling balls in the bowl. The powder mixture is fractured and cold-welded under high energy impact. For example, it consists of a container filled with steel or tungsten carbide balls in which the source material is fed (2:1, Balls:Source material) in the form of flakes. Container may be filled with air or inert gas and rotated at high speed around a central axis (Fig. 9). As a result of high centrifugal force, the source material is forced towards the wall of the container and pressed against it. The size of the silver nanoparticles can be regulated by controlling the speed and duration of the rotation. The mechanical alloying process can be categorized into 4 stages.

Initial stage: The powder particles are flattened by the compressive forces created by the collision of the balls. The milling balls with high kinetic energy change the shapes of individual particles.

Intermediate stage: The mixture of the powder constituents decreases the diffusion distance to the micrometre range. Fracturing and cold welding are the major milling steps at this stage with non-homogeneity of the mixture.

Final stage: This stage results in the homogenous refinement, reduction in particle size and formation of true alloys.

Completion stage: The powder particles thus formed (real alloy) possess an extremely deformed metastable structure.

The major advantages of this method are it produces very fine powder (particle size less than or equal to 10 microns). It is also suitable for milling toxic and abrasive materials since it can be used in a completely enclosed form. On the other hand, contamination of product may occur as a result of wear and tear that may occur primarily from the balls and partially from the casing. It also produces high machine noise level in case of a hollow metal cylinder but much less if the rubber is used as machine material. Furthermore, it takes relatively long milling time and is difficult to clean the machine after use.

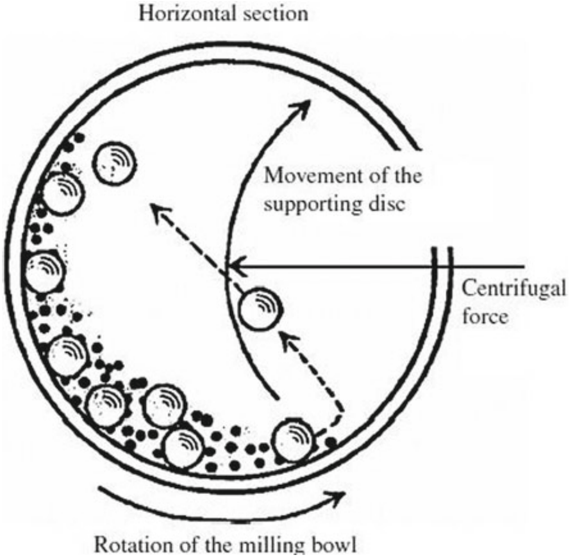

Fig. 9 Schematic view of motion of the ball and powder mixture. [Reproduced from Rajeshkanna and Nirmalkumar (2014) under the license (CC-BY 4.0)]

4.5 Melt Mixing Method

This is a technique to form nanoparticles in glass; an amorphous solid, lacking symmetric arrangement of atoms/molecules. Metals when cooled at very high cooling rates like 10^5–10^6 K/s, can form amorphous solids-metallic glasses. Formation of nanoparticles takes place on mixing molten streams of metals at high velocity with turbulence. They arrest the nanoparticles inside a glass. For example, a molten stream of Cu-B and a molten stream of Ti forms nanoparticles of Titanium boride (TiB_2).

4.6 Evaporation-Condensation Method

A few researchers have also synthesized silver nanoparticles by evaporation–condensation method. In this method, certain solids are heated and evaporated into background gases, followed by a reduction in the temperature leading to mixing the vapours with cold gases. The homogeneous nucleation is thus formed in the vicinity of the gas source and the clusters raise by gas-phase amalgamation of the source atoms. The average particle size of the formed nanoparticles can be increased by increasing gas pressure and the applied inert gas mass. The formation of the atom clusters is controlled by the evaporation rate, at which hot atoms lose their energy in the condensation region and the removal rate of the nucleated clusters from the supersaturation region. The evaporation-condensation process can be considered as a form of the distillation process which removes the volatile impurities and improves the purity of the material.

The above technique can be carried out using a tube furnace at atmospheric pressure where the source material within a boat centered at the furnace is vaporized into a carrier gas (Kruis et al. 2000). However, the generation of AgNPs using a tube furnace at atmospheric pressure has several negatives. A tube furnace occupies a huge area, requires a large amount of energy while increasing the temperature around the material, and also entails a lot of time to acquire thermal stability. In addition, a tube furnace needs a preheating time of several tens of minutes to attain a stable operating temperature and consumes more than several kilowatts of power (Kruis et al. 2000). It is also difficult to control composition in the case of synthesizing more complex materials and this process is restricted to materials possessing low melting points or high vapour pressures.

On the other hand, the evaporated vapor can be cooled at a suitable rapid rate by using small ceramic heaters as the temperature gradient in the vicinity of the heater surface is very steep. In this method, temperature of the heater surface remains almost constant and does not fluctuate with time which facilitates the stable generation of small spherical NPs without agglomeration in high concentrate ion.

A few important chemical, physical and photochemical methods for synthesizing and stabilizing silver nanoparticles have been summarized in Table 1.

Table 1 Some important chemical, physical and photochemical methods for synthesizing and stabilizing silver nanoparticles

Method	Silver precursor	Reducing agent	Stabilizing agent	Size (nm)
Chemical reduction	$AgNO_3$	DMF	–	<25
Chemical reduction	$AgNO_3$	$NaHB_4$	Surfactin (a lipopeptide biosurfactant)	3–28
Chemical reduction	$AgNO_3$	Trisodium citrate (initial) +SFS (secondary)	Trisodium citrate	<50
Chemical reduction	$AgNO_3$	Trisodium citrate	Trisodium citrate	30–60
Chemical reduction	$AgNO_3$	Ascorbic acid	–	200–650
Chemical reduction	$AgNO_3$	$NaHB_4$	DDA	~7
Chemical reduction	$AgNO_3$	Paraffin	Oleylamine	10–14
Chemical reduction (thermal)	$AgNO_3$	Dextrose	PVP	22 ± 4.7
Chemical reduction (thermal)	$AgNO_3$	Hydrazine	–	2–10
Chemical reduction (oxidation of glucose)	$AgNO_3$	Glucose	Gluconic acid	40–80
Chemical reduction (polyol process)	$AgNO_3$	Ethylene glycol	PVP	5–25
Chemical reduction (polyol process)	$AgNO_3$	Ethylene glycol	PVP	50–115
Chemical reduction (microemulsion)	$AgNO_3$	Hydrazine hydrate	AOT	2–5
Chemical reduction (microemulsion)	$AgNO_3$	Hydrazine hydrate	AOT	<1.6
Electrochemical (polyol process)	$AgNO_3$	Electrolysis cathode: titanium anode: Pt	PVP	~11
Chemical reduction (Tollen)	$AgNO_3$	m-Hydroxy benzaldehyde	SDS	15–260
Physical synthesis	Ag wires	Electrical arc discharge, water	–	~10
Physical synthesis	$AgNO_3$	Electrical arc discharge	Sodium citrate	14–27
Photochemical Reduction (pulse radiolysis)	$AgClO_4$	Ethylene glycol	–	17–70
Photochemical Reduction (microwave radiation)	$AgNO_3$	Ethylene glycol	PVP	5–10

(continued)

Table 1 (continued)

Method	Silver precursor	Reducing agent	Stabilizing agent	Size (nm)
Photochemical Reduction (photoreduction)	$AgNO_3$	UV light	–	4–10
Photochemical reduction (X-ray radiolysis)	Ag_2SO_4	X-ray	–	~28
Photochemical reduction (X-ray radiolysis)	$AgNO_3$	CMCTS, UV	CMCTS	2–8

DMF N,N'-dimethylformamide, *NaHB₄* Sodium borohydrate, *SFS* Sodium formaldehyde sulphoxylate, *DDA* Dodecanoic acid, *PVP* Polyvinyl pyrrolidone, *SDS* Sodium dodecyl sulphate, *AOT Bis*(2-ethylhexyl) sulfosuccinate, *CMCTS* Carboxymethylated chitosan

5 Green (Biological) Synthesis of Silver Nanoparticles

As discussed above, the most common method for the synthesis of nanoparticles is chemical reduction through which nanoparticles can be synthesized in bulk in a short span of time. However, as utilization of chemicals leads to non-eco-friendly byproducts, the green route of synthesis of NPs is preferred which is not only environment-friendly but is also cost-effective and can be easily scaled up for large scale synthesis of nanoparticles (Dhuper et al. 2012). In addition, non-requirement of high temperature, pressure, energy and toxic chemicals make the biological synthesis of NPs an upcoming and advocated process.

A wide variety of biological entities can be used for the synthesis of nanoparticles such as; algae, actinomycetes, bacteria, fungus, yeast, viruses and plants; each of which possesses different degrees of biochemical potential that can be efficiently used to synthesize specific metallic or metallic oxide nanoparticles. Nevertheless, all biological entities cannot synthesize nanoparticles depending upon the presence or absence of activities of their enzymes, reduction potential and other intrinsic metabolic processes.

Consequently, for the synthesis of nanoparticles with desired properties, adequate size and morphology, a careful selection of the appropriate biological entity is required. Mostly, biological entities with the potential to accumulate heavy metals provide a good opportunity for synthesizing metallic nanoparticles (Shah et al. 2015). Abundant literature is available regarding the biological synthesis of silver nanoparticles using microorganisms (bacteria and fungi) and plants due to their reducing or antioxidant properties responsible for the reduction of metal compounds in their corresponding nanoparticles.

5.1 Green Synthesis of Silver Nanoparticles Using Microorganisms

Utilisation of microorganisms is one of the most noticeable techniques to produce nanoparticles of desired characteristics. The survival ability of bacteria under difficult situations; i.e. in the presence of a high concentration of metals; is one of the significant factors to choose these organisms. These tolerance mechanisms of bacteria include chemical detoxification, alterations in solubility by changing redox potential of metal ions, energy-dependent efflux system, precipitation and failure in the transportation of special metal system. Nanoparticles synthesized by microbes have biological applications in the fields of bioremediation, bio-mineralization, bioleaching, and bio-corrosion. The biosynthetic methodology of microbe-mediated silver nanoparticles has been presented in Fig. 10.

It is well known that different microorganisms such as bacteria, fungi, yeast and alga are capable of adsorbing and accumulating metals. These biological agents secrete a large amount of enzymes, which have the potential to hydrolyze metals and result in the enzymatic reduction of metals ions. Keeping this in view, various microorganisms are extensively explored for the synthesis of NPs (Table 2). Microorganisms accumulate metal ions from the environment and convert them into the element metal using enzymes generated by cellular activities. The exact mechanism for the synthesis of nanoparticles by biological agents has not been confirmed yet as different biological agents employ different mechanisms and

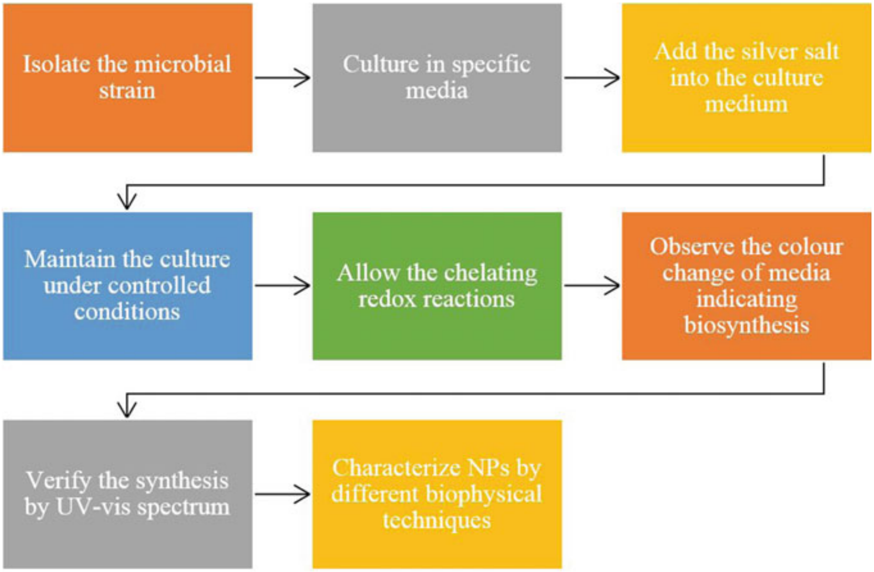

Fig. 10 Biosynthetic methodology of microbe-mediated silver nanoparticles [Self-Created]

different biomolecules response for the synthesis of nanoparticles. The mechanisms considered for the synthesis of nanoparticles include bioaccumulation, efflux system, variations in solubility and altered toxicity through oxidation-reduction, bio-absorption, extracellular complexion or precipitation of metals, and lack of specific metal transportation system (Beveridge et al. 1997).

Microorganisms can synthesize NPs intracellularly (within the cell) or extracellularly (outside the cell). In the intracellular method, metal ions are transported into the microbial cell and convert into NPs in the presence of enzymes. In contrast, the extracellular synthesis of NPs involves trapping of metal ions on the surface of the cells and reducing ions in the presence of enzymes. The presence of anionic functional groups; such as peptidoglycan, teichoic acids, lipoteichoic acids, proteins, and polysaccharides; in the cell wall of bacteria acts as the sites where silver cations are trapped and reduced resulting in the formation of AgNPs.

It has been observed that utilization of microwave irradiation in water, while carrying out bacterial synthesis of NPs, increases the rate of reaction and reduces the aggregation of the NPs (Saifuddin et al. 2009). They suggested that microwave radiations might have heated NPs evenly assisting the digestive ripening of particles without any aggregation. Marine algae like *Chaetoceros calcitrans*, *Chlorella salina*, *Isochrysis galbana* and *Tetraselmis gracilis* can also be used for the reduction of silver ions and thereby synthesis of Ag nanoparticles (Shahverdi et al. 2007). Marine cyanobacterium, *Oscillatoria willei* NTDM01 has also been used for the synthesis of silver NPs (100–200 nm).

The rapid synthesis of silver nanoparticles by utilizing culture of *Klebsiella pneumoniae*, *Escherichia coli* and *Enterobacter cloacae* has been carried out by the role of nitroreductase in bioreduction of Ag^+ (Shahverdi et al. 2007). Likewise, intracellular synthesis of 35–46 nm silver nanoparticles has been reported by using *Pseudomonas stutzeri* AG259 (Klaus et al. 1999). They also observed the formation of large-sized particles (up to 200 nm) when culture was supplemented with high concentrations of silver ions during culturing. Researchers have reported qualitative production of spherical silver NPs; single (25–50 nm) or in aggregates (100 nm); by *Lactobacillus* sp. without optimization (Korbekandi et al. 2012). Analysis by electron microscopy indicated formation of silver NPs not only on the cell membrane, but also inside the cytoplasm and outside the cells. Extracellular synthesis of 5–50 nm diameter AgNPs using *Fusarium oxysporum* were found to possess excellent stability may due to certain proteins (Ahmad et al. 2003). Further, the synthesis of NPs was ascribed to an enzymatic process involving NADH-dependent reductase and nitrate reductase (Kumar et al. 2007). The white rot fungus, *Phanerochaete chrysosporium* could also form silver nanoparticles which were of pyramidal/hexagonal shape and of different sizes (Vigneshwaran et al. 2006). Extracellular biosynthesis of spherical and stable silver NPs using *Aspergillus flavus*, *Aspergillus fumigatus* and *Cladosporium cladosporioides* has also been explored (Bhainsa and D'Souza 2006; Vigneshwaran et al. 2007; Balaji et al. 2009).

Table 2 Synthesis of silver nanoparticles using microorganisms

Microorganism	Size of nanoparticles (nm)	Mode of synthesis	References
Bacteria			
Staphylococcus aureus	160–180	Extracellular	Nanda and Saravanan (2009)
Bacillus aureus	4–5	Extracellular	Babu and Gunasekaran (2009)
Bacillus licheniformis	40	Extracellular	Kalishwaralal et al. (2008)
Bacillus subtilis	5–50	Extracellular	Saifuddin et al. (2009)
Lactobacillus casei	25–50	Extracellular	Korbekandi et al. (2012)
Pseudomonas sutzeri AG259	35–36	Intracellular	Slawson et al. (1992)
Rhodopseudomonas sp.	6–10	Extracellular	Manisha et al. (2014)
Bacillus megaterium	10–20	Extracellular	Prakash et al. (2010)
Bacillus cereus	10–30	Extracellular	Prakash et al. (2011)
Pseudomonas fluorescens	85.46 nm	Extracellular	Silambarasan and Jayanthi (2013)
Vibrio alginolyticus	50–100	Extracellular and intracellular	Rajeshkumar et al. (2013)
Pseudomonas aeruginosa	20–100	Extracellular	Jeevan et al. (2012)
Exiguobacterium mexicanum PR 10.6	5–40	Extracellular	Padman et al. (2014)
Fungi			
Verticillium	25 ± 12 nm	Intracellular	Mukherjee et al. (2001)
Aspergillus aureus	1–20	Extracellular	Li et al. (2011)
Bryophilous rhizoctoni	20–50	Extracellular	Raudabaugh et al. (2013)
Aspergillus flavus	8.92 ± 1.61	Extracellular	Vigneshwaran et al. (2007)
Pleurotus ostreatus	8–50	Extracellular	Devika et al. (2012)
Fusarium oxysporum	5–50	Extracellular	Ahmad et al. (2003)
Fusarium acuminatum EII	5–40	Extracellular	Ingle et al. (2008)
Aspergillus fumigatus	5–25	Extracellular	Bhainsa and D’Souza (2006)
Trichoderma reseei	5–50	Extracellular	Vahabi et al. (2011)
Yeast and Actinomycetes			
MKY3	2–5	Extracellular	Kowshik et al. (2002)
Cryptococcus laurentii		Extracellular	Fernández et al. (2016)

Several physical and chemical factors such as optimum metal ion concentration, pH and the temperature of the reaction mixture, influence the shape and size of nanoparticles (Marooufpour et al. 2019).

Concentration: The rise in the concentration of silver ions (from 1 to 5 mM) in reaction mixture results in the formation of NPs with large size and their aggregation hinder the availability of silver ions and functional group; while at lower concentration (such as 1 mM) the nanoparticle synthesis and size reduction start quickly due to the availability of more functional groups in the mixture.

pH: Alkaline pH is considered suitable for the synthesis of nanoparticles with maximum production of silver nanoparticles.

Temperature: Temperature is one of the important physical parameters for synthesis of nanoparticles. Low temperature conditions result in the fabrication of large-sized nanoparticles whereas, high temperature synthesizes the comparatively small-sized nanoparticles. Hence, a higher temperature is considered optimum for nanoparticle synthesis.

Time: The increase in the reaction time increases the absorbance resulting in the rise in concentration of AgNPs.

5.2 Green Synthesis of Silver Nanoparticles Using Plants

Amongst the biological methods of silver nanoparticle synthesis, utilization of plant extracts is potentially advantageous over microorganisms because of ease of improvement, less biohazard, no culturing cost and no requirements of highly aseptic conditions and their maintenance (Kalishwaralal et al. 2010). Furthermore, plant-based biosynthesis is a relatively straightforward method that can be simply scaled up for large-scale production of nanoparticles. These factors stimulated attention for the acceptance of a clean, benign, reliable, biologically compatible, and environment-friendly green approach to synthesize nanoparticles.

The utilization of plants as reducing agents for the synthesis of silver nanoparticles has drawn much attention nowadays, because it is a single step technique which is facile, environment-friendly, non-pathogenic and cost-effective. Plant-mediated synthesis of AgNPs allows advancement over chemical and physical methods, and can be easily scaled up for large-scale synthesis (Rajeshkumar and Bharath 2017). The major advantage of opting green route for the synthesis of silver nanoparticles is that it does not require additional chemicals to stabilize the nano-mixture as the reduction and stabilization of silver ions is governed by the combination of biomolecules that are already present in the plant extracts. These biomolecules include amino acids, enzymes, proteins, polysaccharides, vitamins; and various secondary metabolites such as tannins, phenolics, saponins, terpenoids, alkaloids etc.

Different parts of plants; such as leaves, stem, root, seed, fruit, callus, peel, and flower are explored for the synthesis of metallic nanoparticles in various shapes and sizes using different biological approaches (Kuppusamy et al. 2016). A large number of plants reported to facilitate silver nanoparticles synthesis are presented in the Table 3.

Extracts prepared from plants; such as lemongrass (*Cymbopogon flexuosus*), alfalfa (*Medicago sativa*) and geranium (*Pelargonium graveolens*) have been used as successful reactants in the manufacture of silver nanoparticles (Kesharwani et al. 2009). The biomolecules present in the extracts of *Camellia sinensis* (green tea), *Citrus sinensis* and *Datura metel* such as caffeine, flavonoids, alkaloids and polyphenols, amino acids and polysaccharides, etc. have served as reducing agents and stabilizers during the formation of various shapes of AgNPs (Vilchis-Nestor et al. 2008; Begum et al. 2009; Kesharwani et al. 2009).

Similarly, leaf extracts from *Nelumbo nucifera* could reduce silver ions and produce different shapes of silver NPs of 45 nm diameter (Santhoshkumar et al. 2010); whereas leaf extract of *Euphorbia hirta* produced spherical silver NPs of 40–50 nm diameter (Elumalai et al. 2010). Prasad and Elumalai (2011) obtained silver NPs of 57 nm diameter by using *Moringa oleifera* leaf extract combined with 1 mM $AgNO_3$ solution. *Ocimum sanctum* leaf extract was used to form crystalline AgNPs (4–30 nm) within 8 min of reaction time (Singhal et al. 2011). They revealed that ascorbic acid present in *O. sanctum* leaves assisted in the reduction of silver ions, while proteins acted as capping agents increasing their stability. Reducing sugars and flavonoids present in *Cacumen platycladi* extract played a significant role in the reduction of silver ions resulting in the formation of silver nanoparticles of 18.4 ± 4.6 nm diameter and narrow size distribution (Huang et al. 2011). The extract prepared from the bark of *Cinnamon zeylanicum* was found to be successful in the biosynthesis of 31–40 nm cubic/hexagonal silver nanocrystals (Sathishkumar et al. 2009).

5.3 Biosynthetic Methodology of Plant-Mediated Silver Nanoparticles

Plant-mediated silver nanoparticles are synthesized based on the following methodology though optimization of the procedure is essential based on the type of plant, desired size of NPs and other characteristics required.

1. *Collection of the Plant of Interest*: The desired plants can be collected from the available sites. The collected plant parts should be examined for any disease spots or infection, epiphytes and necrotic plants that can be removed. The selected parts then are washed thoroughly twice/thrice under running tap water to clean dirt or any other trapped particles if any, followed by thorough cleaning with distilled water. These selected, clean and fresh sources of NPs can be used

Table 3 Utilization of different plant species for the synthesis of silver nanoparticles

Plant	Size (nm)	Shape	References
Abutilon indicum	7–17	Spherical	Mariselvam et al. (2014)
Acalypha indica	0.5	–	Kumarasamyraja and Jeganathan (2013)
Acorus calamus	31.83	Spherical	Nakkala et al. (2014a)
Acalypha indica	20–30	Spherical	Krishnaraj et al. (2010)
Achyranthes aspera	1–30	Spherical	Sharma et al. (2017)
Aloe vera	50–350	Spherical, triangular	Chandran et al. (2006)
Alternanthera dentate	50–100	Spherical	Kumar et al. (2014)
Allium sativum	4–22	Spherical	Ahamed et al. (2011)
Argyreia nervosa	20–50	–	Thombre et al. (2014)
Boerhaavia diffusa	25	Spherical	Nakkala et al. (2014b)
Brassica rapa	16.4	–	Narayanan and Park (2014)
Camelia sinensis	30–40	Spherical, triangular, irregular	Vilchis-Nestor et al. (2008)
Carissa carandas	25–50	Spherical	Govindarajan and Benelli (2016)
Citrullus colocynthis	31	Spherical	Satyavani et al. (2011)
Cocos nucifera	24	Spherical	Roopan et al. (2013)
Couroupita guianensis	10–45	Cubic	Vimala et al. (2015)
Cocous nucifera	22	Spherical	Mariselvam et al. (2014)
Calotropis procera	19–45	Spherical	Gondwal and Pant (2013)
Centella asiatica	30–50	Spheupregulate or downregulaterical	Rout et al. (2013)
Coccinia indica	10–20	–	Kumar et al. (2013)
Cymbopogan citratus	32	–	Geetha et al. (2014)
Carica papaya	25–50	–	Jain et al. (2009)
Citrus sinensis	10–35	Spherical	Kaviya et al. (2011)
Delphinium denudatum	< 85	Spherical	Suresh et al. (2014)
Datura metel	16–40	Quasilinear superstructures	Kesharwani et al. (2009)
Eclipta prostrate	35–60	Triangular, pentagonal, hexagonal	Rajakumar and Rahuman (2011)
Eucalyptus hybrid	50–150	–	Dubey et al. (2009)
Eucalyptus macrocarpa	10–100	Spherical, cube	Poinern et al. (2013)
Ficus carica	13	–	Ulug et al. (2015)
Garcinia mangostana	35	–	Veerasamy et al. (2010)
Musa paradisiacal	20	–	Bankar et al. (2010)

(continued)

Table 3 (continued)

Plant	Size (nm)	Shape	References
Moringa oleifera	57	–	Prasad and Elumalai (2011)
Memecylon edule	20–50	Triangular, circular, hexagonal	Elavazhagan and Arunachalam (2011)
Mangifera indica	20	Spherical, triangular, hexagonal	Philip (2011)
Melia dubia	35	Spherical	Kathiravan et al. (2014)
Nelumbo nucifera	25–80	Spherical, triangular, decahedral	Santhoshkumar et al. 2010
Psoralea corylifolia	100–110	–	Sunita et al. (2014)
Premna herbacea	10–30	Spherical	Kumar et al. (2013)
Portulaca oleracea	<60	–	Firdhouse and Lalitha (2012)
Pogostemon benghalensis	>80	–	Gogoi (2013)
Rhododendron dauricum	25–40	Spherical	Mittal et al. (2012)
Rizophora mucronata	60–95	Spherical	Gnanadesigan et al. (2011)
Swietenia mahogani	50	–	Mondal et al. (2011)
Tea extract	20–90	Spherical	Suna et al. (2014)
Tribulus terrestris	16–28	Spherical	Gopinath et al. (2015)
Trachyspermum ammi	87, 99.8	–	Vijayaraghavan et al. (2012)
Thevetia peruviana	10–30	Spherical	Rupiasih et al. (2013)
Vitis vinifera	30–40	–	Gnanajobitha et al. (2013)
Vitex negundo	5 and 10–30	Spherical and fcc	Zargar et al. (2011)
Ziziphora tenuior	8–40	Spherical	Sadeghi et al. (2015)

fresh or can be shade-dried at room temperature (27 ± 2 °C) for about 2–3 weeks until they dry completely.

2. *Preparation of Plant Extracts*: The plant extracts can be made by following hot percolation method. In the case of fresh plant material, around 10 g of fresh plant part is cut into small pieces, while if extracts are made from dried plant material, the plant parts can be powdered using a domestic electric blender. Thereafter, the plant material is boiled in 100 mL of distilled water at 60 °C in a water bath for about 15–20 min with intermittent manual agitation to ensure homogeneity of plant extract solution. After boiling, the plant extract solutions is left undisturbed for about 2–3 h and then filtered using muslin cloth followed by filtration through Whatman No. 1 filter paper disc (125 mm) to eliminate

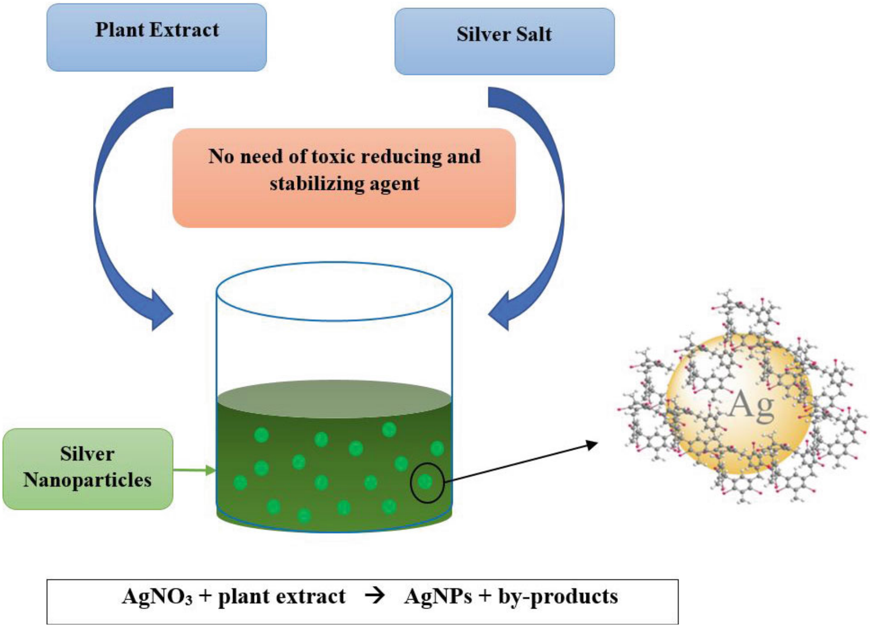

Fig. 11 One pot green synthesis of silver nanoparticles using plant extracts [Self-Created]

particulate matter. A clear plant extract formed, then can be stored in amber colored culture tubes at 4 °C for further use.

3. *Biosynthesis of Silver Nanoparticles*: Biosynthesis of silver nanoparticles can be carried out by simple addition of a few mL of freshly prepared plant extract to 10 mL of silver salt solution (Silver nitrate; $AgNO_3$). The volume of plant extract and concentration of silver nitrate (1–10 mM) solution needs to be optimized by screening various combinations, which can be achieved by varying the volume of plant extract in extract-silver salt mixture (Fig. 11). The reduction of pure Ag(I) ions to Ag(0) can be monitored by measuring the UV–visible spectra of the solution at regular intervals.

5.4 Factors Affecting Synthesis of Plant-Mediated Silver Nanoparticles

The composite mixture of plant extract and silver salt should be provided controlled conditions of concentration, reaction time, temperature and pH to synthesize the silver nanoparticles.

1. *Effect of concentrations and volume (plant extract: silver salt)*: For the green synthesis of silver nanoparticles, both variables; the volume of plant extract and concentration of silver salt; need to be optimized by screening different ratios. The volume of the biological source should be screened first. Observations can be made by recording change in colour (primary indicator) and through UV–vis scan in order to see whether the synthesis of nanoparticles is successful or not. A slight change in volume can upregulate or downregulate the green synthesis process of silver nanoparticles (Sharma et al. 2017).

The synthesis of silver nanoparticles has been attempted using aqueous leaf extract of *Thevetia peruviana* Juss (Oluwaniyi et al. 2016). Figure 12a shows the spectral scans obtained at varying silver ion concentration. The reaction was carried out at the optimum temperature of 30 °C and time (30 min). The intensity was found to be increased with increasing concentration of silver ion with the SPR peak for all the different concentrations at 460 nm.

They also fabricated nanoparticles by varying volume ratios of 1 mM silver nitrate to *T. peruviana* aqueous leaf extract (ranging from 4:1, 3:2, 2:3 and 1:4). From the UV–Vis spectrum (Fig. 12b), it was observed that with 4:1 ratio of 1 mM silver nitrate and leaf extract of *T. peruviana,* the extract bio-reduced and stabilized the nanoparticles with the plasmon resonance at 460 nm. Other volume ratios, 3:2, 2:3 and 1:4 were failed to produce distinct characteristics SPR for silver nanoparticles at the visible region of the UV–Vis spectrum. Therefore, it is important to screen different ratios of plant extracts and silver salts for the optimum synthesis of nanoparticles.

Effect of contact time at room temperature: The time factor plays a very important role in order to understand the rate of synthesis of silver nanoparticles. The duration and incubation of the synthesis reaction mixture determine the rate of

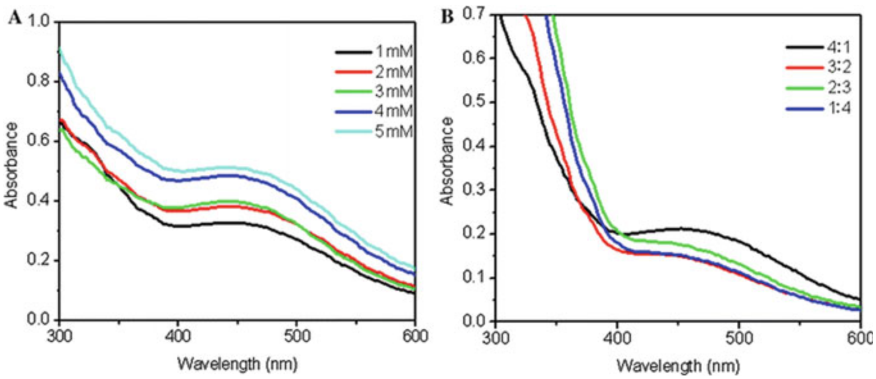

Fig. 12 The UV–vis absorption spectra for silver nanoparticles synthesized using aqueous leaf extract of *Thevetia peruviana* Juss at different (A) concentrations and (B) volume ratio at 30 °C for 30 min. [Reproduced from Oluwaniyi et al. (2016) under the license (CC-BY 4.0)]

the silver nanoparticles synthesis. The duration of contact between the silver salt and the reducing agent may vary as per the source of the plant used.

The rate of synthesis of silver nanoparticles from plant extracts can be monitored through UV–vis spectroscopy (Fig. 13). The primary indication of synthesis of nanoparticles is marked by the change in colour of the reaction mixture within few minutes of reaction time. Generally, during the formation of silver nanoparticles, the colour changes from pale yellow or green to light brown followed by deep brown within 10–15 min of contact. Initial hours of UV–vis scans show broad peaks with much lower absorbance. As the reaction time between Ag^+ and the reducing agent in the extract increases, a gradual increase in the intensity of the Surface Plasmon Resonance (SPR) peak can be observed.

The optimum time span required for reduction of silver ions range from 24 to 48 h (Chandran et al. 2006; Lin et al. 2010; Khalil et al. 2014). If the synthesis of AgNPs takes longer incubation time of about one week, the nanoparticles show better stability and are without aggregation with a slight decrease in the absorbance (Dipankar and Murugan 2012; Bindhu and Umadevi 2013; Khalil et al. 2014).

2. *Effect of temperature*: The plant-mediated synthesis of silver nanoparticles is generally temperature-dependent which may vary from plant to plant. Some plant extracts exhibit the ability to reduce the silver salt at room temperature while some may require a certain degree of heat of activation. Higher temperature, if provided to the composite mixture, can increase the reduction rate of silver salt by the plant extract. The AgNPs synthesized from olive leaf extract at different temperatures displayed increased absorbance with an increase in temperature (Fig. 14) (Khalil et al. 2014). They concluded that increasing the reaction temperature reduces Ag^+ ions rapidly and leads to the consequent homogeneous nucleation faster resulting in the formation of small-sized AgNPs.

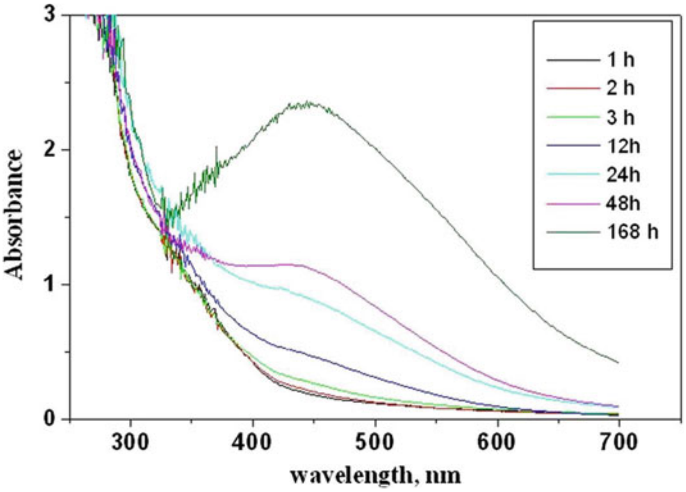

Fig. 13 UV–visible spectra of silver nanoparticles as a function of time at room temperature. [Reproduced from Khalil et al. (2014) with permission]

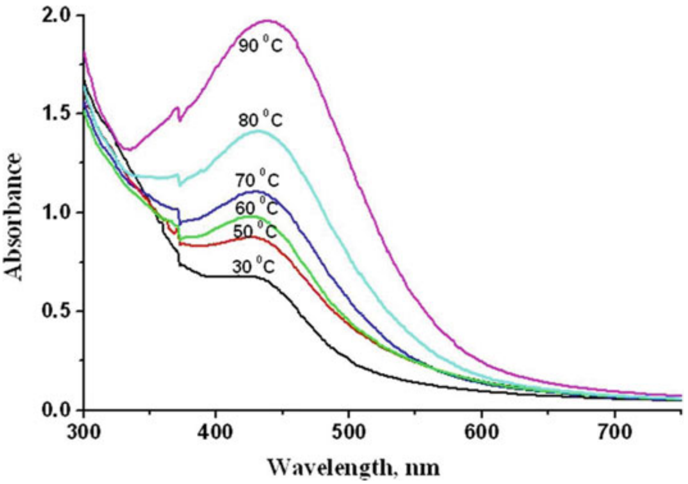

Fig. 14 UV–vis spectra of AgNPs as a function of temperature. [Reproduced from Khalil et al. (2014) with permission]

3. *Effect of pH*: Just like temperature, pH also has a considerable effect on the synthesis of nanoparticles. The shape and size of biosynthesized nanoparticles can be regulated by altering pH of the nano-reaction mixtures. The particle size of the AgNPs is expected to be larger in the acidic medium while smaller in the basic medium. The alkaline pH of the reaction mixture provides optimum conditions enhancing the reducing and stabilizing capability of biomolecules resulting in rapid synthesis of silver nanoparticles.

Figure 15 depicts the effect of pH on the synthesis of silver nanoparticles from olive leaf extract. The absorbance of the silver nanoparticle synthesis medium increases with the rise in pH. The absorption band possesses a narrow peak and shifts towards the shorter wavelength. The figure clearly shows that low absorbance at lower pH (2–5) indicate a lower rate of synthesis, while a moderate synthesis at pH 6 to 7 and rapid synthesis at the pH ranging from 7 to 8. It is significant to note that the synthesis of Ag nanoparticles downregulates when the pH of the synthesis medium reaches at/around 10 or above.

It has been advocated that pH of the reaction mixture can influence the electrical charges of the biomolecules which affect capping and stabilizing capabilities of biomolecules impacting the growth of nanoparticles (Khalil et al. 2014).

5.5 Mechanism of Plant-Mediated Synthesis of Silver Nanoparticles

The chief mechanism involved in the plant-mediated synthesis of silver nanoparticles is plant-assisted reduction due to the presence of various phytochemicals;

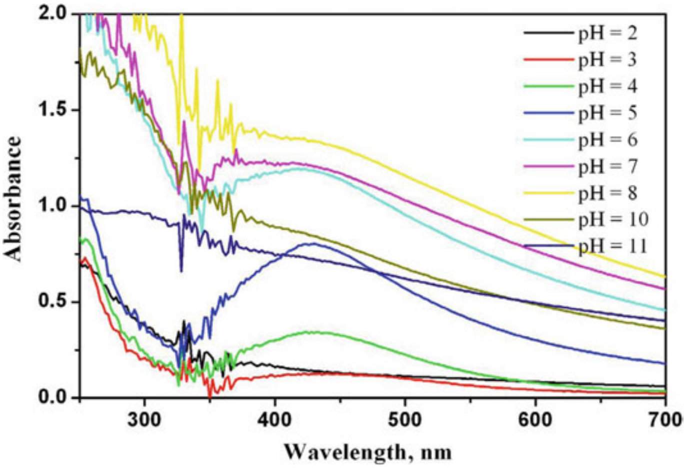

Fig. 15 Effect of pH on the formation of AgNPs from olive leaf extract at room temperature. [Reproduced from Khalil et al. (2014) with permission]

such as ketones, terpenoids, amides, flavones, carboxylic acids and aldehydes, etc. (Khatoon et al. 2017). Water-soluble phytochemicals; organic acids, quinones and flavones; are responsible for the rapid reduction of the Ag^+ in the reaction mixture (Jha et al. 2009). It is believed that due to the electrostatic interactions between the silver ions and proteins present in the plant extract, Ag^+ is trapped on the protein surface. Proteins reduce these ions, cause a change in the secondary structure which lead to the formation of silver nuclei. Further reduction of Ag^+ leads to the formation of more silver nuclei and their build-up results in the formation of silver nanoparticles (Fig. 16) (Iravani et al. 2014).

A schematic diagram showing the silver ion reduction, agglomeration and stabilization to form a particle of nano size is presented in Fig. 17 (Srikar et al. 2016).

A large number of organic biomolecules; such as flavonoids, terpenoids, alkaloids, phenols, gum, carbohydrate, fat, proteins, enzymes and coenzymes, etc.; act as both reducing and stabilizing agents; and donate electron resulting in the reduction of Ag^+ to Ag^0. The dual role of phytoconstituents facilitates the reaction and use of a large number of chemicals is not needed as required in chemical reduction methods. However, the bioactive phytoconstituent, responsible for silver ion reduction, varies based on the explored plant species/extract.

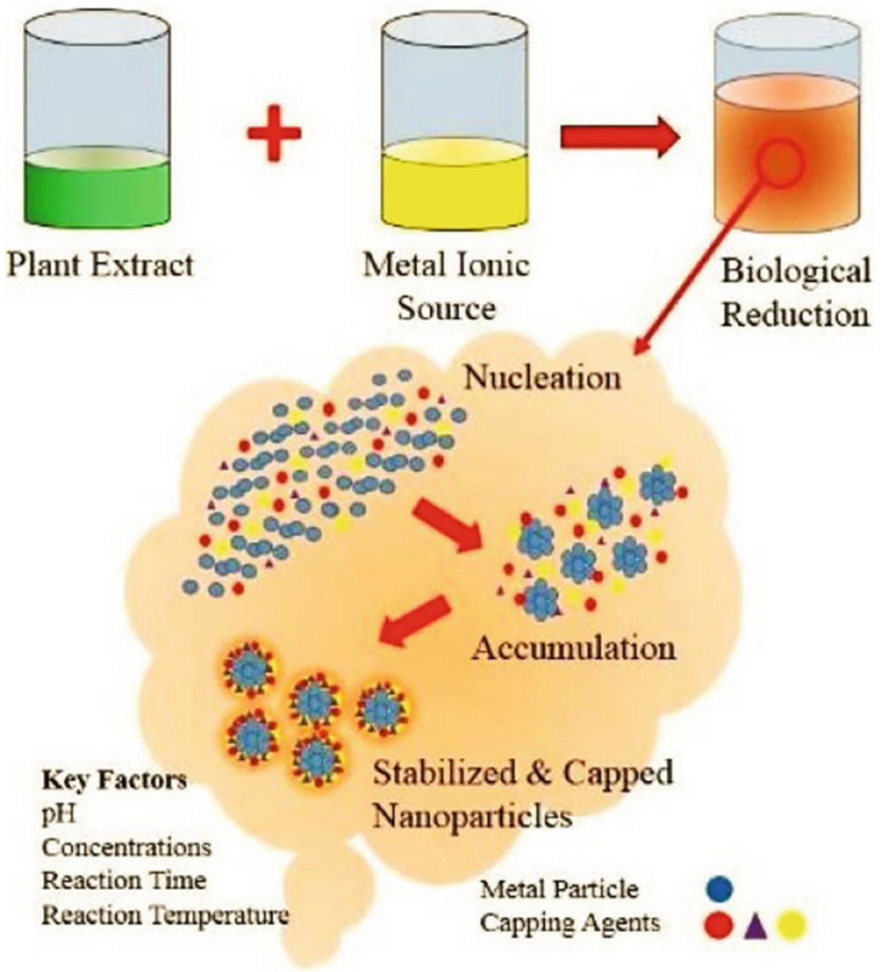

Fig. 16 Biological synthesis of silver nano-composites using plant extract. [Reproduced from Shah et al. (2015) under the license (CC-BY 4.0)]

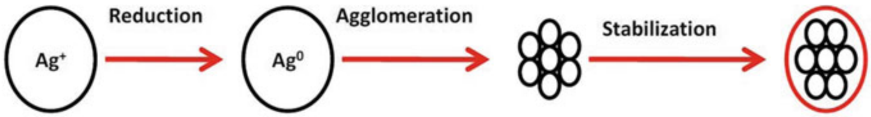

Fig. 17 Synthesis mechanism of AgNCs. [Reproduced from Srikar et al. (2016) under the license (CC-BY 4.0)]

6 Conclusion

Silver nanoparticles have drawn the attention of researchers because of their unique properties, and applications in diverse areas. Various chemical, physical and biological synthetic methods have been explored to synthesize silver nanoparticles of various shapes, sizes, and stability. A few such methods include irradiation, laser ablation, chemical reduction, photochemical methods and synthetic methods using microbes and plants. Most of these techniques are still under investigation to optimize the structure, size, shape, stability and aggregation of nanoparticles. Selection of reducing agent, stabilizer, solvent medium, temperature, etc. are a few regulatory factors to decide the particle size and morphology of silver nanoparticles.

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Physical and Chemical Modification of Silver Nano Particles

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Abstract Silver Nano Particles (AgNPs), as a class of nanomaterials, exhibit many unique properties such as small size effect, surface effect, and dielectric confined effect similar to other types of nanomaterials (Chakravorty and Giri in Chemistry for the 21st Century, “Chemistry of Advanced Materials”, Oxford Blackwell Scientific Publication, London 1993). Thanks to these unique effects, nanoparticles are significantly different from macroscopic bulk materials in microscopic and macroscopic properties such as catalysis, electromagnetism, optics, thermology, and superconductivity. Therefore, like other types of nanomaterials, AgNPs has also been widely applied in many fields including biomedicine, aerospace, industry and agriculture.

1 Introduction

Silver Nano Particles (AgNPs), as a class of nanomaterials, exhibit many unique properties such as small size effect, surface effect, and dielectric confined effect similar to other types of nanomaterials (Chakravorty and Giri 1993). Thanks to these unique effects, nanoparticles are significantly different from macroscopic bulk materials in microscopic and macroscopic properties such as catalysis, electromagnetism, optics, thermology, and superconductivity. Therefore, like other types of nanomaterials, AgNPs has also been widely applied in many fields including biomedicine, aerospace, industry and agriculture.

Nevertheless, the application of AgNPs is still limited by some objective problems. On the one hand, due to the small particle size, large specific surface area, high surface energy, abundant surface atoms and insufficient atomic coordination of the nanoparticles, the surface atoms are highly active and extremely unstable. Nanoparticles are prone to agglomeration or adsorption with other sub-

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stances during preparation, storage, and use. On the other hand, the application of AgNPs in the fields of catalysis, environmental protection, microelectronics, biomedicine and chemical engineering requires specific surface physicochemical properties and functions. Therefore, in order to obtain stable AgNPs with specific physicochemical properties, it is necessary to carry out reasonable surface modification in the process of preparing or dispersing nanoparticles, that is, to change the surface structure and state of the nanoparticles by physical or chemical methods.

The surface modification of nanoparticles refers to treatment, modification and processing of the surface of nanoparticles by physical and chemical deep processing methods. Thus, controlling the internal stress, increasing the repulsive force between the nanoparticles, reducing the gravitation between the nanoparticles, and purposefully making change in surface physical and chemical properties. The treatment of nanoparticles such as altering the morphology, crystal structure, defect state, stress state, surface functional group, surface hydrophobicity, surface wettability, surface potential, surface adsorption and reaction characteristics, etc. are commonly employed for the surface modification of nanoparticles. The science and technology gives new functions to nanoparticles and meets the needs of nanoparticles processing and application (Kang et al. 2019).

After surface modification of nanoparticles, a series of properties such as adsorption, wetting and dispersion will change due to the changes in surface properties. Through surface modification, some new properties can be achieved: ① Improve or change the dispersion of nanoparticles, ② Improve the surface activity of nanoparticles, ③ Create new physical, chemical, and mechanical properties on the surface of the nanoparticles, ④ Improve the compatibility between nanoparticles and other substances. Based on that information, reasonable surface modification is essential for the widely application of AgNPs.

Due to the high requirements and high standards of practical applications and the development of nanoscience research, the physical and chemical modification methods of AgNPs have been greatly developed and are becoming more advanced. This chapter mainly introduces the surface modification of AgNPs, including physical modification method, chemical modification method and surface modifiers of AgNPs, and the problems and solutions for modification of AgNPs also are presented shallowly.

2 Problem Statements and Solutions for Chemical and Physical Modification of AgNPs

The particle size of AgNPs is mostly between 1 and 100 nm, and most of the atoms are at the surface of the particles with a large surface area, so they have special surface properties as follows:

(1) The crystal field environment and binding energy of the surface atoms are different from the internal atoms. There are many unsaturated bonds and many active centers. They have high chemical activity and are easy to combine with other atoms to stabilize.

(2) Nanoparticles have a large surface Gibbs free energy and are thermodynamically unstable systems. Therefore, the nanoparticles can spontaneously agglomerate, oxidize or surface adsorb to reduce the number of unstable atoms on the surface and reduce the energy of the system.
(3) Surface electron effect. During the nanocrystallization process, a large amount of positive or negative charges accumulate on the surface of the nanoparticles. These charged particles are extremely unstable. In order to stabilize, they attract each other and agglomerate the particles. The main force is the electrostatic Coulomb force.
(4) Proximity effect. When the size of nanoparticles decreases to a certain particle size or less, the distance between the particles is extremely short. Then the van der Waals force between the particles is much larger than the gravity of the particles themselves, and the particles tend to attract each other and agglomerate.

These characteristics of nanoparticles also provide the possibility of surface modification. The surface modification of nanoparticles mainly includes three aspects:

① studying the surface characteristics of the nanoparticles in order to modify them in a targeted manner,
② using the above results to analyze and evaluate the surface characteristics of the particles,
③ determine the type of surface modifier and the treatment process.

The principle of surface modifier selection is to reduce the surface energy state of the particles and eliminate the surface charge and surface gravity of the particles. Considering the properties of AgNPs, the surface modification mainly starts from these aspects:

(1) Improve the dispersibility of AgNPs and protect nanoparticles. The surface modifier is grafted onto the surface of the AgNPs, and a coating layer is formed on the surface to change the charge distribution on the surface of the nanoparticles and prevent agglomeration and oxidation.
(2) Improve the surface activity of the AgNPs. By modification, the surface of the nanoparticles is provided with a large amount of active groups. Thereby greatly improving the reactivity of the AgNPs with other reagents, and creating conditions for further modification of the AgNPs.
(3) The selection of suitable modifiers: the suitable modifier is selected to achieve a good wetting state of the AgNPs and the dispersion medium, and improve the compatibility between the nanoparticles and the dispersion medium.
(4) In some cases, the modifier has both the function of stabilizing and functionalizing nanoparticles. According to the specific requirement of different application, suitable modifiers should be selected to meet the requirements of sensing, analysis and other applications. Surface modification of AgNPs has been systematically studied for many years, and a variety of surface modifiers with different functional groups have been used to stabilize and functionalize AgNPs (Olenin and Lisichkin 2018). The surface modification methods of

AgNPs can be divided into the physical modification and chemical modification. The surface modifiers, physical modifications, and chemical modification methods of AgNPs are described in detail below.

3 Surface Modifiers Used for AgNPs

The synthesis of AgNPs has been thoroughly and systematically studied for years, and surface modifiers are becoming more and more abundant. Similar to other metal nanoparticles, AgNPs also have excess surface energy and cannot exist in the "bare" form. Therefore, the AgNPs are surrounded by dispersion medium molecules or additionally added stabilizers (primarily surfactants). This type of stabilizer is based on the principle of steric effect and is used to reduce the excess surface energy of nanoparticles regardless of surface interactions between AgNPs and stabilizers. Such stabilizers can form a protective layer on the surface of AgNPs through absorption, coating or deposition, etc. Another kind of stabilizer depends on the strong chemical bonds between stabilizers and the nanoparticles surface, which also are named surface modifiers. In this case, the ligands are charged species, such as molecules containing amino or carboxyl groups, which produce a double electric layer and induce the coulombic repulsions among nanoparticles. Here, the stabilizers, surfactants, chemical modifiers, etc. are collectively referred to as modifiers. In addition, the surface modifiers will be introduced from the following aspects including chemical modifiers, surfactants, and biomolecules stabilizers that involve organic molecules, polymers, and DNA.

3.1 Conventional Organic Molecule Modifiers

Liquid phase synthesis is the most used method way to obtain various shapes and size AgNPs with monodispersity (Homola et al. 1999). In all kinds of liquid-phase synthesis methods, the chemical modifiers must be present not only to control the size and morphology and prevent aggregation but also to functionalize the surface of AgNPs for further application. The liquid phase preparation of AgNPs generally requires three chemical functional compounds: a silver precursor, reducing/stabilizing agent and solvent, and a reducing/stabilizing agent. Surface chemical modified nanoparticles usually contain several fragments: binding group, linker, and surface functional group. The synthesis of AgNPs by using citrate as a reductant and stabilizer in water was first reported in 1982 (Lee and Meisel 1982). From then, lots of modifiers with different binding groups were researched to stabilize and functionalize the AgNPs via direct interaction of the surface silver atoms with the anchor group of the modifier. These binding groups of modifiers all possess a high affinity for silver atom, manly including carboxyl (–COOH), amino (–NH_2), thiol (–SH), sulfide (–S–), and disulfide (–S–S–). The structures of several common chemical modifiers are listed in Fig. 1.

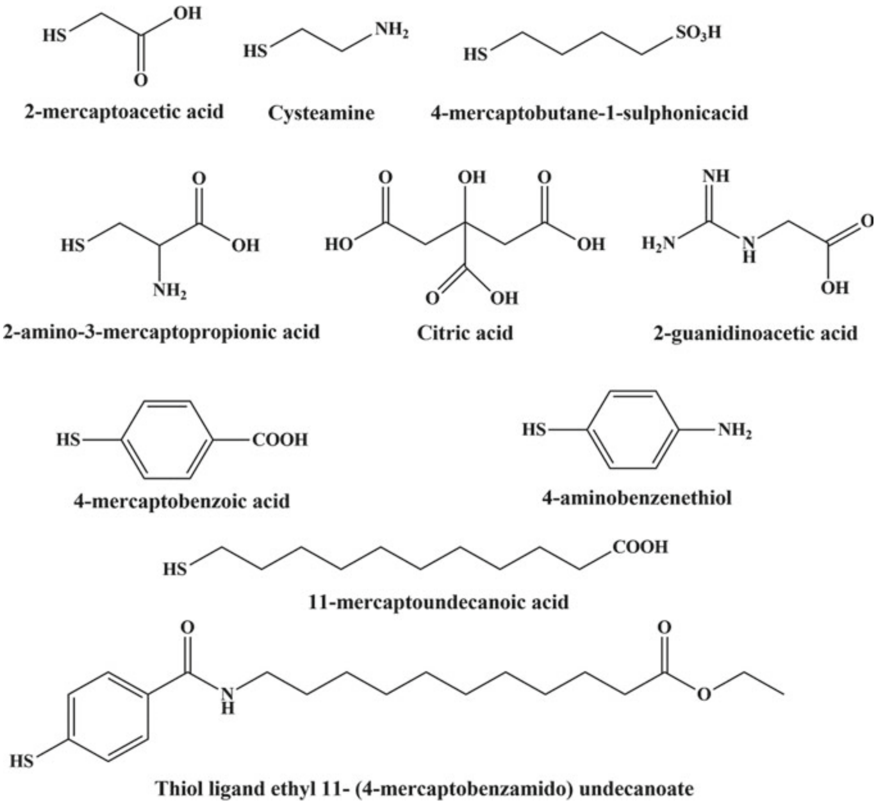


Fig. 1 Examples of modifiers used for coating AgNPs

Surfactants can not only adsorb on the surface of AgNPs to prevent the aggregation of nanoparticles but also can regulate the particle size and morphology of nanoparticles in the synthesis process of nanoparticles. Up to now, some organic molecule surfactants were used for improving the stability of AgNPs, changing the surface properties, and controlling the stereochemical structure of AgNPs, such as sodium dodecyl sulfonate, sodium sulfosuccinate (anionic surfactants), and cetyl trimethyl ammonium bromide (CTAB, cationic surfactant). According to the research results of Zaheer and Aazam (2017), the position of the surface plasmon resonance band strongly depends on CTAB (cetyl trimethyl ammonium bromide). The intensity and position of the absorption band can be tuned by changing CTAB. CTAB plays a vital role in the synthesis of stable, perfect transparent yellow color AgNPs at room temperature.

3.2 Polymers

A series of polymers also are used as the surface modifiers of AgNPs. Among them, the most widely used is polyethylene glycol (PEG) and polyvinyl pyrrolidone (PVP). PEG is the most utilized polymer to improve the biocompatibility of AgNPs. In many biomedical or therapeutic applications that AgNPs need to be dispersed in complicated media, the surface of AgNPs should be modified by thiolated-PEG ligands through strong metal-S bonds to stabilize and exploit the properties of AgNPs effectively. Pandian et al. (2019) have reported that the synthesis and modification of AgNPs by using Sesbania aegyptiaca leaf extract and PEG, respectively. PEG was to improve the stability and biocompatibility of AgNPs. The toxic effect of PEG-AgNPs was studied through macrophage and HeLa cells. When the concentration of AgNPs is 1.5 μg/mL, the growth of HeLa cells can be inhibited to 50%, but no toxic effect was observed to inhibit the macrophages.

PVP, as a nonionic polymer, has been widely applied in the synthesis of nanoparticle, especially for AgNPs. PVP contains a polar lactam group in the pyrrolidone ring and a non-polar methylene group (–CH2–) in a macromolecular structure. Hence, PVP possesses highly soluble both in water and in nonaqueous solvents. In a wide pH range, PVP can act as a stabilizer in colloidal AgNPs through its hydrophobic carbon chain repulsion and physical and chemical inertia. The interaction between PVP and AgNPs during and after synthesis has been researched for years. The PVP plays a critical role in the crystal facet regulation and stabilization of AgNPs. The PVP-AgNP interaction also investigated through density functional theory by Al-Saidi et al. (2012). In this research, the authors found that the interaction between PVP and {100} and {111} crystal facets of AgNPs occurs via van der Waals forces and direct binding. The PVP molecules bind to silver in a flat conformation, and the binding energy of oxygen atoms in the carbonyl group is stronger with {100} than {111} crystal facet. Therefore, the PVP can be used to control the morphology of AgNPs during synthesis process based on the surface-selective of PVP to silver. Xia and co-workers showed that different AgNPs shapes, including cubes, truncated cubes and octahedral, can be obtained through changing the concentration and molecular weight of PVP (Xia et al. 2012). The surface free energy of AgNPs facets can be controlled through changing the concentration of PVP, and that the effective coverage of PVP on the surface of AgNPs can be affected by the molecular weight of PVP, both lead to alter final morphologies of the nanoparticles. As shown in Fig. 2, the stereochemical structure of AgNPs exhibits obvious change with the amount of PVP decrease.

The PVP can weakly reduce silver ions in aqueous solution (Hoppe et al. 2006). From the research done by Hoppe and co-workers they prepared AgNPs solution by mixing PVP with $AgNO_3$ in a one-step process at low temperature in an aqueous solution. PVP acts as a reducing agent and a surface modifier in the reaction. Different specifications of PVP were used to study the reducing ability of PVP with different molecular weights on precursors. AgNPs with different morphologies, sizes and optical properties were synthesized by varying the ratio of PVP to metal

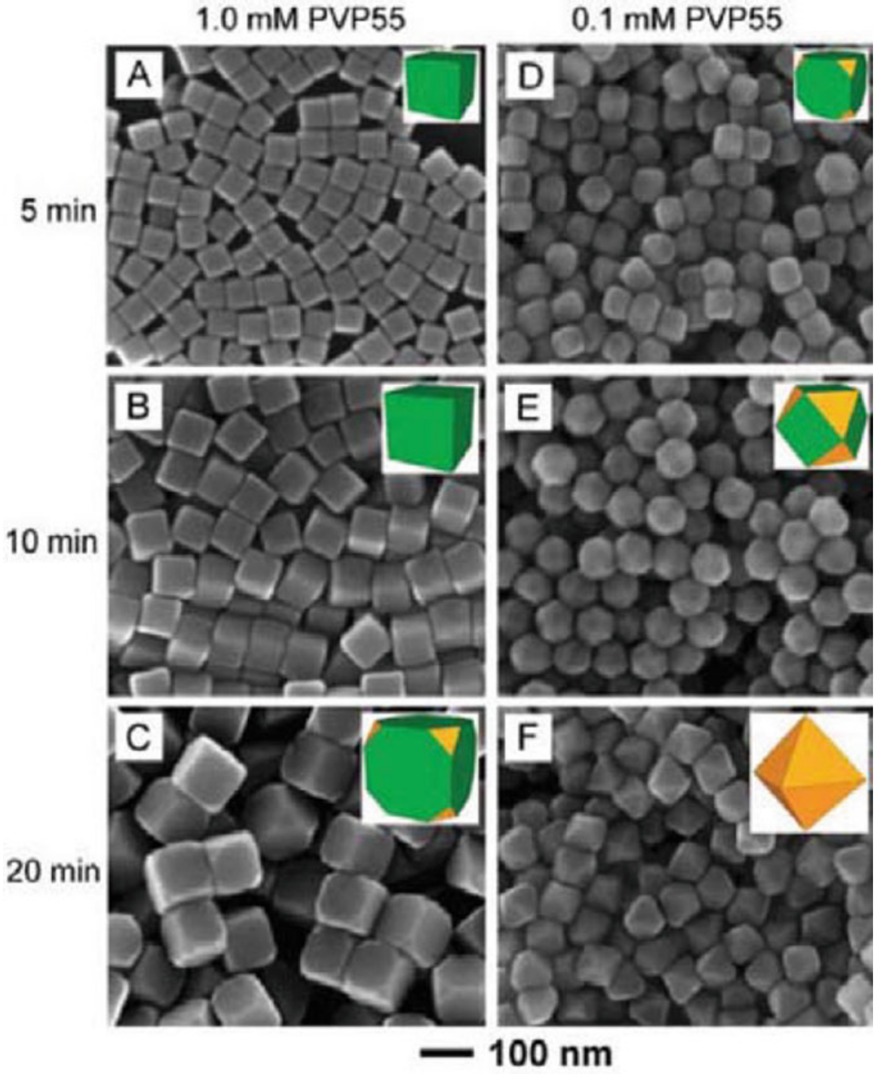


Fig. 2 SEM images of AgNPs grown from 40 nm cubic seeds in the presence of 1.0 mM (A–C) and 0.1 mM PVP55 (D–F), respectively. Reused with permission from reference Xia et al. (2012)

salt. As described here, PVP can act not only as a stabilizing agent and morphology inducing agent, but also as a reduce agent similar to weakly binding molecules. More recently, PVP has also been applied to gold nanoparticles synthesis, where PVP adsorption enables the formation of octahedral, triangular plates and other morphologies of gold nanoparticles.

3.3 Biomolecules

The biochemical properties of AgNPs have attracted great interest from many scientists because the behavior of nanoparticles is not only related to their function, but also to their toxicity and induction of inflammation (Nel et al. 2009). Because the conventional pathways for many contemplated biomedical applications, such as drug delivery and disease diagnosis, are intravenous, then the interaction and stability of nanoparticles with plasma is very important. When stabilizers such as citrate, CTAB or PVP are used, the stability, biocompatibility and functionalization of the nanoparticles are difficult to achieve in blood. These stabilizers have insufficient stability at high ionic strength and may be cytotoxic. Thus, bioactive modifiers hold great promise as coating agents for biomedical applications, such as sugars, amino acids, proteins, peptides, aptamers, DNA, etc. Most biomolecules have a primary amine, carboxylic acid, phosphate, alcohol, or a thiol group on their surfaces and hence molecules can be attached to the AgNPs surface to make the surface of the AgNPs functional.

Chitosan is found in the exoskeleton of some insects and crustaceans, which is produced by the deacetylation of chitinis, and it is a non-toxic, biodegradable, biocompatible, and natural polysaccharide. This natural polysaccharide is applied successfully for the nanomedicine fields for the delivery of drugs, proteins and genes. Especially, AgNPs have also been coated with chitosan through different techniques to develop a novel biocompatible nanosystem. On the one hand, chitosan can be covalently bonded to the surface of the AgNPs by a coupling reaction, and the chitosan chain can be chemically modified with an organic molecule. The functional groups of organic molecule not only can react with chitosan through carboxylation, acylation and alkylation, but also can coordinate with the silver ion (Affesa et al. 2020; Rashki et al. 2021). Mi et al. (2015) have synthesized chitosan-capped AgNPs through reducing the chitosan-Ag^+ low temperature complex. The fluorescence emission and surface plasmon resonance absorption of prepared AgNPs was affected by the degradation time and concentration of chitosan. Badr et al. (2020) reported the AgNPs capped with anionic chitosan surfactant and surface behaviors were analyzed in detail and the TEM images of AgNPs capped with anionic polymeric chitosan is represented in Fig. 3.

Functionalization of AgNPs with amino acids, peptides and proteins has been another effective method to enhance efficacy and stability of nanoparticle based delivery systems. Each peptide or protein is composed of a primary amino and carboxylic group at its ends, while the amino acid side chains attach additional properties or functional groups depending on their molecular structure. In cases when nanoparticles are functionalized with primary amines, carboxylic acids and thiol surface groups, they are covalently conjugated with biomolecules via amide, disulfide and ester bonds. Proteins are particularly suitable for use as a coating material for stabilizing AgNPs for use in biological systems due to their high molecular weight, chargeability, complex but well-defined structure, multifunctional chemical groups, and high affinity for metal surfaces. Here are some

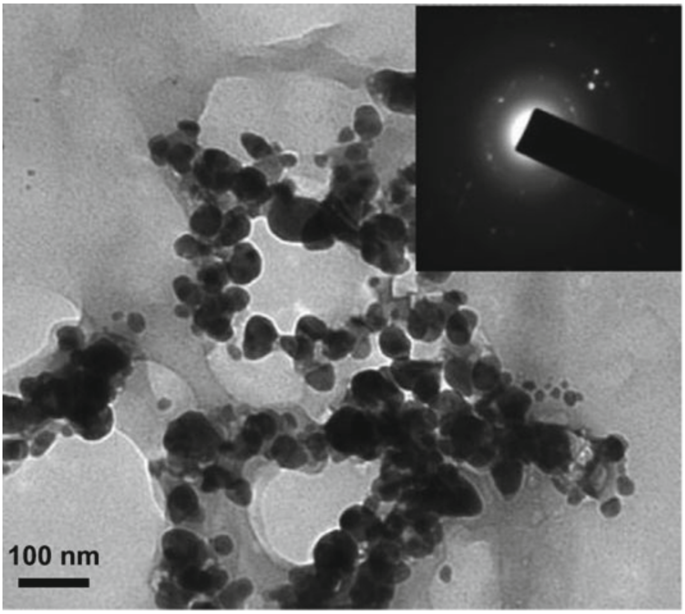
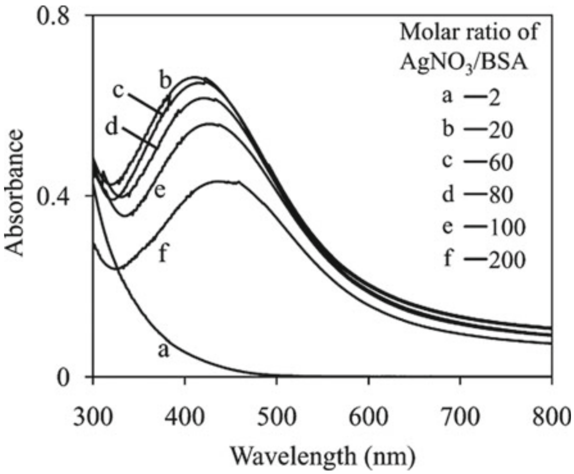


Fig. 3 TEM images of prepared AgNP capped with synthesized anionic polymeric chitosan. Reused with permission from reference Badr et al. (2020)

examples of these modifiers used in AgNPs modification. Nidya et al. (2014) has synthesized L-Cysteine capped AgNPs through a chemical reduction method. Cysteine is bound to the surface of AgNPs through the thiolate moiety. Kalakonda and Banne (2018) have prepared sodium citrate-stabilized AgNPs and coated with peptide. Peptide-coated AgNPs shows high stability in high salt concentration with no any aggregation. The results also indicated that the reactivity of the peptide on the surface of AgNPs is governed by the conformation of the bound peptide on the reconstructed nanoparticle surface. Gautam et al. (2013) showed that bull serum albumin (BSA) capped AgNPs can be formed by the reduction of silver ions in neutral aqueous solution within 30 min. The size and spherical shape of AgNPs could be controlled and nanoparticles with diameters ranging from 8 to 140 nm could be obtained depending upon the molar ratio of $AgNO_3$/BSA (Fig. 4), and the reaction time.

Biopolymers possess high potential as stabilizers for colloidal AgNPs based on their biocompatibility, which will allow for various applications in sensing and biological diagnosis. DNA, as a kind of biomolecule, has been widely applied to stabilize AgNPs in different colloidal conditions as a ligand. The strong negative charge on the phosphate backbone in DNA produces high electrostatic repulsion of the nanoparticles, and the DNA layer also provides steric stabilization. In the majority of cases, the DNA or oligonucleotide is functionalized at the end with an alkyl thiol to covalently bind with the AgNPs surface. DNA can also act as counter

Fig. 4 UV-Vis spectra of BSA conjugated AgNPs formed at different molar ratios of Ag^+/BSA. Reused with permission from the reference Gautam et al. (2013)



ions and interact with silver ions non-covalently to balance the negative charge of the phosphate backbone. Besides, the high physicochemical stability and the great mechanical rigidity of the double helices that DNA possesses makes it the most suitable biomolecule for modifying the surface of AgNPs. Fu et al. (2018) have reported a blue-emitting AgNPs, which was prepared in a matrix of single-stranded DNA through ambient hydrothermal reactions. DNA acted as the coating or stabilizer agent in the process.

The surface modifiers for AgNPs have been extensively studied for years, and many modifiers were developed. Thus, future research will likely focus on the enhancement and improvement of the stabilities and viabilities of the developed AgNPs systems and design of more simplified and market-friendly fabrication methods for the production of functionalized AgNPs.

4 Physical Modification Methods

Physical modification is a method to modify the surface of nanoparticles through a series of physical processes, such as adsorption, coating, and cladding, etc. In addition, the surface modification of nanoparticles by ultraviolet and plasma rays also considered as physical modification method. There are two main methods for the surface physical modification, the first one is adsorption method (directly adsorb the special material on the surface of nanoparticles by van der Waals force) and the other is the surface coating method. Physical modification has been widely applied to modify the surface of AgNPs. Reasonable physical modification can improve the stability and control the hydrophilicity and hydrophobicity of AgNPs.

In general, the surface modification of AgNPs by surfactants belongs to adsorption method. Surfactant molecules contain two functional groups with distinct properties, one is a polar group with hydrophilicitya, and the other is a non-polar functional group with hydrophilicity. When the nanoparticles are dispersed in aqueous solution, the non-polar lipophilic group of the surfactant is absorbed to the surface of the nanoparticles, while the polar hydrophilic group is compatible with water, which achieves the purpose of good dispersion of nanoparticles in water, and vice versa. Surfactants are inexpensive, large in production, large in variety and easy to obtain, so they are extremely suitable for initial surface modification of nanoparticles.

The mechanism of the surfactant as a dispersing agent is mainly to utilize the adsorption effect of the surfactant on the solid and liquid interface. The surfactant can form a molecular film on the surface of the nanoparticle to prevent the particles from contacting each other, and at the same time increase the distance between the particles, so that the contact of the particles is not tight, and the formation of bridging hydroxyl groups and true chemical bonds is avoided. In addition, the addition of polymeric surfactants can also play a role in steric hindrance.

There also have some reports about those surfactants as a stabilizing agent for the synthesis of AgNPs through adsorption. Kora et al. (2009) have synthesized sodium laurylsulfonate (SDS) capped AgNPs through UV photo-reduction of silver nitrate aqueous solution. They found that SDS capped AgNPs show better colloidal stability over citrate, PVP and CTAB capped AgNPs, which can be attributed to the formation of double layer of SDS on the AgNPs surface. The results of zeta potential suggest that SDS molecules are assembled on the surface of nanomaterials by physical adsorption. Unfortunately, surfactants generally do not have functional groups that can functionalize AgNPs, which limits their application to some extent. Feng et al. (2017) have reported adenosine monophosphate (AMP) and SDS co-modified AgNPs. SDS-modified AgNPs is not selective for metal ion recognition. However, for the co-modified AgNPs only the presence of Ni^{2+} led to the color change of AgNPs (Fig. 5), which mainly results from the coordination interaction between Ni^{2+} and AMP.

Surface coating method is also called the surface deposition, which is to deposit a substance on the surface of nanoparticles to form a heterogeneous coating layer without chemical bond with the surface of particles. The surface coating is mainly divided into two ways: inorganic cladding and organic cladding. The surface inorganic coating of nanoparticles is to coat an inorganic substance on the surface of the nanoparticle to change its surface properties. Through this method, the excellent properties of different particles can be fused, and the composite functional materials with required new properties can be prepared.

The inorganic coating of nanoparticles can be realized by sol-gel method and microemulsion method, and the properties of nanoparticles can be improved. The most commonly used surface modifier in the sol-gel process is silica, the function of which is diverse. It not only improve the colloidal stability, but also protect the nanoparticles from dissolution, photolysis, etc. Silica nanoparticles possess high dispersibility and colloidal stability, and these properties are conserved when silica

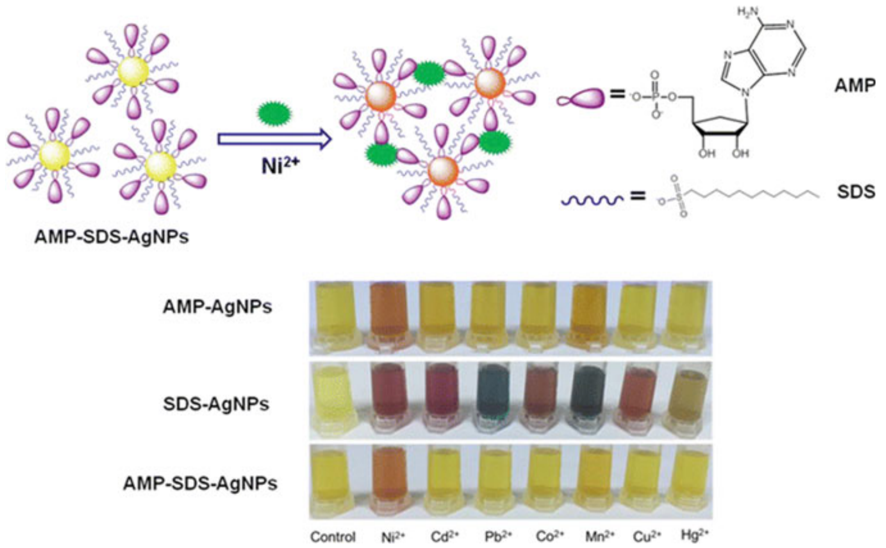


Fig. 5 AMP-AgNPs, SDS-AgNPs, and AMP-SDS-AgNPs solution in the presence of different metal ions. Reproduced with permission from reference Feng et al. (2017)

is used for coating AgNPs. Furthermore, silica is also known to be biocompatible; then the cytotoxicity of the AgNPs is often reduced with the addition of silica shell. Ghimirel et al. (2016) studied the optical properties and morphology of bare AgNPs and silica coated hybrid AgNPs. Direct coating of silica is carried out in water-in-oil microemulsion on pre-synthesized AgNPs by using tetraethyl orthosilicate as silica precursor.

The surface coating of the organic substance is mainly carried out by in situ grafting method. Either already-prepared polymers or monomers are introduced to the silver nitrate salt reduction solutions and serve as a stabilizing and shape-guiding agent. The polymer monomer reaction is directly polymerized to the surface of the nanoparticle by using ultrasound wave and ultraviolet light. For example, several cationic polyelectrolytes, such as poly(diallyl dimethylammonium) chloride, poly(2-(methacryloyloxy)ethyl phosphorylcholinephosphorylcholine), and poly (2-hydroxy-3-methacryloxy-propyltrimethylammonium chloride), has been commonly applied in situ to produce AgNPs coated by these charged polymers (Mayer et al. 2000). Jayeoyea et al. (2020) have reported a nanocomposite stabilized AgNPs through in situ chemical reduction of silver nitrate by using 3-Aminophenyl boronic acid as reductant (Fig. 6), and the composite exhibited satisfactory antibacterial and antioxidant activities.

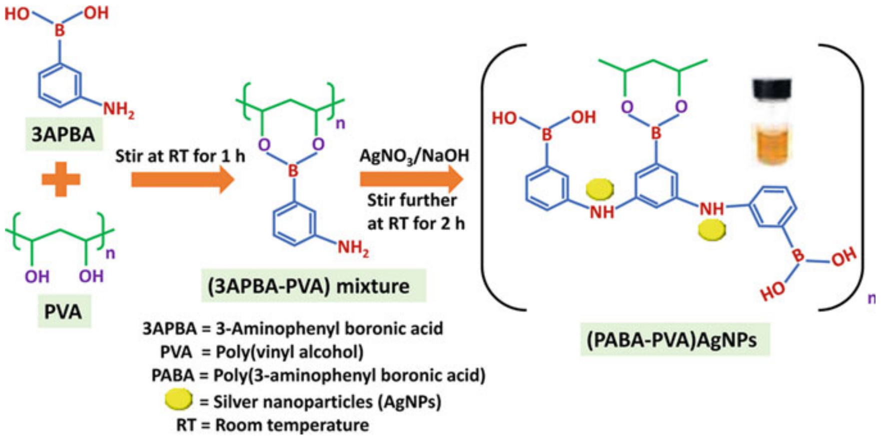


Fig. 6 Schematic illustration of the synthesis protocol for (PABA-PVA) AgNPs. Reproduced with permission from reference Jayeoyea et al. (2020)

5 Chemical Modification Methods

The surface chemical modification is to change the surface structure and state of the nanoparticle by the chemical reaction between the surface of the nanoparticle and the treatment agent to achieve the purpose of surface modification. Since the specific surface area of the nanoparticles is large, the surface bond state and the electronic state are different from the inside of the nanoparticles, and the surface atoms are not fully coordinated, resulting in a large number of dangling bonds, making these surface atoms highly reactive, extremely unstable, and easily associated with other atoms. Combined, this provides favorable conditions for the surface modification of nanoparticles by chemical reaction methods. The chemical modification method mainly include coupling method, surface grafting method, and ligand exchange method, etc.

Due to the higher surface energy of the nanoparticles, they have a lower affinity for organic substances with lower surface energy. When the two are combined, they are incompatible, and gaps appear on the interface, which leads to easy degradation and embrittlement of the polymer at the interface. The coupling method involves, surface of the nanoparticles is treated with a coupling agent to make it compatible with organic substances. The coupling agent molecule generally has two groups, one capable of chemically reacting with the surface of the inorganic nanoparticles and the other being reactive or compatible with the organic substance. Silane coupling agent is one of the common coupling agents, and it is very effective to modify inorganic nanoparticles with hydroxyl groups on the surface. The concept of silane coupling agents was reported by Plueddemann and his coworkers (Plueddemann et al. 1962). After that publication, numerous research works were proceeded on modified nanoparticle surfaces using silane coupling agents to

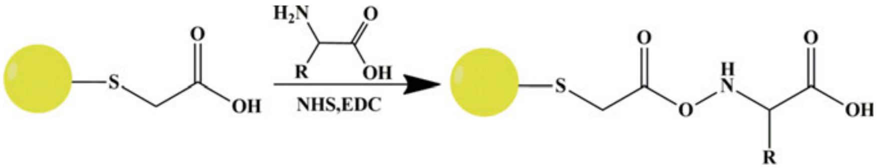


Fig. 7 Schematic diagram of amidation reaction

improve the compatibility between the polymer and nanoparticles surface. However, for AgNPs, many polymers can be directly adsorbed on the surface of AgNPs, such as PVP mentioned above. Therefore, silane coupling agents are not commonly used in surface polymer modification of AgNPs. Han et al. (2008) reported a reverse microemulsion method for the preparation of monodispersed silica-coated AgNPs with no use of silane coupling agent as the surface primer. Therefore, whether it is organic coating or inorganic coating, silane coupling agent is not necessarily need.

Coupling agent also used for further chemical modification of the surface of AgNPs. For example, thioglycolic acid modified AgNPs can be subsequently brought into chemical reactions with amino groups from amino acids and proteins by using 1-Ethyl-3-(3’-dimethylaminopropyl)carbodiimide (EDC) and N-Hydroxy succinimide (NHS) as amide coupling agent (Fig. 7).

The surface grafting modification method is divided into: (1) Coupling grafting method; the nanoparticles surface functional groups react directly with polymeir to achieve grafting. The method has the advantages of easy control of the grafting amount and high efficiency. Krystosiak et al. (2017) reported a perfectly homogeneous polystyrene/silver nanocomposite with antibacterial activity through coupling grafting method (Fig. 8). The polymer nanocomposite also has the potential to be applied to the fields of manufacturing chemical and biochemical sensors, and so on. (2) Polymerization growth grafting method; monomer polymerization growth on the surface of nanoparticles, forming the coating of nanoparticles. The method possesses high grating efficiency commonly. Surface grafting modification brings the advantages of inorganic nanoparticles and polymers into full play and can realize the optimal design of functional materials. In addition, the surface grafting of nanoparticles greatly improved the dispersibility of nanoparticles in organic solvents and macromolecules, and composite materials with high nano powder content and high uniform distribution could be prepared.

The reaction in which the original ligand in the coordination compound is replaced by another ligand is called ligand exchange reaction. Ligand exchange method also is an effective method to modify the surface of AgNPs. Based on the difference of binding affinity of functional groups and silver, modifier with stronger affinity to silver can replace weak affinity ligand. In many cases, the modifier solution is introduced after the reduction of the starting compound and formation of the AgNPs. According to Noh et al. (2015), 1-(2-mercaptoethyl)-1,3,5-triazinane-2,4,6-trione functionalized AgNPs have been synthesized through this procedure.

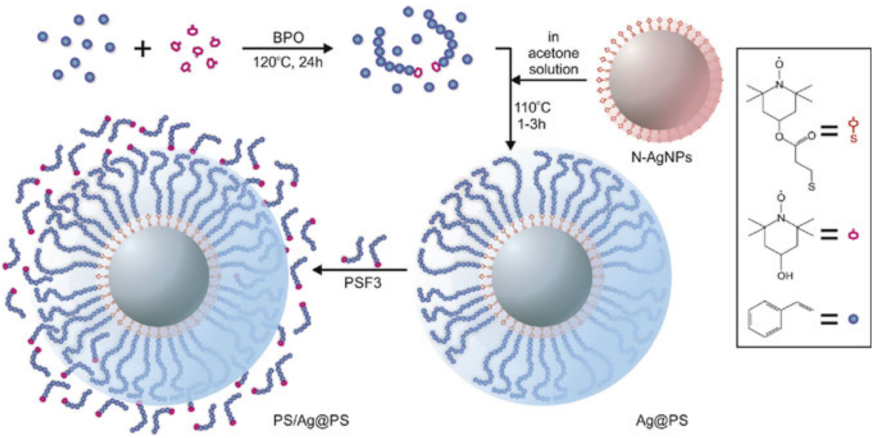


Fig. 8 Schematic illustration of the synthesis process of polystyrene grafted AgNPs. Reused with permission from reference Krystosiak et al. (2017)

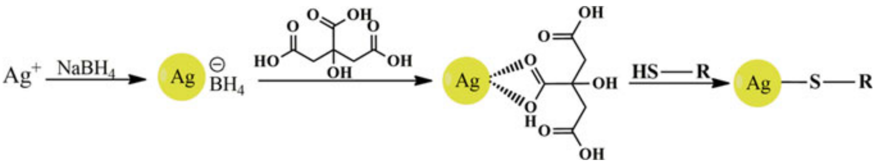


Fig. 9 Schematic illustration of ligand exchange method

If the surface chemical modification of AgNPs is considered to secondary interaction relative to the redox reaction, actually in the reaction system a surface layer component is displaced by another component with higher affinity. Therefore, the excess surface energy of the system decreases, and the system becomes more stable. There also has a classic example, silver nitrate was reduced by borohydride in the presence of sodium citrate, and silver sol containing citrate ions was formed on its surface. Due to the weak coordination ability of carboxyl groups of citric acid to silver, citric acid can be replaced by a sulfhydryl compound with stronger coordination ability. The reaction mechanism can be graphically reflected in the Fig. 9. Ma et al. (2016) have synthesized a p-aminobenzenethiol functionalized AgNPs through a ligand exchange method based on the different affinity of sulfydryl and carboxyl to silver.

6 Conclusions

AgNPs possess unique properties as a representative metal nanoparticles for various application such as antimicrobial and sensing as well as for academic research. The AgNPs are prone to form aggregates or adsorption with other substances in the process of synthesis, storage, and use. Surface modification is an effective way to improve the dispersion stability through by bonding small molecules and grafting polymers. Furthermore, directional surface modification can realize the functionalization of AgNPs to replay the demand of different application fields. Reasonable surface modification not only can improve the stability of AgNPs based on the interfacial interactions between AgNPs and polymers or small molecules, but also can result in new unique properties, such as optical, electronic and catalysis properties. Thus, the surface modification of AgNPs is essential to prepare high-performance and multifunction AgNPs and the surface modification method should be selected according to the practical requirement.

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Characterization of Silver Nanoparticles

Shenghong Yang

Abstract Analytical science is an important tool for observing and exploring the world, especially the microworld. With the development of nanomaterials science and technology, there is a need to not only upgrade and develop new analytical methods, technologies, and new concepts; but also to improve the sensitivity, accuracy, and reliability of analytical test equipment, in order to obtain more information and improve the quality, efficiency and economy of testing.

1 Introduction

Analytical science is an important tool for observing and exploring the world, especially the microworld. With the development of nanomaterials science and technology, there is a need to not only upgrade and develop new analytical methods, technologies, and new concepts; but also to improve the sensitivity, accuracy, and reliability of analytical test equipment, in order to obtain more information and improve the quality, efficiency and economy of testing.

Nanoscience and nanotechnology are a subject to study the properties and interactions of matter at the microscopic scale, and these properties can be applied to multiple disciplines and technology fields. Nanotechnology is the foundation of future high technology. The instrumental analysis methods, that can be suitable for nanotechnology research, are essential components of nanotechnology. Therefore, the characterization and analysis of nanomaterials is of great significance and can affect the development of nanomaterials and nanoscience.

Silver nanoparticles (AgNPs) are widely used nanomaterials. The means of their characterization are quite diverse and gradually becoming more complete due to the development of analytical instruments and technical methods. This chapter mainly

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introduces the most common technologies and methods of characterization of AgNPs. Several aspects such as spectral analysis, morphological analysis, structural analysis, particle size analysis, and so on are described shallowly.

2 UV-Vis Absorption Spectroscopy for AgNPs

One of the major characteristics of metal nanoparticles is that there is an absorption band in the ultraviolet-visible (UV-Vis) region, which is caused by plasmon resonance excitation on the surface of the metal particles (Wu et al. 2001). Mie (1908) first proposed the conductive ball model theory of metal colloids, which is suitable for the colloidal particles with particle size smaller than the absorption wavelength. According to the theory of Mie, the size, shape, spacing and dielectric constant of metal nanoparticles can affect the UV-Vis absorption spectrum of metal colloid. Later, in 1912, Gians extended the theory to apply it to flattened or oblate particles with a particle size less than one-tenth of the wavelength of light. The UV-Vis absorption of colloidal particles was observed not only related to the size of the particles but also closely related to the shape of the particles (Wang and Kerber 1981). In theory, the UV-Vis absorption spectroscopy can be applied to the study of particles with various shapes. With the accumulation of research, UV-Vis absorption spectroscopy has become one of the simplest and most convenient methods for studying metal colloids.

UV-Vis absorption spectroscopy is a very reliable, convenient, and useful technique for the primary characterization of various synthesized nanoparticles, which is also utilized for monitoring the synthesis and stability of AgNPs (Sastry et al. 1998). Besides, UV-V is absorption spectroscopy is simple, fast, sensitive, selective, and easy to operate for different types of metal nanoparticles. It just needs a short time duration for measurement, and even the calibration is not required for the characterization of these nanoparticles. Furthermore, the UV-Vis absorption spectroscopy can be measured directly using a simple commercial UV-Vis spectrophotometer at quite a low cost.

AgNPs possess unique optical properties, which can strongly interact at specific wavelengths of light. The conduction band and valence band of AgNPs lie very close to each other and the electrons can move freely. Due to the collective oscillation of electrons of AgNPs in resonance with the light wave, a surface plasmon resonance absorption band comes into being (Das et al. 2009; Link and Ei-Sayed 2003). The absorption of AgNPs depends on the dielectric medium, particle size, and chemical surroundings. According to the majority of studies carried out, the AgNPs colloidal solution can exhibit an obvious absorption peak at 400 ~ 450 nm. Detsria and Seeharaj (2017) prepared phthalic acid-modified AgNPs by reducing $AgNO_3$ with $NaBH_4$ in the presence of phthalic acid. The UV-Vis absorption spectrum of the as-prepared phthalic acid-capped AgNPs showed a single peak at the wavelength of 400 nm, which is consistent with the surface plasmon resonance phenomenon. Manivannan et al. (2018) reported one kind of silicate sol-gel matrix stabilized AgNPs, which displayed intense absorption at a wavelength of 418 nm. Therefore, the UV-Vis absorption spectrum of AgNPs can be affected by surface stabilizers and ligands.

The UV-Vis absorption spectroscopy can also use for monitoring the formation process of AgNPs. During the reaction, the silver ions from $AgNO_3$ are reduced to silver nanoparticles, which can be monitored by observing maximum absorbance wavelength and intensity change. Ahmad et al. (2015) reported about the biosynthesis of AgNPs by using phytochemicals from a Chinese medicinal plant "*Sargentodoxa cuneata*". The UV-Vis absorption spectroscopy was applied to study the growth process of AgNPs under different amounts of the reactant. As shown in Fig. 1, the intensity of the absorption peak of AgNPs increased gradually with the passage of reaction time. Besides, the stability of AgNPs can also be evaluated through UV-Vis absorption spectroscopy. For example, the aggregation of AgNPs can give rise to the redshift of the absorption wavelength of AgNPs (Fig. 2).

The UV-Vis absorption spectrum of AgNPs also has a strong dependence on both the size and shape of a particle. Xia et al. (2012a) has reported that as the size of the AgNPs increased from 36 to 58, 99, and 144 nm, the major UV-Vis absorption peaks of these nanoparticles exhibited a constant redshift from 430 to 468, 497, and 600 nm. The AgNPs with well-defined shapes were also synthesized

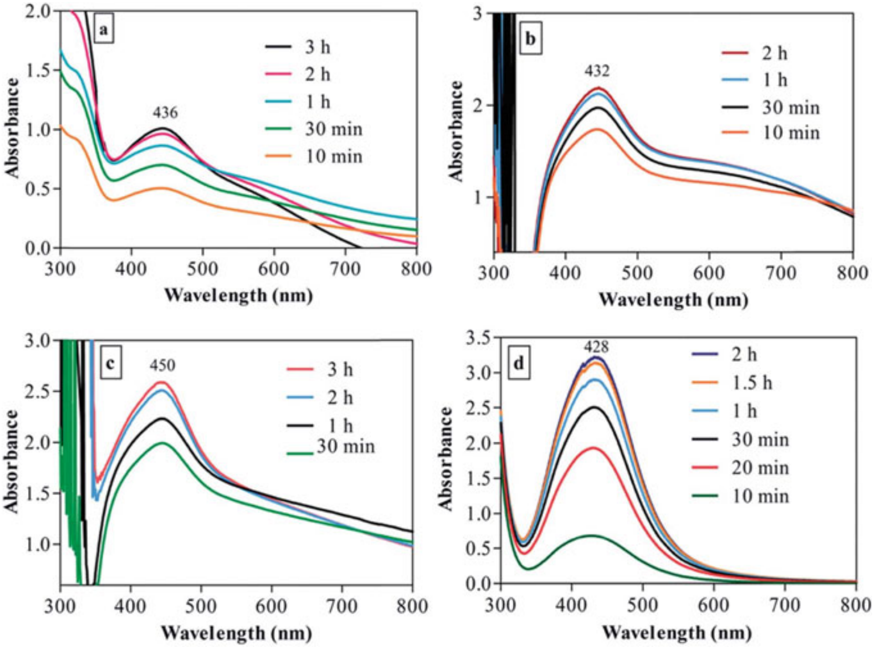


Fig. 1 Time-dependent evolution of UV-visible spectra of AgNPs under the varying amounts of reactant. Reused with permission from the reference Ahmad et al. (2015)

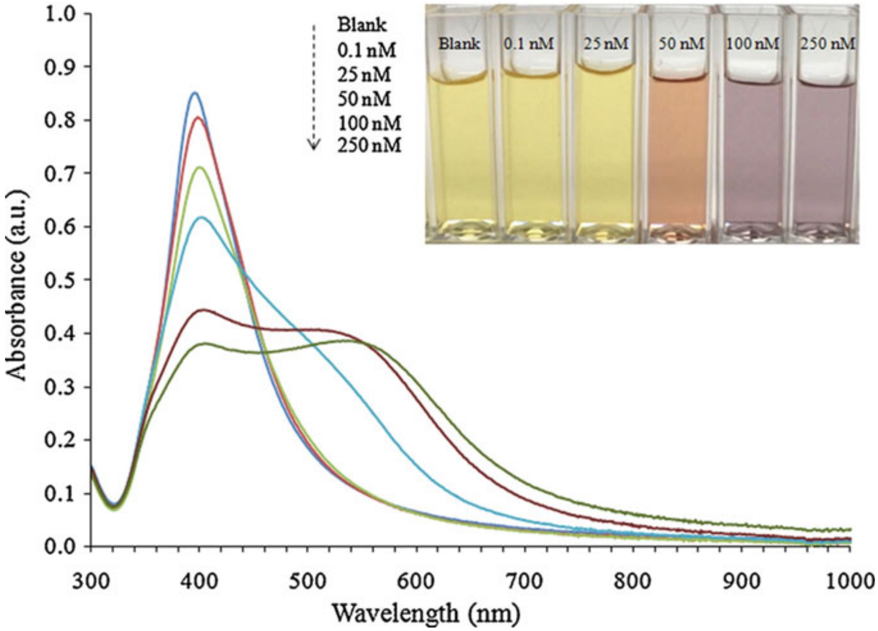


Fig. 2 UV-visible spectra and photographic images of the AgNPs formed in the presence of different glutathione concentrations (0.1–250 nM). Reused with permission from reference Detsria and Seeharaj (2017)

to systematically investigate the effect of shape on the UV-Vis spectrum of AgNPs. The 40 nm cubic particles displayed three absorption peaks with a major peak at 435 nm and two shoulder peaks at 345 and 380 nm. However, the truncated cubes showed only two peaks at 345 and 435 nm and the cuboctahedrons just showed one peak at 435 nm.

3 Scanning Electron Microscopy Analysis

Scanning Electron Microscopy (SEM) is used for the observation and detection of small substances. Compared to optical microscopy, SEM possesses unparalleled advantages in resolution, depth of field, and microanalysis. Since the advent of the mid-twentieth century, the efforts of scientists in various countries and the development of the technology level of the electronics industry have enabled SEM performance to be continuously improved and applied more widely. In the research of nanomaterials and nanotechnology, SEM is widely utilized for the characterization of microstructure and morphology of nanomaterials.

SEM is an all-round analytical microscope for observing the surface microscopic world. It uses a very fine focused electron beam as the illumination source, which

Fig. 3 Scanning electron microscope (Model: ZEISS Sigma 300)

reaches the surface of the sample through a raster scan, and images the information generated by the interaction of incident electrons with the matter. Thereby several times to several tens of times magnified images can be obtained. Figure 3 represents the photograph of an SEM analysis machine.

SEM mainly includes a lens system, electronic signal collection, and processing system, electronic signal display and recording system, vacuum system, and the power supply system. Among these, the lens system can reduce the size of the virtual light source from tens of microns to several nanometers, and control the opening angle of the electron beam in the range of $10^{-2} \sim 10^{-3}$ rad. The function of the electronic signal collection and processing system is to achieve photoelectric signal conversion after which the signal sent to the grid of the picture tube (cathode ray tube). The image of SEM is displayed on the picture tube is photographed by a camera. Commonly, two picture tubes are necessary, one for observation and another one for taking pictures. For SEM, the vacuum degree is usually higher than 10^{-3} Pa, which ensures the flexible manipulation of electron beams. The power supply system is used to supply a specific power source for each component.

SEM, compared with an optical microscope and transmission electron microscope, has several advantageous features: ① The surface structure and morphology of the sample can be visually analyzed, the sample can be translated and flipped in three dimensions and observed through different angles. ② The depth of field is long, hundreds of times higher than an ordinary optical microscope and the image has a three-dimensional effect. ③ Image magnification can be adjusted from tens of thousands to hundreds of thousands of times and the resolution is up to 3 nm, which is between the optical microscope and transmission electron microscope. ④ It causes less radiation damage and pollution. ⑤ The technique has a multi-functional analysis feature; micro-component analysis can be done while observing the morphology.

With decades of research, various sizes and shapes of AgNPs have been obtained. SEM can be used as an effective and visualized way to analyze the surface and three-dimensional structure of AgNPs. So far, researchers have synthesized nanoparticles with various shapes like spherical, diamond, rod-like, and cubic with a wide range of sizes starting from as small as 1 nm to several hundred nm graded in diameter (Rycenga et al. 2011; Pietrobon and Kitaev 2008; Wiley et al. 2007; Cobley et al. 2009) (Fig. 4). We can prepare AgNPs with different shapes and sizes through a formulated solution and standardized procedures according to our interests.

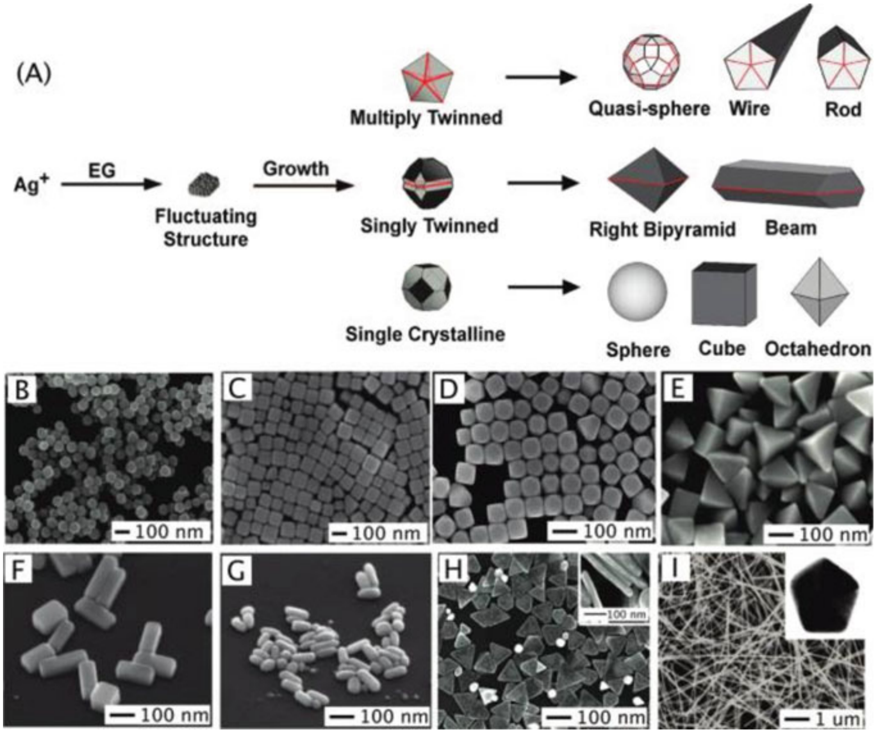


Fig. 4 SEM images of AgNPs with different shapes. Reused with permission from reference Rycenga et al. (2011)

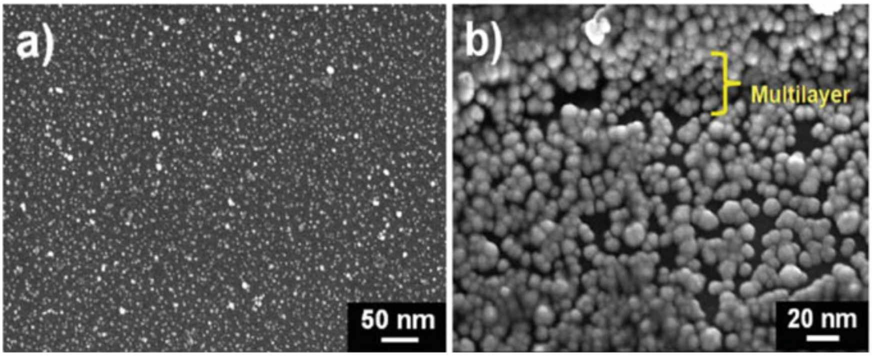


Fig. 5 SEM images of AgNPs immobilized on the amine-modified glass surface (**a**) and silanized glass substrate (**b**). Reused with permission from reference Agnihotri et al. (2013)

Agnihotri et al. (2013) synthesized AgNPs using $NaBH_4$ and trisodium citrate as the reducing and capping agent, respectively, at the required stoichiometric ratios. The results of SEM indicated a highly dense and uniform immobilization of AgNPs on the glass surface. The as-prepared AgNPs were uniformly dispersed with a size range of 10–15 nm and an obvious spherical structure. Thus, the surface and stereoscopic structure of nanoparticles can be clearly observed by SEM (Fig. 5).

Xia et al. (2012b) have studied the influence of facet-specific capping agents on the shape evolution of AgNPs in a seed-mediated synthesis by using SEM. They have demonstrated that poly(vinylpyrrolidone) and citrate can selectively bind to Ag(100) and Ag(111) surface, respectively. Based on the mechanistic understanding, a series of AgNPs with controlled shapes and sizes have been synthesized successfully by using different combinations of seeds and capping agents. The above example can illustrate that SEM is a very useful and convenient technology for the morphological observation of AgNPs.

4 Transmission Electron Microscopy Analysis

After sixty years of development, transmission electron microscopy (TEM) has become an important tool for scientific research in the fields of chemistry, medicine, biology, agriculture, forestry, and material science. TEM also has become an important means for human beings to understand nature and study the tiny structure of the body. For this reason, the operation technique of TEM has become a basic skill that researchers in all fields of research should master. The inventor of TEM (Professor E. Ruska) also won the Nobel Prize in Physics in 1986.

TEM is a high-resolution and high-magnification electro-optical instrument that uses an extremely short wavelength electron beam as an illumination source for focus imaging with a magnetic lens. The basic principles of TEM and optical microscopy are alike, the microscopic magnification process is basically similar, and the optical path and some terms are fundamentally the same. The difference is that the light source of the TEM is not visible light but an electron beam, and instead of a glass lens, it has an axisymmetric electric field or a magnetic field. Therefore, the TEM is still substantially different from the optical microscope in terms of the overall structure, imaging principle, and operation mode.

The TEM consists of three parts: electro-optical system (lens barrel), vacuum system, and power supply system. Figure 6 shows the image of TEM and the modular construction of a whole lens barrel. The arrangement of parts from top to bottom comprises the electron gun, the double spotlight, the sample chamber, the objective lens, the intermediate mirror, the projection mirror, the observation room,

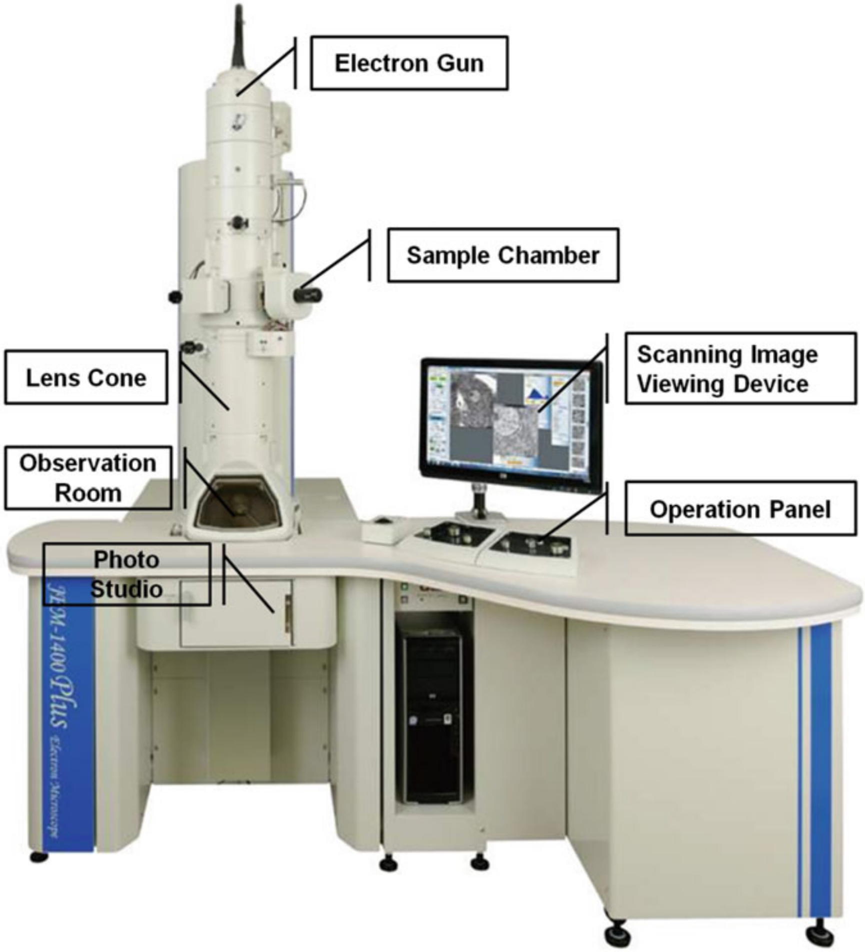


Fig. 6 Transmission electron microscope (Model: JEM 1400)

and the photo studio. The functions of the electro-optical system mainly include illumination, imaging, and observation. The main function of the vacuum system is to maintain a very high vacuum degree inside the mirror by continuously eliminating the air inside the mirror. On the one hand, the extremely high vacuum can keep the electron beam stable ensuring that the stable image on the screen; on the other hand, it can reduce the oxidation of the filament and prolong the life of the filament. The power supply system has two independent supplies, accelerating voltage and electron microscope current. The accelerating voltage requires a small current and a high voltage, while the electron microscope current requires a large current and a low voltage. Stable accelerating voltage and electron microscope current can help eliminate chromatic aberrations and improve resolution.

TEM is one of the most important instruments for studying the morphology of nanomaterials. When using TEM to research the microstructure of nanomaterials, the sample must be of nanometer thickness that the electron beam can penetrate. The samples of TEM are generally divided into powder, film, and sections of the biological sample. The preparation methods of the three types of samples are different and the scope of application is also different. For the TEM analysis of AgNPs, the sample is usually dispersed in a solvent such as water or ethanol and further dispersed by ultrasonic vibration. Subsequently, a small amount of liquid is dropped on the carbon-coated copper grids by a dropper or pipetting gun. It should be noted that the sample rod can be loaded only after the copper grid is dried. For samples with water as a dispersant, it is generally baked with an infrared lamp to speed up the drying speed.

Newly synthesized materials are usually characterized by a variety of methods, and TEM is frequently used as an effective technique for the characterization of nanomaterials, which can visually reflect the particle size, size distribution, and morphology (Lin et al. 2014). TEM, compared with SEM, possesses two advantages: It can provide better analytical measurement capability and spatial resolution (Williams and Carter 2009). Therefore, TEM characterization is essential for the systematic study of AgNPs. Yin et al. (2002) reported a simple, facile, and easy to water phase synthesis method for the preparation of water-soluble AgNPs with narrow size distributions in the range of 20–50 nm. From Fig. 7, we can see that the

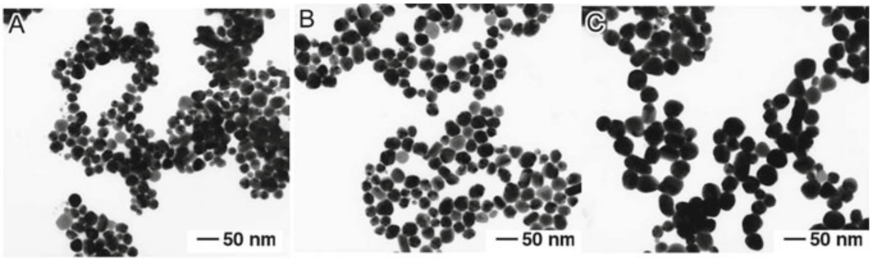


Fig. 7 The TEM images of AgNPs that was prepared at 27 °C (**a**), 30 °C (**b**), and 35 °C (**c**), respectively. Reproduced with permission from reference Yin et al. (2002)

prepared AgNPs show good monodispersity, which also provides evidence for its good water-solubility. Furthermore, they have demonstrated that the size of AgNPs can be flexible controlled just by changing temperature. As the temperature rises, the average size of these AgNPs changed from 20 to 30 and 40 nm.

Xiong et al. (2007) reported the synthesis method for obtaining high yields of Ag nanoplates using polyacrylamide that slowdown the reduction of silver nitrate. The authors utilized TEM to monitor the evolution of the shape by drawing samples from different periods of reaction time (Fig. 8a, b). The sample used was a circular nanoplate with a mean size of 10 nm and at a reaction time of 45 min. When reaction time increased to 100 min, most of the nanostructures took a triangular or hexagonal shape.

Ma et al. (2010) have successfully prepared small silver nano-cubes in a hydrophobic solvent. The TEM images are shown in Fig. 9, the samples exhibited a relatively narrow size distribution with an average size of 14 nm. The high-resolution TEM image (Fig. 9c) taken from an individual particle suggests a multiply-twinned structure that matches an icosahedron.

The important information of AgNPs, such as particle size, morphology, structure, and dispersibility, can be obtained directly from a TEM image. Compared with

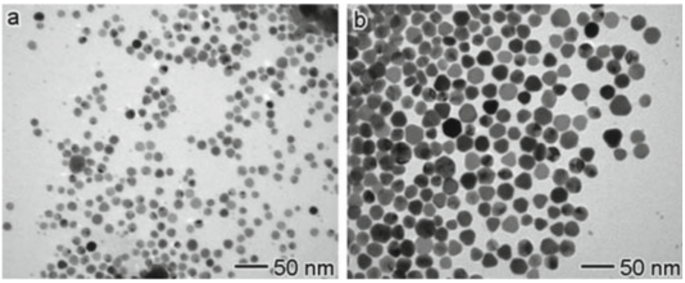


Fig. 8 TEM images of AgNPs prepared under different reaction time (**a**, **b**). Reproduced with permission from reference Xiong et al. (2007)

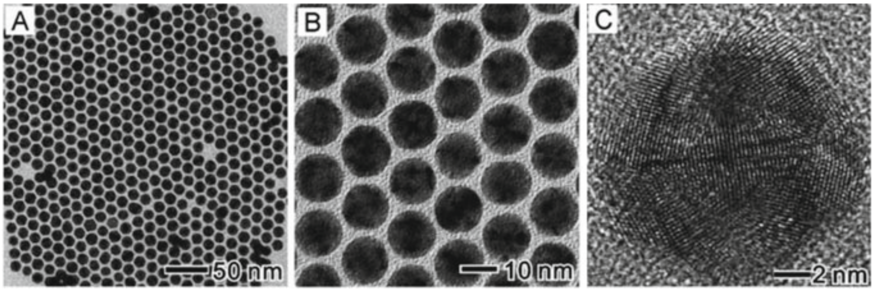


Fig. 9 TEM images of AgNPs with different magnifications (**a**, **b**), high-resolution TEM image of an individual silver particle (**c**). Rreproduced with permission from reference Ma et al. (2010)

SEM, the TEM can easily obtain the inside structural information, but stereo images of particles cannot be obtained. TEM combined with other characterization methods thus can provide a more comprehensive description of the properties of AgNPs.

5 Optical Microscopy

An optical microscope is a precision optical instrument with a history of more than 300 years that uses optical theory to magnify and image tiny objects that cannot be distinguished by the naked eye to extracting fine structure information. Classical optical microscopes are just a combination of optical components and precision mechanical components that use the human eye as a receiver to view and magnify images. Later, a photographic device was added to the microscope, using photographic film as a receiver that can record and store the image. One of the important features of a modern optical microscope is photoelectric integration. It generally uses photoelectric components, TV camera tubes, and charge couplers as the receiver of the microscope, and is equipped with an electronic computer to form a complete image information acquisition and post-processing system.

Although traditional optical microscopy has a certain spectral and temporal resolution, its spatial resolution is “insurmountable” limited by the diffraction limit of the grating. The resolution of a conventional optical microscope is about 200 nm, which is difficult to apply to the observation of phenomena at the ultra-micro scale. Though electron microscopy has incomparable resolution with optical microscopes, these microscopes that do not use light waves (photons) as information carriers and also have some fundamental weaknesses. First of all, there are many restrictions on the observation of the sample, for example, the sample must be a conductor, not a non-conductor and a solution; secondly, there are strict requirements on the sample environment, such as the need for a vacuum, etc.; and finally, they may cause more or less damage to observed objects.

Optical microscopes have very few restrictions regarding samples compared with electron microscopy. They can be liquids and non-conductors, animate and inanimate, transparent or opaque, or even illuminating. Besides, the optical microscope can not only observe the sample in a static state but also observe the sample under dynamic conditions. Therefore, the optical microscope has great advantages for the measurement of the sample over electron microscopy in some way and cannot be replaced by electron microscopy completely.

To cope with the development and demand of nanoscience research, breaking the limitations of diffraction limits and improving the resolution of optical microscopes is fundamental to expand its application range. In recent years, researchers have made breakthroughs in the research of the optical microscope through a series of efforts, and successively invented some methods beyond the diffraction limit, such as near field the optical microscope, light activation the localization microscope, and stimulated emission depletion microscopy, and so on. Wang et al. (2011) have reported nano-scale optical microscopy with a resolution of 50 nm, where the white-light diffraction limit was overcome by using optically transparent glass

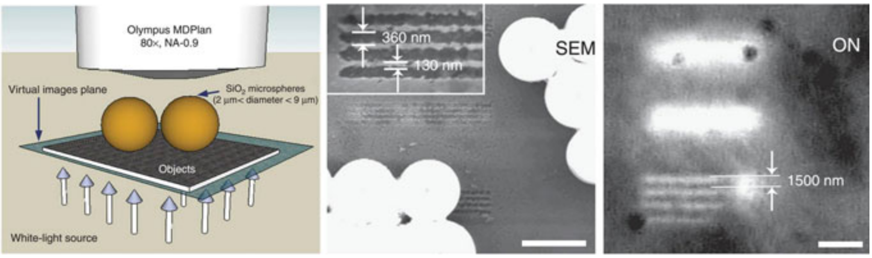


Fig. 10 Schematic of the microsphere superlens with transmission mode integrated with a classical optical microscope (left image), microsphere superlens imaging of 360-nm-wide lines spaced 130 nm apart by SEM (middle image) and optical microscopy (right image). Reproduced with permission from the reference Wang et al. (2011)

microspheres as far-field super-lenses. The optical microscopy operates in both reflection and transmission modes and generates virtual images with a magnification of up to ×8. As shown in the left image of Fig. 10, these microspheres can collect the near-field object information and form virtual images that can be captured by the conventional lens. The middle and right image of Fig. 10 suggests that the 360-nm-wide lines spaced 130 nm apart can be resolved clearly. Such a super-resolution white-light optical microscopy opens up new opportunities for imaging viruses, DNA, and nanoparticles in real-time.

Optical microscopy has been used in the characterization and analysis of nanomaterials in recent years due to its unique advantages such as low cost, easy operation, and non-invasiveness. Optical microscopy is also one of the essential tools for studying certain specific formation processes and the biological effects of silver nanomaterials. Lemineur et al. (2018) have used a nano-scale optical microscopy technique, backside absorbing layer microscopy, to quantify the electrodeposition process in situ of AgNPs. It is the first time that the backside absorbing layer microscopy was used to explore their electrodeposition. The optical microscope could realize the imaging of deposition and the stripping process of AgNPs in situ through positive and negative voltage switching. The AgNPs prepared by electrodeposition varied in sizes from 10 to 80 nm.

Yan et al. (2018) observed the deposition and distribution of AgNPs in microorganisms like *Daphnia Magna* as a biological model through optical microscopy. As shown in Fig. 11, it can be observed that the AgNPs are distributed in the intestines and other parts. Furthermore, the fluorogenic tetrazole-functionalized tetraphenylethylene derivative 1 (TEZ-TPE-1, the silver ions capture reagent) was used for selectively sensing the Ag^+ released from AgNPs and monitoring the time-dependent dissolution of different sized AgNPs in *Daphnia*.

The development and synthesis of AgNPs with photoluminescence performance offers a new opportunity for the application of AgNPs in biology. Combined with laser confocal microscopy, fluorescent AgNPs have been used widely in the field of

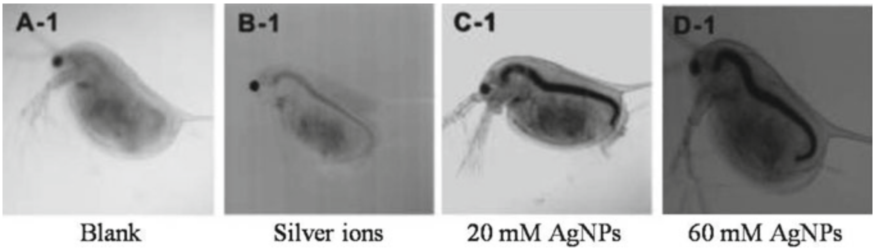


Fig. 11 The microscopy images of daphnid exposure in the SM7 medium containing (TEZ-TPE-1,) for 12 h. From left to right: TEZ-TPE-1 alone, $AgNO_3$, 20 nm AgNPs and 60 nm AgNPs. Reproduced with permission from the reference Yan et al. (2018)

bioimaging and cell labeling as a new and effective optical probe. Li et al. (2018) synthesized highly stable and multi-emissive AgNPs in situ in a DNA hydrogel. The prepared fluorescence AgNPs were successfully applied to the intracellular hydroxyl radical sensing.

6 Fourier Transform Infrared Spectroscopy for AgNPs

Infrared rays have been gradually applied to various fields since these were discovered by British astronomer Herschel in 1800. The chemists investigated the absorption of infrared radiation with different wavelengths by various substances to infer the composition and structure of the material and molecules. This method of studying the relationship between the material structure and infrared absorption is called Infrared (IR) spectroscopy. Fourier Transform Infrared (FTIR) spectroscopy is a method for measuring the infrared spectrum of the substances through measuring interferogram and performing Fourier transform of the interferogram, mainly composed of optical detecting part and computer part. At present, a large number of IR spectrum data of various substances have been systematically summarized. According to the different characteristics of the spectrum, the unknown functional group can be determined, the chemical structure can be elucidated, the chemical reaction process can be observed, the isomers can be distinguished, and the purity of the analyte can be estimated, etc. Therefore, FTIR spectroscopy has become a routine analytical method for qualitative and structural analysis. For example, the stretching vibration of the carbonyl group is at about 1600–1900 cm^{-1}, and the stretching vibration of –NH is at about 3300–3500 cm^{-1}. In the analysis of nanomaterials, information on the group and structure of the substance can be obtained simply by comparing the spectrum library.

Typically, a molecule with a time-variant dipole moment may absorb IR radiations; the oscillating frequency of which corresponds to the frequency of incident IR light (Johal 2011). The absorption of IR radiation transfers energy to the molecule, inducing a corresponding covalent bond stretching, bending, or twisting

(Cantor and Schimmel 1980). But the molecules with no dipole moments, such as O_2 and N_2, cannot absorb IR radiations. The FTIR spectrum, illustrating absorption or transmission versus incident IR frequency, can thus offer a fingerprint of the structure of the molecule.

For the measurement of FTIR spectroscopy, different types of samples require different methods of sample preparation. For nanoparticle powder samples, the halide tableting method is usually used. The analytically pure potassium bromide (KBr) is placed in an agate mortar for fine grinding (particle diameter less than 2 microns) followed by the addition of the sample in a certain ratio (the mass ratio of sample to KBr is about 1:100). The sample is thoroughly ground again to mix the KBr with the sample and finally pressed with a hydraulic press to form a uniform transparent sheet with a thickness of 1 mm.

FTIR has the advantage of rapid data collection, strong signal, large signal-to-noise ratio, and less sample heat-up (Kumar and Barth 2010). It is also a non-invasive technique and has been applied widely to study the surface structure and composition of AgNPs, such as the conformation of functional molecules grafted onto the surface of AgNPs. Chen et al. (2016) have reported a simple and feasible method for the preparation of AgNPs in water with a high molecular weight microbial exopolysaccharide (EPS1). FTIR was used to analyze the reduction of silver ions and the surface structure of AgNPs. As shown in Fig. 12, the peaks at 3000–3600 cm^{-1} attributed to the stretching vibrations of –OH and $–NH_2$. The absorption peak at 3482 cm^{-1} in the spectrum of EPS1 corresponded to the stretching vibration of –OH. In the FTIR spectrum of AgNPs, the peak shifted to 3458 cm^{-1}, suggesting the interactions between hydroxyl groups of EPS1 and the AgNPs. The phenomenon was further verified by the shift of the deformation vibration of –OH at about 1100 cm^{-1}. No obvious difference shown at about 1380 cm^{-1} suggested the excess removal of $AgNO_3$ by dialysis. Nsengiyuma et al.

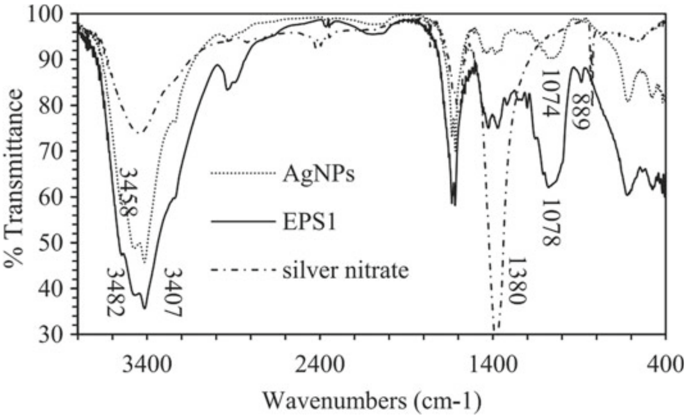


Fig. 12 FTIR spectra of silver nitrate, exopolysaccharide, and AgNPs. Reused with permission from the reference Chen et al. (2016)

(2016) have synthesized 1,3-alternate calix[4]arene-modified AgNPs. On comparing the IR spectra of bare AgNPs and 1,3-alternatecalix[4]arene-modified AgNPs, they successfully demonstrated that 1,3-alternate calix[4]arene had been successfully attached to the surface of AgNPs.

FTIR can provide IR absorption spectra to study the changes in surface properties, as well as identification of chemical properties on the AgNPs surface through matching the fingerprints of specific functional groups. However, since the depth of penetration of FTIR is of the same order of magnitude as the incident infrared wavelength, FTIR still is not a very sensitive surface-analysis method at the nanometer scale.

7 X-Ray Diffraction for Silver Nanoparticles

Since the German physicist, Röntgen discovered X-rays in 1985. After more than a hundred years of development, the X-ray diffraction (XRD) technology has been widely applied in various engineering subjects, chemistry, material science, physics, etc., and has become an important analytical method. XRD can realize the analysis of crystal structures, the qualitative identification of various compounds, and the quantitative resolution of particle sizes and chemical species by using the diffraction principle. The reflection of the X-ray light on the crystal results in the formation of different diffraction patterns, which depicts the physicochemical properties of the crystal structure. Therefore, the analysis of structural features of various materials, such as polymers, biological molecules, and inorganic catalysts, etc., can be achieved with the aid of XRD (Robin 2009). Each material has a unique diffraction beam which can be defined and identified by comparing the diffracted beams with the reference database.

Recently, the applications of XRD have extended to the characterization of various nanomaterials and conforming their properties (Das et al. 2014). The working principle of XRD is Bragg's law based on the wide-angle elastic scattering of X-rays and measuring the diffraction intensities in the range of 8–80° 2θ angles.

XRD, an effective characterization method, has also been used to study the crystalline structures, size, and diffraction patterns of AgNPs. The XRD pattern of AgNPs with a face center cubic crystalline structure displayed four main peaks at (111), (200), (220), and (311) according to the Silver Joint Committee on Powder Diffraction Standards Database (File NO. 04-0783) (Anbu et al. 2019). Anbu et al. synthesized environmentally benign AgNPs using leaf extract of *Platycodon grandiflorum* at different temperatures and performed XRD analysis to confirm the crystalline structure of prepared AgNPs. The XRD spectrum of AgNPs displayed the face-centered cubic crystalline nature with four intense peaks at 38.19°, 46.31°, 67.41°, and 76.88°, which were attributed to the crystal face of (111), (200), (220), and (311), respectively (Fig. 13). The existence of additional peaks was suggested to be probably due to the attachment of the plant extract on the AgNPs.

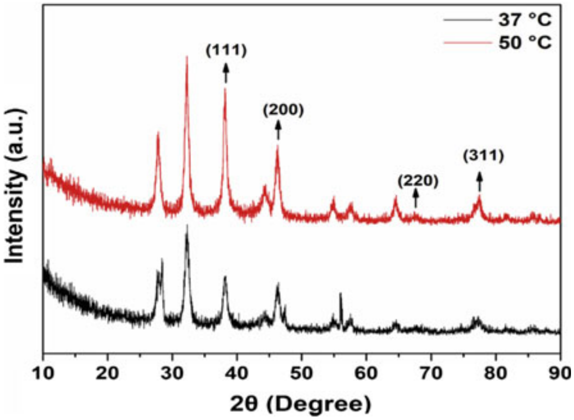


Fig. 13 XRD pattern of prepared AgNPs using platycodon grandiflorum extract at different temperature. Reused with permission from the reference Anbu et al. (2019)

In the research of nanomaterials, XRD not only study the crystalline structure of nanomaterials but also could calculate their grain size. According to the X-ray diffraction theory, when the crystal grain size is less than 100 nm, the smaller is the grain size, the larger is the peak width of the diffraction peak. Considering the influence of the structure and absorption of the sample on the diffraction line shape then the grain size of the nanomaterial can be calculated by the Debye-Scherrer formula:

$$D = k\lambda/\beta\cos\theta$$

where *D* is the crystallite size of the AgNPs, λ is the wavelength of the x-ray source (0.1541 nm), β is the half-peak width of the diffraction peak, *k* is the Scherrer constant (0.9 to 1), and θ is the Bragg's angle (Nabikhan et al. 2010).

Tanvir et al. (2012) have reported that the efficient synthesis of a stable aqueous dispersion of AgNPs at room temperature by just using a coenzyme as the reducing agent with no aid of organic solvents, toxic reagents, and other biological materials. According to the XRD data of prepared AgNPs and Scherrer equation, the average size of AgNPs was calculated to 20 nm, which was found consistent with the TEM results. Renganathan et al. (2018) have prepared AgNPs with different sizes through simple biosynthesis. The average sizes of AgNPs were calculated in the range $\sim$18–26 nm through the Scherrer formula, which is in good agreement with the results of the atomic force microscope.

XRD, as a well-established technique, has been widely used to analyze the material structure from the atomic scale, but the applications of the XRD technique are limited due to the difficulty of crystals growth and the ability to get results only from a single conformation/binding state of the sample. Compared with electron diffraction, XRD still suffers from the low intensity of the diffracted X-rays, especially for low atomic number materials.

8 Dynamic Light Scattering for AgNPs

Dynamic Light Scattering (DLS), also known as Photon Correlation Spectroscopy and Quasi-elastic Scattering, is widely used to characterize the physicochemical characteristics of small particles. DLS, as one of the light scattering modalities, can explore the size distribution of polymers, biomacromolecules, and nanomaterials in the range of one nanometer to submicron down in solution or suspension using a monochromatic light source (Brar and Verma 2011). The principle of DLS is to monitor the temporal fluctuation of Rayleigh scattering intensity of particles, induced from the Brownian motion of the particles with size much smaller than the incident light wavelength at a fixed scattering angle. The particle size can be obtained from the analysis of the motion-dependent autocorrelation function using the Stokes-Einstein equation (Sapsford et al. 2011). The size determined by DLS is usually bigger than XRD and TEM, which may be due to the influence of the capping agent present on the particles. In the particle size measurement, DLS technology has the advantages of accuracy, rapidity, and good repeatability, and has become a more conventional characterization method in nanotechnology.

DLS, however, requires several precautionary steps during sample preparation. The sample should be well dispersed in the liquid medium. The dispersant should be transparent and have a different refractive index than the solute particles, without causing swelling, resolution, or association of the particles. Besides, the solvent must be clean and capable of filtration. The analysis of particle size is commonly carried out with the scattering angle of 90° and the instrument temperature at 25 °C. Sample concentration can also significantly affect the accuracy of measurement results. Further, the optimal concentration measurement range for different samples is different. If the sample concentration is too low, there may not be enough scattered light to measure. If the sample is too concentrated, then one particle's scattered light will also be scattered by other particles. Therefore, in the actual measurement, the appropriate measurement concentration should be selected according to the particle size to obtain reliable measurement data.

DLS is widely used as a simple and effective tool for the characterization of the size distribution and aggregation state of AgNPs. Lin et al. (2003) have reported a direct synthetic route for preparing narrowly dispersed AgNPs with no extra size-selection processes. As shown in Fig. 14, the size distribution of these AgNPs was characterized systematically using DLS. The particle sizes of these AgNPs were mainly distributed in the range of 7–11 nm with a narrow size distribution, found well consistent with TEM results.

Ma et al. (2016) have developed a rapid and simple colorimetric method for the analysis of 6-benzylaminopurine based on *p*-aminobenzenethiol (ABT) functionalized AgNPs. The DLS technique suggested the mean size of citrate-stabilized AgNPs as 7 nm (Fig. 15a). The average hydrodynamic diameter of citrate stabilized AgNPs (Cit-AgNPs) was slightly increased from 7 nm to 10 nm after ABT combined to the surface of Cit-AgNPs (Fig. 15b). When ABT-AgNPs binded with 6-benzylaminopurine, a huge conjugate network could form, resulting in the

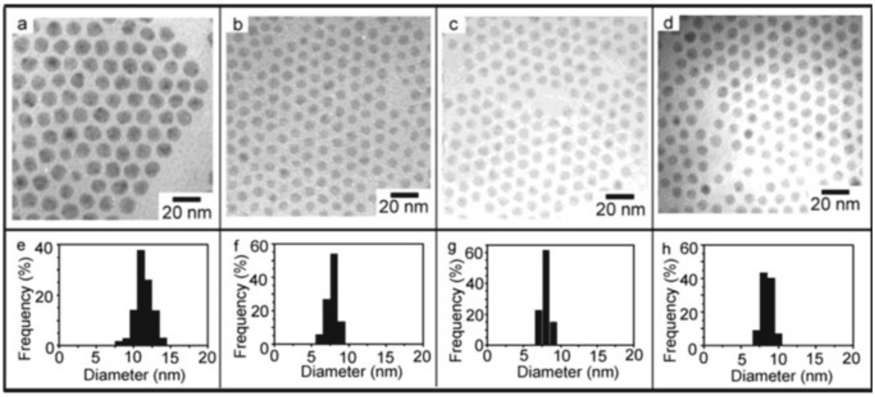


Fig. 14 TEM images (**a**–**d**) and the corresponding particle size distribution analyses (**e**–**h**) of AgNPs obtained at different molar ratios of reactants. Reproduced with permission from the reference Lin et al. (2003)

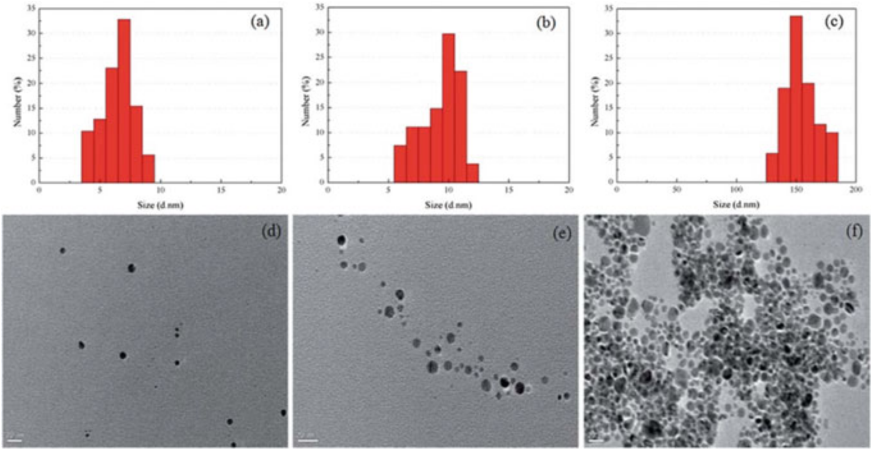


Fig. 15 The size distribution by number and corresponding TEM images of **a** Cit-AgNPs, **b** ABT-AgNPs and **c** ABT-AgNPs in the presence of 6-benzylaminopurine. Reproduced with permission from reference Ma et al. (2016)

aggregation of analyte-ABT-AgNPs. DLS was also used to monitor the size of ABT-aggregated AgNPs and the average size increased to 150 nm (Fig. 15c). TEM data further proved the accuracy of DLS results.

DLS has a series of advantages in the characterization of nanomaterials, including short analysis time, non-invasiveness, high accuracy, wide application range, along with low instrument cost and better reproducibility measurements, etc,. However, DLS also suffers from several disadvantages. It is difficult to correlate size fractions with a particular composition when certain amounts of aggregates are present. DLS has limited utility for analysis of samples with heterogeneous size distributions. Besides, due to the assumption of the spherical nature of particles in the analysis, DLS is just suited to accurately measuring the size of spherical nanomaterials.

9 Raman Spectroscopy

Raman Spectroscopy (RS), a kind of scattering spectrum, was developed from the Raman scattering effect discovered by Indian scientist C.V. Raman in 1928. RS can obtain molecular vibration and rotation information of molecules by analyzing the scattering spectrum difference from the incident light frequency, which is an analytical method for studying molecular structure. Furthermore, RS can provide submicron spatial resolution for light-transmissive materials with no need of sample preparation process. Thus, RS is also an in situ characterization technique. The principle of RS is to measure the inelastic scattering of photons that possessing different frequencies from the incident light after interacting with the electric dipoles of the molecule. RS, as a fingerprint spectrum for characterizing molecular vibration levels, has been widely used in the fields of physics, chemistry, biology, and material science.

The principle and mechanism of RS are different from those of infrared spectroscopy but can provide similar structural information, including various normal vibration frequencies and the related vibration energy levels in the molecule. Therefore, RS can also be used to identify functional groups in a molecule just similar to that via infrared spectroscopy. The change of molecular dipole moment is the cause of infrared spectroscopy, while the spectral intensity of RS depends on the change of polarizability during the corresponding normal vibration process. In molecular structure analysis, RS and infrared spectroscopy complement each other. For example, infrared absorption of C–C is weak, while the RS is strong. Therefore, some information that cannot be detected by the infrared spectrometer can be expressed well by RS.

RS can be used for qualitative and quantitative analysis with the advantages of being fast, simple, repeatable, and non-destructive. The process does not involve any sample preparation, and samples can be measured directly through fiber-optic probes, glass or quartz, etc. Furthermore, RS is suitable for studying chemical compounds and biological samples in aqueous solution because of the weak RS of water molecule. Besides, since the diameter of the laser beam is usually only 0.2–2 mm at the focus of the sample, conventional RS requires only a small amount of sample. This is a big advantage of RS over conventional infrared spectroscopy. Moreover, the Raman microscope objective can further focus the laser beam to 20 microns or less to analyze smaller areas of the sample.

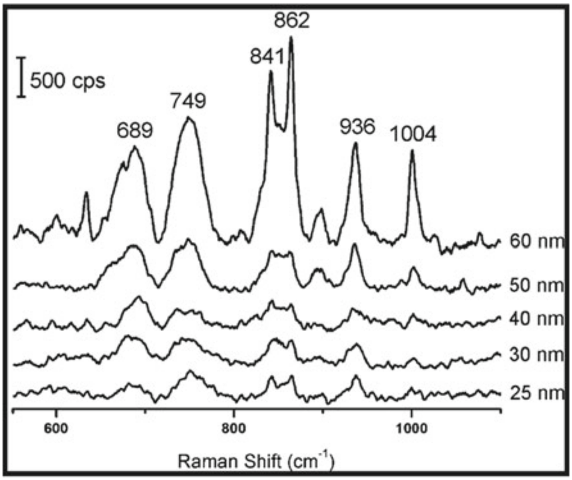
RS is the inelastic scattering spectrum of matter that provides unique information about the vibration and electronic properties of a material. In nanomaterials research, RS can help to evaluate the effect of nanoparticles size change on RS signals and the effect of nanoparticle's introduction on the glass phase structure. RS possesses the advantages of high sensitivity, no damage to samples, convenience, and rapidity. Consequently, RS is widely used for structural analysis, bond state analysis, and qualitative identification of nanomaterials.

The traditional RS technique can provide indirect characterization information of nanomaterials by analyzing spectral broadening and shifting, but it lacks the spatial resolution necessary to characterize the different fields of nanotechnology applications. Other downsides of conventional RS include the requirement of extremely small cross-sections and interference of fluorescence, demanding intense laser excitation to provide sufficient RS signals. In contrast, the Surface-Enhanced Raman Scattering (SERS) can strongly enhance RS signals and increase spatial resolution. SERS can provide topological information of the nanomaterials, in addition to their structural, chemical, and electronic properties.

As an effective and convenient method, RS is also applied to the characterization and analysis of AgNPs. Zhang et al. (2010) have synthesized AgNPs (nano-cubes) with edge lengths from 30 to 200 nm using a seed growth strategy. RS is used to characterize the size change and surface molecular structure of AgNPs. As shown in Fig. 16, it is clear that the intensity of SERS peaks increased as the nanoparticles became bigger. Some of the key vibrational bands of polyvinylpyrrolidone on the surface of AgNPs were also observed in the RS spectrum. The strong peaks located at 841 and 862 cm^{-1} were assigned to the pyrrolidone ring. The peaks at 689 and 936 cm^{-1} were ascribed to the C–C stretch and the CH_2 groups on the pyrrolidone ring, respectively.

Oćwieja et al. (2017) synthesized stable cysteine-capped silver AgNPs by using sodium borohydride as a reductant and L-cysteine as a modifier (Fig. 17). The SERS was used to confirm the chemisorptions of cysteine molecules on the AgNPs surface. For example,the disappearance of the band at 2548 cm^{-1}, due to the –SH stretching vibration of L-cysteine, suggested the formation of Ag–S bonds on the AgNPs surface.

Fig. 16 SERS spectra of the as-prepared AgNPs with five different edge lengths. Reused with permission from reference Zhang et al. (2010)



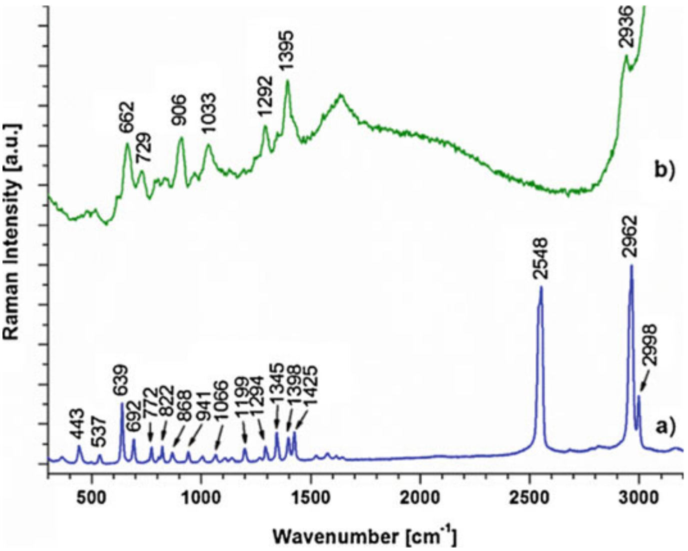


Fig. 17 RS spectra of L-cysteine powder (**a**) and L-cysteine-stabilized AgNPs (**b**). Reused with permission from reference Oćwieja et al. (2017)

10 Nuclear Magnetic Resonance Spectroscopy

Nuclear Magnetic Resonance (NMR) spectroscopy is mainly applied to study the absorption of radio-frequency radiations by the atomic nucleus. It is one of the most powerful tools for the qualitative analysis of the composition and structure of various organic and inorganic substances, and sometimes it can also be used for quantitative analysis. NMR technology plays a very important role in the determination of organic molecular structures. From the traditional one-dimensional spectrum to the multi-dimensional spectrum, from the continuous wave nuclear magnetic resonance spectrum to the pulsed Fourier transform spectrum, the NMR technology carried a significant role with a more extensive application field.

NMR is a non-invasive technique causing no damage to the sample, as it needs simple sample preparation. However, the sensitivity of NMR spectroscopy is lower than that of optical technology, and a relatively large number of samples are required for measurement. If a certain level of the signal-to-noise ratio is necessary for NMR spectral analysis, it can also be time-consuming.

NMR spectroscopy is one of the important techniques for characterizing the structure and properties of materials. Like other spectroscopy methods such as infrared spectroscopy and ultraviolet spectroscopy, NMR spectroscopy involves the determination of the energy difference between different energy states. The difference is that NMR requires an external magnetic field, and it is associated with the nucleus rather than the electrons. In NMR spectroscopy, radio frequency radiation can cause energy level splitting of the nucleus only when placed in a strong magnetic field. When the absorbed radiant energy is equal to the difference of the energy levels of the nucleus, an energy level transition occurs to generate a resonance signal. The position of the resonance signal can reflect the chemical structure (functional group, molecular conformation, etc.) of the sample molecule; the signal intensity is often related to the amount of the relevant nucleus present in the sample.

NMR can be divided into the hydrogen spectrum (^{1}H–NMR) and carbon spectrum (^{13}C–NMR) technique according to the object to be measured. Though other NMR techniques, such as ^{15}N, ^{19}F, ^{31}P, etc., are also present, the most widely used ones are ^{1}H–NMR and ^{13}C–NMR. NMR can also be divided into liquid nuclear magnetic and solid nuclear magnetic spectroscopy according to the measured sample state. Liquid NMR is used most commonly, while solid NMR plays an important role in the research of polymers and nanomaterials structure.

At present, NMR is not only an important method for molecular structure analysis but also an indispensable research tool in the field of nanomaterials science. NMR spectroscopy has been applied to characterize several physiochemical features of nanomaterials, including structure, polymers and fullerene derivatives, purity, and functionality in dendrimers, and conformational changes occurring in the interactions between ligands and nanomaterials. Pulsed-field gradient NMR has been used to evaluate the diffusivity of nanomaterials, to calculate the size and interactions of species.

Because of the advantages of NMR, it can also be used for the characterization of AgNPs. Neelgund et al. (2015) reported a single-step method for the preparation of size-controlled AgNPs using a bifunctional molecule, octadecylamine (ODA) and observed the resonance at 2.66 ppm, typical of α–CH_2 protons in pure ODA, which shifted to 2.17 ppm in the ODA-capped AgNPs sample (Fig. 18). The resonance shift suggested that the ODA molecules were bound to the surface of AgNPs. Kumar et al. (2017) synthesized sodium benzoate-functionalized AgNPs

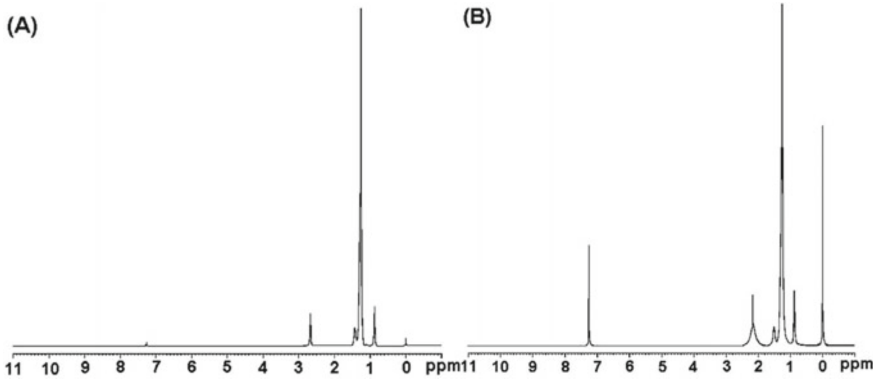


Fig. 18 NMR spectra of pure octadecylamine (**a**) and octadecylamine-modified AgNPs (**b**) in $CDCl_3$,. Reused with permission from the reference Neelgund et al. (2015)

and used ^{1}H–NMR to study the interaction of sodium benzoate and AgNPs. After sodium benzoate was modified to the surface of AgNPs, the resonance shift of benzene ring protons changed from 6.797–6.920 and 7.082–7.248 ppm to 7.302–7.431 and 7.707–7.739 ppm.

11 Conclusions

The characterization technology of AgNPs involves almost all analysis and testing techniques, from basic chemical analysis methods to equipment-based instrument analysis technologies such as spectroscopy and electron microscopy. Among them, UV-Vis absorption is the easiest way to characterize AgNPs with low-cost. TEM and SEM are essential to the morphologic study of AgNPs, where DLS can provide supplement and verification. Furthermore, the surface group's information of AgNPs can be obtained from FTIR. Besides, XRD, NMR, optical microscopy, and Raman spectrum can be as optional characterization technology to provide extra supplementary information and explain the phenomenon in a particular situation.

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Silver Nanoparticle on Various Synthetic Polymer Matrices: Preparative Techniques, Characterizations, and Applications

Arya Uthaman, Hiran Mayookh Lal, and Sabu Thomas

1 Introduction

Polymer nanocomposites achieved significant attention in recent years and also have become essential materials in modern nanotechnologies. This interest arises as a result of their outstanding performance, design flexibility, higher properties compared to constituent materials, low life cycle cost, and enormous applicability of nanocomposites in various engineering and industrial fields. The polymer nanocomposites are advanced functional materials that constitute nanoparticles/ nanofillers dispersed inside the polymer matrix forming in a core-shell structure. The shape of these reinforcement varies (like fibers, platelets, spheroids) at least should have the dimension in the range of 1–50 nm. For manufacturing, nanocomposites follow strict requirements in each step, such as controlled/ optimized mixing, stabilized dispersion, and orientation of the dispersed phase should be controlled for all multi-phase systems.

For particle, the transition from micro to nano is due to changes in their chemical and physical structure, which contributes to their unique properties. The smaller particle size enhances the surface area-to-volume ratio, which leads to the dominant behavior of atoms due to the higher surface area of nanoparticles. There is more possibility to have one-to-one interaction with other particles present inside. Therefore, the nano filled polymer composites pose enhanced thermal resistivity and mechanical strength by the inclusion of nanoscale filler. It is essential to maintain the uniform distribution of nanoparticles as it substantially improves the overall performance of the composites. Among nanoparticles, silver nanoparticles

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(AgNPs) merit special attention due to their efficient applicability in the biomedical field, especially as antimicrobial agents. AgNPs are commonly applied in various industrial applications such as the production of electronic circuits, inkjets, sensors, biomarkers, photography, etc. As mentioned, these properties of AgNPs are strongly influenced by their aspect ratio, shape, size, and distribution.

The synthesizes of AgNPs include various methods such as physical, chemical, photochemical, and biological routes (Natsuki 2015). Each of these methods has its advantages and disadvantages. Physical and photochemical methods for AgNPs synthesis need strict control over the reaction and expensive equipment, but it doesn't include the usage of toxic chemicals. However, the chemical synthesis of AgNPs is comparatively cheaper. The main drawback is the usage of very toxic chemicals. In recent years the AgNPs synthesized using plant-based non-toxic photochemical inclined to use a safer chemical process with an efficient transformation of desires products. The industrial production of AgNPs uses phytochemicals reducing agents and biocompatible polymer-based stabilizers. Thus, this method is considered more environmentally friendly. The microorganism based biological process for the synthesis of silver nanoparticles also recently developed. However, this method also has some disadvantages and is not preferred for the industrial production of silver nanoparticles.

It is well known that due to the size, shape, surface chemistry, and aspect ratio of AgNPs it characterizes quite different from bulk silver. The aforementioned properties of AgNPs give unique and desired properties to the nanocomposites while incorporating within different polymer matrices. The uniform dispersion and strong interfacial interaction of AgNPs with the polymer matrix create a huge nano-dimensional interface in the polymer nanocomposite. Thus, the polymer matrix is found to modify the surface chemistry of AgNPs and prevent the aggregation of nanoparticles. The interfacial interaction between the AgNPs and polymer matrix is responsible for the unique and desired properties, and thus suits many advanced applications. Many polymer matrices incorporated with AgNPs interestingly act themselves as the reductants for silver ions. The silver polymer nanocomposites utilized for wound healing applications can effectively eject silver ions which can act as an anti-microbial agent. The sliver-based nanocomposites can be used as a heterogeneous reusable catalyst and hence can be easily separated using the filtration method from the reaction medium. This chapter includes the elaborated discussions on AgNPs based polymer nanocomposites, synthesis, properties, and various applications.

2 Types of Polymer Matrices

To fabricate polymer nanocomposites almost all types of polymer matrices such as plastics, fibers, and elastomers are commonly used. This list of polymer matrix ranges from low molecular weight elastomers and high molecular weight resins are also utilized for manufacturing various thermosetting polymer nanocomposite. Both thermoplastics and thermosetting polymers are used for manufacturing polymer nanocomposites. By the homogeneous dispersion of nanoparticles in the polymer matrix will improve its performance. The polymer matrix in which the nanofillers or nanoparticles uniformly dispersed is not only a continuous phase but also stabilizes and strongly interacts with nanoparticles.

Polymers are macromolecules (organic or inorganic molecules) constituents formed by the linkage of a large number of repeating units. The repeating units are called monomers which are formed of simple molecules. The process of linkage of simple monomers to giant polymer molecules is known as the polymerization process. The number of repeating units formed in a polymer chain is termed as a degree of polymerization and it is used for determining the molecular weight of polymer from the known molecular mass of repeating unit. The polymers are manufactured using different techniques such as addition, condensation, and rearrangement polymerization techniques. The addition polymerization includes the monomer bond together one after another by covalent bonding without elimination of any by-products. There are different types of addition polymerization, the first type is free radical polymerization that includes controlled radical polymerization such as atom transfer radical, group transfer, and chain transfer. The second type is ionic polymerization such as anionic and cationic polymerization, etc. The examples of polymers manufactured utilizing addition polymerization techniques are polyethylene, polystyrene, polyvinyl chloride, polymethyl methacrylate, polytetrafluoroethylene, polyisoprene, polybutadiene, polychloroprene, polyacrylonitrile, etc. are examples of homopolymers, that includes the combination of the same type of monomer. The different combinations of more than one type of monomers to form as co-polymers include polymers such as ethylene-propylene copolymer, polybutadiene-styrene poly acrylonitrile-butadiene, poly acrylonitrile-butadiene-styrene, poly-vinylidene fluoride-hexafluoropropylene-tetrafluoroethylene), etc. All these polymers are manufactured utilizing the addition polymerization technique. The formation of co-polymers results in improved properties as compared to homopolymers and is also flexible polymers because of the internal plasticization effect. In the condensation polymerization technique, the mutually reactive reactants undergo polycondensation reactions in which the polymers are formed by the step-growth mechanism that involves the elimination of small molecules as byproducts. polyesters, polycarbonates, polyethers, poly(ester amide)s, polyamides polyimides, polysulfones, poly(ether ketone)s, etc. are examples of polymers manufactured utilizing condensation polymerization. On the other hand, if the polymers are formed by a step-growth mechanism without any elimination of byproducts, then the polymerization process is termed as a rearrangement polymerization process. The polymers formed by this process are polyurethanes, polyureas, polyurethanes, etc. All these aforementioned polymerization processes are conducted mainly by four polymerization techniques such as mass/bulk, solution, suspension, and emulsion polymerization. Moreover, these four techniques interfacial, template, electrochemical, and plasma polymerizations are employed depending on the requirements of the products.

The polymers process different structures that include linear chains with low branched, high-branched, and hyperbranched structures (dendrimers). The hyperbranched polymers possess three-dimensionally branched macromolecules with large surface free functional groups and these type polymers are highly compatible with others and highly soluble in a vast number of solvents. Compared to other types of polymers the hyperbranched polymers are easy to process, therefore these polymers are an ideal class of matrices for polymer nanocomposites. Generally, all the polymers mentioned above can be easily processed utilizing different techniques such as solution mixing, suspension mixing, emulsion mixing, melt mixing, and rubbery stage mixing, etc. The general classification of polymers includes thermoplastic polymers that can be processed repeatedly in a controlled manner without losing its property, other classification is thermosetting polymers as once they set or chemically cross-linked in the final stage of processing, they are not possible to process again. The overall properties of a polymer can be identified from its structure and molecular weight. The main drawbacks of polymers are its poor mechanical, thermal, flame retardant properties, and its biodegradability. However, polymers are superior over metals and ceramics because of their advantages like easy processing, versatility in structure, modification, and relatively low cost. Due to these advantages of polymers, they are chosen as superior material as matrices for manufacturing nanocomposites.

Based on the origin of polymers, they can be classified as natural polymers and synthetic polymers. All the polymers we mentioned above are synthetic polymers, natural polymers are the polymers that obtain naturally, including polysaccharides (starch, alginate, chitosan/chitin, hyaluronic acid derivatives) or proteins (collagen, soy, silk, fibrin gel), etc. There are many advantages and disadvantages that characterize these two different origins of polymers, as mentioned synthetic polymers have high mechanical strength and modifiable structure and properties compared to natural polymers. Natural polymers have their potential advantage of biologically reorganizations and, but they have poor mechanical properties compared to synthetic polymers. Natural polymers based nanocomposites where natural polymers act as matrix and nanoparticle act as nanofillers donates great potential to be utilized for various applications such as wound healing, food packaging, biomedical industry, etc.

3 Preparation of Polymer Silver Nanocomposites

Silver/polymer nanocomposites are fabricated using preformed AgNPs or either by introducing silver precursors to polymer matrix followed by the preparation of AgNPs. The other method includes the preparation of polymer in the presence of silver precursors or preformed AgNPs. The electrospinning technique for the fabrication of polymer/silver nanocomposites includes the homogeneous nanoscale dispersion of polymer-AgNPs in a polar solvent or solvent mixture such as methanol, ethanol, acetonitrile, etc. The AgNPs-polymer nanocomposites are manufactured as silver-impregnated nanofibers utilizing an electrospinning technique. Generally, AgNPs- polymer nanocomposites are manufactured by the conventional techniques that are employed for the preparation of polymer nanocomposites. The main objective for the manufacturing of polymer nanocomposite is to fabricate them with a higher amount of interfacial interaction between polymer and nanoparticles, this could be attained by the uniform distribution of nanoparticle throughout the polymer matrix and maximum degree of nano dimensional interface should be achieved in the resultant polymer composite. The presence of an appropriate functional group in the polymer matrix and nanoparticle can increase interaction between nanoparticle and polymer matrix interface. The ultrasonic force and mechanical shearing are also employed commonly for the uniform distribution of nanoparticles inside the polymer matrix. Thus, it is very crucial for choosing the appropriate method for the manufacturing of polymer nanocomposite for exploring their maximum potential. A detailed description of the types of polymer matrices and preparative techniques for manufacturing nanocomposites are discussed below.

3.1 Solution Technique

In this technique, a polymer solution and nanoparticle are well dispersed to a homogeneous mixture, this can be done by utilizing a mechanical shearing followed by ultrasonication. For making the homogenous mixture a polymer solution is prepared separately in a solvent, and the nanoparticle is dispersed in a liquid medium by proper homogenization. The liquid medium used for both polymer and nanoparticle should be miscible. Both the solution is mixed homogeneously, the unwanted solvent is removed from the prepared homogeneous mixture either by evaporating the solvent from the mixture or by precipitation of polymer/ nanomaterial dispersion. The significant interaction between the polymer and nanomaterial must be greater than polymer-solvent and nanomaterial –solvent interactions. The strong interaction between the polymer and nanoparticle helps the polymer chains to penetrate inside the structure of nanoparticles, also the polymer chains are absorbed to the surface of nanoparticle while forming a polymer nanocomposite. In this manufacturing technique, both intercalated and exfoliated nanocomposites are formed. The state of intermixing between the polymer chain and nanoparticle depends on the thermodynamics of mixing, the prepared nanoparticle must be thermodynamically stable, which is governed by favorable enthalpy and entropic factors. The strong interaction between the polymer matrix and nanoparticle results in the higher enthalpy loss, and the Gibbs free energy becomes favorable, the strong interaction between the polymer and nanoparticles also results in a decrease of entropy factor due to the restriction of motions of the polymer chain. The solution technique is a simple process however, it is associated with various drawbacks, such as environmental and health hazards due to the usage of toxic organic solvents, higher cost, flammability, etc., (Xin and Li 2011) decorated carbon nanotubes (CNT) with AgNPs for manufacturing advanced CNT/ polymer nanocomposites utilizing solution technique. The polystyrene is dissolved in reductant followed by the addition of pre-prepared Ag-CNT filler, the mixture is ultrasonicated for 10 min, and the composite was dried in a vacuum oven at 50 °C for 6 h. The composite samples were molded using a hot-press molding machine.

3.2 Melt-Mixing Technique

This technique involves uniform mixing of nanoparticles in preformed polymer matrices utilizing the conventional melt processing equipment for manufacturing polymer nanocomposite with desired properties. The melt-mixing process is commonly preferred by industries because this process avoids the usage of toxic solvents, and is simple and economic. The industrial melt-mixing techniques involve the melting/softening of semicrystalline/amorphous polymers by heating in the mixing equipment such as an extruder, injection molding, Brabender mixer, etc. followed by the incorporation of nanoparticles. The homogenous dispersion of nanoparticle inside the polymer matrix is obtained from the applied mechanical shear force inside the mixing equipment. The environmental friendly processing is the main advantage of this technique, therefor the melt mixing technique for fabrication of polymer nanocomposites is well accepted by various industries. Pre-proofs et al. (2019) prepared AgNPs-polymer nanocomposite by melt-kneading of polymers and silver precursors in an internal mixer. Initially, the polymer was introduced to the mixing chamber, and then the silver precursors were added to the chamber after 2 min of processing of polymer. The polymer/silver precursor mixture was melt-kneaded for a specific duration. Molten silver/polymer nanocomposite was taken out from the chamber and kept at room temperature. The authors employed a one-step solvent less in situ reduction method to convert Ag-precursors to AgNPs during processing, which utilizes a mild reducing environment of thermoplastic polymer melts for reduction.

3.3 In Situ Polymerization Technique

In this technique, the nanoparticle is well dispersed in the low viscous monomer or prepolymer. The polymer is formed in the presence of dispersed nanoparticles and thereby forming the polymer nanocomposites. The dispersion of nanoparticles in the low viscous monomer or prepolymer allows it to adsorb on the surface of dispersed nanoparticle; during the polymerization, the polymer chains help in debundling or delamination or dispersion of nanoparticles. In the case of in situ technique, the viscosity of prepolymers or precursors of the monomer is lower than the respective preformed polymers compared to the solution polymerization technique. Thus the interaction of nanoparticle and the polymer matrix is relatively stronger. The polymer composites formed by this technique are exfoliated polymer nanocomposites because of low viscosity of prepolymer, uniform dispersion of nanoparticles, and strong interfacial interaction between polymer matrix and nanoparticles. This technique is mainly preferable for manufacturing polymer nanocomposites from resin due to the minimum solvent used and lower energy requirement. In addition, it is notable that if the presence of an additional functional group in the nanomaterial can form a crosslinking reaction while processing thermosetting polymer nanocomposites. Eisa et al. (2012) prepared a well-dispersed AgNPs in polyvinyl alcohol (PVA)/polyvinyl pyrrolidone (PVP) blend films using in situ technique where PVP and PVA act as stabilizers and polyol as reductant. The authors used 0.6 ml of 0.05 M of $AgNO_3$ was added to the homogeneous solution of PVA/PVP blend prepared in different polymer ratios (100/0, 80/20 50/50, and 20/80). The polymer composite films obtained exhibit excellent anti-bacterial activities and are suitable for various biomedical applications.

3.4 Sol-Gel Method

In this method, nanoparticles are prepared in the polymer matrix. It involves the gel or aqueous solution containing the precursors, or building blocks of the nanoparticles polymer matrix is subjected to elevated temperature by heating. During the treatment, the polymer aids the nucleation and growth of nanoparticles and thus the nanoparticle formed are trapped inside the polymer matrix. The nanocomposites formed are in the colloidal form and polymer nanocomposites in the colloidal form are usually prepared using this technique. The main advantage of this technique involves the potential of promoting the uniform dispersion of nanoparticles inside the polymer matrix in a one-step process without applying any additional energy. However, this method possesses serious disadvantages like, in case of processing the nanoparticles that require high temperature may decompose polymer matrix. So, this technique is not suitable for manufacturing polymer nanocomposites with clay-based nanoparticle which requires high-temperature processing. Furthermore, the probability of aggregation of nanoparticles is higher due to the harsh processing conditions. Therefore, this technique is less common compared to the aforementioned techniques. synthesized silica silver nanocomposites utilizing the sol-gel process.

3.5 Electrospinning Technique

This is a standard technique for manufacturing polymer nanocomposite based nanofibers. The electrospinning technique involves an automatic hydraulic syringe with a micro-tip needle, a DC source with high voltage, and a collector connected with an electrical earthing. The process of electrospinning involves a polymer solution in the form of a suitable polar polymer melt mixed with the required amount of nanoparticles. The homogeneous dispersion of polymer melt and nanoparticles are achieved utilizing mechanical shearing followed by ultrasonication similar to the solution technique. The high voltage electric field produces electrically charged jets from polymer solution or melt, which on drying of jets solidify through evaporation of solvent to produce nanofibers. The voltage used in this technique should be high enough so that the electrostatic must overcome the surface tension of polymer melt to come out from the needle tip. The highly charged nanofibers are directed towards an oppositely charged collector, which is in various shapes such as, flat, rotating drum, etc., to collect the fibers Subbiah et al. (2005). The uniformity, dimension, and morphology of manufactured nanofibers depend on the concentration, polarity, and viscosity of the polymer solution/melt, hydraulic pressure exerted from the syringe, flow rate, tip diameter, exerted electric field strength, tip to collector distance, etc. (Abdel-Mohsen et al. 2019) fabricated nanofiber mats by electrospinning of polyvinyl alcohol/hyaluronan solutions in the presence of uniformly dispersed AgNPs. Liu et al. (2017) developed PLA-based fibrous mats with graphene oxide-Ag nanoparticles utilizing electrospinning technique, it shows excellent anti-bacterial properties that are suitable for biomedical applications.

3.6 Template Method

In this method, nanoparticles are prepared from their precursor solution utilizing polymers as the template, the polymer nanocomposite is formed in situ. The main advantage of this process is the possibility of uniform distribution of nanoparticle in the polymer matrix in a single-step process. Even though the materials formed by the template method are of great interest because of the manufacturing of inorganic porous materials. This process is not a commonly used method for industrial manufacturing due to the poor quality of nanocomposites, and also this method does not hold good for the production of polymer nanocomposites.

4 Silver Nanoparticle in Different Synthetic Polymer Matrices

4.1 Polyethylene-Silver Nanocomposites

Polyethylene is a thermoplastic polymer with a crystalline structure. These plastics are classified into two types such as high-density polyethylene (HDPE) and low-density polyethylene (LDPE). The main advantages of polyethylene include high tensile strength, ductility, impact resistance, low moisture absorption.

The higher the density of polyethylene the material becomes more rigid and strong. The primary application of polyethylene includes containers and bottles, plastic bags, plastic films, and geomembranes.

The polyethylene used as a matrix polymer for AgNPs to form polyethylene/silver nanocomposites is widely used for several biomedical applications and food packaging industries due to its excellent anti-microbial activities. The LDPE is the most commonly used thermoplastics for the packaging application due to its high flexibility, easy processability, transparency, environment recyclability, thermal stability, and economic efficiency makes LDPE superior as a packing material. Dehnavi et al. (2013) proposed a novel method for the fabrication of antibacterial LDPE-AgNPs nanocomposite film for food packaging. The synthesis of nanocomposites involves three steps; the first step contains the preparation of AgNPs by the chemical reduction of silver salt using fructose as a reducing agent in a stable colloidal solution, the second step involves the corona air plasma treatment on LDEP film surface to increase the adhesion of AgNPs on the surface of LDPE, and the third step involves adhesion of AgNPs on the surface of LDPE by the immersion of pre-treated LDPE in the colloidal silver solution. The corona pre-treatment of LDPE films improved its adhesion of AgNPs on the polymer surface. This was proved by utilizing FTIR-ATR analysis of the untreated and corona treated LDPE films. The presence of polar groups such as C–O and C = O formed on the surface of LDPE by corona air plasma treatment helps the polymer to increase its hydrophilicity and reactivity of LDPE films; therefore, more AgNPs were coated on the surface of LDPE. The authors found the silver ion release rate of 0.00150 μg/mL cm^2 by immersing a nanocomposite sample of $6 \times 10\ \text{mm}^2$ into 125 ml deionized water, and a 2 ml solution was taken at a defined period to identify the presence of silver ions utilizing atomic absorption spectroscopy. The manufactured AgNPs/LDPE nanocomposites exhibits excellent antibacterial properties and were evaluated by agar well diffusion and dynamic shake flask method. Olmos et al. (2018) manufactured homogeneous LDPE/AgNPs nanocomposites using a non-conventional processing method. The high energy ball-milling under cryogenic conditions was utilized to achieve a powder of well-mixed LDPE and AgNPs. The composite film was prepared by hot-pressing. The films possess excellent antibacterial properties against DH5a Escherichia coli cells according to the antimicrobial studies. The AgNPs incorporated with LDPE does not influence its physical, chemical, and thermal properties (Brito et al. 2020).

Several studies are reported on HDPE chosen as the matrix polymer for manufacturing nanocomposites as it has a wide range of biomedical application such as catheters, tubing, syringes, antimicrobial surfaces, device packaging, and several commodity applications such as pipes, water storage containers, kitchen storage plastics, etc. (Roy et al. 2020) manufactured HDPE/silver-clay hybrid nanocomposite by melt mixing technique utilizing a twin-screw extruder. The prepared nanocomposite shows excellent antimicrobial properties. The analysis of in vitro cytocompatible properties of HDPE/silver/clay nanocomposite represents complete compatibility and no viable cell count reduction to human dermal fibroblast and erythrocyte cell lines quantified in vitro in (3-(4,5-dimethylthiazol-2-yl)-

2,5-diphenyltetrazolium bromide (MTT) assay and RBC hemolysis protection assay. In the in vivo analysis, tissue section retrieved from rat skin was surgically stitched with HDPE/silver- clay nanocomposite showed no changes in the morphology after continuous exposure of 21 days.

4.2 Polystyrene-Silver Nanocomposites

Polystyrene (PS) is a hard and stiff thermoplastic polymer produced by the polymerization of its monomer called styrene. These are most commonly used in the food-service industry as containers, disposable eating utensils, and foamed plates, cups, and bowls. The polystyrene matrix for AgNPs could provide effective stabilization nanoparticles and enable the easy processibility for manufacturing AgNPs/PS nanocomposites for the desired application. These nanocomposites can be used in different applications such as surface-enhanced Raman scattering, molecular sensing, a digital memory device, biomedical applications, and antibacterial packaging. Vodnik et al. (2012) manufactured nanocomposites film with AgNPs incorporated in PS matrix in different quantities and its optical and thermal properties were studied as a function of silver content. The nanocomposites were prepared to utilize the solution mixing method. The nanocomposite films exhibited a plasma resonance peak at 470 nm, due to the collective oscillation of free electrons in AgNPs embedded in the PS matrix. The authors compared the experimental bands with theoretical absorption spectra calculated utilizing effective medium Maxwell-Garnett theory. The TGA analysis of the nanocomposite films reveals, the introduction of AgNPs to PS increased slightly the thermal stability of PS and a notable improvement in the thermal-oxidative stability of the nanocomposite films. The glass transition temperature of the nanocomposite film decreased due to the weak interfacial interaction between AgNPs and PS matrix. Ali et al. (2019) manufactured silver/PS-polyvinylpyrrolidone (PVP) nanocomposites utilizing polymerization by γ-ray irradiation. The mechanism of synthesis of silver/PS/PVP nanocomposite is represented in Fig. 1. The AgNPs was dispersed in PVP, the AgNPs was embedded in the PS matrix via subsequent reduction of Ag+ ions by γ-ray irradiation, as it is an effective method for the synthesis of the nanoparticle by the reduction of metal ions. The size of the nanoparticle is controlled by adjusting the values of the irradiation of samples. The PVP not only stabilized the polymer particles but also prevented the nanoparticle from agglomeration. The optical absorption spectra are characterized using UV visible absorption spectroscopy and confirm the redshift of peaks increased within the irradiation dose. As shown in Fig. 2, the absorption band appears at 295 nm is for the PS matrix, while increasing the irradiation dose the intensity peaks are shifted to longer wavelength ranges from $\approx$420 to 430 nm. This confirms the presence of a large number of nanoparticles with higher γ-irradiation doses. The TGA test reported the thermal stability of polystyrene enhanced with the increase in loaded AgNPs in the PS matrix. PS-methyl acrylic acid (MAA)/silver nanocomposites sphere with high catalytic activity is prepared by (Liao et al. 2016). The PSMAA/silver nanocomposite spheres are prepared in the aqueous media where the silver precursor [Ag $(NH_3)_2$]+ ions are absorbed on to monodispersed PS-MMA spheres due to the strong electrostatic attraction between the electronegative carboxyl group and electropositive [Ag$(NH_3)_2$]+ ions. The [Ag$(NH_3)_2$]+ ions reduced to AgNPs are protected by PVP on the surface of PSMAA spheres. Krystosiak et al. (2017) proposed a novel approach for preparing PS/silver nanocomposites utilizing nitroxide mediated radical polymerization. This method involves the late injection of nitroxide-coated AgNPs into a TEMPOL mediated styrene polymerization system, the homogeneous PS/silver nanocomposites formed are with well-defined core-shell structure, high grafting density that varies from 2 to 5.9 chain/nm^2, and exhibits effective antibacterial activity.

4.3 Polycarbonate-Silver Nanocomposites

Polycarbonate (PC) are amorphous thermoplastic polymers, they are generally strong, tough, and some grades of this polymer are optically transparent. Unlike other thermoplastic polymers, the PC can undergo large deformations without breaks or cracking. The general application of PC includes digital disks like DVDs, automotive components, eyewear lenses, medical devices, etc. The incorporation of metal nanoparticles to the matrix of PC enhances its physical properties, the resultant nanocomposite obtained will be appropriate for several applications such as biotechnology, energy storage, packaging, optical devices and food stabilizing systems, etc. Several studies were reported on PC/silver nanocomposites. Nouh et al. (2017) manufactured Makrofol PC/silver nanocomposites films and analyze the effect of gamma irradiation on the structure and optical properties of nanocomposites. The PC/silver nanocomposites were prepared by casting technique, where Makrofol PC is dissolved in methylene chloride. The synthesized AgNPs (PVP reduction of silver nitrate in ethanol solution) is added to the PC solution under magnetic stirring. The aqueous mixture was cast into a petri dish and placed for 3 days in a closed box to evaporate the solvent. The PC/silver nanocomposite films are exposed to gamma radiation in the dose ranges from 20 to 300 kGy. The irradiation up to 150 kGy results in the increases of intermolecular interaction between PC chains and Ag that is attributed to the crosslinking that reduced the ordering structure, giving polymer more resilience. This reduces the optical energy gap and the increase in the refractive index. In another study conducted by (Nouh et al. 2020) synthesized PC/polybutylene terephthalate/silver nanocomposites and exposed to gamma irradiation ranges between 2 and 25 kGy. The resultant effect was characterized by utilizing the microscopic and spectroscopic technique. The authors found, the gamma irradiation causes proper spreading of AgNPs in the PC—polybutylene terephthalate matrix and thus resulted in the increase of amorphous phase with a decrease in the optical energy gap. Further, the nanocomposite exhibits a response to color change as intensity

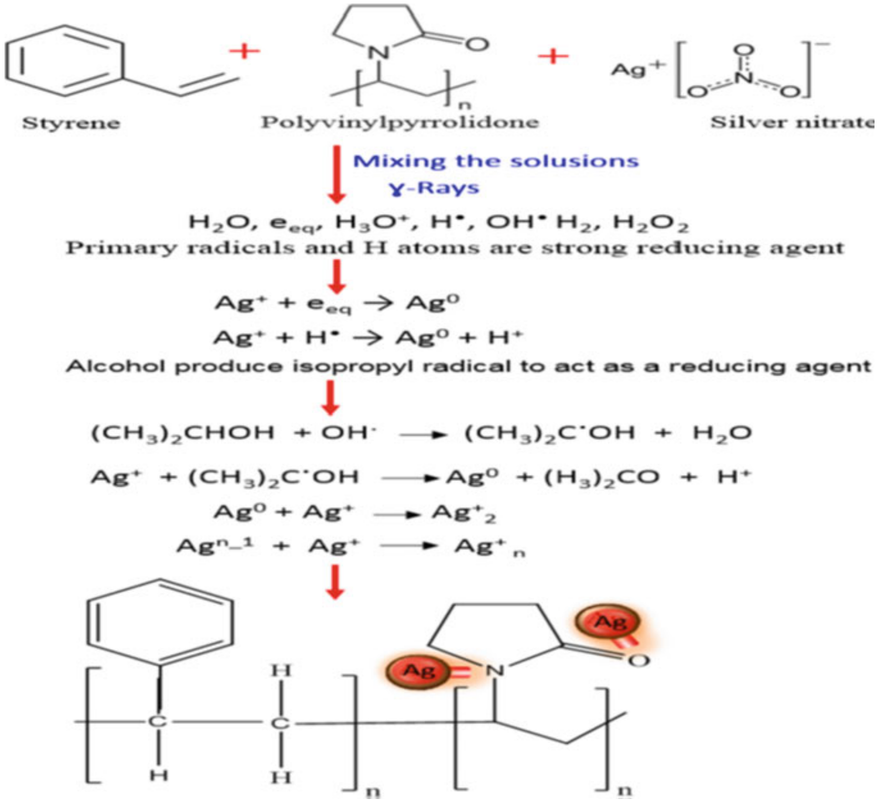


Fig. 1 Chemical structure and proposed mechanism of synthesis of silver/PS/PVP nanocomposites. Reproduced from References Ali et al. (2019) with permission

increases from 0.64 to 4.94. The association of PC matrix with conductive fillers such as Silver nanowires further extended the range of application of PC by the addition of electrical properties to PC/silver nanocomposites (Moreno et al. 2012).

4.4 Polypropylene-Silver Nanocomposites

Polypropylene (PP) is a very common thermoplastic polymer and has been compounded for a wide range of properties such as high resistance to stress and cracking, high melting point, excellent impact strength, biomedical field, etc. The common application of PP includes containers for food storage, household goods such as utensils, area rugs, athletic apparel, etc., automotive parts such as car batteries, etc. The modification of PP with inorganic nanoparticles such as AgNPs may provide additional functionality to the polymer. The presence of AgNPs in the

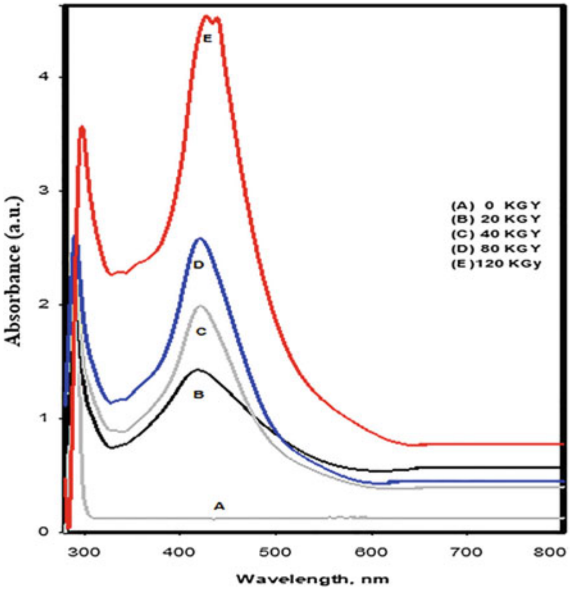


Fig. 2 Spectrum of UV/vis for silver/PS/PVP nanocomposite. Reproduced from Reference Ali et al. (2019) with permission

PP matrix increases the crystallization temperature of isostatic PP even at very low silver content, this represents a high efficiency of heterogeneous nucleation (Oliani et al. 2015). The investigation of the biocidal effect of gamma-irradiated PP/silver nanocomposites was studied by (Oliani et al. 2017). In this study, the PP was modified by gamma irradiation of isotactic PP in the presence of acetylene. The modified PP is with long-chain branching and distinct rheology. The authors blended 50/50 wt% of neat PP and modified PP and mixed using a twin-screw extruder then the AgNPs were infused into the polymer blend matrix at different concentrations of 0.1%, 0.25%, 0.5%, 1.0%, (1% PVP), 2% and 4% by wt%. The characterization of nanocomposite films utilizing Raman spectroscopy revealed the presence of a functional group associated with the stability of AgNps. Figure 3 shows the Raman spectrum of different concentrations of silver in the PP matrix. The band at 237 cm^{-1} represents stretching of Ag–O bond, band range between 397 cm^{-1} represents the Ag lattice vibration modes, intense peak at 1358 cm^{-1}, and 1589 cm^{-1} represents the enhancement of Raman lines by carbon polymeric segments absorbed on the silver oxide. The peak at 659 cm^{-1} represents the presence of PVP stabilized silver nanoparticles.

Using TEM analysis the authors verified the presence of AgNPs clusters with size ranges between 26 and 41 nm. The tensile strength of PP was found to decrease due to the addition of a higher concentration of AgNPs. The nanocomposite film with 1% AgNPs (PP/1.0% AgNPs-PVP) exhibits a comparatively excellent antibacterial effect. The manufactured nanocomposites prepared are

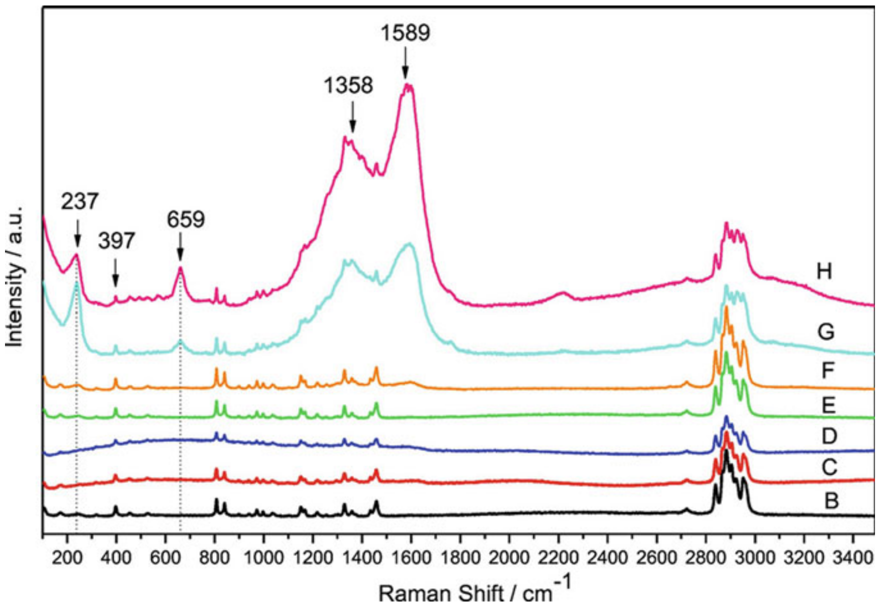


Fig. 3 Raman spectrum of PP films with AgNPs: B) PP/0.1%AgNPs; C) PP/0.25%AgNPs; D) PP/0.5%AgNPs; E) PP/1.0%AgNPs; F) PP/1.0%AgNPsPVP; G) PP/2.0%AgNPs; H) PP/4.0% AgNPs) Reproduced from reference (Oliani et al. 2017) with permission

noncytotoxic to human cells which are confirmed by a cell of a mouse. The authors also found the presence of surfactant-coated AgNPs allows antibacterial protection in contact-active without detectable biocide release. In another study conducted by (Ghorbani and Molaei 2017) the antibacterial properties of PP/silver nanocomposites were investigated. AgNPs were coated on the surface of PP films. For this purpose, the surface of the PP film was treated by corona discharge, and the modified PP films were then immersed in a colloidal solution of AgNPs. The AgNPs in the solution were synthesized by chemical reduction of silver salt using hydrazine hydrate (three silver nitrate solutions of 100 ml with various concentrations of 0.01, 0.005 and 0.001 M). The corona discharge treatment of PP/silver nanocomposite films was done to change the polarity of the nonpolar surface of PP and prepare it for coating. The corona discharge was applied to PP films for three different periods of 1, 3 and 5 min and the experiments were repeated for each time slot at three different powers of 100, 5000, and 10000 W. The SEM analysis of treated PP films confirms that the coating of the film enhances with an increase in time and power. The antibacterial activity of PP/silver nanocomposite films against gram-positive Staphylococcus aureus and Escherichia coli measured using the disk diffusion method reveals by increasing the time and power of corona discharge improves the quality of coating on the film. Ziabka and Dziadek (2019) prepared PP modified with AgNPs were manufactured utilizing injection molding and extrusion.

The authors studied to analyze whether AgNPs could influence the stability of the PP matrix during the 24 months of in vitro testing. It was found that the PP matrix with AgNPs displayed the significantly higher tensile strength and Young modulus during 12 and 24 months of investigation. The DSC analysis revealed that the incubation of composite material resulted in a slight reduction in the degree of crystallinity and melting temperature of PP. The overall performances of nanocomposite are observed stable even during 24 months, thus the authors concluded the material could be confidently applied as biomaterials.

4.5 Polyvinyl Chloride-Silver Nanocomposites

Polyvinyl chloride (PVC) is a lightweight, tough material that is rigid, durable, and is resistant to acids and bases. Most of the PVCs are used by construction industries as drainpipes, roofing sheets, gutters, and vinyl siding. The excellent antimicrobial properties of PVC/silver nanocomposite films are widely applied for food material packaging. Azlin-Hasim et al. (2016) manufactured antibacterial PVC/silver nanocomposite films utilizing the solvent casting method. From the mechanical characterization of nanocomposites film, the authors found that there is no significant difference between tensile strength and elongation at break of PVC films and PVC/silver nanocomposite films. From the thermal analysis, the Tg of PVC/silver nanocomposite decreased from 95 °C (PVC films) to 72 °C. The decrease in Tg may due to the van der Waals interaction between PVC chains and AgNPs. It is also suggested that the decrease in Tg of nanocomposites may due to repulsive force between nanoparticles and interfacial layer may lead to polymer chain mobility, thus yielding plasticizing effect by a reduction in the values of Tg. The antimicrobial activity of PVC/silver nanocomposite films for food packaging is confirmed significantly by extended shell-life of chicken breast fillets and reduced oxidation of chicken breast fillets compared to PVC wrapped equivalents. Afzal and Akhtar (2010) synthesized polyaniline-PVC/silver nanocomposites and analyzed the electrical properties of the nanocomposite. The dedecylbenzenesulfonic acid doped polyaniline (PANDR) has been produced by the doping method. AgNPs are then added to the PANDR solution and then mixed with PVC solution to prepare PANDS-PVC/silver nanocomposites. The incorporation of AgNPs has improved the mechanical properties of nanocomposite blends compared to pure polymer blends. It also reduces charge trapping centers and increases enhances the conducting channels. In another study Ismayil et al. (2020) silver doped polyaniline-PVC nanocomposite films were prepared by the non-solvent-induced phase inversion method. The AgNP's doped nanocomposites exhibit excellent photodegradation efficiency and excellent antibacterial efficiency.

4.6 Polymethyl Methacrylate (PMMA)-Silver Nanocomposites

PMMA is amorphous in nature, a linear polymer, rigid and transparent plastic material. PMMA is a strong and lightweight material with good impact strength. The environmental stability of PMMA is superior compared to other plastics such as PS and PE. PMMA is known for its various applications such as in automotive industries as car windows, car interior, and exterior panels, etc., in Electronic field such as LCD/LED TV screens, laptops/smartphone display, solar panels, etc. PMMA due to its high bio-compatibility it is also widely used in biomedical applications like dental cavity fillings and bone cement. Borse et al. (2016) studied the antibacterial efficiency and water treatment application of PMMA embedded AgNPs. One-pot synthesis by UV irradiation method was performed to synthesis PMMA/silver nanocomposites. The silver precursor was added in Milli-Q water. Low-pressure mercury lamps utilized as a UV source and the solution was irradiated for 24 h. After UV irradiation, the color of the solution changed from colorless to yellow that indicates the formation of PMMA embedded AgNPs. The nanocomposite shows excellent antibacterial properties against Gram-positive and Gram-negative bacteria. The authors also prepared PMMA/silver nanocomposite loaded membrane via the PMMA/AgNps solution through the membrane using a syringe. After passing the PMMA/silver nanocomposite solution through the membrane the color of the membrane changes from white to yellow. The antibacterial study of the treated membrane confirms the excellent antibacterial properties of the membrane. The water treatment was executed by passing sludge water through the treated membrane, and filter effluent water contains dead bacteria which, indicates that the treated membrane exhibits excellent antibacterial properties (Fig. 4).

In another study (Pullanchiyodan et al. 2017), AgNPs decorated boron nitride/PMMA nanosheets were manufactured for high thermal conductivity electronic substrates. The nanocomposites were prepared by considering the facile solution blending process. The dispersion of filler in the polymer matrix is characterized by using the elemental mapping of EDS coupled with SEM. The thermal conductivity analysis of nanocomposite reveals the high thermal conductivity is achieved by the hybrid AgNPs decorated boron nitride/PMMA (PMMA-BAX) nanocomposites than boron nitride/PMMA composites (PMMA-BX) and compared to prism PMMA. The experimentally measured thermal conductivity shows a good agreement with the theoretical model. The dielectric measurement performed at microwave frequencies and radio frequencies reveals that the nanocomposite shows a low dielectric constant (<5) and low alternating current conductivity. The authors concluded that the AgNPs decorated boron nitride/PMMA nanocomposites could efficiently be utilized for effective thermal management (Fig. 5).

Moreno et al. (2016) tuned the rate of silver release from the PMMA matrix to control the rate of release of silver ions, the nanocomposite is produced via the electrospinning technique. PMMA/silver nanocomposite fibers were then subjected

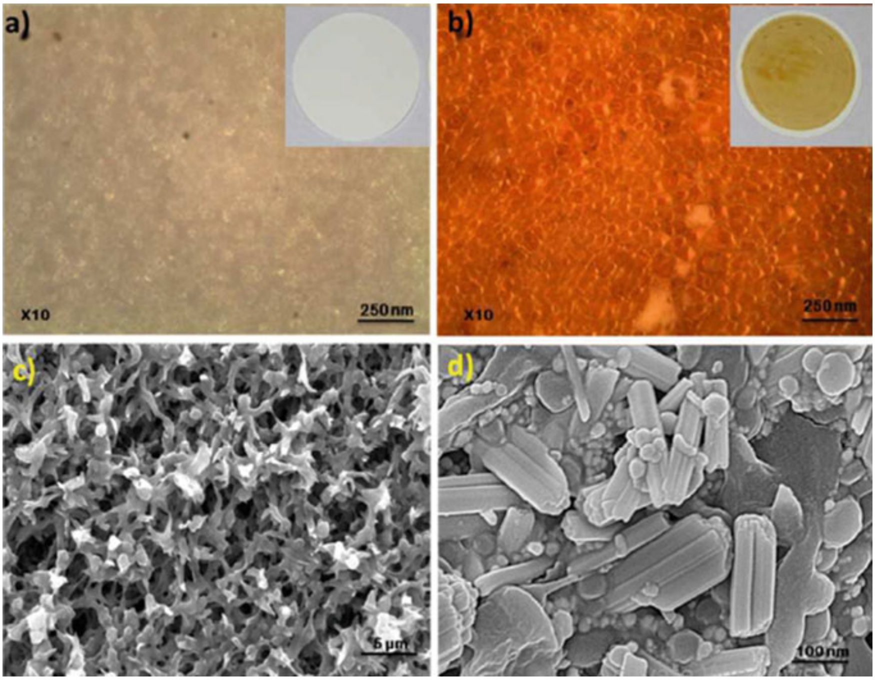


Fig. 4 Optical and FE–SEM images of untreated membranes (**a**, **c**) and treated membrane (**b**, **d**). The inset shows the photographic image of untreated and treated membrane (Borse et al. 2016)

to UV radiation in different levels of exposure to improve the gradual reduction of silver ions to AgNPs. The silver particle size increases from 2 to 5 nm under irradiation. The rate of Ag+ release found directly depends on the degree of exposure to UV. The fast release of Ag+ is observed for non-irradiated samples, in which the higher irradiation time is responsible for a slower release of Ag+, and the higher proportion of AgO and the increase in silver nanoparticle size is responsible for the slower release.

4.7 Polyvinyl Alcohol (PVA)-Silver Nanocomposites

PVA is a colorless water soluble thermoplastic polymer resin derived from the hydrolysis of polyvinyl acetate. PVA forms as a flexible water soluble material when the water evaporates. In general, PVA is resistant to solvents, oils, and fungi. The general application of PVA includes paper coatings, adhesives in packing, printing inks, thickeners, etc. Incorporating inorganic metal nanoparticles such as AgNPs to the PVA enhances its properties and could extend its application to various fields such as electronics, material packaging, biomedical applications, etc. Even as a synthetic polymer, due to the good biodegradability and water solubility

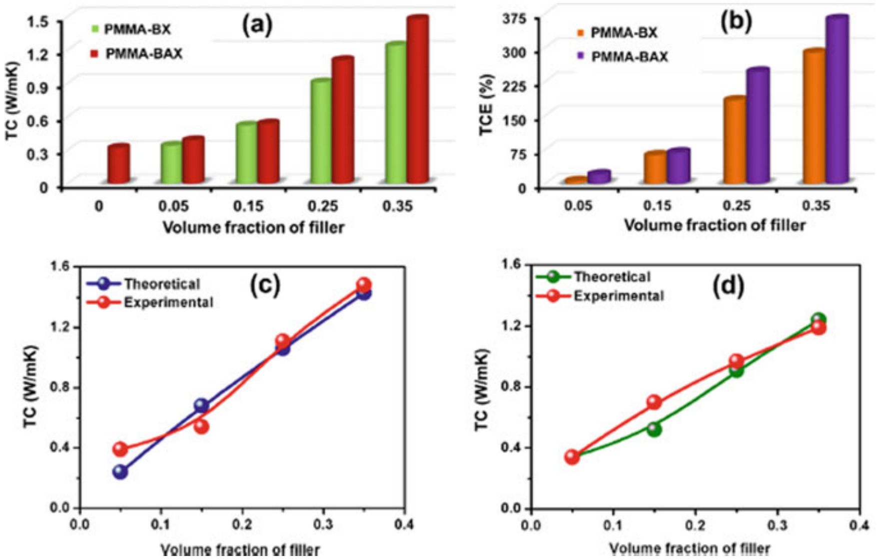


Fig. 5 (TC) Thermal conductivity (**a**), (TCE) thermal conductivity enhancement of nanocomposites (**b**). Measured and calculated thermal conductivity of PMMA−BAX and PMMA−BX nanocomposites respectively (**c**, **d**) (Pullanchiyodan et al. 2017)

of PVA, it is capable to replace conventional petroleum-based polymers from certain biomedical applications. Mukherjee et al. (2017) studied the conduction mechanism, dielectric relaxation, and current voltage of PVA/silver nanocomposites. The synthesis of silver nanotubes involves $AgNO_3$ as silver donor and PVP as a polymeric capping agent, ethylene glycol as the solvent and reducing agent. The preparation steps of PVA/silver nanocomposite involve dilution of PVA (1.2 gm) in deionized water under continuous magnetic stirring (at 353 K). Then AgNPs (2 wt%) dispersed in deionized water (10 ml) added dropwise to PVA solution at room temperature at continuous stirring. The obtained PVA/silver nanocomposite solution was poured to peptides and allowed to dry at room temperature for five days. The electrical properties were studied using a small portion of nanocomposite film the silver paste contact applied to the opposite phase, and it behaves like a capacitor. The DC conductivity of films checked utilizing Keithley 6514 electrometer reveals the conductivity increases with an increase in temperature that suggests the nanocomposite films exhibit semiconducting behavior. The two activation energies of nanocomposite films Ea = 0.73 eV within region (323–368 K) and Ea = 0.84 eV within the region (383–443 K) were determined using Arrhenius equation of conductivity, the variation of conductivity and Arrhenius fitted curve is shown in Fig. 6. The dielectric constant at room temperature and 10 kHz is observed as 8.02 which is higher than pure PVA (6.17). With the increase in temperature, the dielectric constant was observed steeper comparatively at a low frequency than high frequency due to space charge polarization and DC conductivity contribution. The increase of dielectric properties of nanocomposite follows the modified Cole-Cole model, represented in Fig. 7. Mathew et al. (2019) fabricated PVA/chitosan/Ag nanocomposite membrane utilizing gamma irradiation technique with excellent antibacterial activity and for biomedical applications. The preparation of nanocomposite involves mixing PVA and chitosan with different copolymer compositions in the presence of $AgNO_3$ (silver donor) and glutaraldehyde (cross-linker), followed by in situ reductions with gamma irradiation in various doses. As the irradiation dose increases (25–75 kGy), the plasmon band shifted from 430 to 418 nm with high intensity, confirming the formation of smaller particles. The prepared nanocomposite films exhibit excellent antimicrobial and antifungal activities. Thrombogenicity and hemolytic potential studies reveal the weight of blood clotted on the PVA/chitosan/Ag nanocomposite membrane was very low; it confirms the manufactured membranes could be classified as non-thrombogenic and slightly hemolytic, suggesting the nanocomposite membranes are possible for biomedical applications. Mathew et al. (2019) synthesized PVA/AgNPs nanocomposite food packaging material utilizing the solvent casting method. The authors used ginger rhizome extract as a reducing agent, under the influence of direct sunlight. The prepared films show excellent antibacterial activity against foodborne pathogens such as Staphylococcus aureus and Salmonella Typhimurium.

4.8 Polyamides-Silver Nanocomposites

Polyamides are polymers in which monomers are linked together by amide linkage (also known as peptide bonds). Polyamides include synthetic polyamides or nylons and naturally occurring proteins (discussed in Chapter "Synthesis and Green Synthesis of Silver Nanoparticles"). Nylons are thermoplastic polymers that can be melt-processed into various forms such as films, fibers, or shapes. Nylons are produced diamines and dicarboxylic acid and are designated by two numbers, the first number is the number of carbon atoms in diamine and the second number is the number of carbon atoms in the dicarboxylic acid. The hydrogen bonds formed between the polymer chains give the polymer more strength and a high melting point. The nylons are used as textiles, carpets, ropes, also it can be cast into different shapes to manufacture things like bearings and cogs. By incorporating inorganic metal nanoparticle into polyamides can improve its mechanical, chemical, electrical, and optical properties. The AgNPs incorporated in the polyamides matrix is widely applied in many areas due to its unique mechanical, catalytic, electrical, chemical, and anti-bacterial properties. Especially AgNPs/nylon nanocomposites, which have various applications in different areas such as biomaterials, catalysis, electrical, protective clothing, etc. (Pant et al. 2011) synthesized AgNPs impregnated TiO_2/nylon-6 nanocomposite mats with excellent antimicrobial and photocatalytic properties. The nylon-6/TiO_2 nanocomposite mat was first prepared to utilize an electrospinning process. Then the silver photo deposition was done in

Fig. 6 Variation of DC conductivity with temperature of PVA/silver nanocomposite films, the solid lines represents the Arrhenius fitted curve (Mukherjee et al. 2017)

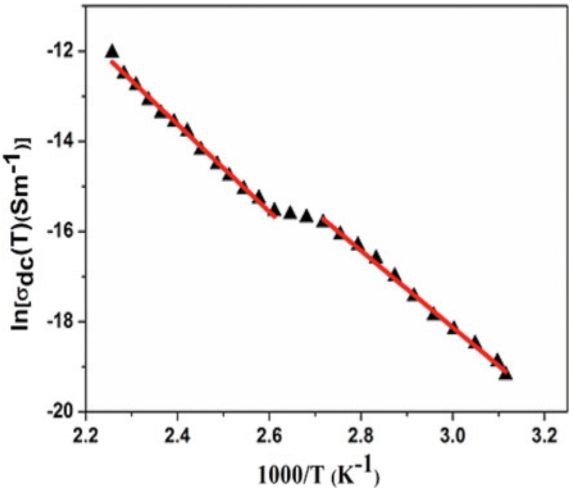
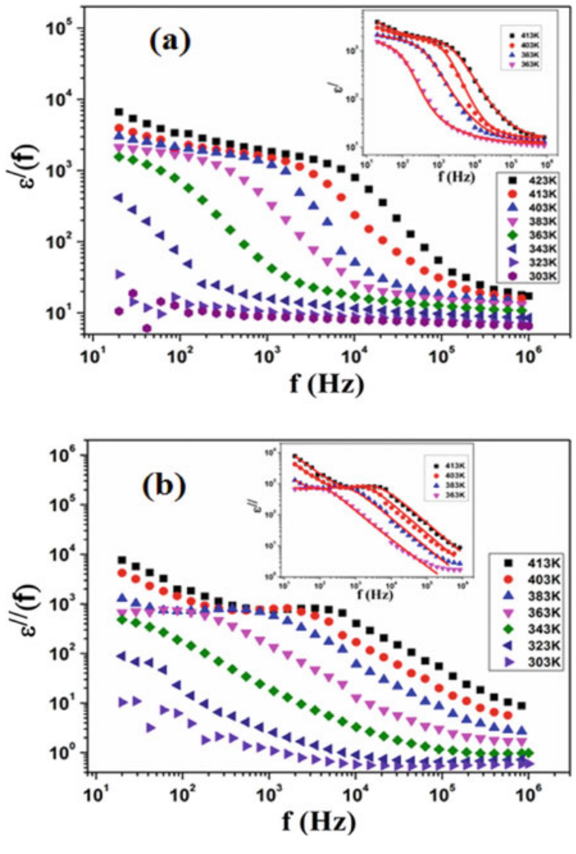


Fig. 7 The frequency variation of real part (ε$^{/}$) (**a**) and imaginary part (ε$^{//}$) (**b**) of PVA/Ag nanocomposite films. The inset plots represent the fit according to Cole-Cole equation (Mukherjee et al. 2017)



nylon-6 and TiO_2/nylon-6 nanocomposite matrices by placing inside the $AgNO_3$ solution. The photo deposition of AgNPs in the polymer matrix was conducted under UV light at 254 nm for irradiation time 15, 30, 60 s, respectively. After the treatment, the mats were washed with distilled water and vacuum dried for 24 h at room temperature. During the electrospinning process, the TiO_2 inside the nylon-6 matrix was formed like a high aspect ratio spider-wave-like structure and facilitated the UV light photoreduction of $AgNO_3$ to Ag. The AgNPs were deposited selectively upon the TiO_2 nanoparticles of the prepared nanocomposite mat, represented in Fig. 8 TEM images and EDX spectra. The antibacterial properties of nanocomposites were evaluated by testing against Escherichia coli, and the photoactive properties of nanocomposite were tested by observing the degradation of methylene blue dye solution in a simple photochemical rector. The result shows the AgNPs loaded TiO_2/nylon nanocomposites are more effective than AgNPs/nylon-6 nanocomposite. The prepared nanocomposite has potential as an economically friendly photocatalyst and can be utilized as a potential water filter medium. Omar et al. (2016) also studied the anti-microbial properties of nylon 6, 10/AgNPs nanocomposite material. The anti-microbial activity of the synthesized nanocomposites is effective against Escherichia coli. Perkas et al. (2007) synthesized ultrasound-assisted coating of nylon 6,6 with AgNPs and the authors also studied its anti-bacterial activity. Maleknia et al. (2015) synthesized nylon 6/silver nanocomposite fibers for the permanent antibacterial activity to common synthetic textiles. The nanocomposites were prepared by a modular twin screw extruder. The anti-bacterial study of nanocomposite against staphylococcus aureus and Klebsiella pneumonia. The results obtained from the anti-bacterial study reveals the nylon 6/silver nanocomposites exhibit excellent anti-bacterial properties.

4.9 Polylactic Acid (PLA)-Silver Nanocomposites

PLA is a thermoplastic aliphatic polyester obtained by condensation of lactic acid or by the ring-opening of lactide, the cyclic dimer of the basic repeating unit. In 2010, PLA was ranked second in the world regarding its consumption volume. The most important specialty of PLA is its biocompatibility, and this makes PLA a perfect choice for medical implants intended to be absorbed by the body. PLA degrades in turn into lactic acid which, is non-toxic to the human body. Among nanocomposites, PLA/silver nanocomposites are widely used in biomedical applications due to the excellent antibacterial properties of AgNPs and the biocompatible behavior of PLA. PLA/silver nanocomposite is also applied in antibacterial packagings and electrical applications. Zhang et al. (2018) synthesized PLA/silver nanocomposites by coating silver on PLA microfibers and then molded via compression molding. The electromagnetic interference shielding effectiveness and electrical conductivity of the nanocomposites enhance due to the silver coating layers on PLA microfibers. Solution techniques are generally used for manufacturing PLA/silver nanocomposites. The electrical properties of the nanocomposite

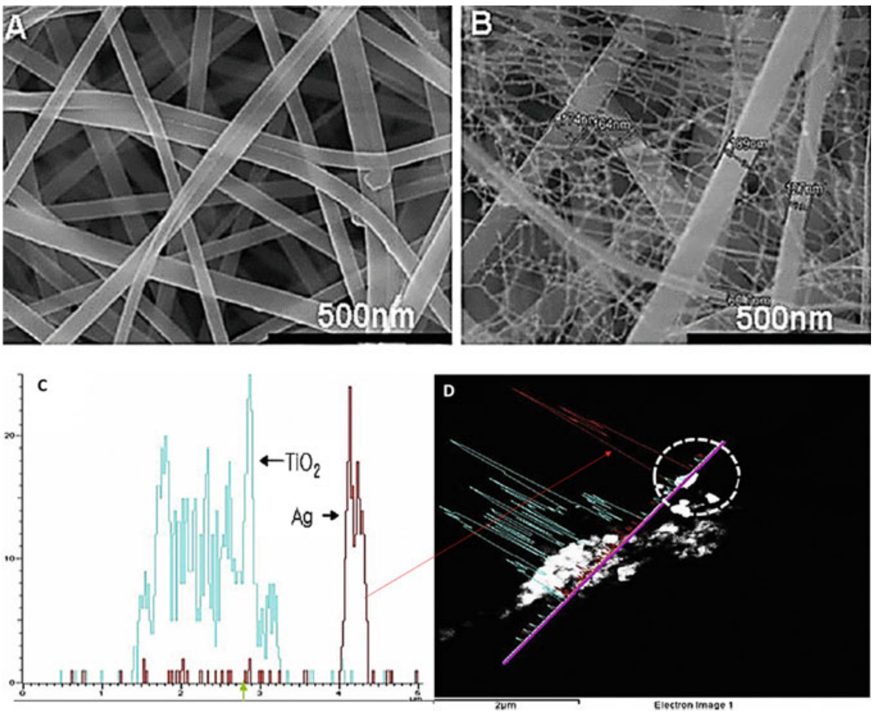


Fig. 8 FSEM images of neat nylon-6 mat (**a**) and TiO_2/nylon-6 mat (**b**), TEM-EDX of Ag–TiO_2/nylon-6 nanofibers: EDX spectra of TiO_2 and Ag NPs (**c**), TEM-EDX image of nanocomposite fibers (**d**) (Pant et al. 2011)

increased with the increase in the amount of silver coating which is controlled by adjusting the coating time. PLA/silver nanocomposite was prepared in a way of wet electroless deposition processing via controlling the deposition time, represented in Fig. 9. The preparation of PLA/silver nanocomposite involves two steps. First, PLA microfibers (3 g) were immersed in acidic $SnCl_2$ solution allowing the deposition of nuclei on the PLA fiber surface. The roughened PLA microfibers were extracted from the solution and washed with distilled water. Second, the roughened PLA fibers were exposed to Tollen's reagent prepared by dissolving $AgNO_3$ (2.0 g) in 100 ml distilled water and stirred well by adding NH_3OH until the solution turned clear. Sodium citrate was used as the reducing agent.

Liu et al. (2017) developed PLA based mats with graphene oxide (GO)-silver hybrid nanofillers. The PLA/GO-silver nanocomposites were prepared by the electrospinning technique. The manufactured nanocomposite exhibits excellent antibacterial properties against Escherichia coli and Staphylococcus aureus and enhanced thermal and tensile properties. These nanocomposite mats could be applied for biomedical applications due to efficient antibacterial properties. Busolo et al. (2010) synthesized silver-based layered silicate in PLA matrix antimicrobial

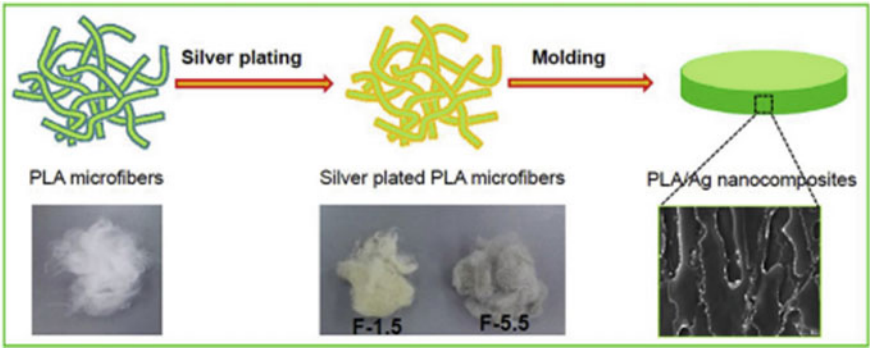


Fig. 9 Fabrication of PLA/silver nanocomposite with chain structures conductive network (Zhang et al. 2018) (sample named as F-x, where x denotes the deposition time in minutes)

food packaging coatings. The nanocomposite was prepared using the solvent casting method. The synthesized nanocomposite exhibits excellent antimicrobial activity against Gram-negative Salmonella spp.

4.10 Polylactic Glycolic Acid (PLGA)/Silver Nanocomposites

PLGA is an aliphatic polyester-based biodegradable polymer that comprises a copolymer of lactic acid (α-hydroxy propanoic acid) and glycolic acid (hydroxy acetic acid). PLGA due to its excellent biocompatible and biodegradable nature it has been used extensively used for several biomedical applications. PLGA is approved by the FDA and found to be both biocompatible and biodegradable for specific human clinical applications. PLGA in water media undergoes hydrolytic chain scission, the mechanism of degradation involves different steps such as penetration, chain scission, and diffusion of the degradation products. It is also possible to control the degradation rate with the influence of several factors such as the ratio of lactic and glycolic acid, molecular weight, length of lactic acid and glycolic blocks, porosity, structure, and morphology. The biodegradable PLGA nanocomposites based on inorganic metal nanocomposite such as gold, titanium, silver, etc. are used for various applications including sensors for diagnosis and antibacterial treatments. The AgNPs loaded on the PLGA matrix could effectively reduce the bacterial development through modification of their surface properties. Rinaldi et al. (2013) synthesized biodegradable PLGA/silver nanocomposite with controlled degradation rate and antibacterial properties. The AgNPs were synthesized using $AgNO_3$ as a silver donor in PVP/$CHCL_3$ solution under continuous stirring for 5 h at a constant temperature. PLGA/silver nanocomposite films were prepared by the solvent casting technique. The PLGA was dissolved in $CHCL_3$ under continuous stirring at room temperature. The nanocomposites were produced by adding AgNPs (1–3 wt%) to PLGA/$CHCL_3$ suspensions with continuous stirring. The dispersion was cast in Teflon sheets and air-dried for 24 h and then 48 h in a vacuum at 37 °C. The effect of silver loading on the polymer matrix degradation was analyzed following the mass loss and morphology of the nanocomposite films at different stages of degradation. The release of Ag+ during the degradation of nanocomposite was analyzed through the diffusion model to have insight into the degradation kinetics. It was found that the release rate and the degradation rate was reduced at higher AgNPs loading. The nanocomposite shows excellent antibacterial properties. Scavone et al. (2016) manufactured and analyzed the antimicrobial properties and cytocompatibility of PLGA/silver nanocomposites. The nanocomposite was manufactured utilizing the solvent casting method. The nanocomposites exhibit excellent antibacterial properties against Escherichia coli and Staphylococcus aureus. The nanocomposite exhibits good cytocompatibility when assayed with L929 and SAOS-2 cells hence, the PLGA/ag nanocomposite is a promising candidate for tissue engineering applications.

4.11 Epoxy/Silver Nanocomposites

Epoxy resins are categorized as thermosetting polymers. Epoxy resins refer to a broad group of reactive compounds that are characterized by the presence of an epoxy ring, which is represented by a three-member ring containing one oxygen atom bonded with two carbon atoms. The molecules with the presence of this functional group define as epoxide, where this molecular base can vary widely resulting in different classes of epoxy resins. Epoxy resins may be cross-linked either with themselves via catalytic homopolymerization, or with co-reactants including acids, amines, alcohols, thiols, and phenols. The co-reactants are referred to as hardeners and the process of cross-linking as curing. The epoxy resins are utilized in a wide range of applications such as electronic components, adhesives, laminates, coatings, aerospace, and marine applications, etc., owing to its high tensile strength and young's modulus, solvent resistance, and good thermal stability (Uthaman et al. 2020). Recently epoxy nanocomposites due to their unique physicochemical properties have gained great interest. In particular silver nanoparticle incorporated in the epoxy matrix gives excellent electrical, mechanical, and antibacterial properties to the resultant nanocomposites. Yagci et al. (2008) synthesized epoxy/silver nanocomposites by simultaneous polymerization-reduction approach. The visible light photoinitiator (camphorquinone) was utilized to generate electron-donating radicals. The oxidation of these radicals to the corresponding cations in the presence of $AgSbF_6$ (hexafluoroantimonate) leads to the formation of AgNPs. These cations formed are capable of initiating cationic ring-opening polymerization of the epoxides. So, the stable AgNPs were formed in the polymerizing medium, the rather formation of AgNPs depends on the radical concentration. Boumedienne and Maaroufi (2020) studied the structural and optical-electronic properties of epoxy/silver nanocomposite films (0.01–0.1 vol.fr

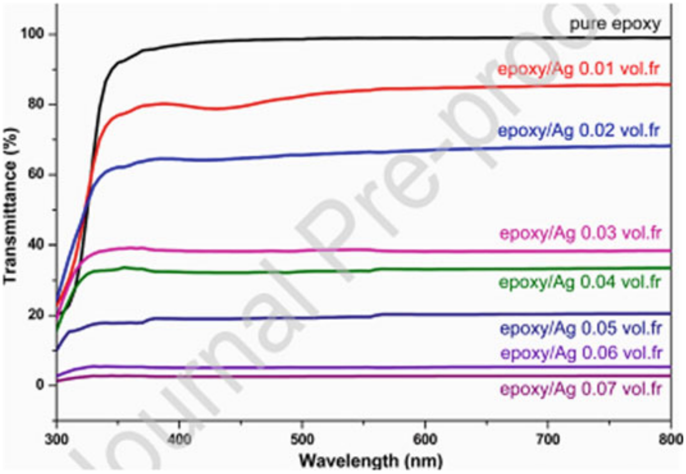


Fig. 10 UV–Vis spectra/Transmittance of epoxy/Ag nanocomposite films (Boumedienne and Maaroufi 2020)

of Ag) prepared to use the extrusion technique. The spectroscopic and microscopic analysis of the nanocomposite reveals good dispersion of AgNPs in the epoxy matrix. The water absorption study of the nanocomposites reveals negligible absorption of water. The electrical properties of the epoxy/silver nanocomposites depend on the filler conductivity, geometry, filler fraction, and interaction with matrix, the electrical conductivity increases with the increase in the amount of silver. The optical properties also depend on the number of silver particles in the epoxy matrix. The transmittance in the wavelength range significantly reduced with the increment in filler content, represented in Fig. 10. The optical band gap for pure epoxy is observed higher due to its optical transparency. However, the optical band gap shifts three times towards a lower value with the increase in AgNPs loading. The authors demanded the synthesized epoxy/silver nanocomposites could vary the bandgap by varying the filler concentration owing to its good chemical stability, electrical conductivity, and optical properties, the prepared nanocomposite could be safely applied as a demanding material in thermoelectricity, optoelectronics, and solar cells.

4.12 Polyurethenes (PU)-Silver Nanocomposites

Polyurethane polymers are composed of urethane linkages in their repeating unit. The PU is formed by the polyaddition reaction between diisocyanate with polyols. PU is generally used in manufacturing high-resilience foam seatings, seals, gaskets, high-performance adhesives, surface coatings, and sealants, etc. PU has been also widely used for manufacturing medical equipment due to its good hemocompatibility and excellent mechanical properties. PU is generally classified as a thermosetting polymer even though thermoplastic PU (TPU) is also available. TPUs are widely applied in the biomedical field and for manufacturing medical devices. The unique chemistry of PU gives them versatility with a wide range of behaviors that ranges from rigid plastics to soft and flexible plastics. Silver nanoparticle as an excellent antibacterial agent while incorporated within the PU matrix enhances the antibacterial properties of the resultant nanocomposites and is widely applied in different biomedical fields. One of the first applications of polymer/silver composites in medicine was the “Erlanger Silberkatether” that was developed in the 1990s by incorporating silver powder with the TPU matrix. Triebel et al. (2011) prepared TPU/silver nanocomposites utilizing two different routes. The first is in situ preparation, AgNPs were produced by thermal reduction of silver acetate during the melt mixing process. The second route involved an ex situ preparation, AgNPs produced in an invertible polyester resulting in smaller particle size. The AgNPs obtained from this method surrounded by a polyester cage that helps to stabilize the nanoparticles and prevent agglomeration. The incorporation of AgNPs in the polymer matrix was done by utilizing the extrusion technique. The silver ion release from the polymer matrix was analyzed using anodic stripping voltammetry. The Ag ions release of various PU/silver nanocomposites as a function of immersion time is evaluated. The amount of silver ions released during a particular immersion time increases with the higher concentration of AgNPs in the PU matrix. At a constant weight percentage of AgNPs in the PU matrix, the composite with ex situ AgNPs exhibits a release of silver ions which is about two orders of magnitude greater than the release from the nanocomposite with in situ AgNPs. Zhao et al. (2019) fabricated waterborne PU/silver nanocomposite foam with enhanced mechanical, thermal, and antibacterial properties. The nanocomposite foams were prepared for the mechanical foaming method. The uniform distribution of AgNPs in the PU matrix facilitated cell growth, leading to an enhanced average pore size, air permeability, thermal stability, etc. The incorporation of AgNPs in the PU matrix also increased the mechanical stability of the PU/silver nanocomposite. The nanocomposite exhibits excellent antibacterial properties against Escherichia coli and Staphylococcus aureus.

5 Conclusions

Polymer nanocomposites based on AgNPs are essential materials in the field of nanoscience and technology because of their excellent properties and capability for applications in various areas. This chapter discussed the preparative techniques of polymer nanocomposites and the synthetic polymer nanocomposites based on silver nanoparticles. The excellent antimicrobial activities, the inhibiting effect of infection, and the microbial proliferation of AgNPs lead the polymer nanocomposites based on silver nanoparticles to apply widely in the various biomedical field. The design of bio-nano composites with specific requirements involves using a wide range of polymer matrices. In this chapter, we discussed the incorporation of silver nanoparticles in various synthetic polymer matrices. Much research are still ongoing, and there is yet to be a definite conclusion on the behavior of nanoparticles on different polymer systems.

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Silver Nanoparticles with Natural Polymers

Sapana Jadoun and K. F. Anna Dilfi

Abstract Natural polymer-based nanocomposites, in which natural polymers act as matrix and silver nanoparticles act as nanofillers, offer great potential to be used in various applications in food packaging, wound healing, biomedical industry, etc. due to its high antimicrobial/antibacterial activity. Natural polymer-silver nanocomposites have been prepared by various methods such as microwave, chemical, sonochemical, photochemical, and radiochemical reducing methods. In this chapter, a brief review of recent research and development of natural polymers used for nanocomposite formation with silver nanoparticles will be presented. The discussion will be focused on categories of various nanocomposites of silver, their preparation, properties, and various applications.

Keywords Natural polymer · Silver nanoparticles · Starch · Chitosan · Antibacterial activity · Wound healing

1 Introduction

"Nanocomposite" term is generally related to those filled polymers having discrete nanofillers with the size of average nanoparticles about less than 100 nm (Zhan et al. 2003). In recent years, nanocomposites have attracted the attention of researchers for their use in various fields such as chemistry, biology, electronics, and medicine (Ahuja and Kumar 2009; Jancar et al. 2010). Nanocomposites comprise metal nanoparticles embedding into polymer matrices by which the advantages of nanoparticles can be achieved (Corbierre et al. 2001). Fabrication of nanocomposites is an effective technique to conserve the properties of the metal by

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avoiding aggregation of nanosized metal (Ma et al. 2011). Nanocomposites of polymer/metal in which polymer acts as a protecting agent, template, or stabilizer show many important qualities (Folarin et al. 2011).

Natural polymers have always been employed as natural fillers or matrices in metallic nanoparticles for their stability against coalescence and oxidation (Rhim and Ng 2007). They occur in nature and can be extracted by some processes (Kulkarni Vishakha et al. 2012). Natural polymers are non-toxic, readily available, safe, and devoid of side effects as well as these are economical, having the potential capability of chemical modifications, biodegradability and also biocompatibility with rare exceptions (Bhatia 2016). These properties make natural polymers useful in pharmaceutical formulations such as the manufacture of films, microparticles, solid monolithic matrix systems, beads, implants, nanoparticles, injectable and inhalable systems along with some viscous liquid formulations (Ogaji et al. 2012).

Silver has attracted a lot of attention because of having outstanding properties such as chemical stability, virtuous electrical, and thermal, as well as good catalytic properties (Srikar et al. 2016). Due to the nanosize of these particles, it is projected to open new paths for preventing and fighting with diseases (Kim et al. 2007). Silver has been known for exhibiting sturdy toxicity to an extensive series of microorganisms and due to this, compounds based on silver have been widely used in fungicidal and bactericidal applications (Roy et al. 2013). Silver has been combined with various polymers for advanced and new soft materials in the form of nanocomposites (Peponi et al. 2014). In these metallic nanocomposites, such as silver nanocomposites, polymers act as stabilizers/matrices and offer them stability against coalescence and oxidation (Ng et al. 2013). Some researchers (Zare and Shabani 2016) have reviewed polymer-metal nanocomposites for their application in the biomedical field. Much research on silver nanoparticles (Ag nanoparticles) with various polymers have been studied such as polyvinyl alcohol (Usman et al. 2016), polyvinylpyrrolidone (Sun et al. 2016), hyperbranched polyurethane (Deka et al. 2010), polyacrylonitrile (Motitswe and Fayemi 2019), polyaniline (Choudhury 2009), etc.

2 Natural Polymer-Ag Nanocomposites

In nanotechnology, the current trend is the use of biological friendly and biocompatible natural polymers which can easily provide stabilization functions and reduction to silver nanoparticles (Singh et al. 2016). Natural polymers are an area of wide interest because of their biocompatibility and non-toxicity (Rogina 2014). Natural polymeric matrix combined with a filler having a dimension in the nanometer-scale is termed as bionanocomposites (Gacitua et al. 2005). Bionanocomposites such as metal/polymer compounds are widely spreading its wings in the research field due to their unique properties and applications (Darder et al. 2007; Siqueira et al. 2010). Natural polymer-silver nanocomposites (Natural polymer-Ag nanocomposites) comprising of a matrix in the form of natural polymer and nanofiller of silver nanoparticles generally reveal many attractive advantages such as mechanical, optical, and electrical characteristics (Abdelwahab and Shukry 2015). In silver nanoparticles synthesis, natural polymers play an important role as stabilizer due to its effectiveness in avoiding precipitation and agglomeration via controlling the preparation of nanoparticles along with dispersion stability (El-Rafie et al. 2011). Natural polymer-Ag nanocomposites can be easily synthesized by mechanical mixing of a natural polymer with silver nanoparticles through in situ reduction of silver salts or complexes in a natural polymer matrix, via melt mixing or in situ polymerization in the presence of silver nanoparticles (Li et al. 2010). For the preparation of these nanocomposites various methods have been adopted such as microwave (Li et al. 2011b; Nadagouda et al. 2011), chemical (Hussain et al. 2003; Khanna et al. 2005a, b; Yagci et al. 2008), sonochemical (Karim et al. 2007; Li et al. 2012), photochemical (Gabriel et al. 2017; Hada et al. 1976), and radiochemical reducing methods (Huang et al. 2009). A schematic representation of fabrication methods used in the synthesis of metal-polymer nanocomposites is given in Fig. 1 (Zahran and Marei 2019). Numerous studies of Ag nanocomposites with natural polymers have been reported up to now with increasing frequency (Cheviron et al. 2014; Faraji et al. 2012; Halder et al.

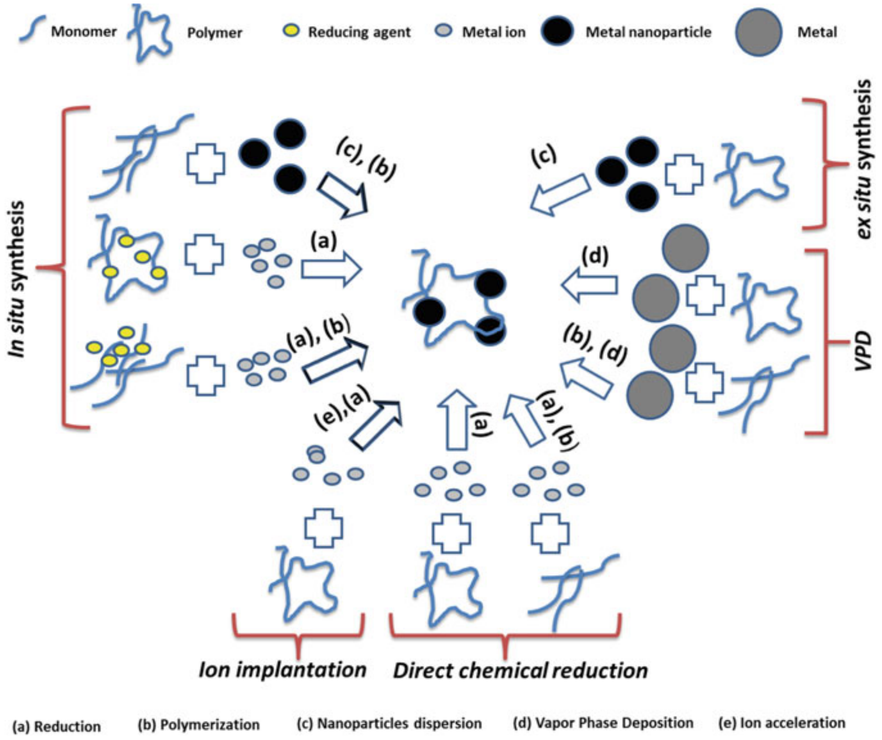


Fig. 1 Schematic representation showing the fabrication methods used in the synthesis of metal-polymer nanocomposites. Reproduced from Ref. Zahran and Marei (2019) with permission

2011; Kumar-Krishnan et al. 2015; Li et al. 2011a; Potara et al. 2011). Nanocomposites of natural polymers such as gelatin (Zhou et al. 2012), sodium alginate (Bhowmick et al. 2013), starch (Valodkar et al. 2010), gum acacia (Bajpai and Kumari 2015), carboxymethyl cellulose (Nadagouda and Varma 2007) with silver nanoparticles produce antimicrobials (Velusamy et al. 2016).

3 Categories and Synthesis of Natural Polymer-Ag Based Nanocomposites

3.1 Natural Rubber-Ag Based Nanocomposites

Natural rubber can be extracted from some trees in the form of latex (milky liquid) having isoprene units with some impurities which can be removed by the vulcanization process to enhance its elasticity, durability, and resilience (Shubhra 2013). Protein found in natural rubber has great potential to be used as a stabilizer and due to that silver ions can be absorbed and bind easily by protein bases (Zuhainis et al. 2015). It is extensively used in industries, such as health care products based on latex, gloves, adhesives, etc. (Yip and Cacioli 2002).

An environment-friendly and cheap-cost nanocomposites of natural rubber/silver were synthesized by a soft thermal reduction for photo-assisted degradation of a dye, methyl orange (Abu Bakar et al. 2018). On the other hand, green synthesis of nanocomposites by in situ reduction of silver nitrate by natural rubber latex was performed. (Rathnayake et al. 2014). Hu and his coworkers had done a great job by preparing rubber composite fibers comprising silver nanoparticles by in situ chemical crosslinking and electrospinning (Fig. 2) (Hu et al. 2012).

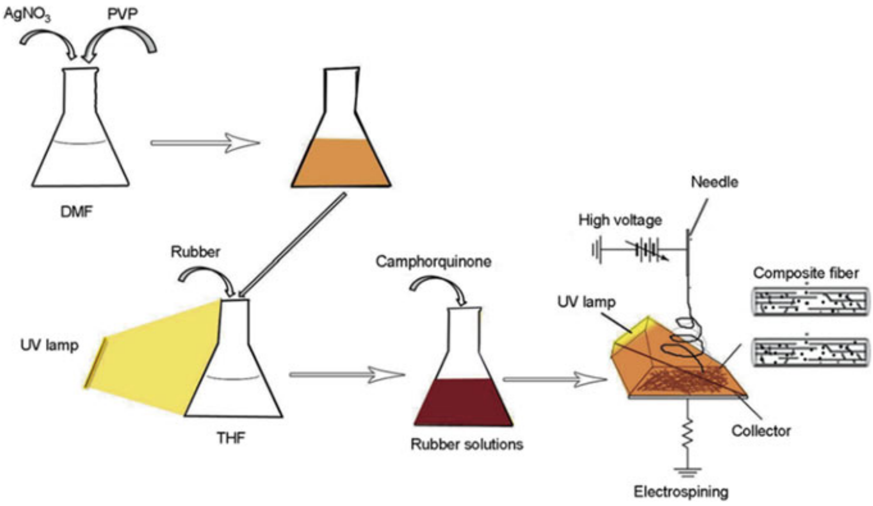


Fig. 2 Schematic diagram of the experimental process for rubber/silver nanocomposites. Rreproduced from Ref. Hu et al. (2012) with permission

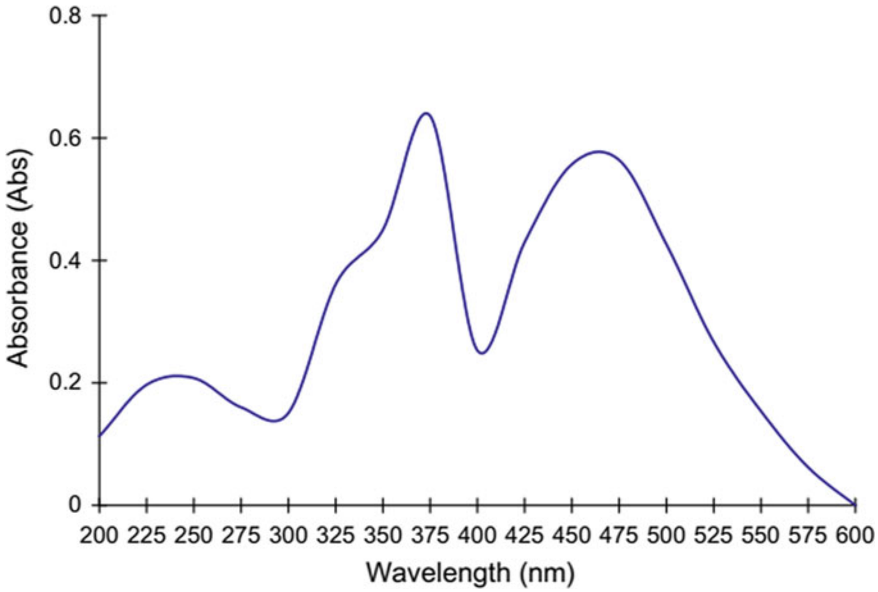


Fig. 3 UV–vis spectra of a typical Ag/PVP-g-NR nanocomposite. Rreproduced from Ref. Bakar et al. (2010) with permission

Bakar and his coworkers synthesized nanocomposites via photoreduction of casting a film by using silver nanoparticles and natural rubber latex (Bakar et al. 2007). These nanocomposites were found centered cubic type and the studies suggested that natural rubber containing protein is responsible for the formation of natural rubber-silver nanocomposites (Bakar et al. 2010). Afterward, they used polyvinylpyrrolidone-grafted natural rubber and silver for the synthesis of nanocomposites whose average diameter was found 4.1 nm. These in situ nanocomposites were formed by using tetraethylenepentamine (TEPA) and cumene hydroperoxide (CHP) as a redox initiator. UV-Visible spectrum was found between 200 nm and 600 nm for these nanocomposites in which a peak at 242 nm was attributed to natural rubber peak and a peak for silver nanoparticles was seen at 375 and 470 nm (Fig. 3) (Bakar et al. 2010).

3.2 *Starch-Ag Based Nanocomposites*

Among natural polymers, starch has received much attention as it is the most auspicious biodegradable and biocompatible material due to its unique and strong advantages of wide availability, low cost, and total compostability with no toxic residues left (Chen et al. 2015). The starch $(C_6H_{10}O_5)_n$ is chemically a homopolymer of α-Glucopyranose units with the composition of two distinct polymer chains named amylose and amylopectin. Amylose is a linear structure while amylopectin is branched structure. The former consists α1-4 glycosidic linkage while the structure of later is made up with α1-4 along with α1-6 glycosidic linkages. The ratio of these two polymers affects the structure of starch such as chemical nature, size of granules, architecture of polymers within the granules and crystallinity. The starch contains a large number of hydroxyl groups which is a precursor for metal complexation. These hydroxy groups provide sites for metal ions for the advantageous properties via good control of shape and size as well as dispersion of nanocomposite formed by starch and metal (Collinson and Thielemans 2010).

Preparation of starch/silver nanocomposites of an approximate size of 24–52 nm via chemical reduction of silver nitrate using sodium borohydride as a reducing agent was firstly prepared by Bashir and coworkers (Bashir et al. 2015). Abreu and his labmates prepared films of nanocomposites of starch and silver nanoparticles. Different concentrations of silver nanoparticles were prepared directly in starch solution via chemical reduction method (Abreu et al. 2015). A starch-based silver bionanocomposite of 8 nm size was synthesized by (Božanić et al. 2011). Preparation was completed in the presence of starch by reduction of the silver salt in aqueous solution and sodium borohydride was used as a reducing agent in this reaction. These nanocomposites were characterized by morphological (Scanning electron microscope and Transmission electron microscopy) and spectral (Ultraviolet-visible absorption spectroscopy). UV visible studies revealed the trapping of a part of silver nanoparticles in the water during the film formation which confirmed partial oxidation to Ag^+ ion. The silver nanoparticle oxidation was then established by X-ray photoelectron spectroscopy. The presumed morphology of nanocomposites with interactions between silver ions, starch molecular chains, and water molecules are shown in Fig. 4.

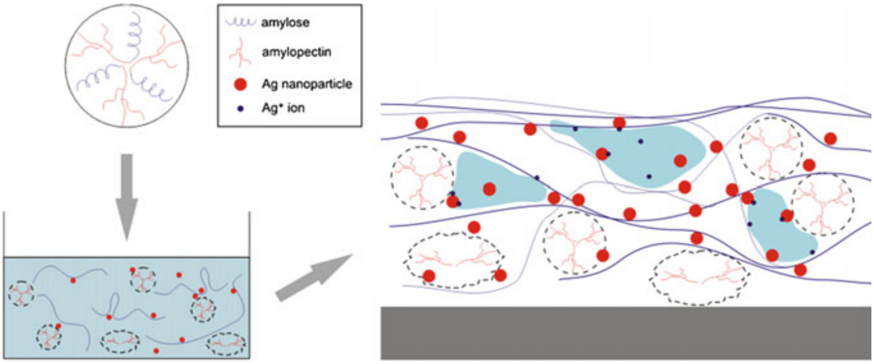


Fig. 4 Schematic representation of the morphology of the system with possible interactions between starch molecular chains, silver ions and/or nanoparticles, and water molecules. Rreproduced from Ref. Božanić et al. (2011) with permission

3.3 Chitosan-Ag Based Nanocomposites

Chitosan, a natural polymer, is derived by Glocan which can be synthesized by chitin monomers polymerization via boiling of monomer in a solution of potassium hydroxide (Muzzarelli 2013). Chitosan is the most natural amino polysaccharide and generally, it is deacetylated chitin (El Knidri et al. 2018). It is a composition of structural polysaccharide poly(β-(1-4)-2-amino-2-deoxy-D-glucose) which is plentifully available after cellulose in nature (Sukkunta 2005). The interaction of chitosan with the bacterium is very easy. It binds to glycosaminoglycans, DNA, and many proteins; and thus it is attractive in the form of enhancing the antimicrobial effect of silver nanoparticles (Rodrigues et al. 2012). Chitosan has numerous applications in the pharmaceutical field and tissue engineering (Cheba 2011).

Vimala et al. (2011) synthesized nanocomposites of chitosan and silver followed by fabricating a film of same by polyvinyl alcohol. They achieved formation of silver nanoparticles by the reduction of silver ions in an acidic solution of chitosan by using functional groups. The presence of these nanocomposites was confirmed by spectral and morphological studies. Some nanocomposites and the films of genipin-crosslinked chitosan and silver nanoparticles were prepared for biomedical applications (Liu and Kim 2012). These films were tested against some of the bacteria like *Staphylococcus aureus, Escherichia coli, Bacillus subtili, Pseudomonas aeruginosa*, etc. and were found to possess high antibacterial activities against these. Hence, these films were recommended to be used in burn dressings and wound.

Huang and his co-workers (2004) synthesized silver-chitosan nanocomposites in aqueous solution by the reduction of silver (Ag) salt using sodium borohydride ($NaBH_4$) in presence of chitosan and confirmed the presence of silver nanoparticles through UV-Vis and TEM analysis (Fig. 5). Some batonet-like structure of chitosan-silver nanocomposites were seen by polarized optical microscopy (POM).

3.4 Gelatin-Ag Based Nanocomposites

Gelatin is a translucent and colorless solid substance that can be attained from the hydrolysis of collagen found inside animals' bones and skin (Asghari et al. 2017). It has a wide area of applications in medical sciences such as shells of pharmaceutical capsules drug delivery systems, preparation of tissue engineering scaffolds, etc. (Faulkner and Fridovich 1993; Padhi 2015; Tiwari et al. 2014).

Ahmad et al. (2011) prepared nanocomposites of gelatin with silver nanoparticles using a reducing agent, sodium borohydride ($NaBH_4$). $AgNO_3$ and gelatin were used as a precursor and natural stabilizers, respectively. These bionanocomposites were characterized by spectral and morphological studies while the size of these was found less than 15 nm. Later, nanocomposites of gelatin and silver were prepared using gamma radiation-induced crosslinking as a new in situ method by

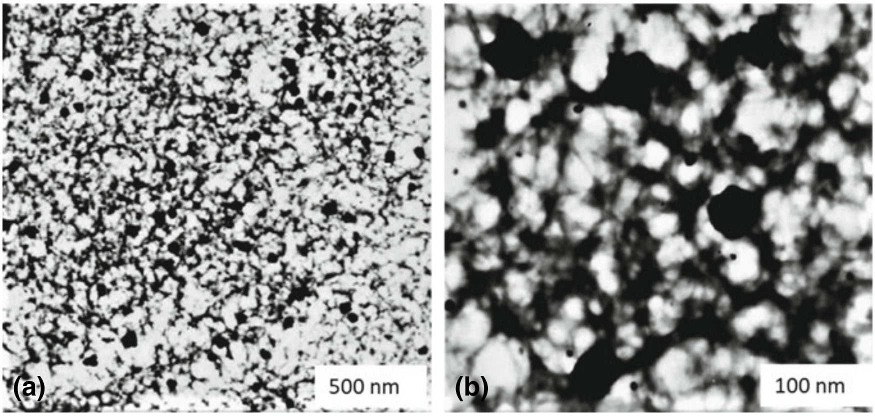
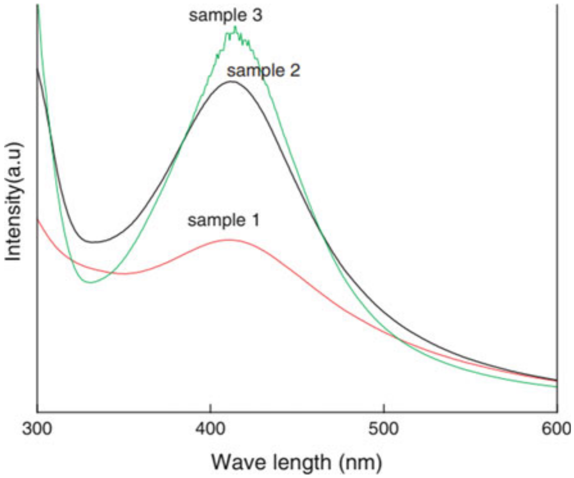


Fig. 5 TEM images of silver nanoparticles distributed in Ag–chitosan nanocomposite prepared with 20 mM $AgNO_3$ illustrated in the different scale bars: **a** 500 nm; **b** 100 nm. Reproduced from Ref. Huang et al. (2004) with permission

Fig. 6 UV-VIS absorption spectra of 2.3 mmol dm^{-3} silver nanoparticle solutions. Sample 1, 0.5 g% gelatin solution; Sample 2, 1 g% gelatin solution; and Sample 3, 2 g% gelatin solution. Reproduced from Ref. Halder et al. (2011) with permission



Abd El-Mohdy (2013). The incorporation of silver nanoparticles in gelatin was confirmed by transmission electron microscopy (TEM), X-ray diffraction (XRD), UV–Vis spectroscopy, Fourier transform infrared (FTIR) spectroscopy, and energy-dispersive X-ray (EDX) analysis. The fabrication of bio-based antimicrobial film of gelatin/silver nanocomposites was done by Halder et al. (2011) by the chemical reducing method. The reduction of silver nitrate solution was carried out by sodium borohydride as a reducing agent with a fixed concentration of silver nitrate solution and a fixed concentration of gelatin. UV-visible spectroscopy revealed that all concentration samples showed the same characteristic plasmonic band at 412 nm (yellow color) for silver nanoparticles (Fig. 6).

4 Applications

4.1 *Antimicrobial/Antibacterial Activity for Food Packaging and Other Applications*

Li and coworkers prepared cellulose/silver nanocomposites which displayed high antimicrobial activity against the microbes *Staphylococcus aureus* (gram-positive) and *Escherichia coli* (gram-negative) which can be seen in Fig. 7 clearly (Li et al. 2011a). Likewise, natural rubber/silver nanocomposites strongly inhibited the bacteria and showed antimicrobial properties against gram-positive *Staphylococcus aureus, Staphylococcus epidermidis,* and gram-negative *Escherichia coli* (Rathnayake et al. 2014).

Films of starch/silver nanocomposites revealed antimicrobial activity against *Candida albicans Staphylococcus aureus* and *Escherichia coli* without significant differences between different concentrations of silver nanoparticles' investigated, hence were found highly useful in food packaging material (Abreu et al. 2015). Usman et al. (2016) discussed the outstanding antimicrobial activity of starch/silver nanocomposite films against gram-positive *Staphylococcus aureus* and gram-negative *Escherichia coli.* Starch-embedded silver nanocomposites also have been studied for microbial growth and viability prevention against common

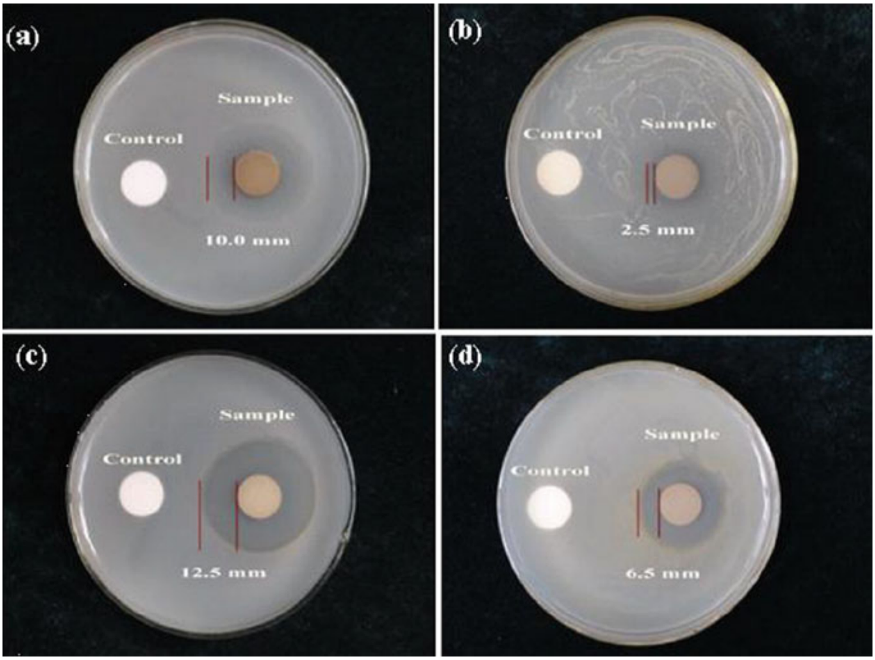


Fig. 7 Antimicrobial activities of cellulose–Ag nanocomposites (**a** and **c**), *Escherichia coli* and *Staphylococcus aureus* (**b** and **d**). Rreproduced from Ref. Li et al. (2011a) with permission

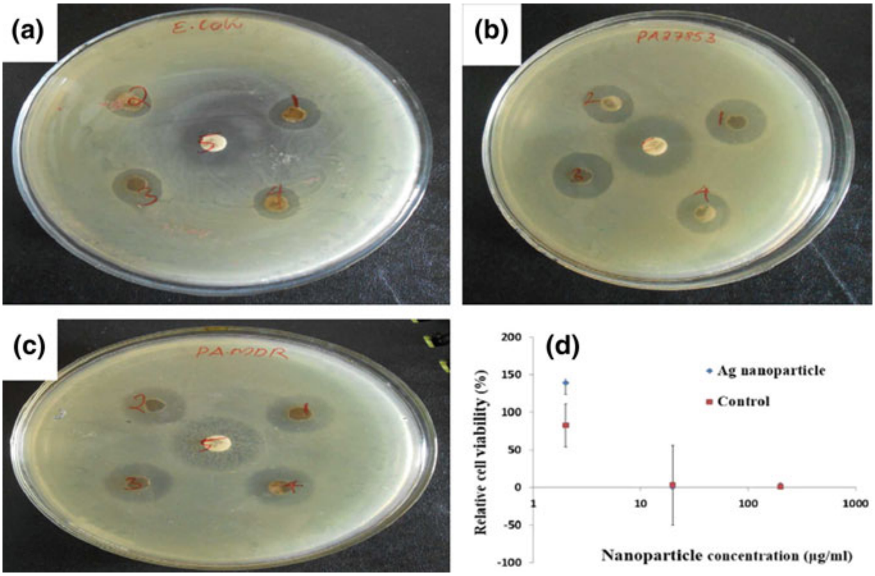


Fig. 8 Comparison of the inhibition zone test for Gram-negative bacteria **a** *Escherichia coli* and **b** *Pseudomonas aeruginosa* (PA27853), **c** *Pseudomonas aeruginosa* (PAMDR) and **d** typical relative cell viability of the starch-capped Ag-NPs against human HTP-1 cell line. Reproduced from Ref. Mohan et al. (2016) with permission

pathogens *Escherichia coli, Staphylococcus aureus* and *Candida albicans* (Božanić et al. 2011). Utilization of biodegradable starch nanocomposites for food packaging applications and the biomedical industry was discussed by *García* and his coworkers (García et al. 2015). Mohan and his labmates studied the cytotoxicity and sensing properties of starch/silver nanocomposites. They suggested good antibacterial activities against *Pseudomonas aeruginosa* and gram-negative *Escherichia coli* (Fig. 8) (Mohan et al. 2016).

Gelatin/silver nanocomposites showed less toxicity to the human cell, hence were preferably more suitable for the potential applications in industrial, consumer, and medical products. These nanocomposites were also tested by the 'cup-plate zone of inhibition' method for antibacterial activity and showed noteworthy antifungal and antibacterial activity (Halder et al. 2011). Cellulose/silver nanoparticles were prepared by a direct chemical reduction method for its application as an antimicrobial agent (*Escherichia coli* and *Staphylococcus aureus*) (Drogat et al. 2011).

4.2 Wound Healing

A wound dressing/healing should have the capability to absorb wound exudates as well as it should give a wet environment to the wound (Coleman and Neilsen 2019;

Khalid et al. 2014). The advanced wound dressings, designed to treat complex and acute wounds, should have added features, such as it should be in solid form, possess fast healing character and exhibit antimicrobial/antibacterial activity along with drug carrier ability (Saghazadeh et al. 2018; Zahedi et al. 2010). Various bionanocomposites synthesized from biopolymers are recommended for advanced biocompatible and biodegradable wound dressing materials (Ahmed and Ikram 2016; Kamoun et al. 2017).

The nanosilver/gelatin nanocomposite hydrogels have revealed antimicrobial activity against numerous bacteria and fungi. A noticeable increment in antibacterial activity was seen by the increment of silver nitrate content. The comparative in vitro antibacterial studies between neat (pure polymers) and nanocomposites elucidated higher inhibition in case of nanocomposite gel which suggested their efficient use as a wound dressing (Abd El-Mohdy 2013). *Arockianathan* et al. (2012) prepared nanocomposites using natural polymers, starch and chitosan, impregnated with silver nanoparticles and studied their wound healing pattern (Fig. 9). They found that the healing rate was faster in the case of experimental wounds (C-F) rather than that of control (A and B).

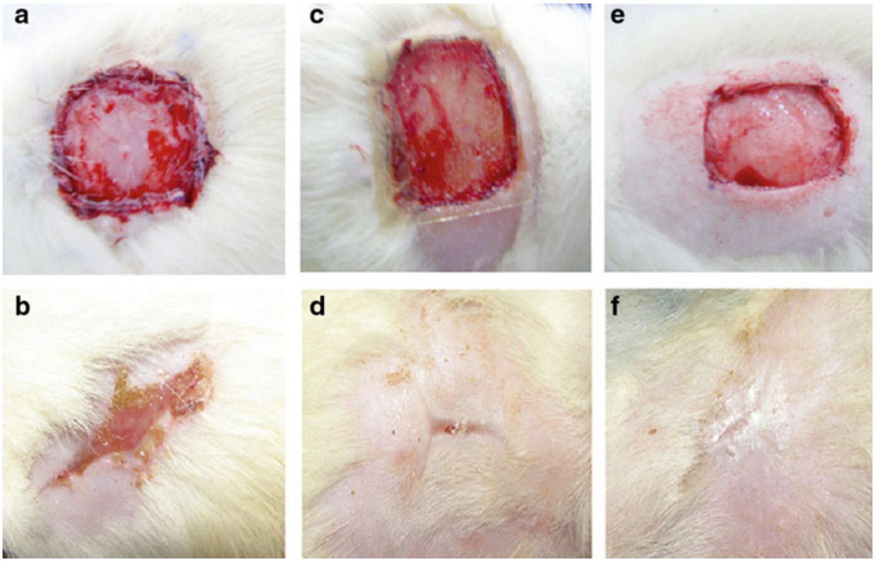


Fig. 9 Photographic representation of wound contraction rate on different days of healing: **a**, **c** and **e** are control, Ch-SG-AgNP (chitosan and sago starch impregnated with silver nanoparticles without antibiotic gentamicin) and Ch-SG-AgNP-G (chitosan and sago starch impregnated with silver nanoparticles with antibiotic gentamicin) treated groups on the 0th day, respectively, **b**, **d** and **f** are control, Ch-SG-AgNP and Ch-SG-AgNP-G treated groups on the 16th day, respectively. Reproduced from Ref. Marie Arockianathan et al. (2012) with permission

4.3 Sensors

To sense or detect some environmental characteristics, a transducer/sensor is required (Timmer et al. 2005). It detects the event and gives a equivalent output usually as an optical or electric signal. Sensors can be classified as chemical sensors, biosensors, etc. (Goepel et al. 2008). A biosensor is an analytical device having a physiochemical detector which detects the analyte that combines a biological target (Castillo et al. 2004). Various metal/polymer nanocomposites have been reported for use in sensing devices such as novel pH-responsive Ag/poly (HEMA–PEGMA–MAA) nanocomposites (Xiang and Chen 2007) and biopolymer–silver nanocomposite for detection of ammonia optical ammonia sensor. This sensor was highly useful in medical and clinical diagnosis for low ammonia level detection in biological fluids, like saliva, plasma, sweat, etc. (Pandey et al. 2012). Chitosan-guar gum/silver nanoparticles were synthesized for effective utilization in glucan and glucose sensors (Bagal-Kestwal et al. 2014).

4.4 Conductive Devices

Natural polymers combined with electrically conductive metal offers a brilliant capability to materials for electrical conductivity (Kaur et al. 2015). These conductive nanocomposites can be useful in numerous conductive device applications such as electrode, sensor, rechargeable battery, shield, etc. (Sanchez et al. 2005). Meena and labmate (2017) studied the conduction mechanism and observed the enhanced conductivity in starch/silver nanocomposites.

The composite films of gelatin/chitosan/nanosilver were prepared by electrodeposition of gelatin/chitosan and nanosilver onto different conductive substrates or electrodes such as titanium plate, stainless steel plate, Indium tin oxide electrode and silver foil, (Fig. 10) and improved conductivity was achieved. Furthermore, it revealed in vitro antibacterial/antimicrobial activity against *Staphylococcus aureus* and *Escherichia coli* which is applicable in biomedical fields such as neuroprosthetic implants, skin biomaterials, and artificial muscles (Wang et al. 2015). Electronic and optical properties of chitosan/silver nanocomposites were studied by Aziz et al. and a decrement in the optical bandgap in chitosan/silver nanocomposites samples containing alumina nanoparticles was observed (Aziz et al. 2017).

4.5 Other Applications

Some nanocomposites of gelatin/silver nanoparticles were fabricated for their potential application in cancer therapy or for their use as an antioxidant. These nanocomposites were observed to behave as an antibacterial agent in preventive and

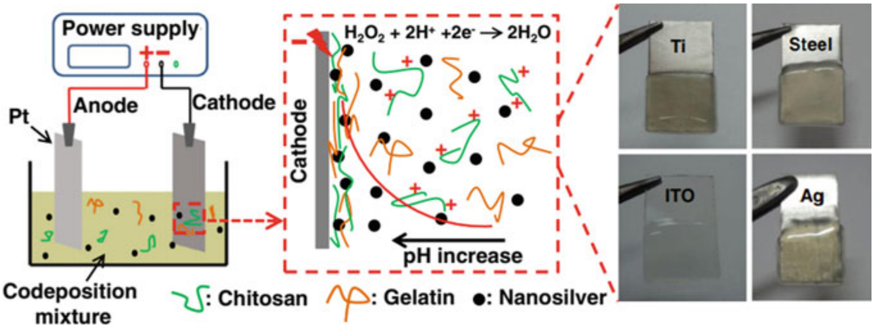


Fig. 10 Electrodeposition of gelation/chitosan/nanosilver and photographs of the electrodeposited hydrogels on Ti (Titanium) plate, stainless steel plate, ITO (Indium tin oxide)electrode, and Ag (silver) foil, respectively. Reproduced from Ref. Wang et al. (2015) with permission

curative health care (Salaheldin et al. 2017). Alginate-gelatin/silver nanocomposites were found useful in the induction of apoptosis in human glioblastoma cells (Sharma et al. 2014). *Ex situ* preparation of chitin/silver nanocomposites was performed and found applicable in antimicrobial and mosquito larvicidal activity (Solairaj and Rameshthangam 2017).

5 Conclusion

Nanocomposites have appeared as an efficient strategy to advance the functional and structural properties of natural polymers for the last two decades. The incorporation of silver nanoparticles into natural polymers has given rise to demand of a unique class of materials (nanocomposites) that has attracted researchers and scientists to employ them in various applications including biological, chemistry, and materials sciences. The present chapter focused on different categories of natural polymers and their composites fabricated with silver metal via various techniques. Lately, higher interest is being aroused on natural polymers (biopolymers) such as starch, gelatin, natural rubber, chitosan, etc. which are biocompatible and biodegradable. These satisfy demands for green chemistry, enhanced sustainability, renewability, environment friendliness, reduced pollution and intrinsic biological activity. Nanocomposites based on biodegradable polymers (natural polymers) for application in the specific biomedical fields such as antibacterial/antimicrobial activity, food packaging, wound healing, sensing, etc. as well as application in conductive devices and other fields are also presented.

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Characterization of Silver/Polymer Nanocomposites

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Abstract In this chapter, we mainly discussed the characterization techniques of polymer nanocomposites based on silver nanoparticles. The main characterization techniques discussed in this chapter includes various methods such as microscopic and spectroscopic characterizations, scattering and diffraction characterizations, thermal, mechanical and viscoelastic characterizations of polymer/silver nanocomposites. The commonly used instruments through which the analysis of morphology, microstructure, elemental composition, mechanical, thermal and viscoelastic properties of silver/polymer composites are discussed in this chapter. The following is a detailed description of each characterization techniques.

1 Microscopic Analysis on Silver/Polymer Nanocomposites

To determine the size and distribution of the Ag hybridized polymer, scanning electron microscopy (SEM) analysis can be used. SEM is a kind of microscopic morphology observation method with size range between transmission electron microscopy (TEM) and optical microscopy (OM). It can be directly used to the sample surface for microscopic imaging. Secondary electron signal imaging is mainly used to observe the surface morphology of the sample, i.e. scanning the sample with a very narrow electron beam, which produces various effects through the interaction between the electron beam and the sample, mainly the secondary electron emission of the sample. Secondary electrons can produce an enlarged image of the sample's surface, which is set up in time sequence when the sample is scanned; even if the enlarged image is obtained by point-by-point imaging. It is a large instrument for measuring the surface morphology of samples. When an

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incident electron beam with certain energy bombards the surface of the sample, the electrons collide with the nucleus and outer electrons of the element in one or more elastic and inelastic collisions. Some electrons are reflected out of the surface of the sample, while the other electrons infiltrate into the sample, gradually lose their kinetic energy, and finally stop moving and are absorbed by the sample. In this process, more than 99% of the incident electron energy is converted to the thermal energy of the sample, while about 1% of the incident electron energy excites various signals from the sample. These signals mainly include secondary electrons, backscattered electrons, absorption electrons, transmission electrons, Auger electrons, electromotive force, cathode-luminescence, X-ray and so on. Thus, SEM is to obtain the observation of the surface morphology of the test sample by receiving, amplifying and displaying the information, and then analyze the samples.

To observe the surface morphology by SEM, the sample preparation process is simple and does not need to be sliced. The samples should be treated accordingly to keep the surface structure of the samples as good as possible, without distortion and pollution, and the samples should be dry and have good conductivity. SEM also can observe the surface structure of samples directly. Since the sample moves and rotates in a three-dimensional space in the sample chamber, the sample can be observed from various angles. Moreover, it has stereoscopic sense, wide amplification range, high resolution and little damage and pollution to the sample. SEM analyses the morphological and structural characteristics of the material by the signals collected from the collision between the electron beam and the sample surface. For the observation of the morphology and structure of silver nanoparticles based polymer nanocomposites, because of the high resolution and clear image of scanning electron microscopy, the profile characteristics, cross-sectional area view, thickness and distribution of silver nanocomposite material can be judged and analyzed by scanning electron microscopy.

Moreover, it can be used for analysis of various functions. When it is connected with X-ray spectrometer, the morphology can be observed and the composition of micro-area can be analyzed at the same time. When equipped with optical microscope and monochrometer, the cathode fluorescence image can be observed and the cathode fluorescence spectrum can be analyzed. The dynamic test can be carried out on a heating, cooling and stretching test bench. Understanding the most basic form of a substance begins with its morphology, and further in-depth analysis of its elemental composition and the micro-structure of its formation. SEM is usually used in conjunction with X-Ray fluorescence (XRF) thickness measurement and EDX. Some EDX machines also have XRF thickness measurement functions. From the relevant common analysis reports, we can see both the SEM diagram of the sample and the result chart of the analysis and measurement.

The advantages and advancement of nanoparticles are due to their nanoscale size. The unique properties of nanoparticles cannot be separated from their ultrafine size. Therefore, the research on the size of silver polymer nanocomposites are the premise and foundation for the good application of these nanocomposites. SEM images could verify the existence of silver nanoparticles, in which form they exist and whether they form dense network structures or are completely embedded below the surface of polymers. At the same time, the existence of large black spots or not would help to judge whether the silver nanoparticle polymer was aggregated or not from the image. SEM images can be used to judge whether silver nanoparticles are uniformly distributed in the matrix of the polymer as well as the influence of polymer introduction on the dispersion of silver nanoparticles (Fig. 1).

For example, when graphene oxide was introduced in the silver/graphene oxide hydrogel, the silver nanoparticles were well dispersed on the surface of graphene suggested by SEM (Jiao et al. 2015). In this case, the introduction of polymer played a good role in the dispersion of silver nanoparticles. As it is well known, porous structure is the basic structure of polymer, which has many advantages, such as large contact area, strong adsorption capacity and so on. SEM can clearly characterize the porous structure of silver nanocomposites and as the content of silver nanoparticles variation. The radius of silver nanoparticles obtained by using low concentration silver ion solution is smaller than that using high concentration silver ion solution. The radius of silver nanoparticles obtained by using high concentration silver ion solution is larger. For example, in graphene oxide hydrogels, the most basic structure is porous structure. Different silver content has a great influence on the size of the hole, which lead to the decrease of the effectiveness of

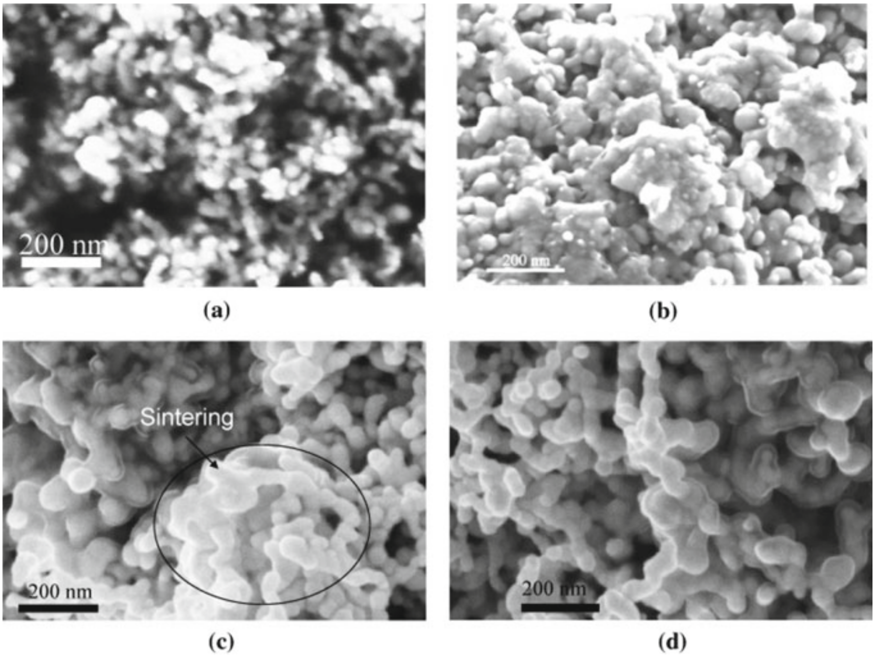


Fig. 1 Morphology difference of silver nanoparticles before annealing with the mixture of bisphenol A and hexahydro-4-methylphthalic anhydride (HMPA) **a** non-annealed, **b** annealed at 150°C for 30 min, **c** annealed at 100°C for 30 min, and **d** annealed at 100°C for 30 min. Reproduced from Ref. Jiang et al. (2006) with permission

hydrogel. With the increase of silver content, the larger the pore structure and radius are, the larger the surface area is, which is conducive to the adsorption of other substances. So the radius has a great influence on the properties of polymers. Scanning electron microscopy (SEM) can be used to analyze the radius of silver nanoparticles with different content, which can create better polymer structure (Fan et al. 2014). Furthermore, the contact structure between silver nanoparticles can be analyzed simultaneously.

Since SEM can observe the micro-structure of polymer very well, thus, tiny changes of the micro-structure of silver/polymer interface could be monitored through SEM (Fig. 2). In this way, the formation mechanism of silver/polymer nanocomposites through comparing the changes of the micro-structure before and after the formation of composites could be understood. In the preparation of silver nanowire-based transparent electrodes, when the initial intense pulsed light (IPL) irradiation intensity is very low, it is obvious that silver nanoparticles are randomly distributed on the polymer surface. The edges of these silver nano-networks are very sharp and not fully fused with the polymer, but there are gaps at the junction of the silver nanoparticles with the polymer. When the irradiation intensity increases, the polymer begins to melt. The melted polymer filled the gap, and the silver nanoparticles begin to embed beneath the surface of the polymer. The parts far away from the polymer are still very clear. When the irradiation intensity increased, the degree of melting increased until it is completely embedded below the surface, forming a perfect physical viscous form with the polymer. The cross section and the formation process of silver/polymer composite were observed by SEM. The surface structure of the composite and the micro-structure between silver nanoparticles were analyzed, indicating potential application for the implementation of this electrode (Song et al. 2015). To further observe morphology in higher magnification, TEM is mainly used to analyze the fine structure (less than 200 nm) that cannot be seen clearly under an optical microscope and SEM. These structures are called submicroscopic structures or ultra-fine structures. If people want to see these structures clearly, a shorter wavelength electron beam as the light source is necessary. The wavelength of the electron beam is much shorter than that of visible light and ultraviolet light. The current resolution of TEM can reach 0.2 nm. Because the penetrating power of electron beams is very weak, the specimens used for electron microscopy must be made into ultra-thin sections with a thickness of about 50 nm. It plays a very important role in the research and application of new materials. It has a wide range of applications in materials science such as the analysis of organic-inorganic composite materials and to study the composition, microstructure and dispersion of composite materials.

In contrast, optical microscope (abbreviated as OM) is an optical instrument that uses optical principles to magnify and image tiny objects that cannot be distinguished by the human eye, so that people can extract detailed structure information. Ordinary optical microscopes cannot see 1 nm which has to be observed under TEM. The microscope uses the magnification imaging principle of the convex lens to magnify the small objects that the human eye cannot distinguish to the size that

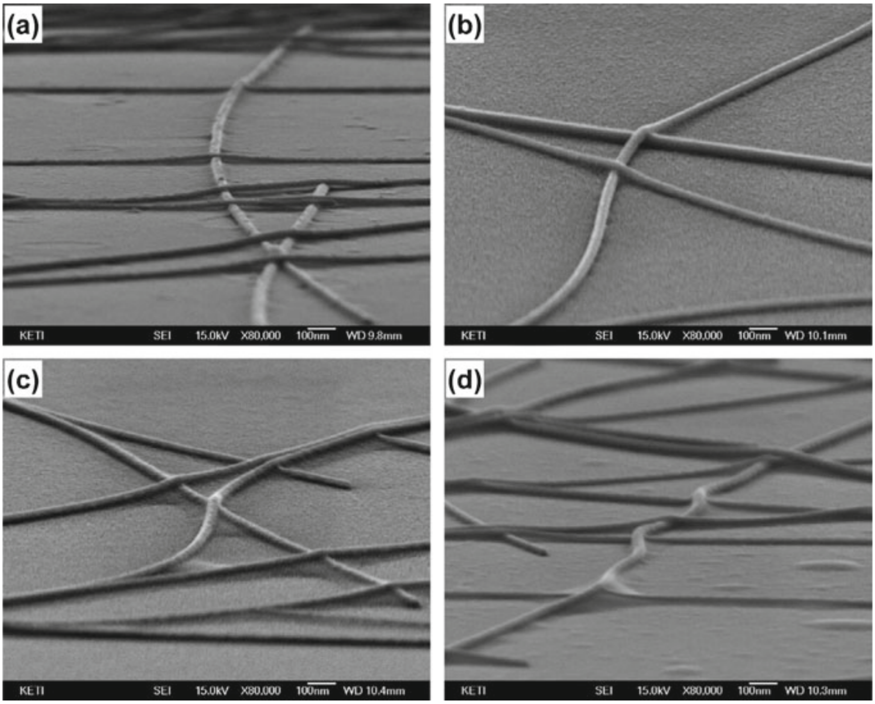


Fig. 2 Tilt-views taken by SEM for samples with increasing number of IPL exposure (500 ls): **a** a single exposure, **b** 2 times, **c** 4 times, and **d** 8 times. Reproduced from Ref. Song et al. (2015) with permission

the human eye can distinguish. It mainly increases the opening angle of the close small objects to the eye (The object with a large angle of view has a large image on the retina.), use the angular magnification M to represent their magnification power. The maximum magnification would be thousands of times. The detailed description on application of TEM and OM on characterization of Ag NPs have been discussed on Chapter 4 and hence they are not discussed here.

2 Spectroscopic Analysis of Silver/Polymer Nanocomposites Analysis

2.1 Energy Dispersive X-Ray Spectroscopy (EDX)

Energy dispersive X-ray spectrometer (EDX) is realized by analyzing the characteristic X-ray wavelength and intensity of the elements emitted by the samples. The elements in the samples are determined according to the different characteristic

X-ray wavelengths of different elements. The content of elements in the sample can be determined by comparing the strength of the specific lines of different elements. Usually EDX combined with electron microscopy can be used to analyze the micro-area components of samples.

The whole atomic system is in an unstable excited state due to the appearance of holes by the inner electron. The atomic lifetime of the excited state is about 10^{-12}–10^{-14} s, and then it spontaneously transits from high energy state to low energy state. This process is called relaxation process. The relaxation process can be either non-radiative or radiative. When the outermost electrons transit to holes, the energy released is absorbed inside the atom and driven out of another outermost secondary photoelectron, which is called Auger effect, also known as secondary photoelectron effect or non-radiation effect. The ejected secondary photoelectron is called Auger electron. The energy is characteristic and independent of the energy of incident radiation. When the energy released by the outer electrons leaps into the inner hole and it is not absorbed by the atom, X-ray fluorescence is produced in the form of radiation. The released energy is equal to the energy difference between two energy levels. Therefore, the energy or wavelength of X-ray fluorescence is characteristic and shows one-to-one relationship with elements. When the K-layer electrons are ejected, the holes can be filled by any electron in the outer layer, which can produce a series of spectral lines called K-line. The X-ray from L-layer to K-layer is called K-alpha ray, and the X-ray from M-layer to K-layer is called K-beta ray.

In addition, the intensity of fluorescence X-ray has a certain relationship with the content of the corresponding elements. Therefore, the quantitative analysis of elements can be carried out.

EDX can characterize the local chemical composition of inhomogeneous samples, the chemical composition of less materials or small particles, the one-dimensional or two-dimensional component distribution of inhomogeneous samples, and the film composition deposited on arbitrary substrates. Qualitative analysis of elements in samples and quantitative analysis of their mass concentration can be carried out quickly. Solids can be directly analyzed, and it is a non-destructive characterization technology, requiring little or no sample preparation, and the sample preparation process is simple. To obtain reliable analysis results, the samples are required to be: (1) the samples are strict, smooth and smooth (especially for quantitative analysis, the samples need polishing), and the atomic number less than five cannot be analyzed. (2) Samples with rough surface can be analyzed, but they are limited to qualitative and semi-quantitative analysis, and the existing forms of elements cannot be analyzed. (3) The sample must be conductive and conductive, and the surface should be sprayed with carbon or gold if necessary.

Typical EDX spectra: the y-axis describes the number of X-rays, and the x-axis is the energy of X-rays. The data generated by EDX analysis contains the spectra corresponding to the peaks of all the different elements in the sample. The location of the peak is to identify the elements, and the peak height is helpful to quantify the concentration of each element in the sample. Characteristic of energy spectrum: it can quantitatively analyze all elements in various types of micro-area, and it can be completed very quickly in a few minutes. The geometric position of sample and detector is low, the requirement of W and D is not very strict, and the results of X-ray scanning and surface distribution can be obtained at low magnification; the probe current of energy spectrum analysis is small, and the damage to the sample is small; the detection limit is generally 0.1–0.5%, medium. The quantitative phase error of the main elements of the non-overlapping peaks of atomic number is about 2%.

Qualitative elemental analysis of silver/polymer composite can be done by EDX spectroscopy. The characteristic X-rays emitted by different elements have different frequencies, i.e. different energies. Elements can be determined by detecting the energies of different photons. The data generated by EDX analysis contains the spectra corresponding to the peaks of all the different elements in the sample. Each element has a characteristic peak of unique energy. By analyzing the energy of the characteristic peak, the elements contained in the polymer composite could be inferred. For example, in the analysis of silver nanoparticles polymer, we can qualitatively judge the appearance of silver nanoparticles in polymer by observing the appearance of characteristic peaks of silver. Different elements have different characteristics. Quantitative elemental analysis of silver/polymer composite also can be done by EDX spectroscopy. Quantitative analysis of EDX energy spectrum can be divided into two methods. One is quantitative analysis with standard sample. Under the same conditions, the X-ray intensity of each element is identified in the standard sample and the composite sample is measured simultaneously. The percentage of each element can be calculated by strength ratio. Therefore, the accuracy of standard sample analysis is high. The second is quantitative analysis method is without standard sample. X-ray intensity of the sample is calculated quantitatively by theoretical calculation or database. In silver/polymer nanocomposites, EDX can be used to determine the percentage of each element in the polymer. Not only the existence of silver nanoparticles and other particles are expected to be characterized, but also the content of each particle. EDX can be combined with other spectrograms to analyze the content of each element, so as to obtain the proportion of each kind of element. In cellulose/silver polymer composite, different characteristic peaks in EDX represent carbon, oxygen, and iron, silver and gold. The ratio of each element is characterized by the simultaneous use of Mapsum spectrum beside it (Maleki et al. 2017). When silver nanoparticle is doped into polymer matrix, its performance is affected not only by the way in which the composite is formed, but also by the specific elements that make up the polymers. Therefore, through the quantitative analysis, the effect of element content on the properties of polymer could be understood in detail. The properties of polymer can be modulated by changing the content of elements in polymer, and the application of silver/polymer nanocomposite in various fields can be expanded.

EDX can be combined with electron-probe micro-analyzer (EPMA), SEM, TEM and so on. The combination of SEM and EDX is the most widely used micro-analysis instrument. SEM equipped with EPMA accessories such as X-ray energy spectrum IEDX and X-ray component analysis can analyze the chemical composition and other information in the sample micro-area.

The lower limit of the detected component content is 0.1%. It also can be used to analyze the modification of dry polymer materials. EDX can not only detect the presence of silver nanoparticles in the analysis of silver nanocomposites, but also judge the dispersion of silver nanoparticles in the polymer matrix. Through the EDX images, if silver nanoparticles are not aggregated, they will be uniformly distributed on the polymer surface. It is proved that silver nanoparticles are well dispersed on the surface at least. In cellulose/silver polymer composite, SEM was combined with EDX to characterize the dispersion of silver nanoparticles (Fig. 3). The results showed that silver nanoparticles were uniformly distributed on the surface of polymer, which proves that silver nanoparticles are well dispersed in the polymer matrix. Each instrument has its own defects. When several instruments are used to analyze polymers together, they can better characterize the polymers (Maleki et al. 2017).

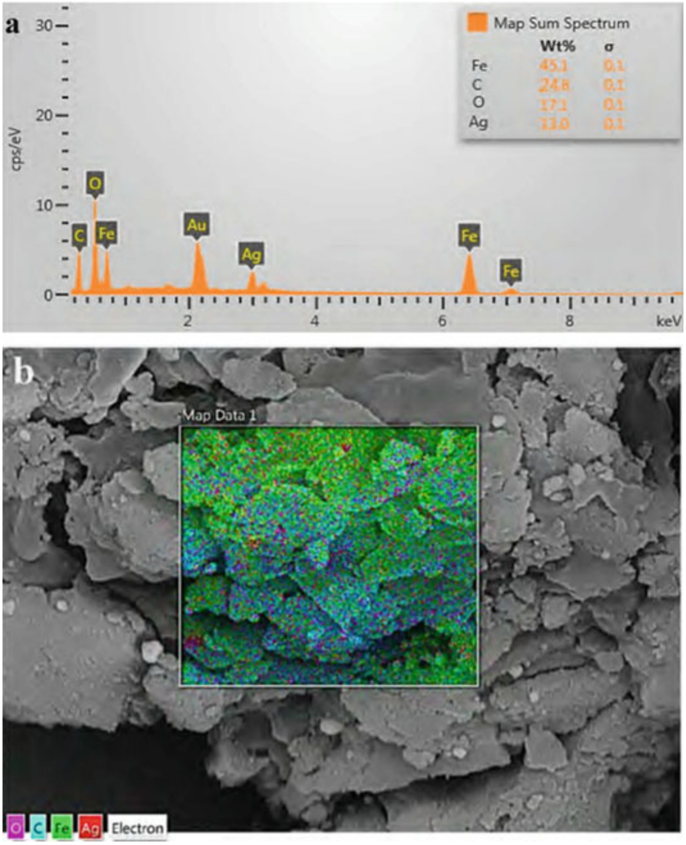


Fig. 3 **a** EDX analysis of the magnetic cellulose. **b** SEM-EDX mapping. Reproduced from Ref. Maleki et al. (2017) with permission

2.2 X-Ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) analysis uses X-ray to irradiate the sample and excite the inner electrons or valence electrons of atoms or molecules. The electrons stimulated by photons are called photoelectrons. The photoelectron spectra can be obtained by taking the kinetic energy of photoelectrons as abscissa and the relative intensity (pulse/s) as ordinate.

XPS is widely used in the analysis of inorganic compounds, alloys, semiconductors, polymers, elements, catalysts, glass, ceramics, dyes, paper, ink, wood, cosmetics, teeth, bones, transplants, biological materials, grease, glue and so on. The composition of typical XPS spectra includes abscissa: electron binding energy or kinetic energy, which directly reflects the shell/level structure of electrons, and ordinate: CPS (counts per second): relative photoelectron current intensity, the peak directly represents the binding energy of atomic orbits and the background is bremsstrahlung (primary and secondary electron generation of inelastic scattering). The number of back electrons with high binding energy increases gradually. Many peaks can be obtained by scanning the sample. The strongest photoelectron line in the main line is usually the peak with the strongest intensity, the smallest peak width and the best symmetry in the spectrum. It is called the main line in XPS spectrum. The photoelectron line is used to identify elements. In addition to strong photoelectron lines, there are photoelectron lines from other shell layers in the atom, but the intensity is slightly weak, some are very weak. The spectral line width of the photoelectron line is a contribution from four aspects: the natural width of the intrinsic signal of the sample element, the natural width of the X-ray source, the instrument and the broadening factor of the sample's own condition. There are other accompanying peaks or lines in the spectra, such as multiple splitting lines, which help to analyze the spectra and provide important information for the study of electronic structures in atoms.

XPS can be used in:

1. Qualitative analysis of elements. All elements except H and He can be identified according to the position of the characteristic lines in the energy spectrum.
2. Quantitative analysis of elements. The atomic content or relative concentration is determined by the intensity of the photoelectron spectrum line (the area of the photoelectron peak) in the energy spectrum.
3. Solid surface analysis. It includes chemical composition or element composition of surface, valence state of atom, energy state distribution of surface, electron cloud distribution and level structure of surface electrons.
4. Structure of compounds. The chemical shift of the inner electron binding energy can be measured accurately, and the information of chemical bond and charge distribution can be provided.
5. The application of molecular biology. i.e. A small amount of CO in vitamin B_{12} could be identified by XPS.

In the characterization of silver/polymer nanocomposite by XPS, the elements in silver nanocomposites can be qualitatively analyzed. According to the different chemical energy and frequency of each element, the intensity of the characteristic main line formed in the spectrum is different, and the particles in silver nanocomposite can be inferred. It can also be used to characterize the change of the intensity of the characteristic main line when the content of silver nanoparticles changes. It can not only analyze the elements existing in silver nanocomposites, but also analyze the chemical structure and energy level structure of the elements. It can specifically characterize the existing form of silver nanoparticles. It can further characterize the properties of the polymer, and has great significance in improving the material and their application. The specific analysis of silver/polymer nanocomposite is as follows.

XPS spectra prove the existence of polymer and determine the form of elements in silver nanocomposite and the corresponding chemical bond type of elements. Each element (except H and He) has its own strongest photoelectron line with characterization, which is the main basis for qualitative analysis of elements. XPS spectrogram characterizes the signal of each element in silver nanocomposites at specific bond energy. Different polymers are composed of different chemical elements, and each element has its own unique crystal structure. Then there are differences in the characteristic peaks in the corresponding spectrogram. Several characteristic main lines appear, which represent several elements. So we can deduce what elements exist in the polymer and what types of bonding elements are by mapping the different bond energies of each element. In the silver/polydopamine composite, the XPS spectrum (Fig. 4) includes several characteristic lines, which is assigned to carbon, nitrogen, oxygen and silver particles, respectively. There are three bond types in the C1s map, carbon-carbon single bond or C–Hx (284.1 eV), carbon-nitrogen bond or C–OH (285.2 eV), carbon-oxygen double bond (287.9 eV), from the N1s map, nitrogen-hydrogen bond can be obtained at bond energy 399.4 eV. O1s map mainly contains two kinds of signals, carbon-oxygen double bond (530.4 eV) and oxygen-hydrogen bond (532.1 eV). The existence of polydopamine can be inferred from these results. The signal of silver nanoparticles can be also obtained, which appears at about 370 eV (Zhang et al. 2015). Therefore, by observing several different characteristic lines and different bond energies in the spectra, we can infer the existence of elements in polymers and the different bonding forms of different elements.

XPS can not only qualitatively determine the presence of elements in polymer, but also quantitatively analyze silver nanocomposites. Quantitative analysis of different chemical structures can be carried out according to the area of different peaks. The relationship between the characteristic peaks and the content of silver nanoparticles can be obtained by XPS in-depth analysis in silver/polymer nanocomposite. The characteristic main line strength of each element will be affected by other elements, where the intensity of the peak of the element will change. When silver nanoparticles are incorporated into the polymer, the peak strength of elements in the polymer will change. When the content of silver nanoparticles is higher, the effect of silver nanoparticles on the characteristic

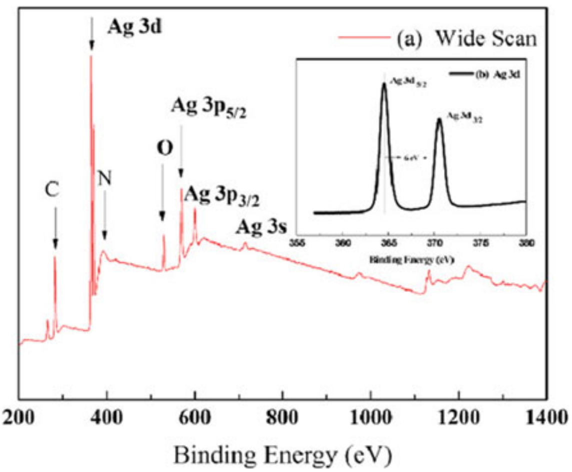


Fig. 4 XPS spectra of AgNPs@PDA particles (Zhang et al. 2015). Reproduced from Ref. Zhang et al. (2015) with permission

mainline strength of other elements is greater. For example, when the mass ratio of silver nanoparticles in graphene oxide changes, the characteristic of silver nanoparticles in XPS spectra will be different. With the increasing content of silver nanoparticles, the characteristic main line strength of C1s decreases gradually. The influence of the content of silver nanoparticles on the XPS spectra and the influence of the content of silver nanoparticles on the main line strength of carbon elements are also explained. It shows that the presence of adjacent elements affects the structural characteristics of polymers to certain extent (Fan et al. 2014).

In addition to the main line, there are also many splitting lines in XPS spectra. The reason is that when the valence shell of atoms has unpaired spin electrons (e.g. transition elements in D region, lanthanide elements in F region, most gas atoms and a few molecules NO, O_2, etc.), the inner vacancies formed by photoionization will couple with them, resulting in more than one final state of the system, which is reflected in the splitting of spectra in XPS spectra. In XPS spectra, the splitting lines of spin-orbit coupling energy levels are usually obvious. The main splitting lines are: $p_{3/2}$, $p_{1/2}$ of p orbital, $d_{3/2}$, $d_{5/2}$ of d orbital and $f_{5/2}$, $f_{7/2}$ of f orbital. The energy splitting distance varies with the element. However, not all elements have obvious spin-orbit coupling splitting spectra, and the energy spacing of splitting varies with chemical states. When silver nanoparticles exist, the internal chemical structures are different, and the energy levels are different in the polymer. The characteristic peaks under different bond energies represent different orbital forms in silver nanoparticles. Therefore, energy level and charge distribution information of silver nanoparticles in silver/polymer composites can be easily analyzed according to the characteristic peaks of XPS. In the XPS spectra of a silver/polydopamine (Fig. 4), the spectra of silver nanoparticles can be observed. There are two different peaks in the spectra, corresponding to Ag $3d_{5/2}$ and Ag $3d_{3/2}$ at 368.1 eV and 374.1 eV bond energies respectively, which proves that the energy level structure of silver nanoparticles is different (Zhang et al. 2015).

2.3 Ultraviolet-Visible (UV-Vis) Absorption Spectroscopy

Ultraviolet-visible (UV-vis) absorption spectra belong to molecular spectra. They are all produced by the transition of valence electrons. In organic compounds, there are σ electrons forming single bonds, π electrons forming double bonds, and n-pair electrons without bonds. When a molecule absorbs a certain amount of radiation energy, these electrons will jump to a higher energy level. At this time, the orbit occupied by the electrons is called anti-bond orbit, which is closely related to the internal structure. In the UV-vis spectra, there are four types of electron transitions: $\sigma \rightarrow \sigma^*$, $n \rightarrow \sigma^*$, $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$. The energy required for various transition type decreases in the following order: $\sigma \rightarrow \sigma^* > n \rightarrow \sigma^* > \pi \rightarrow \pi^* > n \rightarrow \pi^*$. Accordingly, the composition, content and structure of substances can be analyzed, determined and inferred.

Detection can be qualitatively and quantitatively when the matter undergoes n-π^* and π-π^* transition upon light irradiation.

Lambert-Beer's law is the theoretical basis of quantitative analysis in UV-vis spectroscopy. It is mathematical expressed as $A = \varepsilon\ b\ c$. where ε is the molar absorptivity (sometimes called the extinction coefficient), c is the concentration of the solution in moles per liter, and l is the length in centimeters of the sample through which the light passes.

UV-vis spectroscopy is widely used, not only for quantitative analysis. UV-vis spectroscopy also has been particularly useful in identifying the impurities in polymers such as monomer inhibitors residuals and simple structural analysis, equilibrium constants, coordination ratios of complexes, etc. because of its sensitivity ($\sim 10^{-5}$ molar).

UV-vis spectra of substances are basically chromophores (referring to the atomic groups or structural systems that can absorb ultraviolet and visible light) absorption in their molecules. Conjugated systems do absorb there, however, and the greater the conjugation, the longer the wavelength of maximum absorption. UV-vis spectra can be chosen for the understanding of the chromophore information of silver/polymer nanocomposites. Because of its high sensitivity, the UV-vis peaks of silver nanoparticles are usually only two or three, and the peak shape is gentle. It mainly depends on the chromophore characteristics, which conforms to Bill's law, so it is suitable for qualitative and quantitative study of silver nanoparticles. The silver nanoparticle polymers are characterized from several aspects.

According to Lambert-Bill's law, same concentration of solution measured has different absorbance at different wavelengths of light. The absorbance of the same substance at different concentrations is different at a certain wavelength, especially the maximum absorption wavelength. For the same solution to be measured, the higher the concentration, the greater the absorbance will be. For the same substance, regardless of the concentration, the wavelength corresponding to the maximum absorption peaks the same, and the shape of the curve is exactly the same. In the characterization of silver/polymer nanocomposite, the concentration of solution can be changed to change the content of silver nanoparticles. Through the characterization of ultraviolet-visible absorption light, the change of absorption peak intensity can be observed from the obtained curves. Therefore, the change of silver nanoparticles on the peak intensity can be analyzed. Because it is the same substance, its absorption wavelength has no effect. By observing the absorption peak height at the same wavelength, the influence of solution concentration on polymer can be deduced.

UV-vis spectroscopy can be used to analyze the existence of silver nanoparticles. For example, by comparing the absorption peaks in the ultraviolet-visible absorption spectra of silver nanoparticles with those of non-silver nanoparticles, we can judge whether silver nanoparticles are incorporated into polymers. If silver nanoparticles are not existed polymers, no absorption peaks will be observed (Chen et al. 2015).

Ultraviolet-visible absorption spectra can characterize the state of silver nanoparticles in polymers. The absorption peak is due to the plasma resonance of nanoparticles, which is related to the size and shape of nanoparticles. When there are nanoparticles, it will appear absorption peaks, which can identify the existence of silver nanoparticles. For example, in the silver/graphene oxide hydrogel, the plasma resonance of silver colloidal results in the appearance of absorption peaks, which indicates that silver, exists as nanoparticles in the silver graphene oxide complex (Fan et al. 2014). When silver nanoparticles are assembled into polymer matrix, the characteristic peak absorption wavelength of UV-vis spectrum changes, which may be due to the reduction of the distance between adjacent silver nanoparticles in the film compared with silver nanoparticles in aqueous solution (Fig. 5), indicating that the size and morphology of silver nanoparticles can change when they interacted with polymers (Chen et al. 2015).

Each polymer has different chemical bonds. The types of chemical bonds also can be analyzed by UV-vis spectroscopy. UV-vis spectroscopy can be used to

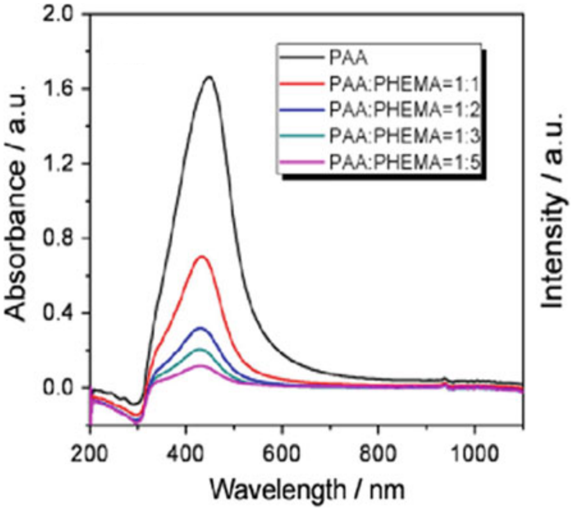


Fig. 5 UV-Vis spectra of different polymer films contained Ag NPs, where PAA stands for polyacrylic acid, PHEMA stands for poly (2-hydroxyethyl methacrylate). The Ag was generated by soaking the coated PAA:PHEMA film in a 0.3 M aqueous solution of $AgNO_3$ for 12 h before UV irradiation. Reproduced from Ref. Chen et al. (2015) with permission

deduce whether there are conjugated structure systems in the molecular skeleton of compounds, such as C=C–C=C, C=C=O, benzene ring, etc. We can judge how electrons transit. Different conjugated systems correspond to different absorption peaks at different wavelengths. By analyzing several absorption peaks, we can judge how many conjugated systems there are and how many transitions there are. By comparing the types of chemical bonds, the formation process and the formation mechanism can be analyzed. UV-vis spectra show two absorption peaks in silver/graphene oxide hydrogel composites which is 232 and 300 nm, representing the π-π* transition of carbon-carbon double bond electrons and the n-π* transition of carbon-oxygen double bond electrons (Fan et al. 2014).

The formation of new chemical bonds can be judged by UV-vis spectra. When silver nanoparticles react with polymers, new chemical bonds, such as hydrogen bonds and covalent bonds, are formed. This is important to the formation of polymer composites. Through the characterization of silver nanoparticles polymer by UV-vis spectroscopy, the changes of absorption peaks before and after polymer reaction can be used to judge the formation of some new chemical bonds, and also prove the formation of polymers. For example, in the silver nanowire/chitosan composite films, silver enhanced the properties of polymers by forming silver-sulfur covalent bonds. Therefore, the formation of covalent bonds is the key to the formation of polymers. UV-vis absorption spectra were used to analyze nanowire/chitosan composites and silver nanowire mixed chitosan polymers respectively. By comparing the absorption peaks formed by the polymers before and after the analysis, the change of absorption peak intensity can be observed obviously. The formation of silver-sulfur covalent bond is proved (Pan et al. 2018).

2.4 *Infrared Spectroscopy (IR)*

Infrared Spectrum (IR) is also called molecular vibration rotation Spectrum. It is caused by the transition of molecular kinetic energy level (accompanied by the transition of rotational energy level). Material absorbing electromagnetic radiation should satisfy two conditions: (1) radiation should have the energy just needed to meet the transition of matter; and (2) there is occasional interaction between radiation and matter. When a molecule is irradiated by infrared light with a constant frequency (constant energy), resonance absorption will occur if the vibration frequency of the molecule is consistent with that of the external infrared radiation. Because the atoms of the molecule show different electronegativity due to the different difficulty of gaining and losing valence electrons, the molecule also shows different polarity. These dipoles themselves have some original vibration frequencies. When the external radiation frequencies are the same as the dipole vibration frequencies, the molecules interact with radiation (vibro-coupling). By increasing their vibration energy, the vibration is stimulated and the amplitude is increased, and the molecules transit from the original ground state vibration to a higher vibration level. This frequency range corresponds to energies of about 2–12 kcal/

mol. This amount of energy is sufficient to affect bond vibrations (motions such as bond stretching or bond bending) but is appreciably less than would be needed to break bonds. The second condition for the generation of infrared absorption spectra is that there is a dual interaction between infrared light and molecules. In order to satisfy this condition, the dipole moments of molecules must change when they vibrate. This actually ensures that the energy of infrared light is transmitted to molecules, which is achieved by the change of the molecular vibration dipole moment. Not all vibration will produce infrared absorption, only the vibration of dipole moment changing can cause observable infrared absorption, which is called infrared active vibration; molecular vibration with dipole moment equal to zero cannot produce infrared absorption, which is called infrared inactive vibration. Molecular vibration can be divided into two types: stretching vibration and bending vibration. The former refers to the reciprocating motion of atoms along the bond axis, and the bond length changes during the vibration process. The latter refers to the vibration of atoms perpendicular to chemical bonds. By using infrared spectroscopy, the bond length and bond angle of the molecule can be determined, and the stereo configuration of the molecule can be deduced.

The strength of chemical bonds can be determined by the yield constant. According to the position of absorption peak in the spectrum, the structure of the unknown substance can be inferred, and the content of each component in the mixture can be determined according to the intensity of characteristic absorption peak. Therefore, the main advantage of infrared spectroscopy is that it has good characteristics and can even be used to analyze isomers and stereoisomers. Therefore, it is mainly used for qualitative analysis. The application of infrared spectroscopy has a wide range, but its limitations are lack of sensitivity, difficulty in trace analysis and poor quantification. The interpretation of spectra relies mainly on experience.

FTIR instrument has the advantages of high signal-to-noise ratio, high energy output, high wavenumber accuracy, wide-band measurement range and fast scanning. Therefore, it has a special important position in the analysis of polymer materials. Infrared spectroscopy is often used to identify polymers because of its simple operation and strong spectral characteristics. Infrared spectroscopy can distinguish not only different types of polymers, but also some polymers with similar structures.

IR can be used to characterize different chemical functional groups of silver/polymer nanocomposites. Each polymer has different chemical structure, so their corresponding chemical bond types are different, so different polymers have characteristic infrared absorption spectra, just as everyone is a special existence, no two are exactly the same. Atoms that make up chemical bonds or functional groups are in a state of constant vibration, and their vibration frequencies are comparable to those of infrared light. Therefore, in infrared spectroscopy, when a certain frequency of infrared light irradiates the polymer, its energy will be absorbed by chemical bonds with the same vibration frequency in the molecule. If the vibration frequency of chemical bonds in the molecule is different from that of infrared light, its energy will not be absorbed by the polymer. The vibrational frequencies of chemical bonds in molecules are different. Therefore, according to the absorption spectra of polymers to continuous infrared light, the characteristic chemical groups and their chemical bond types of polymers can be analyzed, so as to judge the chemical structure and distinguish different polymers. In the analysis of polymer spectrogram, the position of the peak, i.e. the characteristic vibration frequency of the band, should be taken into account in the analysis of chemical bond type, which is the basis for qualitative analysis of functional groups. The type of polymer can be determined according to the position of the characteristic peaks. In the infrared spectra of polymers, the bands with the strongest absorption often correspond to the absorption of their main groups, and have certain characteristics. At the same time, each absorption band in the infrared spectra represents a certain vibration form of an atom group or group in the compound. Their vibrational frequencies (corresponding to the wave numbers of absorption bands appearing on the spectra) are directly related to the atomic mass and the strength of chemical bonds in the groups. Of course, they are also indirectly affected by different adjacent structures and chemical environments. For example, in silver/graphene oxide hydrogels, graphene oxide absorptions in infrared spectra is corresponds to the stretching vibration energy of oxygen-hydrogen bond, the vibration energy of carbon-oxygen double bond and the vibration energy of carbon-carbon double bond and carbon-oxygen single bond, respectively. When the content of silver nanoparticles increased, the absorption peak intensity of infrared spectra changed obviously, which indicated that silver nanoparticles reacted with graphene oxide.

Infrared spectroscopy can also be used to characterize the formation mechanism of silver nanoparticles and identify the formation of new chemical bonds. A simple semi-quantitative prediction of the sequence structure of copolymer can be made by characterizing the change of the signal intensity of the absorption peak of a chemical bond in the infrared absorption spectra of polymers, according to the transfer of the absorption peak and the inference of the reaction mechanism in the synthesis. In addition, another important basis for the analysis of infrared spectra of polymers is the band. The band form includes information on whether the band is split or not. It can be used to study the existence of association in molecules and the symmetry, rotational isomerization and tautomerism of molecules. The intensity of the band is related to the change rate of the dipole moment when the molecule vibrates, but it is also proportional to the molecule content, that is, the stronger the band, the more the molecule content. Therefore, it can be used as the basis of quantitative analysis. The dynamic process of polymer formation can be studied according to the change of the intensity of some characteristic bands with time. As shown in Fig. 6, the absorption peak of carbon-oxygen double bond in pure mercapto-chitosan is 1630 cm^{-1}, the absorption peak of carbon-oxygen double bond turns to 1655 cm^{-1} in silver/chitosan polymer films, which is caused by the electron departure effect of silver nanoparticles. Moreover, with the increase of the content of silver nanoparticles, the absorption peak of silver nanowires sulfhydryl chitosan polymer in infrared spectra becomes more and more flat, the peak band becomes wider, and the peak strength decreases. The disappearance of sulfur-hydrogen bond vibration in silver/chitosan polymer films shows that

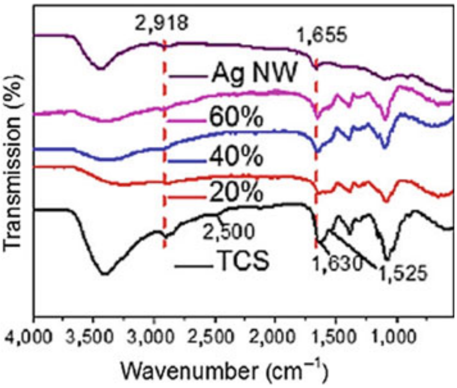


Fig. 6 FT-IR spectra of Ag NWs, pure TCS, and Ag NW-TCS composite films with different Ag NW contents. Reproduced from Ref. Pan et al. (2018) with permission

silver-sulfur covalent bonds are formed on the surface of silver nanoparticles and sulfhydryl chitosan. The reason is that the organic mercaptan molecule absorbs silver nanoparticles to form a covalent bond between silver and sulfur, which results in the red shift of the corresponding absorption peak band (Pan et al. 2018). Red-shift refers to the movement to the red band, that is, the energy of photons becomes lower, the wavelength increases and the wavenumber decreases, so moving to the low wavenumber is red shift, and vice versa is blue shift. Infrared spectroscopy is a vibration spectroscopy, which usually requires very low energy. Moving to low wave number means that the energy required for vibration is lower and the group is more unstable. The formation mechanism of silver/polymer can be inferred by the change of absorption peak intensity in infrared spectra, and the formation of new chemical bonds can be judged.

3 Scattering Methods for the Analysis of Silver/Polymer Nanocomposites

X-ray is the light radiation produced by the transition of the inner electrons of an atom under the bombardment of high-speed moving electrons. XRD is a nondestructive technique that provides detailed information about the crystallographic structure, chemical composition, and physical properties of materials. Crystals can be used as gratings for X-rays. The coherent scattering of these large numbers of particles (atoms, ions or molecules) will interfere with light, thus enhancing or weakening the intensity of scattered X-rays. Because of the superposition of scattering waves of a large number of particles, the maximum intensity of the beams produced by mutual interference is called X-ray diffraction lines. By analyzing the diffraction patterns, we can obtain information about the composition of materials, the structure or morphology of atoms or molecules in materials. The crystal structure causes the incident X-ray beam to diffract in many specific directions. By measuring the angle and intensity of these diffracted beams, crystallographers can generate three-dimensional images of electron density in crystals. Based on this electron density, the average position of atoms in crystals, their chemical bonds and other information can be determined.

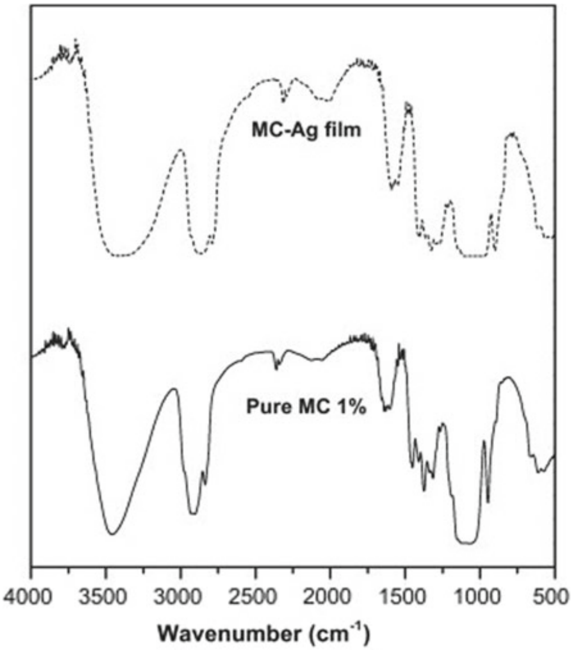
X-ray is a kind of electromagnetic wave with very short wavelength (about 20–0.06 Å). It can penetrate a certain thickness of substances, and make fluorescent substances emit light, photographic latex sensitizes light, and gas ionizes. X-rays produced by bombarding metal targets with electron beams contain X-rays with specific wavelengths corresponding to various elements in the target, which are called characteristic (or marking) X-rays. X-ray is the light radiation produced by the transition of atom inner electrons under the bombardment of high-speed moving electrons. There are two main types: continuous X-ray and characteristic X-ray. Crystals can be used as gratings for X-rays. The coherent scattering of these large numbers of particles (atoms, ions or molecules) will interfere with light, thus enhancing or weakening the intensity of scattered X-rays. Because of the superposition of scattering waves of a large number of particles, the maximum intensity of the beams produced by mutual interference is called X-ray diffraction lines. XRD is based on the coherent scattering of X-rays and the Bragg formula $2d\sin\theta = n\lambda$, crystal theory and reciprocal lattice Ewald diagram. The basic conditions of diffraction are: (1) the integral multiple of the spacing between layers and the radiation wavelength; (2) the spatial distribution of scattering centers is regular. Main Measurements: Crystal structure information. The main methods include X-ray powder diffraction and single crystal diffraction.

XRD is mainly used to analyze the composition, size and crystallinity of nanoparticles by comparing with standard spectra. With the aid of X-ray diffractometer and the diffraction effect of microcrystalline on X-ray, the diffraction pattern of the sample, i.e. the relationship between the diffraction intensity and the diffraction angle can be obtained. The analysis of its diffraction patterns can be used to investigate the properties of chemical bonds and the relationship between structure and properties. It is a means to obtain information about the composition of materials, the structure or morphology of atoms or molecules in materials. At the same time, it can be applied to the structure analysis of crystallization analysis. From the Bragg formula and the known wavelength λ, the angle of θ can be measured, and the spacing d between crystals can be calculated. Given the d value, θ can be measured to calculate the characteristic radiation wavelength and determine the elements contained in the sample. Particle size can be estimated also. According to the spectral line width and the calculation formula, the average grain size can be calculated.

At present, X-ray diffraction (including scattering) has become an effective method to study the microstructures of crystalline and some semi-crystalline materials. For the application of silver/polymer nanocomposite, XRD can be used in chemical analysis, i.e. qualitative and quantitative analysis, which is a widely used aspect of X-ray diffraction in polymer. For qualitative analysis, by comparing the X-ray diffraction of polymer composites before and after the chemical reaction, one can analyze the diffraction spectrum, comparing the differences of the diffraction peaks to check whether there are new diffraction peaks. If new diffraction peaks appear, silver nanoparticles might be generated in the polymer matrix, otherwise there will be no silver nanoparticles. If there is no load of silver nanoparticles, there is no characteristic peak in the spectra which could be used to verify the existence of silver nanoparticles. For the quantitative analysis of silver/polymer nanocomposites, each element has its own special diffraction peaks, and the corresponding peaks of silver with different content are different. The area under the general diffraction peaks represents the content of the element. By analyzing the intensity of the diffraction peaks, we can roughly determine the content of silver nanoparticles and determine the content of silver nanoparticles in materials (Fig. 7).

X-ray diffraction can also be used for phase analysis of silver/polymer nanocomposites. General chemical analysis is used to analyze the kinds and contents of the elements in the constituent substances, but the internal structure of the polymer composite cannot be analyzed. Phase analysis can provide the state of chemical bonding between elements and the aggregation structure of substances. The chemical composition can be same, but the chemical bonding state or aggregation state of substances can be different. As in the case with SiO_2, amorphous silica gel, crystalline quartz and white silica can be formed due to different aggregates. For silver/polymer nanocomposite, the chemical bonds formed by silver nanoparticles may be different in different polymers, thus, the aggregation states are different, and the ways in which silver nanoparticles linked with polymers are different. When X-ray diffraction scans over silver/polymer nanocomposites, the

Fig. 7 FTIR spectra of methylcellulose (MC) and methylcellulose–silver (MC–Ag) nanocomposite film. Reproduced from Ref. Maity et al. (2012) with permission



characteristic peaks of silver nanoparticles can be obtained in the spectra. Different silver phase will lead to different characteristic peaks, and the corresponding angles are also different. The appearance of those X-ray diffraction peaks essentially represents the existence of different crystalline structure, that is, the substance is crystalline. According to the diffraction spectra, the diffraction peaks formed by silver nanoparticles at different angles can be used to infer the crystal planes of silver nanoparticles in polymers, and to better understand the phase of silver nanoparticles in polymers. For example, silver nanoparticles in poly(vinylidene fluoride) and in polydopamine matrix, four characteristic peaks corresponding to 38.150, 44.194, 64.156 and 77.624 degrees of silver nanoparticles can be observed (Fig. 8). The corresponding characteristic peaks of PVDF are 20.08, 36.34, and 40.56 degrees. And the poly(vinylidene fluoride) shows a single peak at 20.5 and 38.8 degrees, corresponding to the [110] and [200] planes and the [002] planes, respectively (Zhang et al. 2015). The plane of silver nanoparticles corresponding to different bond angles was characterized. The orientation of silver nanoparticles in polymer can be well analyzed by X-ray diffraction, and the three-dimensional structure of silver nanoparticles can be understood.

In another case, when ammonia water is added into silver nitrate solution, silver-ammonia complexes begin to form. When graphene oxide is added, silver-ammonia complexes are easily absorbed into oxygen-containing functional groups with negative charges on graphene oxide because of the positive and negative phase absorption of charges. With the addition of glucose, silver-ammonia complex was reduced to silver nanoparticles by aldehyde group of glucose. The characteristic peaks of silver nanoparticles appeared in the related XRD spectra, which proved the formation of silver nanoparticles, explained the formation mechanism of silver nanoparticles polymer. Therefore, reaction process between silver nanoparticles and polymer can be speculated (Fan et al. 2014).

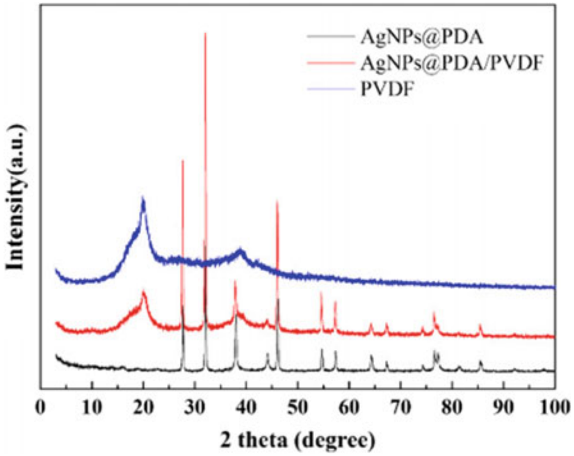


Fig. 8 XRD patterns of Ag nanoparticles@polydopamine (AgNPs@PDA) particles, poly(vinylidene difluoride) (PVDF) film, and AgNPs@PDA/PVDF composite film. Reproduced from Ref. Zhang et al. (2015) with permission

In summary, the application of XRD in silver nanoparticles polymer is very extensive. It can not only qualitatively and quantitatively analyze silver nanoparticles, but also analyze the internal chemical structure of silver nanoparticles polymer, and characterize the corresponding crystal planes of silver nanoparticles at different angles. At the same time, it has a good tool to speculate formation mechanism in silver/polymer nanocomposite.

Laser particle size analyzer is an instrument that used to analyze particle size by means of diffraction or spatial distribution of scattered light (scattering spectrum). It is characterized by fast test speed, wide test range, good repeatability, easy operation and so on. It can be divided into static light scattering (SLS) and dynamic light scattering (DLS) laser particle size analyzer. The SLS is mainly suitable for testing micron particles. The size of nanoparticles can be analyzed by detecting the dynamic light scattering signals of one or two scattering angles according to the Brownian motion of particles. The data obtained is the average particle size.

The diffusion coefficient is inversely proportional to the particle size according to the Stokes Einstein equation. Photonic correlation spectroscopy (PCS) is a technique that used to determine the diffusion coefficient of small particles in liquid by accurately measuring the light scattering intensity of particles as a function of time. When the particles are small, the particles in the liquid are affected by Brownian motion and show a random motion state. When the laser is irradiated onto these particles, the laser light scatters in all directions. The wave frequency of the scattered light contains the information of the particle size. For larger particles that move more slowly, the fluctuations will be slower. When the beam is blocked by particles, part of the light will be scattered. The scattering light will travel at an angle of theta to the direction of the main beam. Scattering theory and experiments show that theta is related to the size of the particle, and the larger the particle, the smaller the scattering light. The smaller the particle, the greater the theta angle of the scattered light. The scattered light is collected at a selected angle and measured by a highly sensitive detector.

Figure 9 shows TEM images and DLS analysis results. The particle size distribution of the prepared nanoparticles is narrow, spherical and pseudo spherical. In DLS analysis (inset), silver nanoparticles exhibit peaks centered at 98 nm in the sample. These results confirm the good stability of gallic acid for nanoparticles (Espinosa-Cristóbal et al. 2009).

Zeta potential is an important characterization parameter of nanomaterials. The net charge on the surface of particles affects the distribution of ions in the region around the particle interface, which leads to the increase of the concentration of counter ions close to the surface. Therefore, there are electric double layers around each particle. There are two parts in the liquid layer around the particles: one is the inner layer, which is called Stern layer, in which the ions are tightly bound to the particles; the other is the outer dispersion area, in which the ions are less closely adsorbed on the particles. In the dispersion layer, there is an abstract boundary, in which ions and particles form stable entities. When a particle moves (e.g. due to gravity), ions within this boundary move with the particle, but ions outside the

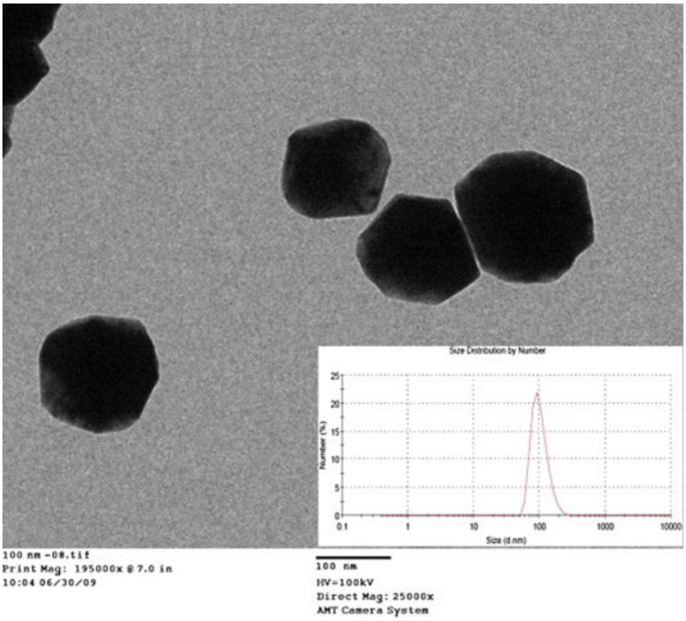


Fig. 9 TEM and DLS results of the silver nanoparticles prepared by the addition of gallic acid to $AgNO_3$ solution method. The mixture was irradiated with UV light (254 nm, 15 W) during 30 min. Reproduced from Ref. Espinosa-Cristóbal et al. (2009) with permission

boundary do not. This boundary is called a hydrodynamic shear layer or sliding plane. The potential at this boundary is called zeta potential.

Zeta potential can be used as an indicator of the stability of colloidal system. If the particles have a lot of negative or positive charges, that is, very high zeta potential, they will repel each other, so as to achieve the stability of the whole system; if the particles have few negative or positive charges, that is to say, their zeta potential is very low, they will attract each other, thus reaching the instability of the whole system. Generally speaking, the higher the zeta potential is, the more stable the dispersion system is. The dividing line of particle dispersion stability in aqueous phase is considered at +30 mV or −30 mV. If all particles have zeta potential higher than +30 mV or lower than −30 mV, the dispersion system should be relatively stable.

Zeta potential of dispersion system can be changed by the following factors: pH, conductivity of solution and the concentration of a particular additive, such as surfactant, polymer. The stability of the product can be obtained by measuring zeta potential energy of a particle as the above variables, and in turn, the best conditions for flocculation can be determined.

For instance, Sankar et al. formulated the biodegradable poly-D, L-lactide-co-glycolide (PLGA) polymer based biogenic silver nanocomposite by modified solvent casting method. The zeta potential value of Ag NPs was −33 mV with

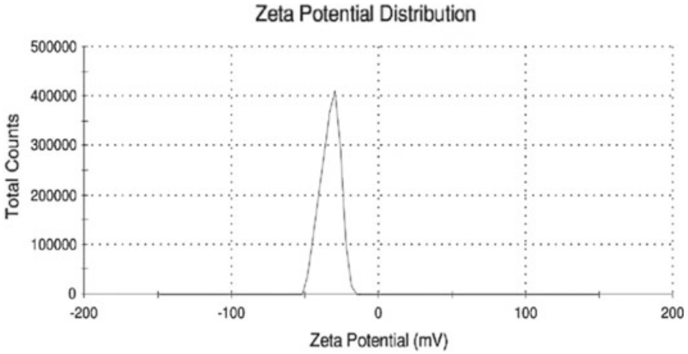


Fig. 10 Zeta potential measurement of Ag NPs. Reproduced from Ref. Sankar et al. (2016) with permission

average particle size distribution was 115 nm (Fig. 10). It is well accepted that a zeta potential value of about −25 mV approves a high energy barrier for the stabilization of nano suspension (Sankar et al. 2016).

4 Silver/Polymer Nanocomposites: Thermal Characterization

Thermal gravimetric analyzer (TGA) is a kind of instrument which uses thermogravimetric method to detect the relationship between temperature and mass of substances. TGA is to measure the change of mass of substance with temperature (or time) under programmed temperature control, in which changes in physical and chemical properties of materials are measured as a function of increasing temperature (with constant heating rate), or as a function of time (with constant temperature and/or constant mass loss). The important characteristic of thermogravimetric method is that it has strong quantification and can accurately measure the change of mass and the rate of change. It can be said that as long as the change of mass occurs when the material is heated, the thermogravimetric method can be used to study the change process.

When the substance under test sublimates, vaporizes, decomposes into gas or loses crystalline water during heating, the quality of the substance under test will change. At this point, the thermogravimetric curve is not a straight line, but a decline. By analyzing the thermogravimetric curves, we can know how much the measured substance changes at different degrees. According to the weight loss, we can calculate how much substance has been lost. The thermogravimetric analyzer is mainly composed of balance, furnace, and temperature control system by program and recording system.

There are two commonly used measuring principles: displacement method and zero-position method. The so-called displacement method is based on the proportional relationship between the inclination of the balance beam and the change of mass, using differential transformer to detect the inclination, and automatically record it. Zero-position method is to use differential transformer method and optical method to measure the inclination of balance beam, and then to adjust the current of coil installed in balance system and magnetic field, so that the coil rotation restores the inclination of balance beam, that is, the so-called zero-position method. Since the force exerted by the coil rotation is proportional to the change of mass, and this force is proportional to the current in the coil, the curve of mass change can be obtained by measuring and recording the change of current. The most widely used TGA method is based on continuous measurement of weight on a sensitive balance (called a thermobalance) as sample temperature is increased in air or in an inert atmosphere. Data are recorded as a weight loss versus temperature.

The important characteristic of thermogravimetry is that it can measure the change of mass and the rate of change accurately. The main measurement is the decomposition temperature of the material. The temperature at which the general mass loses 95% is denoted as the decomposition temperature normally.

Thermogravimetric analysis can study the changes of crystal properties, such as the physical phenomena of melting, evaporation, sublimation and adsorption, the thermal stability, decomposition process, dehydration, dissociation, oxidation, reduction, quantitative analysis of components, the influence of additives and fillers, water and volatiles, reaction kinetics and other chemical phenomena. The TGA curve takes mass as ordinate, decreases mass from top to bottom, temperature (or time) as abscissa, and increases temperature (or time) from left to right. TGA is mainly the relationship between temperature e and mass, so temperature has a great impact on the measurement. The higher the heating rate, the greater the impact it will be. With the increase of heating rate, both the starting and ending temperatures of decomposition increase correspondingly, but the weight loss is not affected by heating rate. With different heating rates, the shape of TGA curve changes, the heating rate increases and the resolution decreases, this is not good to the detection of intermediate products. After the TGA curve is finished, the weight loss percentage of each temperature range can be calculated according to the amount of original sample and the weight loss of each temperature range. It is used to study the thermal stability and composition of materials. Generally, there are several methods to judge the thermal stability of materials. Firstly, the direct comparison the TGA curves of several materials on the same drawing to make an intuitive comparison. Secondly, stipulates a temperature value and then calculates the weight loss percentage at this temperature. The greater the weight loss, the worse the thermal stability of the material will be. Thirdly, the method of constant weight loss temperature stipulates a percentage of weight loss and calculates the corresponding temperature. The higher the temperature, the better the thermal stability will be. Or it can be judged by the starting and ending temperatures of material weightlessness. The higher the starting and ending temperatures, the better the thermal stability will be.

TGA can be used to determine the thermal stability of silver/polymer. TGA has strong quantification and can accurately measure the change of mass and its rate of change, whether the change is chemical or physical, so it is the most widely used analytical technique for the analysis of polymer content, as shown in Fig. 11. The mass loss of silver nanoparticles varies with the content of silver nanoparticles in polymers when TGA is run at the same temperature. In the TGA curve, the load of silver nanoparticles can be analyzed by observing the mass loss of polymers with different silver nanoparticles content. The temperature value on the weight loss curve is used to compare the thermal stability of materials. The thermal stability of silver nanoparticles polymers with different content is different. According to the different decomposition temperature of polymers, the influence of silver nanoparticles content on the thermal stability of polymers can be judged. For example, in silver/chitosan polymers, the mass of silver nanoparticles is not lost when the temperature changes, while the mass of mercapto-chitosan is greatly lost. As shown in Fig. 11, when the silver nanoparticles are assembled into the polymer, the mass loss of the mercapto-chitosan polymer is obviously reduced. When the content of silver nanoparticles is more and more, the mass loss of the polymer is less and less. It shows that the thermal stability of the polymer increases with the increase of silver nanoparticles content (Pan et al. 2018). TGA can be used in combination with differential thermal analysis to better judge the thermal stability of silver nanoparticles polymer, and can also speculate whether there are impure substances.

Differential Thermal Analysis (DTA) utilizes a reference sample which does not undergo any chemical reaction and physical change at a certain experimental temperature to compare with an equal amount of unknown sample in the same environment. Any chemical and physical changes of the unknown substance will increase or decrease temporarily compared with the temperature of the reference sample in the same environment. The decrease is endothermic reaction and the increase is exothermic reaction. When the unknown sample and the reference sample are given the same temperature, the rise of temperature for both the samples will be different because of their different thermal properties. The purpose of the analysis is to measure the temperature difference between them. The curve obtained by taking the temperature difference between the reference material and the sample as the

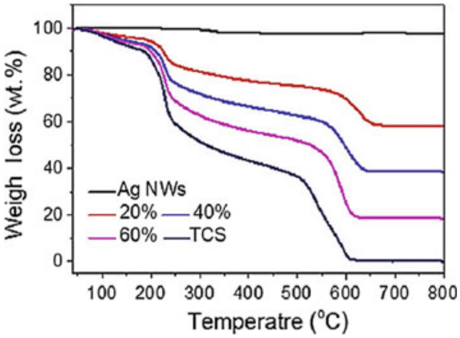


Fig. 11 TGA of silver nanowires (Ag NWs) and different doping ratio with TCS. Reproduced from Ref. Pan et al. (2018) with permission

longitudinal coordinate and the temperature as the abscissa coordinate is called DTA curve. When analyzing the thermal stability of silver/polymer composite, two different curves were obtained when the thermogravimetric analyzer and differential analysis were used together. By comparing the different temperatures corresponding to the mass loss of silver/polymer in the two curves, the thermal stability of polymer can be inferred. For example, in silver/cellulosic, the mass loss temperature of cellulose is at about 250–260 degrees. The main mass loss temperature ranges from 370 to 410 degrees which is due to the degradation of organic substances in the composites, which is much higher than the decomposition temperature of cellulose itself. It is shown that the thermal stability of the material is enhanced when the silver/cellulose composites is formed. At the same time, it was also observed that the mass loss of silver/cellulose polymer composite occurred between 300 and 320 degrees, which is possibly due to the decomposition of other impurities. Through mass loss, it can be inferred whether there are other impurities in the polymer, and the purity of the polymer can be qualitatively judged (Maleki et al. 2017). As shown in Fig. 12, the pure and 1% Ag doped CdO examples in the TG-DTA curve show that the decomposition peak/melting temperature is 208 and 105°C, corresponding mass loss is 9% and 7%, respectively, as shown in the first step of the curve. In the second step, the organic decomposition temperature of the pure sample and the silver-doped sample were 333 and 233°C respectively, and 6% and 8% mass were lost respectively. This result shows that the percentage of organic decomposition increases from pure silver to silver doped (2%). Step 3: DTA curve shows the inorganic decomposition of 1% Ag doped samples at 380, 384 and 373°C, and the mass loss corresponding to TG curve is 2% respectively (Sivakumar et al. 2015).

Differential scanning calorimetry (DSC) is a thermos analytical technique in which the difference in the amount of heat required to increase the temperature of a sample and reference is measured as a function of temperature. Both the sample and reference are maintained at nearly the same temperature throughout the experiment. Generally, the temperature programed for a DSC analysis is designed so that the temperature of sample holder increases linearly as a function of time. The reference sample should have a well-defined heat capacity over the range of temperatures to

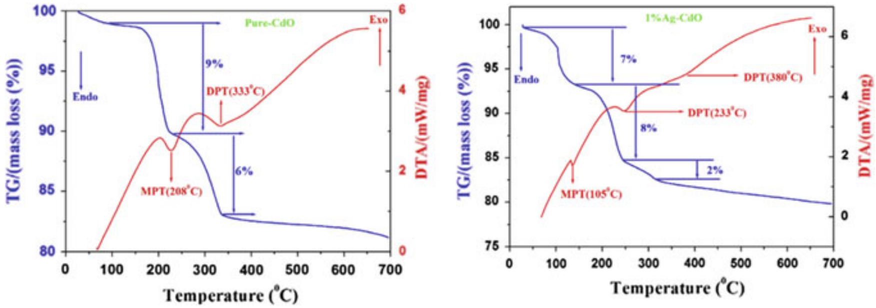


Fig. 12 TG–DTA curve for pure-CdO and 1% Ag-CdO nanoparticles. Reproduced from Ref. Sivakumar et al. (2015) with permission

be scanned. Since DSC can measure a number of characteristic properties of a sample, like glass transition, heat capacity and crystallization temperature, DSC is used widely for examining polymeric materials to determine their thermal transitions. Melting points and glass transition temperatures for most polymers are available from standard compilations, and the method can show polymer degradation by the lowering of the expected melting point, T_m, for example. T_m depends on the molecular weight of the polymer and thermal history, so lower grades may have lower melting points than expected. The percent crystalline content of a polymer can be estimated from the crystallization/melting peaks of the DSC graph as reference heats of fusion can be found in the literature. DSC can also be used to study thermal degradation of polymers using an approach such as Oxidative Onset Temperature/Time (OOT).

Satyendra Mishra et al. synthesized the highly stable, semicon-ducting polyaniline/silver nanocomposites which are prepared in situ by employing the acoustic cavitation mechanism to obtain the composite in nanophase. Phase transitions were investigated over the range of 35–300 °C at 10 °C/min under nitrogen atmosphere on a DSC 60 differential scanning calorimeter. TGA and DSC results indicated greater thermal stability for the nanocomposites along with higher crystallinity (Mishra et al. 2012). Mohammad et al. reported an nanocomposites of poly (2-hydroxyethyl methacrylate) (PHEMA) hydrogels with silver nanoparticles (Ag NPs). The DSC experiments was found to vary with conversion in a different way compared to neat PHEMA (Siddiqui et al. 2016).

5 Mechanical and Viscoelastic Characterization of Silver/Polymer Nanocomposites

Dynamic mechanical analysis (DMA) is a technique that used to study the viscoelastic behavior of polymers. A sinusoidal stress is applied and the strain in the material is measured, allowing one to determine the complex modulus. The temperature of the sample or the frequency of the stress are often varied, leading to variations in the complex modulus. This approach can be used to locate the glass transition temperature as well as to identify transitions corresponding to other molecular motions of the material.

Lavinia Balan et al. reported a new method for the preparation of silver nanoparticles/polymer nanocomposite materials by UV-radiation curing of multifunctional acrylate monomers. Silver nanoparticles possessing an average diameter of 6.6 nm were first prepared by chemical reduction of silver nitrate with *t*-BuONa-activated sodium hydride in THF. The viscoelastic properties of the nanocomposite were monitored by DMA (Fig. 13). Silver nanoparticles were found to have no detrimental effect on the photopolymerization kinetics and the incorporation of metal nanoparticles allowed to reduce the gloss of UV-cured coatings. An increase of the diameter of silver nanoparticles to 20 nm was observed during the curing process (Balan et al. 2008).

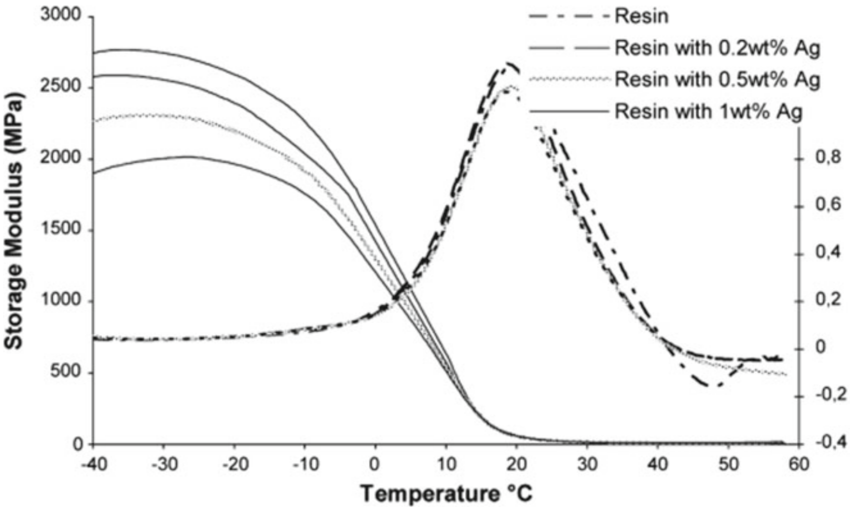


Fig. 13 Influence of silver nanoparticles on the viscoelastic characteristics and tan δ profiles recorded by DMA for a UV-cured polyurethane-acrylate. Reproduced from Ref. Balan et al. (2008) with permission

Antoine Lonjon et al. prepared highly conductive composites of silver nanowires and semicrystalline polyamide 11 for different content. DSC and DMA have shown high stability of the composite physical structure and an optimization of the mechanical properties as a function of nanowires content of 3.6 vol.%. A simultaneous enhancement of the electrical conductivity of polyamide 11 was also obtained (Lonjon et al. 2013).

Different chemical structures of polymers can be designed and synthesized to produce polymers with different glass transition temperature (T_g), melting temperature (T_m), crosslinking, and crystallinity that will result in different mechanical behaviors. Usually, polymers are used as matrix materials, which requires that they have good mechanical properties, durability and adaptable to various needs (e.g. as fibers to withstand tension; as plastic products to withstand knocking; as rubber to be elastic and wear-resistant, etc.). Mechanical properties refer to the mechanical responses of materials after being subjected to force, such as deformation, reversibility of deformation and damage resistance. These responses can be expressed by some basic parameters.

The mechanical properties of polymers indicate the relationship between stress and strain of polymers under external forces. When polymers are used as structural materials, their mechanical properties are particularly important, basic parameters of mechanical properties including strain and stress plot, elastic modulus, hardness and strength.

Polymer materials are viscoelastic. When the stress is removed, part of the work is used for frictional effect and converted into heat energy. This process can be expressed by stress-strain curve. The abscissa of the curve is strain, and the longitudinal coordinate is external stress. The shape of curves reflects various deformation processes such as brittleness, plasticity, yield and fracture of materials under external forces. This stress-strain curve is usually called engineering stress-strain curve. It is similar to the load-deformation curve, except that the coordinates are different.

Stress is usually expressed as changes in unit length (area, volume). When the material is deformed under the action of external force, the additional internal force against external force will also be generated in order to keep the material in its original state. When the external force is eliminated, the internal force will make the material return to its original state and gradually eliminate itself. When the external force is in balance with the internal force, the internal force and the external force are equal in size and opposite in direction. Internal force per unit area are defined as stress.

Strain is the relative change in shape or size of an object due to externally-applied force. When a material is loaded with a force, it produces a stress, which then causes a material to deform. Engineering strain is defined as the amount of deformation in the direction of the applied force divided by the initial length of the material.

Stress-strain curves are most commonly used to describe the mechanical properties of polymers. Its shape depends on the polymer's chemical structure, physical structure, experimental conditions, chemical composition, structure, molecular weight and its distribution, polymer branched bonding, crystallization and orientation, size and shape of crystal region, processing state, temperature, rate and so on, which will affect the distribution of stress-strain curve of polymer. According to these characteristics, stress-strain curves can be divided into the following categories. (1) The material is hard and brittle: under the action of larger stress, only minor strain occurs, and fracture occurs before yield point. It has high modulus and tensile strength, but the stress is brittle fracture, and the impact strength is poor. (2) Material is hard and strong: under greater stress, the material has smaller strain, breaks near the yield point, has high modulus and tensile strength. (3) Material is strong and tough: has high modulus and tensile strength, fracture elongation is larger, when the material is subjected to force, it belongs to ductile fracture material: low modulus, low yield strength, high fracture elongation, high fracture strength, can be used for demanding deformation. (4) Soft and weak materials: low modulus, low yield strength, medium breakage, crack elongation. (5) Weak and brittle materials: generally, oligomers, it cannot be directly used as materials.

The mechanical properties of polymer composites depend on different parameters. The intrinsic properties of polymer composites have great influence on the mechanical behavior of hydrogen bond, van der Waals force and covalent bond, and these chemical bonds and intermolecular forces will ultimately affect the mechanical properties of polymer. For the characterization of mechanical properties of silver/polymer nanocomposites, the stress-strain curves were used to analyze. In the stress-strain curve, the mechanical properties of silver nanocomposites are related to the formation of new chemical bonds and the content of silver nanoparticles in the polymer. Silver nanocomposites exhibit excellent mechanical properties because of the formation of chemical bonds between silver nanoparticles and the polymer matrix. Moreover, the curves of different silver nanoparticles are changed. When the content of silver nanoparticles changes, the strain decreases and the stress increases, this indicates that the mechanical properties of the polymer increase. If the stress decreases and the strain increases, the mechanical properties of the polymer decrease. The mechanical properties of mercapto-chitosan with silver nanoparticles are higher than that of chitosan because disulfide bonds are formed when silver nanoparticles form polymers with chitosan, which leads to the increase of mechanical properties (Pan et al. 2018). The mechanical properties of the polymer vary with the content of silver nanoparticles. When the content of silver nanoparticles increases, very small strain occurs in the polymer under great stress, which indicates that the mechanical properties of the polymer are enhanced with the increase of the content of silver nanoparticles.

The tensile strength of silver nanoparticles can be characterized as explained below. When the material is subjected to external forces that exceed the material's bearing capacity, the material will be destroyed. Mechanical strength is a measure of material's ability to resist external forces, which means the maximum stress that material can bear under certain conditions. Tensile strength measures the ability of materials to resist tensile damage. Stress-strain curve can also characterize the tensile strength of a polymer. When the stress of a polymer is larger and the strain is smaller, hence the tensile strength of polymer is higher. Silver nanoparticles can enhance the ultimate mechanical properties of polymer, so the more the content of silver nanoparticles, the greater the mechanical properties of polymer, the corresponding tensile strength of polymer is enhanced. As shown in Fig. 14, when the content of silver nanoparticles in mercapto-chitosan polymer increases, the tensile strength of the polymer increases gradually. When the content of silver nanoparticles increased to 70%, the tensile strength of the polymer will decrease. The reason is that when the content of silver nanoparticles is too high, silver nanoparticles will gather on the surface of the polymer, resulting in poor dispersion of silver nanoparticles. Therefore, the tensile strength of the compound decreases (Pan et al. 2018).

Elastic modulus and toughness are also important basis for characterizing the mechanical properties of polymers. Modulus refers to the magnitude of stress required per unit strain in the range of elastic deformation. It is a characterization of

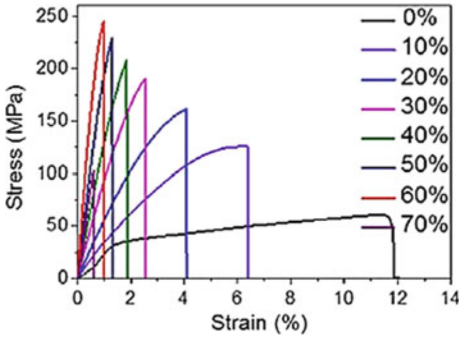


Fig. 14 Stress–strain curves of a series of Ag NW-TCS composite films with increasing Ag NW content. Reproduced from Ref. Pan et al. (2018) with permission

material rigidity. For ideal elastic solids, the relationship between stress and strain obeys Hooke's law, that is, stress is proportional to strain. The proportional constant is called modulus of elasticity, or modulus for short. Elastic modulus characterizes the material's resistance to deformation. The greater the modulus, the less easy it is to deform, and the greater the stiffness of the material. Toughness, a physical concept, represents the ability of a material to absorb energy during plastic deformation and fracture. The better toughness, the less possibility of brittle fracture will be. Toughness can be found in materials science and metallurgy. Toughness refers to the resistance of a material to fracture when subjected to forces that deform it. It is defined as the ratio of energy absorbed by a material to its volume before fracture. When the content of silver nanoparticles reaches 60%, the mechanical properties of silver nanocomposites are the largest. The elastic modulus and toughness of silver nanocomposites are 32.8 GPa and 1.4 MJ/m^3, which are many times higher than those of polymer composites without doping. Moreover, the fracture surface of Ag/polymer is very irregular and trapezoidal (Pan et al. 2018).

In the application of silver/polymer nanocomposites, one of the most important properties is that they are durable and have good toughness. Therefore, the fatigue resistance of polymers will be tested before they are used. Fatigue strength refers to the maximum stress of materials under infinite alternating loads without damage, which is called fatigue strength or fatigue limit. In the fatigue test of silver/polymer nanocomposites, the fatigue strength of the polymer was observed by multiple strains. Whether the polymer could be reduced to its original shape after strain, the more the cycle times, the weaker the reduction degree of the polymer. Recording the reduction times of polymer fracture can effectively characterize the fatigue strength of the composites. For example, in silver/mercapto-chitosan, the strength of the polymer decreased slightly. After 100 bending experiments, the fatigue resistance of the polymer was very high (Pan et al. 2018).

Different polymers have their unique mechanical properties. Stress-strain curves, Young's modulus, tensile strength and hardness are important parameters to characterize the mechanical properties of materials. Therefore, by analyzing these parameters, we can explore how silver nanoparticles affect the mechanical properties of polymer and judge the strength of the mechanical properties of silver/polymer composites.

6 Conclusion

Various commonly used characterization methods and recent progress towards silver/polymer composites include SEM, TEM, EDX, XRD, XPS, IR, UV-vis, TGA, DTA, DMA and characterization of mechanical properties, through which the morphology, microstructure, elemental composition, mechanical properties and thermal properties of have been explained and analyzed in this chapter.

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Applications of Polymer Silver Nanocomposites

Noel Babu and Nikhila Babu

Abstract The antibacterial property and high conductivity that can be provided by silver nanoparticles have generated great interest among researchers to use them in solving problems in real life and to improve the current state of its use. Polymers can provide an easier and affordable platform to keep silver nanoparticles so that it can give a longer life span when put into use. In addition, polymer nanocomposites often offer the possibility of achieving multifunctional features from it. Even though there has been numerous studies with polymer silver nanocomposites its findings have not been put into useful applications primarily because of lack of complete understanding of the mechanisms involved with them. Silver nanomaterials have huge potential for changing the face of medical and industrial use if utilized properly. In order to achieve this more research is needed to understand its mechanism, compatibility, toxicity, process ability, degradation etc. This chapter deals with applications of silver nanocomposites and the need for further research into composites containing silver nanomaterials.

Keywords Polymer silver nanocomposites · Antibacterial coatings · Sensors · Textiles · Membranes

1 Introduction

Silver nanoparticles have attracted the interest of researchers for long time with much progress being achieved over the past decades. The most sought property still remains is their antibacterial activity that makes it suitable for various biomedical applications which include treating wounds, coating of medical instruments, packaging etc. Similar to other nanoparticles, silver nanoparticles also agglomerates to

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form clusters due to high surface energy. Agglomeration drops the properties, which can be obtained from them. In addition, nanoparticles can be lost from a determined deposition site due to abrasion, weak bonding, washing or long term use that can also hinder its optimum use. Uncontrolled release of any nanoparticles into environment is hazardous for both animal life and plant life as toxicity of nanoparticles is not yet fully understood. Silver nanoparticles can be cytotoxic to living cells. So if its release to the environment is unchecked, it will endanger the life cycle of microbes that are very essential for a balanced ecosystem. Use of polymers can help in controlling both agglomeration and its unchecked release while obtaining desired properties from the nanocomposites so formed. The use of polymer nanocomposites also offers another advantage which is the ease by which different nanoparticles can be combined together to give multifunctional features such as antibacterial activity, catalytic property etc. in one system. For these reasons, polymer silver nanocomposites are getting huge attention, which could be understandable from the number of research studies being conducted over the past years.

Many studies have been done to explore different properties of silver nanoparticles that may find numerous uses in day-to-day life such as wound dressing, treatment of burns or cuts, industrial coatings, food processing and packaging industries, clothing, water purifiers etc. Researchers have tried to incorporate silver nanoparticles into polymers in diverse approaches to fabricate nanocomposites. Some examples are dendrimer–silver nanocomposites, polymer-nanosilver composites, silver-titanium dioxide Nano powders, silver nanoparticles coated on polymer fabrics etc. The antibacterial activity of silver nanocomposites is the most studied feature, which have found its use in membrane technology, wound dressings, food packaging and storing among various others. The high conductivity of nanosilver has gathered research interest in applications involving electrical industry and the easier electron transfer capability in its nano form has wide catalytic applications for chemical industry. This chapter reviews various research advances using silver nanoparticle (AgNP) polymer composites for its potential use in medical and engineering applications.

2 Application of Polymer Silver Nanocomposites

2.1 Antibacterial Coatings

Over the course of time, humans have developed different kinds of coatings for wood, metals, buildings, utensils, fabric etc. In most cases, it is for protection of the coated object from external factors such as moisture and sunlight. Such coatings may also be coupled with an approach for lubrication as in protection of machines components against wear and tear. Thus, coatings have become an important aspect of any manufacturing by giving improved life span, saving wastage, adding aesthetics and recyclability. It is now well known that bacteria are not only useful to human beings for fermentation processes and agricultural activities but also in biosynthesis of nanoparticles (Zhang et al. 2020; Zhu et al. 2011; Ahmed et al. 2016), cancer therapeutics (Laliani et al. 2020; Felgner et al. 2016), water treatment (Li et al. 2019a, b), self-healing of concretes (Luo et al. 2015; Wang et al. 2014) and various others. On the other hand, bacteria can also pose a serious risk and health hazard to both terrestrial and aquatic life. Use of coatings against bacteria is an important research direction as bacteria keeps on evolving resulting in changed physiology and can even colonize on top of protective coatings used. It has been noticed that bacteria are able to strongly adhere to surfaces such as surgical instruments, utensils, food packages, medical implants often endangering lives and causing grave public health concerns (Manninen et al. 2016). The colonization of bacteria on surgical instruments and medical transplants can result in infections, which pose great risk to humans. In many cases, it can endanger the health of patients after surgeries. This situation is often referred to as multidrug resistant-hospital associated infection (MDR-HAI) (Alias et al. 2019).

Many studies are being done with silver nanoparticles in polymer matrix due to the enhanced antibacterial activity of silver arising from its higher surface area to volume ratio as compared to in bulk form. Antibacterial property of both silver nanoparticles and ions can be applied as a successful strategy to mitigate the harmful and unwanted growth of bacteria. Many researchers have proposed various mechanisms on how nanosilver can act as a biocide against bacteria but an agreement has not yet been arrived on this. One of the commonly proposed mechanism of antibacterial effect include release of silver ions so that it will cause generation of reactive oxygen species (ROS) inside the cell leading to rupture of the cell membrane (Liu et al. 2010). In other studies it is suggested that AgNPs can attach to the surface of bacterial cell thereby affecting its permeability and normal functions (Sharma et al. 2009). In addition, there are different opinions on which among the two, silver nanoparticles or silver ions, is more effective as an antibacterial agent. Another drawback is that only very few studies are available to understand the toxicity of AgNPs and Ag^+ ions. A direct comparison between the two, in order to have an understanding on their toxicity to cells, suffers limitations arising from controlling size, shape and agglomeration of particles in the polymer matrix (Kumar-krishnan et al. 2015). Most of the conclusions point towards effectiveness in release of Ag^+ ions rather than mere presence of AgNPs in itself and smaller the size of nanoparticles, better its release of Ag^+ ions (Sotiriou and Pratsinis 2010). The release of Ag^+ ions from silver nanoparticles is also dependent on its surface chemistry (Le Ouay and Stellacci 2015). One of the most sought out property and commercialized application from silver nanoparticle composites is its usefulness against bacteria. Polymer silver nanocomposites has been tested and studied against both gram negative and gram positive bacteria such as *E. coli*, *Staphylococcus aureus*, *Pseudomonas aeruginosa*, *Bacillus subtilis* and *Staphylococcus epidermidis* among others (Zhou et al. 2020; Lee et al. 2018; Maziya et al. 2020; Zarnegar et al. 2019).

It is known that silver nanoparticles, as such, in higher concentrations are harmful to both terrestrial as well as aquatic life as its accumulation and uptake inside cells may prove to be cytotoxic. In addition, uncontrolled release of nanoparticles into environment will also have an adverse impact on food chain as every species is interdependent for its survival on another. Polymer nanocomposites offers a possible solution to such concerns by providing better adhesion to substrates, acting as a reservoir and controlling the release of silver ions. Kuzminova et al. (2016) investigated the release of silver ion and antibacterial performance of Ag/plasma polymerized hexamethyldisiloxane (HMDSO) and Ag/SiO_x nanocomposites fabricated using a gas aggregation source (GAS). Inductively coupled plasma mass spectrometry can be used to study the release of silver ions and its antibacterial property can be tested against gram negative or gram-positive bacteria in laboratories. After investigating the release of Ag^+ ions against various parameters such as amount of AgNPs, role of polymer matrix and number of layers of nanoparticles, their study concluded that it is possible to achieve a controlled leaching or a sudden burst of nanoparticles depending on the design of nanoparticles. Also the antibacterial test proved the efficacy of AgNPs against *E. coli* with silver ions release as is demonstrated in other studies (Adibelli et al. 2020) compared to coatings without AgNPs. In many other studies, use of AgNPs along with other nanoparticles such as Fe_3O_4, MnO_2 have shown promising results against bacterial growth, colonization and formation of biofilms which can cause food spoilage and medical device related infections (Tri et al. 2019). Ngo et al. (2019) and Tri et al. (2019) have proposed that the increased antibacterial activity by AgNP—Fe_3O_4 nano hybrids are due to (i) electron transfer from AgNPs to Fe_3O_4 nanoparticle can result in faster Ag^+ release (ii) Fe^{3+} ions can accelerate ionization of Ag nanoparticles (iii) high catalytic activity of AgNPs which is helped by the good dispersion and aggregation stability provided by Fe_3O_4 carrier and (iv) large surface area between the hybrid nanoparticles and bacterial cell membrane. In developing hybrid nanoparticles as bactericides one must make sure that it will function as expected in the real environment as laboratory studies. For example, to understand the ionization behaviour of free AgNPs, several studies have been done in milli-q and complex biological environment simulating human body. Such studies indicate that the ionization mechanism of AgNPs tend be lower in the presence of Cl^- or PO_4^{3-} because of formation of silver complexes and formation of silver—thiol complexes can neutralize the antimicrobial activity (Liu et al. 2010, Liau et al. 1997). In order to address such concerns, various new strategies are being explored such as making use of formation of nano-galvanic couples within the coatings (Manninen et al. 2016), doping of AgNPs with other inorganic materials such as TiO_2 (Li et al. 2018), Fe_2O_3 and MnO_2 nanoparticles as previously mentioned. For coating medical implants and instruments, a sustainable flux of ions should be produced to ward off bacterial infection. This also put forward challenges such as selection of polymer matrix, stabilization of nanoparticles, incorporation method and mobility of ions. When planning to use or produce antibacterial coatings from polymer nanocomposites one has to keep these fundamental aspects in mind and design appropriately to meet the objective.

2.2 Sensors

Metallic silver nanoparticles have attracted research interest in applications such as chemical and biological sensors owing to their high surface plasmonic response to change in chemical or physical environment. Many studies have reported the use of polymeric silver nanocomposites in sensing applications such as detection of chemicals, gas, pressure, strain, heavy metals, humidity etc. Sangamithirai et al. (2017) reported a poly(oanisidine)-silver nanocomposite which can be used as a sensing electrode for detection of NADH (β-nicotinamide adenine dinucleotide) and dopamine (DA) which are essential chemicals in human metabolism. It was found that the prepared electrochemical sensor could sense NADH and DA with a low detection limit of 0.006 μM and 0.052 μM respectively. They have attributed the good response to increased surface area and good electron conductivity of AgNPs present in the electrode. It is also noteworthy to understand that agglomeration of nanoparticles and increment in polymer layers over nanoparticles will decrease the charge transfer ability of the electrode in general. Liu et al. (2011) developed a theophylline sensor by molecular imprinting technique using AgNPs, which demonstrated good selectivity and was able to detect the target molecule in concentration as low as 10^{-6} M. Molecular imprinted polymers can act as synthetic receptors, which can mimic enzyme or antibody receptors in function. The target recognition cavities generated through molecular imprinting technique are capable of selectively binding a target molecule, which then can be monitored and detected using spectroscopic techniques. The theophylline molecules when got bind to the recognition cavities were absorbed on the surface of AgNPs, which were then analysed by surface enhanced Raman spectroscopy. Many studies have been done with AgNPs incorporated along with graphene and its derivatives or carbon nanotubes in polymer matrix to use them as sensing electrodes. In this direction, Guo et al. (2017) used silver nanoparticles, carbon dots and reduced graphene oxide to develop a ternary dendritic nanocomposite which was electrodeposited on a glass carbon electrode to be used as the working electrode for sensing doxorubicin (DOX). The obtained results showed high sensitivity, selectivity and reliability in detection of DOX in real biological samples with good recovery rate. Pathak et al. (2018) also successfully developed a reduced graphene oxide/silver nanocube hybrid nanocomposite using molecular imprinting technique on the surface of a carbon electrode to detect temozolomide, an anticancerous drug, which in higher doses can cause serious health issues. In their study it was found that silver nanocubes gave a high surface to volume ratio and greater electron kinetics, which improves the sensitivity. Another interest of silver nanoparticles is to use them in making gas sensors. Usually AgNPs are used in combination with other nanomaterials and to enhance the detection and sensitivity towards the analyte. Raj et al. (2015) developed a AGNPs/PVP/PVA hybrid coated on a tapered plastic optical fiber to detect Ammonia gas. They used PVP as a reducing and capping agent for the nanoparticles and PVA as the matrix. The hybrid formed a reusable sensing film over the fibre core of the tapered optical fibre and the gas detection studies were conducted for emissions of ammonia. The gas sensing was attributed to change in refractive index due to interaction between ammonia gas and the hybrid and change in the evanescent wave absorption due to localized surface plasmon resonance (LSPR) of the silver nanoparticles. Adsorption of ammonia molecules during the operation is dependent on the amount of AgNPs and more the molecules on the surface implies an increase in refractive index of the medium. As the light pass through the fibre, it interacts with modified cladding resulting loss intensity of output light. AgNPs/PVP/PVA hybrid with 6.6% of Ag showed a sensitivity of 0.88 counts/ppm. This implies that a low amount of nanosilver can help in enhancing the detection of analyte. Nitrogen dioxide (NO_2) is another gas which has attracted great interest as it hazardous even at very low concentrations. Karmakar et al. (2017) studied about NO_2 sensing properties of nanocomposite films made of silver–polypyrrole (Ag–Ppy) doped with p-toluenesulfonicacid at room temperature. The film produced showed a good response of 68% at 100 ppm of NO_2 and it gave a 21% response at a lower concentration of 5 ppm. This response was attributed to both p-toluenesulfonic acid given the porous structure generated from doping and charge transfer due to ohmic contact between Ag–Ppy so that the change in resistance can be easily detected. It is not necessary that silver nanoparticles alone be used as the main sensing component in polymer composites. It can be used for serving other functions along with other main sensing components. Many studies have tried this approach successfully. In a study done by Chen et al. (2015) it was suggested that supramolecular assembled materials can give out multifunctional properties either from host, for example graphene, or any guest (organic molecules, nanoparticles etc.) which is chemically conjugated with the host or dispersed separately in a polymer composite. Using this approach they fabricated a sensor using reduced graphene oxide, silver nanoparticles and naphthalene-1-sulphonic acid (Ag–NA–rGO). AgNPs were attached to rGO through electrostatic forces and NA through π-π stacking. The silver nanoparticles were incorporated in order to increase the NO_2 adsorption. By separating different layers of rGO, the chance and space for gas adsorption can be increased. The gas adsorption of Ag–NA–rGO system was compared with rGO and NA–rGO and was found to be more efficient and sensitive than the latter with 2.8 times greater response to NO_2 at 10 ppm levels. Cannilla et al. (2014) fabricated a resistive sensor to detect ammonia using AgNPs in a poly-methacrylic acid (PMA) matrix loaded with MWCNT capable of operating within room temperature to 50 °C. Ammonia find wide applications in chemical industries but if left unchecked can be very harmful as it is corrosive, explosive and harmful to internal organs. In their study it was concluded that addition of silver nanoparticles could improve the sensing capability of carbon nanotubes towards NH_3. In addition, as amount of AgNPs in PMA increased, so did Ag^+ ions and these ions have immensely contributed in sensing mechanism by forming $Ag(NH_3)_2^+$ complex. In another study conducted by Ragachev et al. (2015), polyaniline—based conductive coatings were studied for ammonia gas sensing applications. It was found that the incorporation of AgNPs enhanced stability, sensitivity and selectivity of the nanocomposite to ammonia gas. The sensing mechanism was mainly dependent on the conductance chance arising from charge transfer between ammonia gas adsorbed and the sensing components. The silver nanoparticles were helpful in transport of charge carriers and also modulated the electrical resistance around the interfacial layer. Using impedance spectroscopy the coating demonstrated a response up to 10 ppm concentration of ammonia gas. Kariuki et al. (2016) fabricated a sensor by spin—coating AgNPs in a poly(amic) acid (PAA) nanocomposite film on a glass carbon electrode to detect nitrobenzene. At a constant scan rate of 100 mV/s it was observed that the current at modified PAA–AgNPs/GC electrode increased with concentration of nitrobenzene from 50 to 300 μM. The developed sensor also exhibited a correlation coefficient of 0.9735, sensitivity of 7.88 μA/μM and low limit of detection (LOD) of 1.68 μM. From above studies, it can be concluded that AgNPs modified electrodes give greater surface area and better electrochemical properties which can be advantageous in detecting gases.

In sensor applications polymer silver nanocomposites have found other uses like in sensing pressure and strain. Measuring pressure using sensors is gaining interest as it has become crucial to precisely measure its change in robots, prosthetic devices, space research etc. You et al. (2016) developed a stretchable piezocapacitive pressure sensor having a single layer of silver nanowire based elastomeric electrode, which could give reproducible results even with a deformation up to 35%. The silver nanowire was deposited on a poly-(dimethylsiloxane) (PDMS) substrate using a stretchable and transparent polyurethane urea adhesive forming a AgNWs/PUU/PDMS pressure-sensitive capacitor. The sensing mechanism involved detection of change in capacitance when there is a mechanical deformation. These characteristics could help piezocapacitive sensors to be used in touch sensors and wearable pressure sensitive fabrics detecting even weak interactions. In most cases, a dielectric polymeric material is placed between two electrodes. A capacitance is formed between the electrodes which changes as distance between them is decreased due to an application of pressure. This rise in capacitance can be used to detect pressure change. In developing flexible pressure sensitive polymer nanocomposte sensors, the main difficulties arise are from poor adhesion between polymer and nano fillers and individual flexibility of the components used. One important aspect of any such sensors is the reproducibility of testing parameters. The capacitance which changed on application of pressure should return to the initial value on disengaging the load and the sensor should give good measurements even after substantial stretching. In stretchable sensors, silver nanowires have thus gained attention. In many cases they are incorporated into the nanocomposite along with other nanoparticles to aid and boost the sensing ability. Aziz et al. (2019) developed a stretchable strain sensor using one dimensional silver nanowires and three-dimensional zinc stannite nanocubes, which gave a stable response when the film got strained from 0 to 100% with no visible change in structure and morphology. The main sensing component in the film was $ZnSnO_3$ nanocubes, which make use of piezoelectric property and silver nanowires merely acted as a conducting filler which reduces the total internal resistance of the composite by increasing number of conduction paths.

Interestingly, humidity sensors are gathering research importance along with industrial and technological advancement. Electronics industries, pharmaceutical and food processing factories, warehouses clean labs etc. need precise control of temperature and humidity for their proper functioning. Currently humidity detection uses properties such as optical, capacitive, piezoresistivity etc. of certain materials. Power et al. (2010) developed a simple humidity sensor using a polyvinyl alcohol (PVA) silver nanocomposite. The prepared nanocomposite was coated on an interdigital electrode array. When a potential of 1 V was applied, a current was developed which was found to be directly proportional to the humidity levels from 10 to 60% RH. Even though the precise mechanism was not clear in their study, it was believed that exposure to water vapour stimulated a form of ionic migration which occurred along one nanoparticle's double layer to the next along which the current flowed. Similarly Bhadra et al. (2019) fabricated a humidity sensor using silver nanoparticles and two polymers namely polyaniline and polyvinyl alcohol to form a nanocomposite, which also exhibited antimicrobial properties. The effect of humidity on the electrical resistance was measured and was used as the criteria for sensing mechanism. With increase in humidity, the resistance also increased. This phenomenon was explained by the fact that the molecules of water can donate electrons to the valence band of PANI, which could reduce the number of holes and increase the band gap. In addition, PVA being hydrophilic can absorb water molecules resulting in swelling which could increase the distance between the AgNPs. This implies that along with silver nanoparticles the matrix, which we use to fabricate the nanocomposite, also plays a vital role in sensor applications. In most cases we use a conducting polymer to make a nanocomposite sensor which help in charge transfer. However, there are also limitations when dealing with conducting polymers such as difficulty in processing, low flexibility, poor adhesion with the filler etc. These issues should be carefully addressed while fabricating sensors out of polymer silver nanocomposites. Another important use of sensors is in measuring temperature, which is undoubtedly gather huge interest in biomedical, food packaging, automotive and heavy industries among others. In this case, silver nanoparticles can act as a secondary filler which can help in enhancing the charge flow or act as an agent which can reduce the tendency of agglomeration in carbon based nanomaterials by separating various layers as previously mentioned. Neella et al. (2017) have used AgNPs with reduced graphene oxide to fabricate a piezoresistive thin film sensor to detect temperature. As the film got exposed to heat, the conductance of the film changed, there was a corresponding change in resistance which was noted down. The electrical resistance decreased linearly with increase of temperature. The sensor developed showed repeatability with negligible hysteresis and non-linearity proving to be highly sensitive.

Another possible use of sensors made of polymer silver nanoparticles is in the detection of leakage heavy metals and toxic ions in environment that can prove to be disastrous for both terrestrial and aquatic life. One of the most harmful and major concern in this area is water contamination. Detection of the presence of such harmful constituents need in-lab testing and reporting in most cases as there may be many contaminants present in a single analyte solution. Developing a contaminant detector with high reliability and sensitivity can give out fast results with minimum cost. Li et al. (2013) developed a sensor with fluorescent silver nanoclusters which were embedded with polymer nanoparticles to detect Cu^{2+} ions. Even though the sensing mechanism is still unclear, silver nanoclusters can be a good candidate in the detection of Cu^{2+} through a fluorescent turn-off reaction. In their study, a template was prepared with PMMA/PMMA-PMMA polymeric nanoparticles having a core shell structure, which later was used to generate silver nanoclusters. It is believed that fluorescent quenching happens when Cu^{2+} ion will react with free carboxylic group present in PMMA that acts as a stabilizer for silver nanoclusters. The selectivity of a sensor is of great importance when used to detect one specific metal cation from a solution and it should be immune from interference of other constituents. Teodoro et al. (2019) developed a ternary nanocomposite combining electrospun nanofibers, cellulose nanowhiskers and silver nanoparticles to be used as an impedimetric electronic tongue to detect heavy metal ions. E tongues can collect information from the sample which can be interpreted using statistical tools to retrieve the data needed for distinguishing the contaminants present. The silver nanoparticles performed the function of Increasing the conductivity of the sensor. They successfully conducted experiments to distinguish four heavy metal ions namely Cd^{2+}, Cu^{2+}, Ni^{2+} and Pb^{2+}. It is therefore possible to detect different heavy metal ions in solution once the sensing units and frequency are selected.

Two types of biosensors namely, enzymatic and non-enzymatic, have gathered research interest in determination of glucose level in human blood. Considering the long life time, good sensitivity, selectivity and low cost, non-enzymatic glucose biosensors based on composite materials has a wide research domain with huge potential. It is a well-known fact that abnormal glucose levels in blood can cause severe health concerns. Deshmukh et al. (2020a) developed a non-enzymatic glucose sensor using polyaniline/rGO nanocomposite which was functionalised with silver nanoparticles. Silver nanoparticles helped to increase the electron transfer rate during the electrochemical sensing operation and acted as an active sensing material for sensing the analyte. The sensor fabricated showed good sensitivity of 2.7664 $\mu A\ \mu M^{-1}\ cm^{-2}$, a range of detection of about 50–0.1 μM and had limit of detection of 0.79 μM. Similarly in another study Ponnaiah et al. (2018) reported a electrochemical sensor prepared using silver doped Fe_2O_3 in polyaniline matrix deposited on a glass electrode for selectively detecting uric acid in urine and human serum. The high catalytic performance of the modified electrode for uric acid oxidation was attributed due to the high surface area and conductivity of the nanocomposite. The ternary nanocomposite electrode exhibited high stability and reproducibility with limit of detection (LOD) of about 102 pM in the linear range of 0.001–0.900 μM for uric acid detection and had a sensitivity of 128.29 $\mu A\ mM^{-1}\ cm^{-2}$. Thus, polymer nanocomposites having silver nanoparticles offer many advantages and is a suitable candidate in medical applications as sensors. Also combining other nanomaterials such as TiO_2, graphene etc. along with AgNPs can provide synergetic properties, which can enhance the sensing ability of the sensors.

2.3 Textiles

The antibacterial property of silver nanoparticles is well known by now and many researchers have tried to study, understand and improve the performance of them in textiles. High performance clothing is a topic of interest in areas such as refineries, manufacturing industries, space exploration where people have to wear clothes for long hours under stressful work conditions. Even, for day to day uses, people usually prefer clothes made of cotton because of its comfort and breathability especially in summer season and places close to seas with high humidity. However, the sweat soaked cotton fabric can be an ideal place for the growth of bacteria and other microorganisms. This can lead to generation of foul odour, itching, allergies etc. A possible remedy for this problem is incorporation of antibacterial agents into the cotton fabric as an add-on feature. Polymer nanocomposites could be utilized in solving these issues by suitable selection of nanoparticles and polymer. Many researchers to make use of its antibacterial activity and to get multifunctional properties out of the modified textiles have tried silver nanoparticles in different shapes. Even when using silver nanoparticles, there are still issues such as loss of whiteness of cotton fabric, cytotoxicity to human cells, leaching of silver nanoparticles during washing and subsequent pollution of water bodies. It is usually observed that after nanosilver deposition, there is a colour change in the white fabric from grey to brown that is attributed to surface plasmon resonance of silver nanoparticles. This could be solved by UV light exposure, Radio frequency (RF) plasma treatment, chemical plating or using suitable polymer matrix. Silver nanoparticles can be added to clothing in two ways either by incorporating silver ions into the polymer or by coating the cotton fibres with silver. Bozaci et al. (2015) developed a Fumaric acid cross-linked carboxymethylcellulose hydrogel/silver nanocomposite which could impart antimicrobial property to the cotton fabrics. The modified cotton fabric was tested for antibacterial effect against gram-positive *Staphylococcus aureus* and gram-negative *Klebsiella pneumonia* bacteria and it was found that there was 99.9% reduction in growth. However it was noticed that with subsequent washing, there was drop in the antibacterial properties. The whiteness of the fabric was also affected slightly and it was dependent on the amount of silver concentration. Nischala et al. (2011) has reported in their study that using particle size well around 1–2 nm can help in retaining the whiteness of the cotton fabric which otherwise may change to colours like yellow, green, brown etc., based on surface plasmon resonance which is shape and size dependent on the NPs. This is because at such small size silver don't behave like a metal and there is no metallic band structure present to exhibit surface plasmon resonance. In another study Hebeish et al. (2013) fabricated a multifunctional antimicrobial and self-cleaning cotton textile using TiO_2 nanowire doped Ag-1% PVP nanocomposite. The self-cleaning ability of the nanocomposite was tested against methylene blue under exposure to sunlight. The photo degradation was explained by 2 reasons; (a) AgNPs deposited can act as electron-hole separation centres which results in formation of Schottky barrier at the interface of TiO_2 and AgNPs, which aids in charge separation and enhancing photocatalytic activity of TiO_2 (b) PVP helped in increasing the transport of charge carriers. The treated fabric also demonstrated good antibacterial property against both gram positive and gram-negative bacteria. Zhao et al. (2019) fabricated a wear resistant and conductive polyester fabric with water soluble polyurethane and AgNPs. They utilized a two-phase structure of polyurethane and sandwich micro-structure decoration (PU–Ag–PU) for the coating, which enhanced the wear resistance. The inner PU layer acted as a binder, the middle Ag layer as a conducting layer and the outer layer being a shield layer. In quest for multifunctional textiles Babu et al. (2012) modified cotton fabrics with Ppy–Ag nanocomposite to make it both antimicrobial and conductive. In most cases, the silver nanoparticles are formed by reduction of Ag^+ ions to Ag atoms, which are deposited on to the fabric. But in their study they have used a redox reaction mechanism in which Ag^+ ions get reduced while it also oxidise the pyrrole monomer. Naturally, the conductivity also increased with an increase in nanosilver concentration. Meanwhile it also demonstrated good antibacterial effect against both gram-negative and gram-positive bacteria. Shahid-ul-Islam et al. (2019) reported application of chitosan-silver nanoparticles synthesized through green synthesis onto linen fabric. Use of biomolecules from pineapple in the synthesis step helped in reducing metallic silver to nano form, which also helped in binding of NPs on to the linen. The treated fabric showed good antioxidant activity and efficient antibacterial property. They explained the improvement in antioxidant activity to synergistic effect from chitosan, silver ion and biomolecules. Use of green synthesis approach thus helps in reducing the carbon footprint and release of toxic reagents as residual waste after the chemical synthesis. Rehan et al. (2018) used chitosan, silver and clay to develop durable multi-functional properties out of cotton fabrics. Chitosan was reported to be a stabilizing agent for AgNPs that helps in reduction of Ag^+ to Ag^0 then forms silver nanoparticles. AgNps helped in providing antimicrobial property while clay improved the flame retardancy and thermal stability of the treated fabric. Thus by using AgNPs, it is possible to impart conductivity and antimicrobial property to textiles. Also by incorporating other engineered materials together with AgNPs and optimising the parameters, it is possible to impart several other properties giving a multifunctional aspect to textiles.

With regard to textiles that have been modified using nanoparticles, the main concern as mentioned before is the leaching-off of nanoparticles during laundering and subsequent loss of property, which it is supposed to deliver. The nanoparticles, which were washed out from the textile, could end up in water bodies resulting in contamination and might enter food chain. Therefore, an important aspect of modified textiles using nanoparticles should be introduced to prevent or minimize leaching of these materials even after many cycles of washing. Usually nanosilver is coated on to textiles by UV irradiation, sol-gel processing, in situ reduction of silver ions into metallic silver, grafting of particles, ultrasound vibration, gamma irradiation, layer by layer deposition method etc. (Rehan et al. 2018). However, the deposited silver nanoparticles maybe held on to the fabric by weak molecular or electrostatic interactions that might result in leaching out of nanoparticles with washing or long-term use. Therefore, it has become an important area of research to find out possible ways to keep silver nanoparticles without leaching off from the modified textiles. Liu et al. (2014) reported an antibacterial cotton fabric fabricated by utilizing polymer wrapped in AgNPs demonstrated excellent antibacterial and washing durability. The approach they utilized involved pomegranate-shaped silver NPAs wrapped by poly(2-aminoethyl methacrylate) graft chains by radiation induced reduction and simultaneous graft polymerization. The modified textile exhibited good antibacterial activities and an excellent laundering durability, where it was able to inactivate higher than 90% of both *E. coli* and *S. aureus* even after 250 commercial or domestic laundering cycles. We have to look into such solutions so that we can utilize the full potential of nanosilver treated textiles. Also we have to be equally careful of the possibility of leaching off of nanosilver from commercially textiles available (Lorenz et al. 2012) and also cytotoxicity of the these particles when in contact with human cells (Rehan et al. 2018).

2.4 Membranes

The increasing need for separation or filtration of liquids, gases, heavy metals at wastewater treatment plants, pharmaceutical and chemical industries etc. has inevitably led to rising innovation and research in membrane technology. At present various types of pressure driven filtration procedures have been evolved depending on the size of separable components such as microfiltration (0.1–10 μm), ultrafiltration (10–1000 Å), nanofiltration, reverse osmosis (average pore size of 0.0005 μm) (Flower et al. 2019). Membrane technology make use of a membrane that essentially acts as a filter for physically separating components. By using nanoparticles, it is possible to improve the performance and service life of such membranes. For example, one of the main problems that membranes face is biofouling. Biofouling occurs with time as microorganisms are attached on to the surface of the membrane forming a colony through multiplication eventually culminating into a biofilm. It remains as a serious challenge especially at wastewater treatment plants causing decline in flux and increasing operational cost. The difficulty with biofouling is that there are limitations in accurate detection and cleaning methods available often lead to membrane damage and subsequent replacement. Membrane surface modification is an available option that is cost effective in controlling biofouling compared to other strategies such as post cleaning and feed water pre-treatment. Usually polymer composite membranes are fabricated such that it tends to be more hydrophilic. The reason behind this approach is that since most bacteria are hydrophobic in nature and therefore they find hydrophobic surfaces as convenient places to grow and colonize. Therefore, hydrophilicity of the membrane can help in initial anti-adhesion and growth of microorganisms on membrane surface. However when considering longer service life, hydrophilicity of the membranes alone cannot prevent or counter the attachment of cells and biofilms can still form (Wu et al. 2017). By modifying, the hydrophilic membrane additionally with antimicrobial materials can help in inactivating the growth of microorganisms on the surface of membranes. Silver nanoparticles being an effective biocide can be a suitable candidate in this scenario for controlling biofouling of membranes. Zhang et al. (2013) fabricated a thin film composite (TFC) membrane for water treatment having a modification of silver—polyethylene glycol PEGylated dendrimer on its surface. Firstly, TFC membrane was made using a polymer solution comprising of polyethersulfone/N-methyl-2-pyrrolidone/polyethylene glycol/water in a specific formulation and after careful post treatments the membrane was conjugated with a 0 generation PAMAM dendrimer. This step was then followed by immersion of the membrane in poly(ethylene glycol) methyl ether acrylate and subsequently in $AgNO_3$ solution to get in situ reduction of Ag^+ ions to silver nanoparticles under sunlight. The modified membrane exhibited enhanced hydrophilicity and permeability without significantly affecting the transport properties. The silver—polyethylene glycol PEGylated dendrimer modified TFC membrane showed good anti-adhesion against both live and dead bacteria with attaching density reducing from 0.15 to 0.02%. The presence of silver nanoparticles in the membrane additionally helped the membrane against biofouling along with the hydrophilicity induced by PEGlation and PAMAM dendrimer is toxic in nature to bacteria cells. In another study, Zhang et al. (2014) extracted silver nanoparticles of an average size of 6 nm using a gram positive Lactobacillusfermentum bacterium and then incorporated into Polyethersulfone to get membranes suitable for ultrafiltraion process. The fabricated biogenic nanocomposite membrane exhibited excellent antifouling properties arising from smoother surface and enhanced hydrophilicity which hindered protein adsorption and formation of biofilm. In membrane nanocomposites, various combinations of nanomaterials have also been explored for preventing fouling and to improve its performance. Ko et al. (2018) reported fabrication of a membrane using silver–graphene oxide coated on polyvinylidene fluoride which effectively decreased the fouling. The application of GO and AgNPs using pressure filtration on PVDF membrane helped in developing a synergetic effect which increased the hydrophilicity, decreased the surface roughness and enhanced the antibacterial property. The leaching of Ag–GO and Ag^+ from the membrane were also studied and it was found that the release of Ag^+ ions are within safe limits. Interestingly Ag–GO was not found in the permeate water which was attributed to the polymer structure of PVDF membrane which prevented the particles from escaping the membrane. Cheviron et al. (2016) studied about the barrier properties of nanocomposite films fabricated using AgNPs, starch and montmorillonite. They reported that the in situ prepared silver nanoparticles played a significant role in improving the oxygen and water barrier properties of the film which was attributed to the crystalline structure of AgNPs and the cohesive interface that which it developed with the starch matrix. Qiu and He (2018) reported a combination of zwitterion with AgNPs for achieving antifouling property for polyethersulfone thin film forward osmosis membrane. They used 1,4-Bis(3-aminopropyl)-piperazine propane carboxylate (DAPPC), a zwitterionic monomer to modify the membrane which reportedly improved the hydrophilicity and transport properties. The in situ generated silver nanoparticles was alone the predominant factor that helped the membrane to inhibit growth of bacteria on the surface of the membrane which was proved by the fact that only 4% *E. coli* remained on the surface modified by a combination of zwitterion and AgNPs as compared to 58% with just zwitterionic surface. Thus by suitable selection of components it is possible to generate membrane surface which can prevent biofouling without losing transport properties. Polymeric silver nanocomposite membranes have also shown their efficacy in handling effluents. In this direction, Anwar and Arthanareeswaran (2019) reported a polyphenylsulfone membrane with silver nanoparticle coated hydroxyapatite as fillers capable of removing organic matter present in palm oil mill effluent using ultrafiltration and preventing its biofouling. It was found also that fillers played an important role in determining membrane characteristics and permeate flux. Another important and noteworthy application of membranes is in detection and separation of gases. The separation of a gas from a stream of gases depends on selectivity and permeation rate of the gas. Consider a case of a stream of gases involving H_2S, CO_2 and CH_4 for separation. It is possible to first separate H_2S and CO_2 from the mixture using membranes which can be later on individually separated using other methods (Bernardo et al. 2009). Industrial gases such as H_2S, NO_2 is dangerous, toxic and acidic. Nour et al. (2014) using catalytic polymeric nanosilver composite membrane was able to separate H_2S gas from a mixture of gases comprising of CO_2 and CH_4. AgNPs are capable of forming Ag_2S on reaction with H_2S. They utilized Ag/Ag_2S formed on the membrane as a catalyst to decompose H_2S into hydrogen and sulphur ions, which can be chemisorbed on the surface. The hydrogen ions could later form hydrogen gas and sulphur atoms. It is noteworthy to mention that the membrane was capable of efficiently separating H_2S from the stream without significantly affecting the permeation of other gases. In addition, silver is used together with other materials to form polymeric nanocomposite membranes that have shown efficacy in selectively separating metal ions from a mixture. Sun et al. (2017) fabricated an ion imprinted nanocomposite membrane (IINcM) comprising of silver/polydopamine/poly(vinylidene fluoride) which can selectively adsorb lithium ions. This is similar to molecular imprinting technology mentioned earlier by which it is possible to create certain recognition sites during the copolymerization process that could selectively bind the target molecule and thus help in separating the target molecule from a mixture. They synthesized 2-(allyloxy)methyl-12-crown-4 (2AM12C4) functional monomer which during the polymerization was successfully conjugated on to the Ag/PDA/PVDF membrane surface using covalent bonds. Ag nanoparticles on the membrane surface played an important role in improving the hydrophilicity, antifouling performance and permeability of the membrane. It is evident from the above cases that incorporation of AgNPs into membranes can give many possibilities in solving problems we face and further investigation should be directed such that maximum performance and utility is obtained.

2.5 Miscellaneous Applications

Besides the most pursued antimicrobial property from silver nanocomposites, there have been many investigations to combine AgNPs with other nanomaterials to utilize them in other possible applications such as catalytic reduction of molecules, solar energy conversion etc. Here some miscellaneous applications and promising outcomes from polymeric silver nanocomposites will be listed. Many studies in catalytic application of silver nanocomposites are directed towards reduction of nitrophenols and dyes. These are released into water bodies as industrial wastes that cause disastrous damage to both flora and fauna. In humans, exposure to these components can cause vomiting, breathing difficulties and nausea. Catalytic degradation offers simple, cost effective method compared to other options chemical oxidation, physical adsorption etc. Silver nanoparticles has excellent catalytic activity and can be used in the degradation of organic wastes. Since AgNPs have high surface energy, they tend to aggregate and lose their catalytic property. It is also known that AgNPs tend to leach out with continuous interaction with liquids which reduces its catalytic property and reusability. To address these issues, it is a better option to use polymers as a solid support to keep the catalytic property of nanoparticles for a longer time and prevent its leaching. Many studies have made an attempt to use nanocomposites having silver nanoparticles for catalytic reduction of nitrophenols. The reduction of p-nitrophenol to p-aminophenol is done with the help of a reducing agent $NaBH_4$. However, this process is very slow and requires the presence of a catalyst. Al-saida et al. (2020) synthesized a magnetic nanocomposite using titanium dioxide, Fe_3O_4, polyaniline and silver nanoparticles that showed dual catalytic applications in reduction of p-nitrophenol and methylene blue dye under light. The addition of Fe_3O_4 helped in separation of the photocatalyst from the solution after the reduction process while AgNPs helped in reducing the structural defects and thus maintaining a high electron-hole separation efficiency for the photogenerated charge pairs. Thus, it can be seen that by employing nanocomposites it is possible to find solution for various research problems such as enhancing the catalytic activity, retrieval of the catalyst and its reuse. Similarly Tomke and Rathod (2020) fabricated a nanocomposite using Fe_3O_4 and Chitosan in core shell formation and AgNPs conjugated using electrostatic force of attraction resulting in formation of a magnetic nanocatalyst. The nanocomposite was successful as a catalyst in converting 4-nitrophenol to 4-aminophenol with at least 15 cycles of reuse and 93% conversion within 30 min. Deshmukh et al. (2020b) prepared a ternary nanocomposite containing silver nanoparticle supported polyaniline conjugated with multiwalled carbon nanotubes for catalytic reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) using $NaBH_4$. It was noticed that the conversion reaction was completed within 240 s that would not have taken place without the catalyst even in excess amount of $NaBH_4$. There exist many other works in which silver nanoparticles form a constituent of nanocatalyst in the conversion of 4-nitrophenol to 4-aminophenol (Praus et al. 2013; Rarima and Unnikrishnan 2020). The catalytic reduction of H_2S gas to hydrogen gas and sulphur atoms using polymeric nanosilver composite membrane has already been mention in the previous section. Thus, polymer silver nanocomposites can be employed as a catalyst to fasten reactions with reusability and efficiency.

It is known that silver nanoparticles can be used to increase the electrical conductivity of polymer nanocomposites. By selecting suitable polymer matrix, it is possible to get nanocomposites with excellent electrical conductivity and electromagnetic (EMI) shielding. Zhang et al. (2018) fabricated a poly(lactic acid) silver nanocomposite with good electrical conductivity and EMI shielding. The poly (lactic acid) microfibers were coated with AgNPs and it was found that it is possible to tune the electrical conductivity by varying the amount of silver nanoparticles deposited. In addition, the nanocomposite exhibited superior EMI shielding which was attributed to the segregated chain structures present, which effectively was capable to reflect and absorb the EM waves. Besides aiding in improving EMI shielding, AgNPs has also proven effective in paving an electrostatic discharge tunnel to help alleviate accumulation of static charge on insulating polymers. Many studies have tried to incorporate conductive fillers into polymers to address this issue and to make antistatic nanocomposite. Y. Wang et al. (2013) fabricated a nanocomposite using Multiwalled carbon nanotubes (MWCNTs) and AgNPs as fillers and polyetherimide (PEI) as the matrix. MWCNTs were firstly grafted with poly(sodium acrylate) and then silver nanoparticles were deposited using reduction of Ag^+ ions. This modified filler was used to prepare the nanocomposite which exhibited excellent antistatic properties with 0.5 wt% filler loading after balancing moisture absorption from environment.

The antimicrobial property of polymer silver nanocomposites have wide implications in medical field especially in treating wounds. In wound dressing, two important aspects are the prevention of bacterial growth and quick healing of bruised area. Silver nanoparticles for its antibacterial property is a good choice to be an active component in wound dressings. It is always a better option to combine silver nanoparticles as antibacterial agent in scaffolds for tissue generation, hydrogels and fabrics for wound dressing. Thus, AgNPs has a huge role in nanomedicine. Palem et al. (2019) reported a composite hydrogel made using guar gum, acrylamidoglycolic acid and AgNPs demonstrated self-healing, antibacterial activity and flexibility. This was attributed to the porous structure generated that could be triggered by varying the pH/temperature and incorporation of AgNPs played a vital role in this. In another study, Montaser et al. (2016) fabricated a polymer nanocomposites for treating wounds using alginate polymer–silver nanocomposite padded nonwoven fabrics. The treated fabric showed the highest antibacterial activity than its next stage modification by using an additional anti-inflammatory drug. However, it was noticed that healing was quicker in presence of an anti-inflammatory drug. Girard et al. (2013) reported self-healing property for a polymer silver nanocomposite using polystyrene sulfonate, which is a polyelectrolyte. It was seen that silver ions could be slowly reduced to silver nanoparticles over a period of about 1 month through a slow process. These silver ions migrate and are deposited at sites where micro cracks are present in the nanocomposite thus helping in self-healing. This can also help in generating more concentration of silver nanoparticles at the surface of the nanocomposite and thus giving more antibacterial activity. Such nanocomposites can be used for coating medical and surgical instruments to prevent infections arising from microbes.

Coating using polymer nanocomposites are not only limited to medical instruments but also it has been explored in protection of steel for industries. El-Katori et al. (2019) used Ag/TiO_2 nanocomposite prepared using chitosan using sol-gel process. The nanocomposite was spin coated on the surface of the steel followed by heating to get an anti-corrosive porous film coating. In another study, El-faham et al. (2018) fabricated a silver—epoxy nanocomposite as anti-corrosive coating for steel. A hydrazide triazine derivative (mPEGTH) was used as a reducing and capping agent for the silver nanoparticles. The incorporation of the capping agent also increased the barrier performance, improved adhesion to steel, adhesion strength and impact resistance. A 3 wt% Ag/mPEGTH in epoxy also showed self-healing effect which was attributed to the capillary action which moves the fillers to the site of defect and where it gets cured on the surface. It is due to the presence of AgNPs, which accelerate the ring opening of epoxy through electron transfer and subsequent curing of epoxy together with Ag/mPEGTH, and amine groups from curing agent. Such strategies can be used to protection of steel from corrosion.

3 Conclusion

As the market is booming, the demand on industries, health care, transport will also increase. This asks for efficient and high performance materials to satisfy the needs. At present nanomaterials if carefully utilized can address many of these issues and provide answer to present and even future research problems. Though antibacterial activity remain the most sought out property from polymer silver nanocomposites, we can conclude from the above mentioned studies that it can utilized for other applications such as energy conversion, water purification and sensors etc. Silver nanocomposites can be a suitable candidate to addresses many problems in healthcare and industries as it can give dual properties that are its antibacterial activity and enhanced conductivity. It can also provide multifunctional properties together with other nanomaterials either as a host or being a guest in the polymer nanocomposite. It is our responsibility to find the suitable combinations to enhance the performance of the nanocomposite and to address the problems that we are facing. Even though there have been many successful lab results with nanocomposites, its commercial use have not been increased because of lack of full understanding. Many mechanisms remain unclear and there exist many studies, which shows polymer silver nanoparticle composites can make existing machines and instruments more efficient and boost its performance. This also demands for further studies to understand the mechanisms involved, toxicity and degradation of polymer nanocomposites when put to use.

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An Overview of Applications of Silver-Based Polymer Nano Composite as Biomaterials

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Abstract It is well known that polymer materials have been extensively investigated and developed for various biomedical applications due to their palpable advantages, including availability, good biocompatibility and biodegradability, ordinary synthesis and characterizations, viable structure modularization, and simple self-assemble process. Hybrid composition can gain many positive features from both mixing materials, which are able to meet the requirements in the applications. Encapsulation of metal nanoparticles in polymer matrices can serve many purposes: (1) improving stability of metal nanoparticles; (2) reducing toxicity; (3) easy to be multi-functionalized; and (4) improving collective properties. Silver nanoparticles (AgNPs) have attracted increasing attention in general and specially in biomaterial applications. AgNPs have prominent antimicrobial, anticancer, antiviral, antioxidant, anti-inflammatory and wound healing effects. The biosafety of AgNPs is a critical issue. Therefore, hybrid nanomaterials based on AgNPs and polymers are highly significant structures since they integrate synergistically the advantageous physical-chemical and biological properties of both AgNPs and polymeric components, providing excellent functionality to the final material. This chapter critically outlines AgNPs/polymer nanocomposites for various biomedical applications such as antibacterial, anticancer, tissue engineering, wound healing and antiviral applications.

Keywords AgNPs/polymer nanocomposites · Biomedical application · Antibacterial · Anticancer · Tissue engineering · Wound healing · Antiviral

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1 Antibacterial Properties of AgNPs/Polymer Nanocomposites

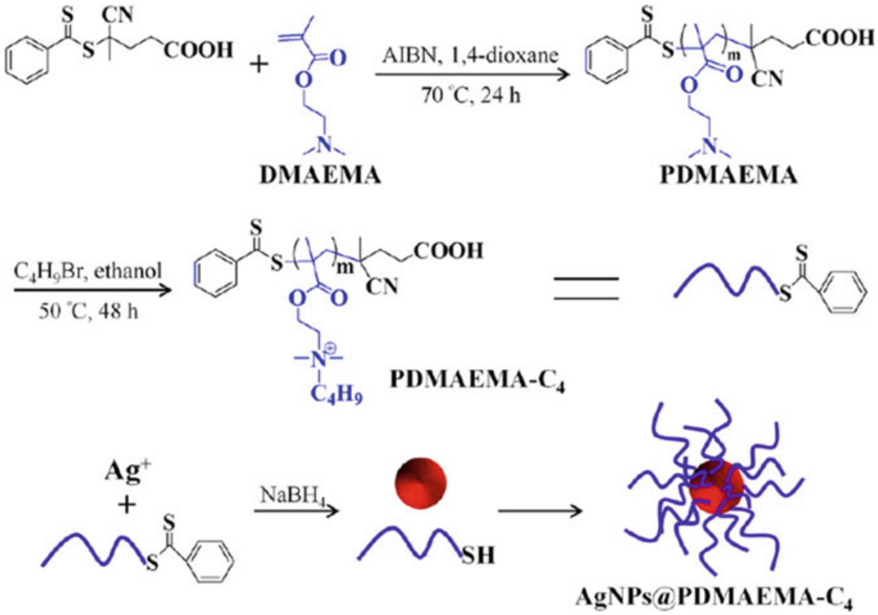
Bacterial infection, the local or systemic inflammatory reaction caused by pathogenic bacteria, is one of the most common diseases in the clinic. Since the birth of mankind, the human health and longevity have been severely affected by harmful bacterium. In history, large-scale infectious diseases such as malaria, yellow fever, and viral hepatitis had become commonplace. In recent years, the industries has developed rapidly, and the population has increased continuously, so the environmental pollution is increasing. The deterioration of environment is conducive to the proliferation of various germs and bacteria. As a result, the incidence and infection rate of bacterium are gradually rising, and human health is threatened. Although antibacterial treatment has made a great progress in the past few decades, according to the International Health Organization, bacterial infection is still the second most common cause of death in the world. In order to protect human health, make the living and working environment more comfortable, and improve people's quality of life, the development of new antibacterial materials with high-efficiency, non-toxic side effects, excellent durability, and good economic returns is crucial.

Antibacterial materials are those functional materials that can inhibit the growth of harmful microorganisms or deactivate various microorganisms, such as fungi and bacteria. They can be classified into three categories: natural antibacterial materials, organic antibacterial materials, polymeric antibacterial materials and inorganic antibacterial materials. Natural antibacterial materials, which are extracted from natural plants and animals, are the earliest antibacterial agents. For example, chitosan extracted from the insect shell with the support of biotechnology has the advantages of non-toxicity, biodegradable and biocompatibility. Depending on the merits, natural antibacterial agents can be used as fertilizers to promote plant growth and improve immunity; or as medical materials to accelerate wound healing and hemostasis. However, natural antibacterial materials are difficult to achieve large-scale marketization due to their shortcomings, such as low antibacterial efficiency, durability and heat resistance. Organic antibacterial materials, also known as sythesized antibacterial materials, have many kinds and have been developed intensively. The organic antibacterial agent includes phenol ethers, biguanides, quaternary ammonium salts, organic halogens, phthalocyanines and so on. The mechanism of the organic antibacterial agents is the presence of positively charged group. The cell surface of bacterium possess negative charge, thus the organic antibacterial agents could attract on the surface of bacterium to kill the bacterium; or the positive charge group reacts with the sulfhydryl group to destroy the protein and the synthesis system of bacteria membranes, thereby killing bacteria. The organic antibacterial agents have the characteristics of fast sterilization speed, strong bactericidal performance and low price. However, the organic antibacterial materials have serious side effects, poor heat resistance and short antibacterial time. Importantly, excessive use of organic antibacterial materials can lead to bacterial resistance. Extensive and abusive use of organic antibacterial materials have caused rapidly increasing antibiotic resistance of bacteria, which makes the treatment of bacterial infection even more challenging. Polymeric antibacterial materials, usually synthesized cationic polymers, possess massive positive charges and membrane-disrupting ability toward negatively charged microbial surface phospholipids exhibit potent antibacterial effects. For example, polymers containing tertiary amino group displayed strong antibacterial activity against bacterial infection. The formed nanocomposites with a large number of positive charge improved their adsorption to bacterial membranes through electrostatic interaction. However, the antibacterial effects of synthesized cationic polymers is limited. Inorganic antibacterial materials including colored precious metals or heavy metals, such as silver, cadmium, gold, mercury, palladium etc., utilize the bactericidal or bacteriostatic ability of metal atoms or ions. The metal atoms or ions are usually supported on the submicrospheres with a large specific surface area by physical adsorption, layer assembly, chemical reduction, photochemical reduction, and so on. A large number of experimental results indicated that the bacteriostasis rate decreased as follow: $Ag^+ > Hg^{2+} > Cu^{2+} > Cd^{2+} > Au^{2+} \approx Co^{2+} \approx Ni^{2+} > Pb^{2+} > H^+ > Fe^{3+} \approx Al^{3+} \approx Zn^{2+} > Mn^{2+} > Ba^{2+}$. However, the toxicity of Hg^{2+}, Cd^{2+}, Pb^{2+} is extremely high, so Ag^+, Cu^{2+} and Zn^{2+} are widely used. Furthermore, Ag^+ has the strongest bactericidal ability. A long time ago, humans have begun to use the antibacterial properties of silver. For example, in ancient China, the aristocrats used silverwares. The first scientifically reports of Ag as an antibacterial application dates to 1881 when silver nitrate was applied as eye drops for the prevention of gonococcal ophthalmia neonatorum. Since then, the antibacterial property of Ag were widely investigated. Silver salts or bulk silver were extensively studied for antibacterial application.

Along with the development of nanotechnology, inorganic AgNPs have extensive applications in the antibacterial field because of its notable physical, chemical and biological properties. The surface-area-to-volume ratio of nanoparticle is greatly higher than its bulk materials due to the nanoscopic dimensions (10^6 times larger for 10 nm compared to 1 cm sized sphere particles). Accordingly, the chemical activity of the nanosized particle is increased. AgNPs possess remarkable antibacterial effects towards a wide spectrum of pathogens (Gram-negative bacteria, Gram-positive bacteria, fungi and even viruses). Furthermore, the pathogens will not cause any resistance to the AgNPs. Therefore, AgNPs are also being developed either as alternatives to antibiotics or in combination therapies to kill multidrug-resistant bacterium.

The antibacterial mechanisms of silver-based materials are complicated. The proposed mechanisms include: (1) sterilization by static adsorption. As mentioned earlier, the cell surface of bacterium are usually negatively charged. Due to the attraction of heterogeneous charges, Ag^+ can be indiscriminately adsorbed by various bacterium, the activity of the bacterium is restricted, the microenvironment of the bacteria is disordered, and the breathing is inhibited, eventually leading to "contact death" of the bacterium. (2) Ag^+ possesses high affinity to a range of biological macromolecules, particularly those with electron rich thiol (–SH) groups. Therefore, the cysteine residues of proteins are often targeted by Ag^+, which disrupts the disulfide bonds, resulting in the denaturation of the tertiary structures of proteins, and thus their functions. (3) Ag^+ can crosslinks the heterocyclic amines in DNA bases, and disrupts the transcription and replication of DNA. Then, the major biological processes including RNA, DNA, protein, and peptidoglycan syntheses are affected. (4) membrane disruption induced by Ag^+. Cell membrane is an important part of bacteria. Therefore, cell membrane damage and destruction would lead to the death of bacteria. Due to the small size and large specific surface area, AgNPs tend to aggregate, and then their antibacterial activity will decrease. Hence, novel methods have been investigated to reduce the aggregation and enhance the antibacterial activity of AgNPs. AgNPs have been incorporated into other materials to form nanocomposites, including graphene-AgNPs, carbon nanotube-AgNPs, polymer/AgNPs, and so on. Among them, polymer/AgNPs nanocomposites have drawn most attention due to their unique stability, biocompatibility, biodegradability and antibacterial property.

Some works about polymer/AgNPs nanocomposites have been reported for antibacterial application. For example, poly(DL-Lactide-co-Glycolide) (PLGA), poly (styrene-co-sodium 4-vinylbenzenesulfonate), poly(2-hydroxyethyl methacrylate) derivative, polydopamine and so on were combinated with AgNPs for antibacterial infection.) (Mei et al. 2014) reported the synthesis of poly(2-(dimethylamino)ethyl methacrylate (PDMAEMA)) by reversible addition–fragmentation chain transfer (RAFT) polymerization, then the tertiary amino groups were quaternized with alkyl



Scheme 1 Schematic representation of the synthesis of AgNPs@PDMAEMA-C_4. Reused with permission Mei et al. (2014)

bromide, the prepared cationic polymers PDMAEMA-C_n with thiol as terminal group were used to stabilize AgNPs (AgNPs@PDMAEMA-C_n) (Scheme 1). The synthesis, characterization, biocompatibility, antibacterial activity, and antibacterial mechanism of AgNPs@PDMAEMA-C_n were systematically investigated. It's well known that the alkyl tail of polymer had great influence on the antimicrobial and cytotoxic properties. A series of PDMAEMA-C_n with different alkyl chain were prepared firstly, 1-bromoethane (C_2), 1-bromobutane (C_4), 1-bromooctane (C_8), 1-bromododecane (C_{12}), and 1-bromohexadecane (C_{16}) were used to quaternized PDMAEMA, respectively. The minimum inhibitory concentration (MIC) assay showed that the antibacterial activity of PDMAEMA-C_2, PDMAEMA-C_4, and PDMAEMA-C_8 against *S. aureus* and *P. aeruginosa* was greater than PDMAEMA-C_{12} and PDMAEMA-C_{16}. However, the cytotoxicity of PDMAEMA-C_2 and PDMAEMA-C_4 against NIH3T3 cell were higher than other synthesized polymers. Therefore, the optimal polymer was PDMAEMA-C_4. The zone of inhibition experiments were conducted to approve the synergistic antibacterial effects between PDMAEMA-C_4 and AgNPs. As shown in Fig. 1, compared with PDMAEMA-C_4, AuNPs@PDMAEMA-C_4 and AgNPs, the diameters of the zones of inhibition of AgNPs@PDMAEMA-C_4 against *P.aeruginosa* and *S. aureus* were largest, which conformed the synergistic effects between PDMAEMA-C_4 and AgNPs. The LIVE/DEAD bacterial cell viability assay against *P. aeruginosa* and *S. aureus* were further progressed to prove the antibacterial activity of AgNPs@PDMAEMA-C_4. In Fig. 2, the live cells were marked as green, and the dead cells were marked as red. The untreated alive bacterial cells exhibited green fluorescence, After treatment with AgNPs@PDMAEMA-C_4 for 20 min, the obvious red fluorescence were both observed for Gram-negative and Gram-positive bacteria, suggesting that the AgNPs@PDMAEMA-C_4 nanocomposites can rapidly and

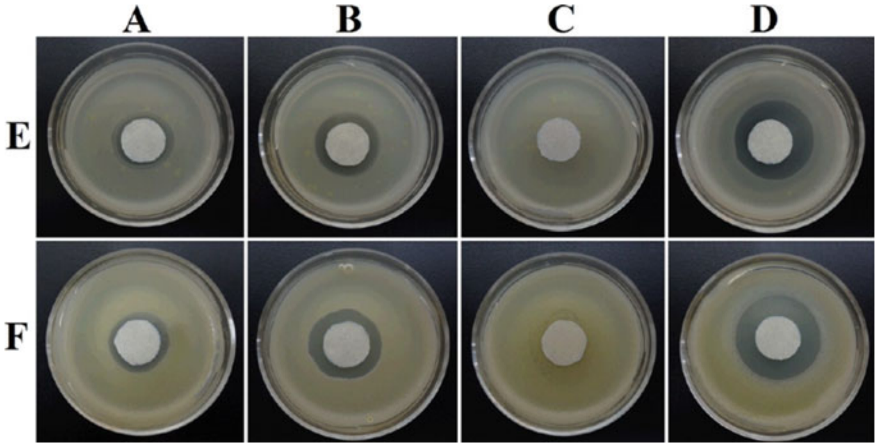


Fig. 1 Inhibition zones of **A** PDMAEMA-C_4, **B** AuNPs@PDMAEMA-C_4, **C** AgNPs, and **D** AgNPs@PDMAEMA-C_4 against **E** *P. aeruginosa* and **F** *S. aureus*. Reused with permission Mei et al. (2014)

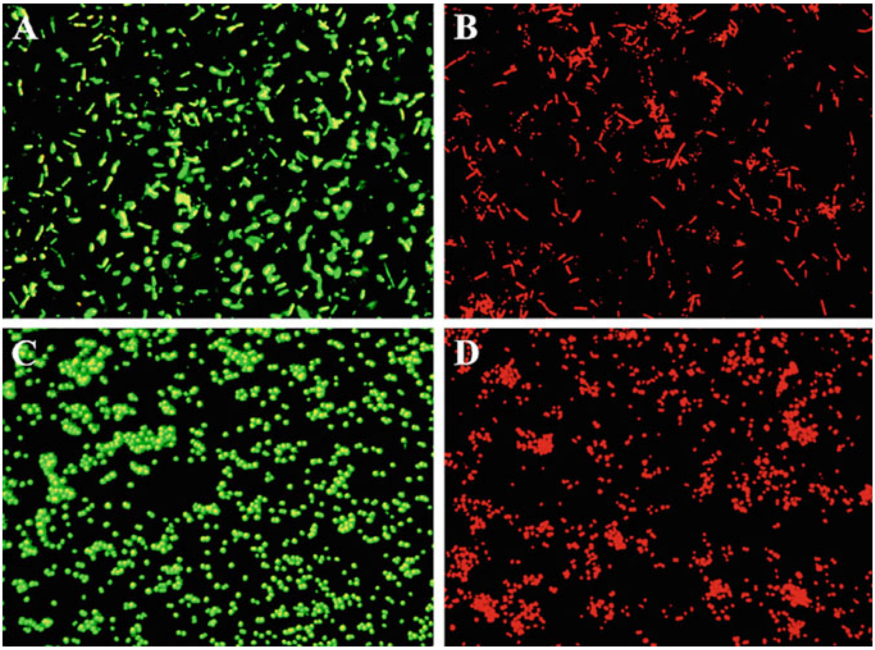


Fig. 2 Fluorescence micrograph of *P. aeruginosa* (**A** and **B**) and *S. aureus* (**C** and **D**) after being treated with AgNPs@PDMAEMA-C_4 for (**A** and **C**) 0 and (**B** and **D**) 20 min. Reused with permission Mei et al. (2014)

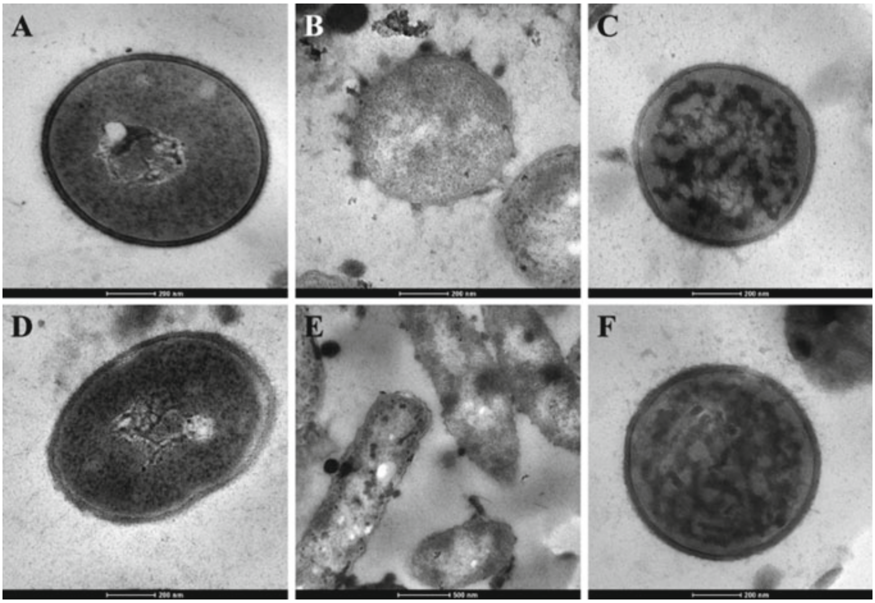


Fig. 3 TEM images of a thin section of *S. aureus* (**A**–**C**) and *P. aeruginosa* (**D**–**F**) before (**A** and **D**) and after (**B**, **C**, **E**, and **F**) cultured with AgNPs@PDMAEMA-C_4 for 30 min. Reused with permission Mei et al. (2014)

efficiently kill the bacterium. Furthermore, TEM were used to clarify the essential antibacterial mechanism of AgNPs@PDMAEMA-C_4 nanocomposites (Fig. 3). Untreated bacterium (*P. aeruginosa* and *S. aureus*) exhibited a smooth surface and distinct nucleoid structures (Fig. 3A, D). After cultured with AgNPs@PDMAEMA-C_4 for 30 min, the cell surface of bacterium became rough, and numerous blebs gererated with cytoplasmic release (Fig. 3B, E) The cationic AgNPs@PDMAEMA-C_4 penetrated into negatively charged bacterium cytomembranes via electrostatic interactions, which accelerates cell division, leading to the production of blebs. Moreover, floccules were observed within bacterium, resulting in the intracellular chaos. The antibacterial mechanism behind AgNPs@PDMAEMA-C_4 may be due to the positively external PDMAEMA-C_4 increase the permeability of the cytoplasmic bacterium membrane. Subsequently, after penetration, the nanocomposite strongly associate with the intracellular enzymes and proteins, resulting in the bacterium death.

Biocompatible AgNPs/polymer nanocomposites having antibacterial/antifouling activity and physical stability in water have gained much attention. AgNPs could be well-dispersed in polymer matrix. Moreover, the polymer and AgNPs may have the synergistic anti-inflammatory effect. Therefore, it is expect that these biocompatible AgNPs/polymer nanocomposites are promising for reducing cytotoxicity and achieving long-term antibacterial properties.

2 AgNPs/Polymer Nanocomposites for Wound Dressing

Skin is the main natural physiological barrier between the body and the external environment, and is the first line of defense against the external factors. It is the most visible and largest human organs. The surface area of adult skin is about 2 square meters, and the thickness is about 2.5 mm. Skin controls the energy of material exchange, such as mechanics, chemistry, thermodynamics, biology, electromagnetics, between inside and outside the body. It can also synthesize some important physiologically active substances, including vitamins, tyrosine, acetylcholine, serotonin, histamine, catecholamines and levodopa precursors. Meanwhile, Skin plays a vital role in the molecular biology and cell biology of the human immune system. The abundant biophysical network of skin can recognizes potential threats and harmful substances through tactile signals, thereby avoiding harmfulness.

Skin damage has also become a widespread medical problem, with approximately 300 million patients around the world every year. The skin is not only the body's largest organ, but also the outermost layer. As a barrier between the body and the outside world, the skin can maintain balance, prevent excessive fluid loss and prevent from the invasion of external microorganisms. In daily life, the skin is vulnerable to external or internal injuries, such as cuts, scratches, bites, burns, refractory bedsore, and chronic ulcers, etc. Although skin has the ability to self-regenerate after loss, this ability can be destroyed under certain conditions, such as large areas of skin loss, deep burns, chronic wounds, difficult-to-heal ulcers, and diabetic foot ulcers. Although the causes of these chronic, difficult-to-heal injuries are not the same, these injuries have some common characteristics. As mentioned above, the function of skin is to prevent the intrusion of bacteria on the skin surface and its surroundings. If this barrier is lost, it can provide microorganisms with a moist, warm and nutrient-rich living environment, so that microorganisms have a chance to colonize, grow and reproduce. Increased infection or cell exudation leads to excessive accumulation of inflammatory cells in the wound site. The inflammatory cells produce more ROS, which eventually damages the structural units of the extracellular matrix and damages the cell membrane, leading to premature cell senescence. ROS and pro-inflammatory cytokines can induce the production of serine proteases and matrix metaloproteinases (MMP), which degrade the extracellular matrix, affect cell proliferation and tissue remodeling in wound repair, and prolong wound healing time. Importantly, wound dressing attached to the wound can reduce the body's water loss, optimize cell regeneration, prevent pathogenic microorganism infection, and avoid wound destruction. Once the wound has been infected, it would recover very slowly, resulting in more pain to the patients. Importantly, improper treatment can cause the wound to enter the chronic phase, which increases the risk of wound biotic infections, thereby affecting health and the quality of life. The common antibacterial agents are antibiotics. However, antibiotics cannot kill bacteria instantaneously, and furthermore, the overuse of antibiotics may lead to the emergence of drug-resistant microorganisms, increased human resistances, and increased human mortality. More importantly, overuse may result in the emergence of "superbugs" that are resistant to most or all antibiotics, thereby threatening human health. The development of new antibacterial drugs far exceeds the speed of bacterial resistance occurs, so new wound dressings with antibacterial effects and no bacterial resistances have attracted widespread attention.

An ideal wound dressing should be nontoxic, nonadherent, nonallergenic to the skin, and able to absorb excess exudates to keep an ideal moist environment for wound. Further, an ideal would dressing should have good biocompatible and excellent antimicrobial properties to improve wound healing, as well as the self-cleaning ability to avoid contamination. Researchers have investigated and developed different kinds of wet dressings to achieve this goal. In recent years, natural, synthetic or hybrid polymers were intensively used for wound dressing. Natural polymers, such as silk fibroin, gelatin, collagen, chitosan, hyaluronate, etc., usually have good biocompatibility, biodegradability, and similar biological characteristics to the skin. These natural polymers can better interact with biomolecules in wound healing process to promote wound healing, so they are widely used in medical treatment. As mentioned above, synthetic polymers also possess palpable advantages, including viable structure modularization, varied synthetic procedures, and simple characterizations. Polymers can self-assemble into nanomaterials, or support nanomaterials as matrix for wound healing. Moreover, nanomaterials play an efficient role in wound dressing due to their large surface area and shape/size-dependent physicochemical characteristics. Compared with conventional antibiotics, nanomaterials possess negligible side effects and are less toxic. It can adsorb on the surface of the bacterial membrane by electrostatic interaction, which destroys the permeability of the membrane and thus affects the integrity of the membrane, thereby exerting an antibacterial effect. Nanomaterials can also be slowly released to improve the local microenvironment, which is beneficial to skin regeneration and repair. In particular, AgNPs have low cytotoxicity and broad-spectrum antibacterial effect, which can effectively kill Gram-negative bacteria and Gram-positive bacteria. Interestingly, AgNPs does not induce bacterial drug resistance. AgNPs have become one of the most commonly used antibacterial nanomaterials, and are widely used in medical fields such as intravenous catheters and surgical scalpels. AgNPs can also reduce the expression of inflammation-related cytokines, reduce the development of inflammation, and promote angiogenesis in wound granulation tissue. However, AgNPs have some drawbacks, such as uncontrolled release of silver ions, aggregation issue, and reduction of antibacterial effect during promoted adhesion of bacteria. Moreover, AgNPs for antibacterial effect often requires a higher concentration, and the antibacterial property is related to its particle size and stability. Therefore, the preparation of AgNPs with small particle size, good dispersion and good stability is

Table 1 A comparative study on various polymer/AgNPs nanocomposites for their potential usage in different types of wounds

Wound type	AgNPs-embedded Biopolymers	Outcomes
Thermal burn injury	Chitosan/AgNPs Nanocomposite	The nanocomposite exhibited excellent antibacterial effect against *S. aureus* and *P. aeruginosa*, the treatment of Wistar rats for 7 days confirmed accelerated wound healing through the promotion
Diabetic wound	Bamboo cellulose nanocrystals/AgNPs	Biocompatible wound dressing lead to wound healing within 18 days, and demonstrated increased expression of growth factors and collagen
Normal wound	Polysaccharides alginate, Hyaluronic acid and Chitlac-AgNPs	In vitro studies showed that the synthesized materials effectively stimulate wound healing and efficiently control bacterial growth
Infected wound	Alginate, Hyaluronic acid and AgNPs	The synthesized materials showed excellent antibacterial activity against both Gram-negative and Gram-positive bacteria compared to AgNPs alone
Chronic wound	Gelatin/Calcium alginate/AgNPs	The synthesized materials exhibited effective antibacterial activity; the scaffolds had potential for the treatment of chronic wounds
Acute and diabetic wound	Cellulose matrix/AgNPs	The nanocomposite acted as a good antibacterial agent and induced enhanced tissue repair in acute and diabetic wounded mice. Treatment with the nanocomposite aids to achieve $\sim$99% wound closure in vivo

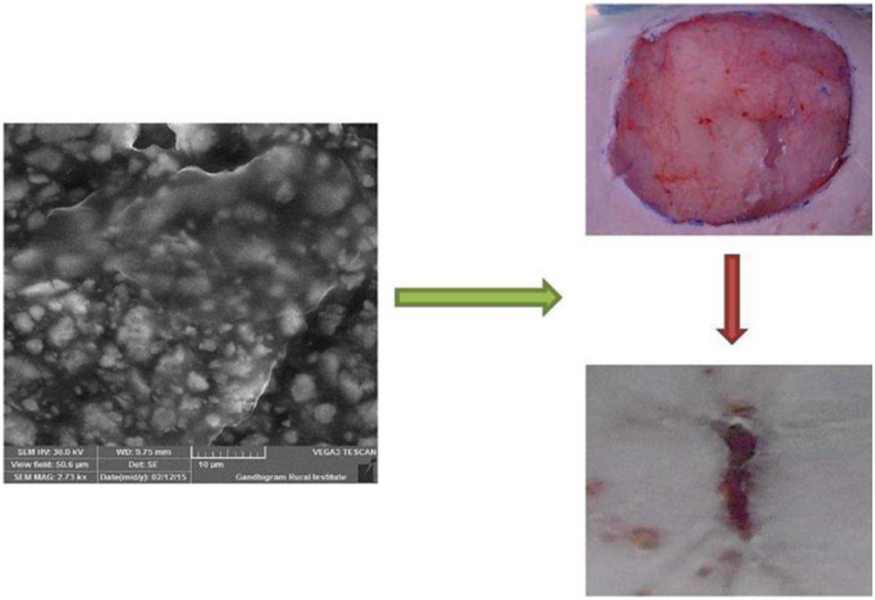
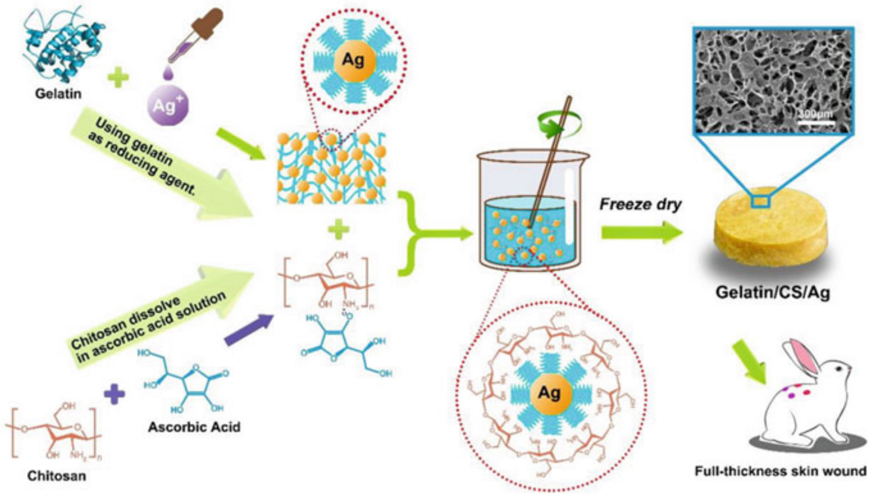


Fig. 4 PLGA/AgNPs nanocomposite for wound healing. Reused with permission Sankar et al. (2016)

a vital issue for wound dressing. In order to overcome the disadvantages of AgNPs, addition of a polymer matrix may be beneficial. Polymeric materials form a similar surface coating on different substrates, have the potential to inhibit aggregation of AgNPs and control the release of silver ions to decrease cytotoxicity, while also having the ability to resist bacteria adhesion. Accordingly, AgNPs/polymer nanocomposite for wound dressing have been extensively developed. Some works about natural, synthetic polymer and AgNPs have been reported for wound healing (Table 1). For example, HA and Na-alginate (SA) were crosslinked by Ca^{2+}, Zn^{2+}, or Cu^{2+}metal cations to prepare films for wound dressing. Furthermore, to enhance the antibacterial effects of HA/SA/Ca^{2+} film, sulfadiazine (SD) in combination with AgNPs as bioactive agents were introduced into the film. The experimental results demonstrated that the HA/SA/Ca^{2+}/SD/AgNPs bio-film had excellent antibacterial activity. In addition, the prepared biofilm was effective dressing for restoring the homeostasis skin tissue of albino rats. Sankar et al. (2016) described the formulation of Poly-D, L-lactide-co glycolide (PLGA) and AgNPs nanocomposite for wound healing (Fig. 4). The PLGA/AgNPs nanocomposite was prepared utilizing a modified solvent casting method. The biogenic synthesized AgNPs solution was added drop by drop in the PLGA solution with stirring at room temperature. After the evaporation of organic solvent, a nanocomposite film was formed. The prepared nanocomposite was carefully characterized by UV-visible spectroscopy, Fourier transform infrared spectroscopy (FTIR), Scanning electron microscopy (SEM), and Dynamic light scattering (DLS) measurement. SEM



Scheme 2 Preparation process and the principle of composite Gelatin/CS/Ag. Reused with permission Ye et al. (2019)

analysis notably showed PLGA/AgNPs nanocomposite was found to be spherical and irregular in shape, distributed in the polymer matrix. Furthermore, PLGA/AgNPs nanocomposite improves wound healing in the excision wound was confirmed by wound closure, protein profiling, histopathology, and matrix metalloproteinases 2 and 9 expression. The analysis results depicted that PLGA/AgNPs nanocomposite enhanced the wound healing activity by sustained release of AgNPs, up regulates protein expression, and inhibit pathogenic bacterial growth.

Gelatin is a natural polymer. Owing to its biodegradability, biocompatibility, and non-immunogenicity, gelatin is a preferred material for wound healing. Chitosan is another kind of functional polymer, which is obtained from the deacetylation of chitin. It has prominent beneficial characteristics, e.g., stability, flexibility, and film-forming ability. They have been extensively investigated for wound healing. (Ye et al. 2019) reported gelatin/chitosan/AgNPs sponge for antibacterial and wound healing application (Scheme 2). In this work, gelatin was applied as the reducing agent and stabilizer to prepare AgNPs in situ, which were mixed with chitosan and ascorbic acid solution, then tannic acid was used to cross-link the materials. After freeze-drying, a new gelatin/chitosan/AgNPs sponge was obtained. The SEM characterization indicated that gelatin/chitosan/AgNPs had a dense and interpenetrating pore structure with a pore size of about 100–250 μm. Importantly, the pore increased with AgNPs concentration increased, which is more conducive to liquid absorption. The existence of AgNPs was confirmed by UV visible spectrophotometry, XRD, and TEM. In particular, TEM results demonstrated that the morphology of AgNPs was sphere and uniform, the particle size was mainly in the range of 2–10 nm. This shape and size meet the requirements for efficient antibacterial performance. In general, wounds are infected with *S.aureus*. Figure 5

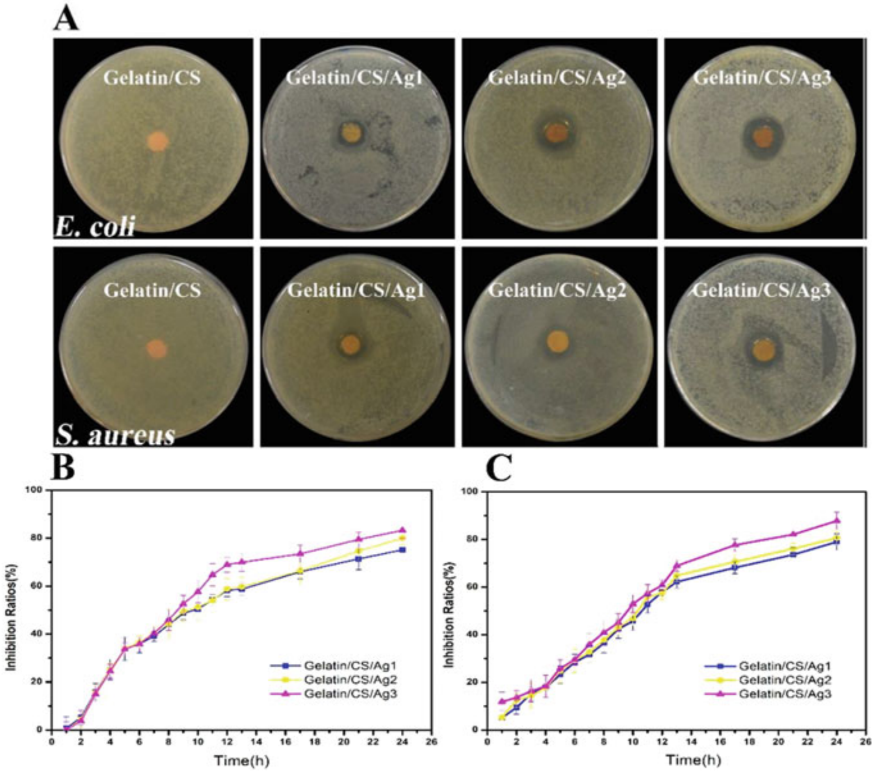


Fig. 5 Antibacterial analysis of the prepared materials using *E. coli* and *S. aureus* (**A**). The antibacterial kinetic curves of the prepared materials for the growth of *E. coli* (**B**) and *S. aureus* (**C**). All values are expressed as means ± SD for each group (n = 5). Reused with permission Ye et al. (2019)

showed the antibacterial effect of four samples, i.e., Gelatin/CS, Gelatin/CS/Ag1, Gelatin/CS/Ag2, and Gelatin/CS/Ag3, on *E. coli* and *S. aureus*. The addition of AgNPs significantly enhanced the antibacterial ability of the material, and the antibacterial capacity increased as the concentration of AgNPs increased. Then, in vitro cytotoxicity measurement was examined to evaluate the biocompatibility of materials. The results indicated that not all the materials were toxic after 24 h incubation with L929 cells. Moreover, after 48 or 72 incubation, the L929 cell viability of all four materials exceeded 100%, indicating that they promoted cell growth. As a wound dressing materials, wound healing text is of vital importance. New Zealand white rabbits were infected with *S. aureus* for 24 h after surgery Fig. 6. Wound growths were recorded on days 1, 5, 10, and 15 after infection. At the 10th day after treatment, Gelatin/CS/Ag2, Gelatin/CS, and control wound shrinkage rates were 90%, 60%, and 43%, respectively. Notably, Gelatin/CS/Ag2 wounds showed approximately complete coverage of new skin, forming a uniform

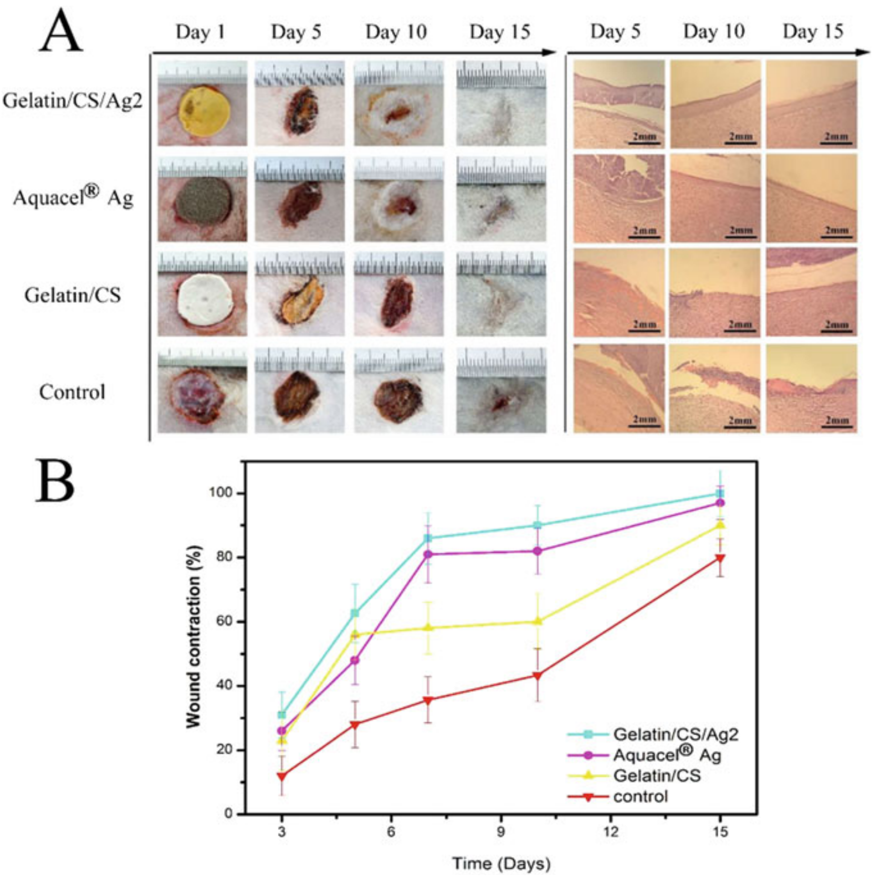


Fig. 6 Wound growth and tissue section of the prepared materials (**A**). Shrinkage of the wound area for the prepared materials group and Control group (**B**). All values are expressed as the mean ± SD for each group (n = 5). Reused with permission Ye et al. (2019)

and thick epithelial tissue. After 15 days treatment, the Gelatin/CS/Ag2 group was more even and the skin was covered with a uniform stratum corneum, which is an important indicator of skin maturation. All findings demonstrated that Gelatin/CS/Ag was an effective antibacterial wound dressing that promoted wound healing.

When biopolymers are coupled with AgNPs, they develop a novel platform and offer great opportunities for wound healing applications. Polymer/AgNPs nanocomposite is easy to apply to the wound site, the material and fabrication methodology is inexpensive, and ultimately it will satisfy the clinician expectation and complies with the patient needs.

3 AgNPs/Polymer Nanocomposites for Tissue Engineering

Langer and Vacanti proposed the definition of tissue engineering in the 1980s. Tissue engineering is a comprehensive discipline that combines engineering and many other natural sciences. It is dedicated to the development of biological materials for the purpose of repair and replacement, and the construction of human organs and their functional substitutes. The core of tissue engineering is to establish a three-dimensional structure composed of cells and biological materials, which is essentially different from the traditional two-dimensional structures (such as cell culture). Its greatest advantage is that it can form living tissue with vitality. Reconstructing the morphology, structure and function of the damaged tissue and achieving permanent replacement; repairing the large tissue defect after culturing in vitro with the least amount of tissue cells; and achieving perfect shape.

At present, there are roughly three kinds of tissue repair methods commonly used in clinical practice: autologous tissue transplantation, allogeneic tissue transplantation and application of artificial substitutes. These three methods have their own shortcomings, such as immune rejection and donor deficiency. The development of modern tissue engineering will fundamentally address the dysfunction or loss of treatment caused by tissue and organ defects. Therefore, the content of tissue engineering research is mainly concentrated on the three aspects of biomaterial scaffolds, seed cells, and three-dimensional construction of tissues and organs. Tissue engineering is a brand new concept put forward in the 1980s. It combines the basic principles, basic theories, basic techniques and basic methods of engineering and life sciences to construct a biologically active implant in vitro and implant it to repair tissue defects. Replace the function of the organ; or as an in vitro device, temporarily replace the organ function to achieve the purpose of improving the quality of life and prolonging life activities. Its scientific significance is not only to provide a new treatment method for relieving the suffering of patients, but also to propose a new idea of copying "tissue organization" and "organ". It marks the arrival of "human era of biotechnology", which is "a far-reaching medical revolution."

Tissue engineering scaffold material refers to a material that can bind to tissue living cells and can be implanted into different tissues of the organism, and according to the specific functions of the alternative tissue. In order to proliferate and differentiate seed cells, it is necessary to provide a cell scaffold composed of a biological material, and the scaffold material is equivalent to an artificial extracellular matrix. Tissue engineering scaffold materials include bone, cartilage, blood vessels, nerves, skin and artificial organs, such as liver, spleen, kidney, and bladder, etc. Various materials have their own unique requirements. For example, the bone tissue scaffold material must be conducive to cell adhesion, non-toxic, non- teratogenic, does not cause inflammatory reactions, provides a good microenvironment for cell growth, and can be safely used in humans. The artificial nerve is a specific three-dimensional structure of the nerve conduit, which can accommodate the regenerative axonal ingrowth. The mechanical guidance of the axial protrusion must provide the required three-dimensional space for the nerve recovery, to ensure the nerve tube has the appropriate strength, hardness and elasticity, so that the nerve has a regenerative passage; Tissue engineering vascular scaffold materials should have good material biocompatibility, degradability, good material-cell interface and certain spatial three-dimensional structure. In addition, there should be some compliance; the ideal artificial skin stent should meet both material and structural requirements. Those material requirements must include: (1) allows cells to adhere to the surface, promote cell proliferation, retain the function of differentiated cells; (2) degradable, materials and degradation products are not cytotoxic, will not cause inflammation; (3) have Good biocompatibility; (4) Wide range of sources, low prices, no risk of disease transmission. Structurally: (1) It should have to have high porosity to provide sufficient space for cell adhesion, regeneration of extracellular matrix and cell diffusion. Pore structure can allow cells to be distributed throughout the scaffold, thus promoting homogeneous tissue formation; 2) should have a three-dimensional scaffold structure to provide structural support and template for specific cells, guide tissue regeneration and control tissue structure.

With the improvement of living standards, people pay more and more attention to their own health. Tissue engineering can help us repair our own damage. Nobel metal nanoparticles have received extensive attentions from researchers due to their high physical and chemical properties. Scientists, particularly in the tissue engineering, have studied the role of silver nanoparticles in the life sciences. (Zulkifli et al. 2017) combined hydroxyethyl cellulose (HEC) and silver nanoparticles with freeze-drying technology as shown in Fig. 7. The authors applied it to inhibit bacterial cell growth in the skin. Since silver nanoparticles are relatively toxic, and tiny nanoparticle sizes can inhibit other cell growth through the stratum corneum of the skin, it is necessary to control the diameter, morphology and silver ratio of the nanoparticles. Therefore, they take some characterization of the nanoparticles.

The formation of silver nanoparticles can be determined by the color change of the solution, from colorless to bright yellow to dark brown. The pore size of the scaffold for skin tissue regeneration is 20–120 μm. The pore size of this synthesis is 50–150 μm, so it is suitable for tissue engineering applications. Non-uniform pore size may be formed during lyophilization, and these pore sizes may indicate the ability of the scaffold to have cell penetration and promote neovascularization. The degradation rate of the stent determines the length of wound healing. It can be seen from the Fig. 8 that HEC/Ag nanoparticles have a good degradation rate, thus making skin wound healing easier. The colorimetric (3-(4,5-dimethylthiazol-2-yl)-5-(3-carboxymethoxyphenyl)-2(4-sulfophenyl)-2H-tetrazolium) (MTS) assay experiments confirmed the relative viability of epidermal cell growth on HEC (Fig. 9). As the incubation time is extended, the relative viability of the cells is significantly improved. However, high concentrations of silver nanoparticles may also cause damage to cells. Therefore, it is necessary to further determine the optimal concentration ratio of HEC and silver nanoparticles.

Deng et al. (2017) got endowing 3D printed polyetheretherketone (PEEK) scaffolds that with superior antibacterial property and acceptable biocompability by mixtured PEEK scaffolds/polydopamine (PDA)/AgNPs, represented in (Scheme 3).

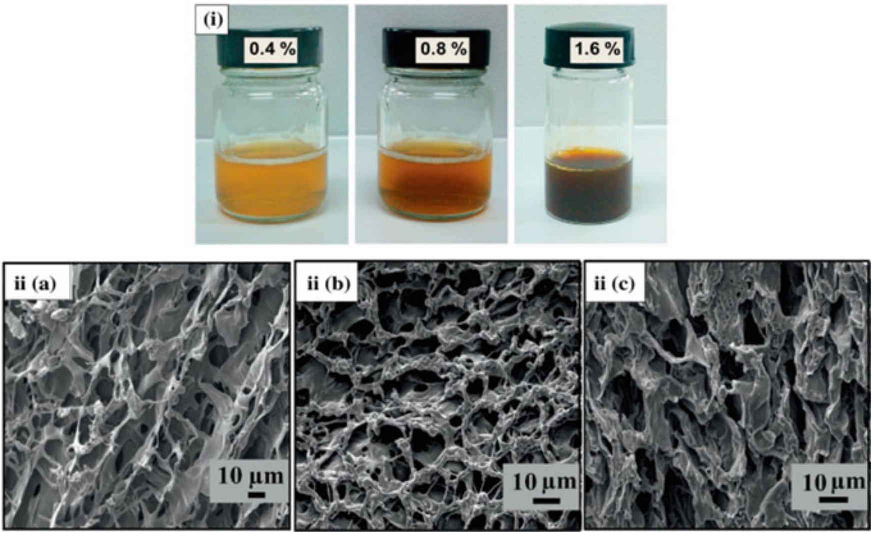


Fig. 7 **i** Photograph of the HEC/AgNPs solutions obtained at different concentrations of AgNO3 and **ii** SEM micrographs of the HEC/AgNPs scaffolds at different concentrations of $AgNO_3$ **a** 0.4%, **b** 0.8%, **c** 1.6% Reused with permission Zulkifli et al. (2017)

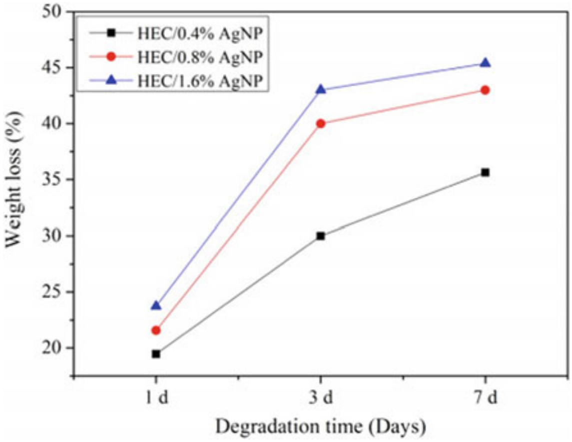


Fig. 8 Weight loss of degrading HEC/AgNPs scaffolds at different $AgNO_3$ concentrations Reused with permission Zulkifli et al. (2017)

As shown in Fig. 10, Ag-decorated 3D PEEK scaffolds displayed significant antibacterial effect towards Gram-negative and Gram-positive bacteria by take some characterization. First, sample's surface morphology and morphology were examined by a field emission scanning electron microscope. Furthermore, they have done the bacterial inhibition ring test to investigate the release of silver and inhibition of

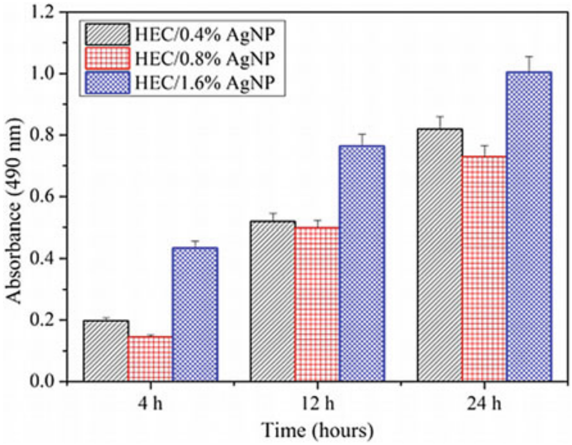


Fig. 9 Human fibroblast viability after 4, 12 and 24 h of incubation **a** 0.4%, **b** 0.8%, and **c** 1.6%. Reused with permission Zulkifli et al. (2017)

bacterial growth and thus evaluating the antibacterial capability. Finally, they tested anti-biofilm ability of the scaffolds in vitro. Figure 11 shows the amounts of adhered microorganism were markedly reduced in the presence of silver. According to SEM observation after an incubation for 7 days, there were almost no bacterial on the surface of 3D PEEK/Ag (1 mm) compared to those on 3D PEEK.

The authors concluded that the bone defects recover quickly, and the addition of silver nanoparticle is more effective. This experiment confirmed that the silver nanocomposites have good biocompatibility, nPLGA and nCS have been proved safe drug carriers, PLGA and CS have been found to have no obvious toxicity to periodontal ligament cells, and the concentration of silver nanoparticles controlled at 50 μg is considered as safe and non-toxic.

4 AgNPs/Polymer Nanocomposite for Anticancer Application

Within the past several decades, cancers have been one of the most serious diseases with high incidence and fatality rate. February 4 is marked as "World Cancer Day" to raise awareness of cancers and encourage the prevention, detection, and treatment of cancers. Cancers are also professionally expressed as malignant tumors and neoplasms, and the basic unit of cancer lesions is cancer cells. Normal human cells can undergo regular metabolism. After cell aging and death, new cell replaces it. This proliferation is restricted due to the limitation of cell divisions. However, the proliferation of cancer cells is infinite, resulting in a large consumption of nutrients in patients. Importantly, cancer cells release a large amount of various toxins, which

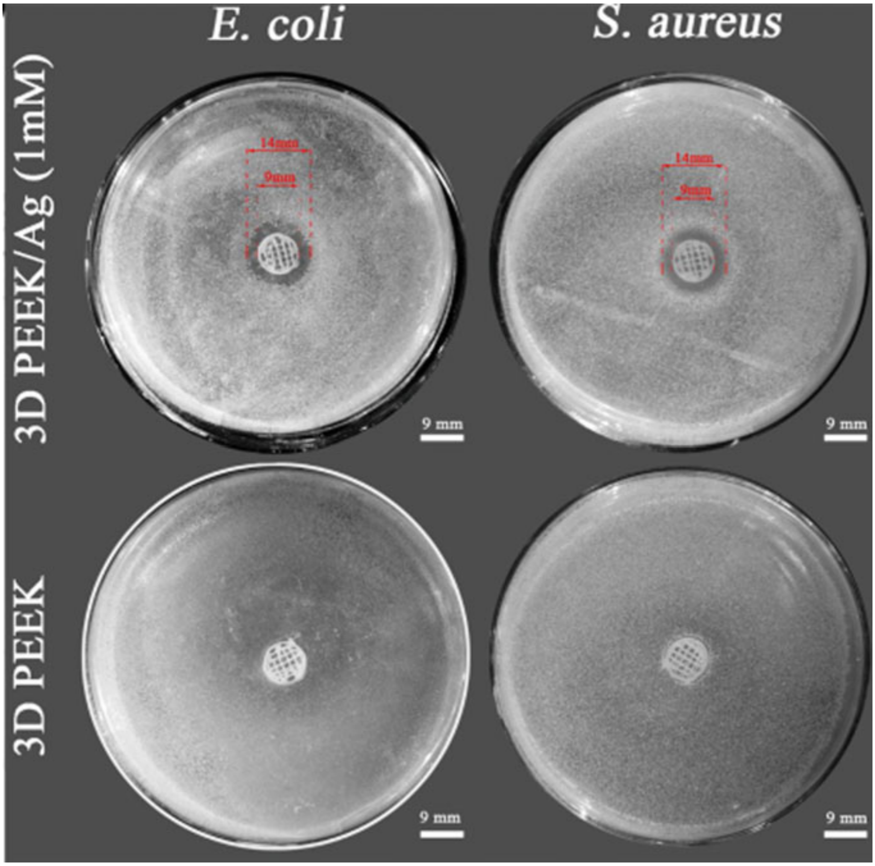
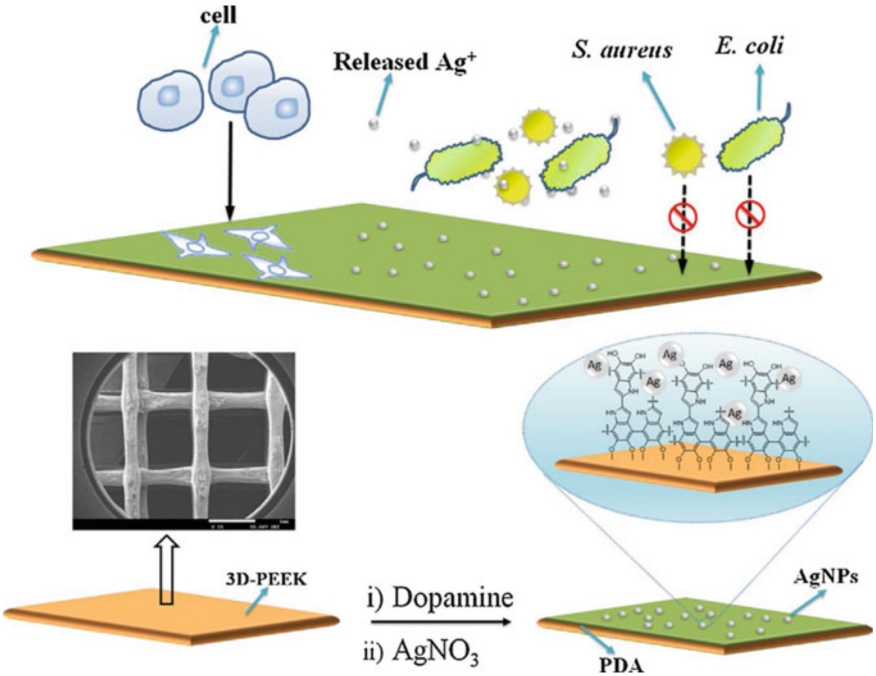


Fig. 10 Inhibition zones of the different samples against *E. coli* and *S. aureus*. Reused with permission Deng et al. (2017)

impair the function of healthy organs. It is worth noting that cancer cells can grow beyond the usual boundaries, attack the adjacent parts and spread to other organs, which is known as metastasis. Metastasis is one of main cause of cancer death. According to the World Health Organization's Global Cancer Report 2014, there were 14 million new cancer cases and 8.2 million cancer deaths in 2012. The main cancers causing death include lung cancer (1.59 million), liver cancer (745 thousand), and gastric cancer (723 thousand), colorectal cancer (694 thousand), breast cancer (521 thousand), esophageal cancer (400 thousand), etc. The report predicts that the number of new cancer cases in the world will reach 19 million by 2025, will increase to 22 million by 2030, and will increase to 24 million by 2035, which will increase 50% in 20 years. The data is terrible.

At present, the main methods for cancer treatment are surgery, radiation therapy, chemotherapy, biological therapy, and light therapy. Surgery is the most direct



Scheme 3 Schematic diagram of the preparation of 3D PEEK/Ag scaffold and its biological evaluation. Reused with permission Deng et al. (2017)

means of cancer treatment. However, the incomplete excision of the pathological tissue will result in the high risk of recurrence and metastasis. Radiation therapy usually uses alpha, beta, gamma, or X-rays with high energy to kill cancer cells, but normal cells are killed at the same time, and the side effects are more serious. Biotherapy is the use of specific biotechnology to stimulate the body's own anti-cancer cells and factors, and return to kill cancer cells. The toxicity of biotherapy is minimum, but the anticancer effect is unsatisfactory for patients with large tumor size. Light therapy, including photodynamic therapy and photothermal therapy, uses infrared or near infrared light to motivate photosensitizer for cancer treatment. The development of fiber optic technology offers more possibilities for light therapy. Light therapy is clinically and theoretically investigated. Chemotherapy is a way to kill cancer cells by using chemotherapeutic drugs. It is a systemic therapy and a widely used method in clinic.

Paul Ehrlich proposed chemotherapy. The origins can be traced back to the First World War. It was found that mustard gas could kill normal white blood cells; it was believed that mustard gas can also kill leukemia-derived leukocytes, and then chemotherapy begins. After a century, currently, there are more than 50 chemotherapeutic drugs, some of which are derived from natural plants such as paclitaxel, vincristine, vinblastine, elemene, etc., but most chemotherapeutic drugs

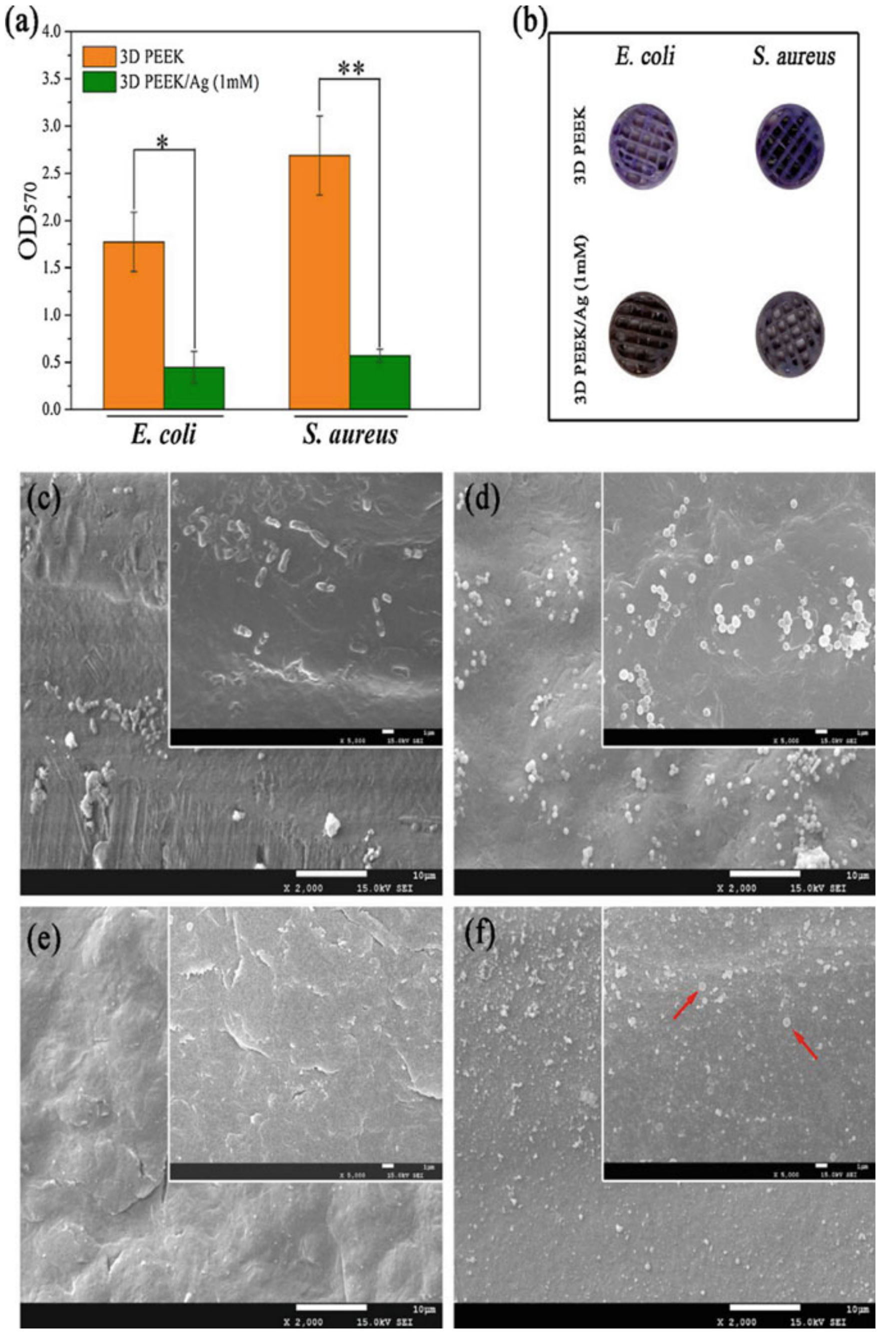


Fig. 11 Antibiofilm formation of the different scaffolds: the biomass of different specimens (**A**); the crystal violet staining results (**B**). * and ** represent $p < 0.05$ and $p < 0.01$ between groups. SEM observation of *E. coli* and *S. aureus* morphologies on different PEEK scaffolds, and the red arrows indicated the bacteria. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article). Reused with permission Deng et al. (2017)

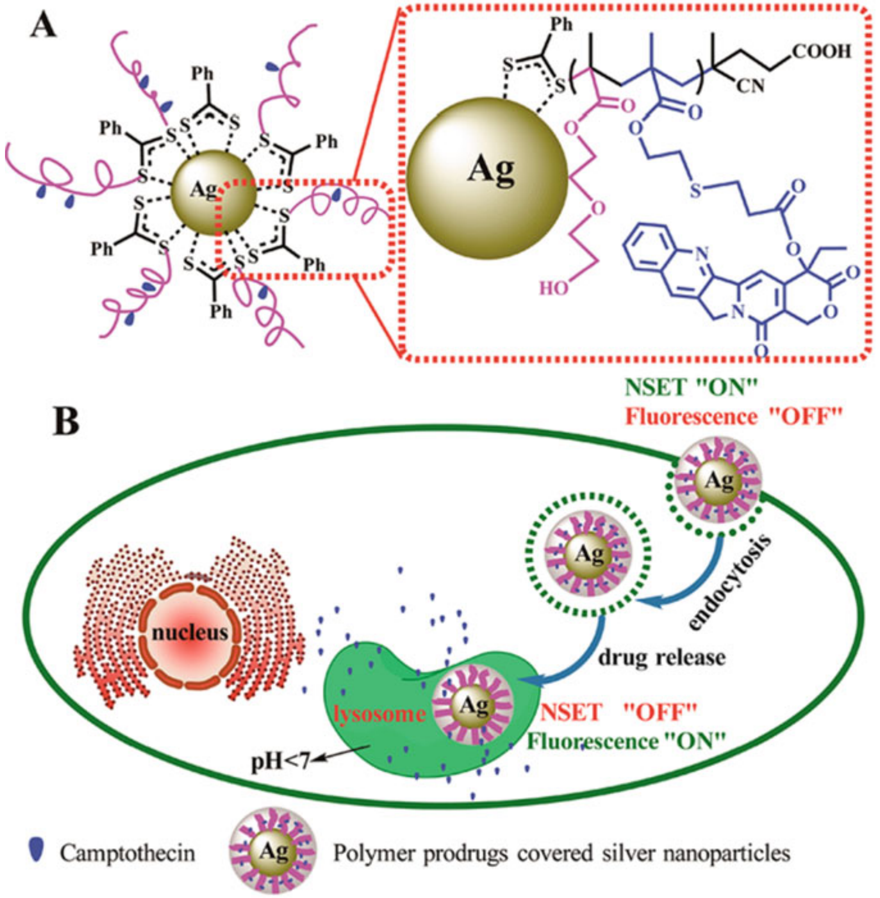
are chemically synthesized. Clinically, these chemotherapeutic drugs are usually combined in different association and concentration for cancer therapy. The application of single-agent chemotherapy will gradually become history in the clinic. It is worth noting that most of the current chemotherapeutic drugs have no selectivity. The normal cells are also killed while killing cancer cells. It is a systemic therapy with serious side effects. The common toxic side effects include body weakness, digestive disorders, decreased immune function, cardiotoxicity, renal toxicity, neurotoxicity, liver toxicity and other organ damage. Moreover, many useful anticancer drugs in clinic, such as doxorubicin, vinblastine, cisplatin, gemcitabine, etc., have poor water solubility, drug resistance, short blood circulation time, and are easily cleared by the reticuloendothelial system (RES), severe liver metabolism and renal exclusion, low bioavailability, minimal selectivity, severe systemic side effects, etc., restrict their clinical application. Therefore, a more effective drug delivery system is needed to deliver anticancer drugs to the cancer site, improve bioavailability, reduce systemic side effects, and reverse drug resistance to some extent. With the rapid development of nanotechnology and advances in characterization techniques, nanomaterials have been extensively used as carriers to carry anticancer drugs as nanomedicine for efficient drug delivery. Nanomedicines have more obvious advantages than small molecule anticancer drugs, (1) nanomedicines can improve the solubility of poorly soluble drugs to certain extent, and can protect anticancer drugs from being degraded; (2) nanomedicines can achieve controlled drugs release and prolonged blood circulation time; (3) nanomedicines have the ability to improve the pharmacokinetics and biodistribution of the anticancer drugs; (4) nanomedicines can reduce the side effects of the drugs; (5) due to the high permeability of tumor tissue vessels, nanoparticles can accumulate at the tumor site through enhanced penetration and retention effects (EPR effect), improving the bioavailability of anticancer drugs; (6) nanocarriers can simultaneously deliver different anticancer drugs with distinct physical, chemical properties and anticancer mechanisms; (7) nanomedicines can pass through a series of barriers, such as epithelial and endothelial cells; (8) nanocarriers can simultaneously achieve treatment and imaging effects, real-time tracking of anticancer drugs and evaluation of drugs efficacy. Nanomedicines have been developed rapidly in recent decades, and various types of nanocarriers have been widely studied, for instance, mesoporous silica nanoparticles, quantum dots, carbon nanotubes, magnetic nanoparticles, gold nanoparticles, silver nanoparticle, polymeric nanoparticles and liposome etc. Importantly, some nanomedicines, such as Doxil, Myocet, Depocyt, Abraxane, Genexol-PM, and Daunoxome have entered the clinical applications.

So far, cancer is still a worldwide problem. A large number of researchers are engaged in the research of nanomedicines for cancer therapy. Among the nanomedicines, polymer/AgNPs hybrid nanocarriers have received extensive attention due to their unique traits. The advantages of AgNPs have been discussed in other chapters, so they are not described here. Interestingly, AgNPs could inhibit the efflux activity of drug-resistant cells and modulate the P-glycoprotein (Pgp) activity. Therefore, AgNPs can serve as possible candidates for cancer therapy. However, free AgNPs can easily pass through the cell membrane, and then accumulate in the cells and tissue sites. As a result, the direct application of AgNPs for cancer therapy may cause cytotoxicity and genotoxicity to normal cells. Accordingly, the development of nanocarrier systems that not only reduce the dosage of free AgNPs but also maintain the anticancer effect is highly desirable. Importantly, AgNPs have unique optical characteristics, such as strong localized surface plasmon absorption and scattering from visible to NIR region. Then the intracellular uptake of AgNPs can be quantified with noninvasive surface-enhanced Raman scattering (SERS). It's well known that SERS is ultrasensitive, which can reach unimolecular concentration. Furthermore, AgNPs are promising candidates for photothermal therapy of cancer due to the high light-to-heat conversion,photostability,great molar extinction coefficient, and tumor selective accumulation. The photothermal effects of AgNPs can be regulated via adjusting morphology, particle size, and architectural organization (e.g., hollow structure or aggregation of particles). Therefore, the polymer/AgNPs hybrid nanocarriers are promising for cancer therapy.

Qiu Liang's group had reported a novel polymer/AgNPs for anticancer application. Camptothecin (CPT)-based polymer prodrug poly(2-(2-hydroxyethoxy)ethyl methacrylate-co-methacryloyloxy-3-thiahexanoyl-camptothecin) (P(HEO$_2$MA-co-MACPT)) was successfully synthesized for the coverage of AgNPs (Scheme 4), (Qiu et al. 2017). For this unique drug delivery system [P(HEO2MA-co-MACPT) @AgNPs], the polymer thickness is around 5.9 nm. In the copolymer, anticancer drug CPT is chemically conjugated to the polymer side chains via the acid-labile β-thiopropionate bond. Importantly, CPT is a fluorescent drug, which can be used as "donor" molecule of the nanoparticle surface energy transfer (NSET). In addition, AgNPs have unique optical properties, which is a good candidate as "acceptor" molecule of the NSET. The AgNP-based NSET effect could be used to study the CPT drug release process in the living cells.

It's well known that nanoparticles usually enter the cells via endocytosis processes, and the size, morphology, zeta potential and surface functionality are the significant factors accounting for AgNPs-induced toxicity and biologic responses. As shown in Fig. 12A, the AgNPs are uniform, and in quasi-spherical shape. The average diameter and the PDI are 51 nm and 0.195, respectively, which was determined by DLS (Fig. 12C). In Fig. 12B, polymer layer could be clearly observed on the surface of AgNPs. After coating with P(HEO2MA-co-MACPT), both the average diameter and the PDI of P(HEO2MA-co-MACPT)@AgNPs were slightly increased. All the results demonstrated that the P(HEO2MA-co-MACPT) were successfully coated on the surface of AgNPs.

The pH-responsive platforms have been extensively investigated as an important anticancer drug delivery system. Compared with normal tissue, extracellular pH of tumor tissue is slightly lower (~6.5–7.2). Moreover, the endocytic compartments, endosomes and lysosomes, is much lower (~4.0–6.5). The functional polymers with acidity-labile linkage, such as acetal, hydrazone, orthoester Schiff base, and boronic ester bonds, etc., were synthesized as pH-responsive polymer-drug conjugates for cancer therapy. In this work, CPT was linked to the polymer via



Scheme 4 Schematic Article (**A**) and Intracellular Release Process of CPT (**B**). Reused with permission Qiu et al. (2017)

β-thiopropionate bond, which was a acid-labile group. First, the thin-layer chromatography (TLC) was conducted to investigate the stability of the P (HEO_2MA-co-MACPT) and the P(HEO_2MA-co-MACCPT) (control polymer, CPT was conjugated by carbonate linkage). As shown in Fig. 13A, after incubation with the solution at pH 7.4 for 6 h, only one single point at the original point were observed. However, a new point at Rf = 0.65, which was ascribed to free CPT, could be obviously seen for P(HEO2MA-co-MACPT) group at pH 5.0 for 6 h. However, for the P(HEO_2MA-co-MACCPT) group, the signal corresponding to CPT could not be observed due to the acidic stability of the carbonate linkage. Moreover, the CPT release behavior from the hybrid P(HEO_2MA-co-MACCPT) @AgNPs were investigated under different pH (Fig. 13B). About 5 wt% CPT was released in PBS solution at pH 7.4 after 96 h incubation, the CPT release was

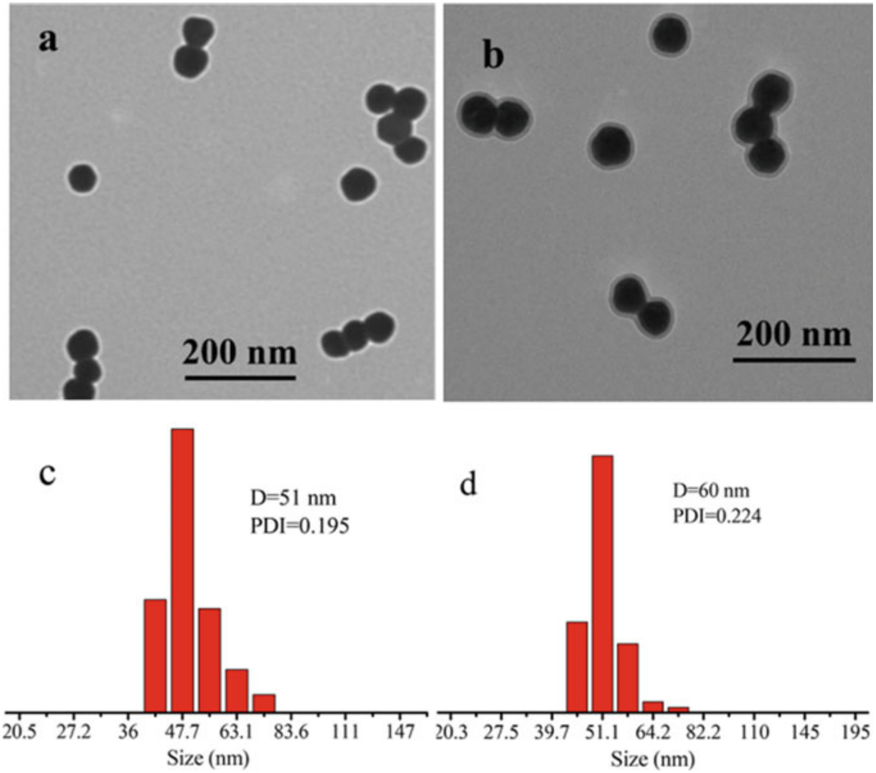


Fig. 12 Size and morphology characterizations of the AgNPs and the P(HEO2MA-co-MACPT)@AgNPs. TEM images (**A**, **B**) and DLS curves (**C**, **D**) of the AgNPs (**A**, **C**) and the P(HEO2MA-co-MACPT)@AgNPs (**B**, **D**). Reused with permission Qiu et al. (2017)

gradually increased in acidic environment. The CPT release result was consistent with the results of TLC analysis. The schematic illustration of β-thiopropionate bond cleaving under acidic conditions was shown in Fig. 13C.

The use of the AgNP-based NSET effect for studying the drug release process in the living cells was reported for the first time. Fluorescence spectra were used to characterize the NSET effect. As shown in Fig. 14A, when the P(HEO$_2$MA-co-MACPT)@AgNPs were incubated with PBS solution (pH 7.4) for 48 and 96 h, no obvious increase of the fluorescence intensity was observed with increase of the culture time, which was ascribed to almost no release of the CPT from the P(HEO$_2$MA-co-MACPT)@AgNPs because the β-thiopropionate bond is stable at neutral solution. However, when the P(HEO$_2$MA-co-MACPT)@AgNPs were treated in the PBS solution (pH 5.0), the CPT fluorescence was gradually increased with the culture time from 6 to 96 h as shown in Fig. 14B, which demonstrated that CPT molecules was gradually released from the hybrid nanoparticle via cleavage of the β-thiopropionate linkage. After CPT release, the

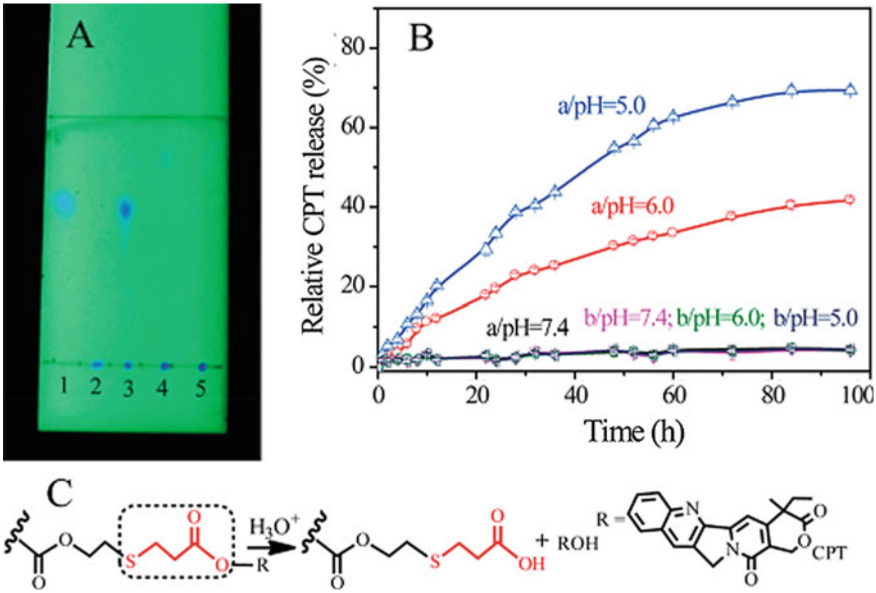


Fig. 13 Acid-responsive property. **A** Acidic cleavage of the β-thiopropionate bond tested by thin-layer chromatography (CH3OH/CH2Cl2 = 1/10, v/v) after incubation of the free CPT (sample 1), the P(HEO2MA-co-MACCPT) solution at pH 7.4 (sample 2) and pH 5.0 (sample 3) and P(HEO2MA-co-MACCPT) solution at pH 7.4 (sample 4) and at pH 5.0 (sample 5) for 6 h. **B** In vitro CPT release profiles of the P(HEO2MA-co-MACPT)@AgNPs (a) and P (HEO2MA-co-MACCPT)@AgNPs (b) after their incubation in buffer solutions (pH = 7.4, 6.0, 5.0) for different time. **C** Schematic illustration of β-thiopropionate bond cleaving under acidic conditions. Reused with permission Qiu et al. (2017)

distance between CPT and AgNPs were enlarged, resulting in the NSET "off" to fluorescence"on" (Fig. 14C).

Because the P(HEO$_2$MA-co-MACPT)@AgNPs system displays the NSET effect, it is reasonable to investigate whether the NSET effect of the hybrid nanoparticle occurs in a living cell, and the confocal laser scanning microscope (CLSM) was used to study the cellular uptake assay and the intracellular NSET effect. As shown in Fig. 15, the HeLa cells were stained with nuclear fast red (red), CPT was displayed as blue fluorescence. For P(HEO$_2$MA-co-MACPT) and P (HEO$_2$MA-co-MACPT)@AgNPs, with incubation times increased, the CPT fluorescence signal were enhanced. The results indicated that NSET effect of P (HEO$_2$MA-co-MACPT)@AgNPs could be used to illustrate the intracellular CPT release.

MTT assay was used to evaluate cytotoxicity of drug-free copolymer, AgNPs CPT-free P(HEO$_2$MA)@AgNPs and CPT conjugate hybrid nanoparticle [P (HEO$_2$MA-co-MACPT)@AgNPs], the results were shown in Fig. 16. We could see that P(HEO$_2$MA), AgNPs, and P(HEO$_2$MA)@AgNPs showed low toxicity to the HeLa cells at high concentrations of 500 μg/mL. After the HeLa cells are cultured

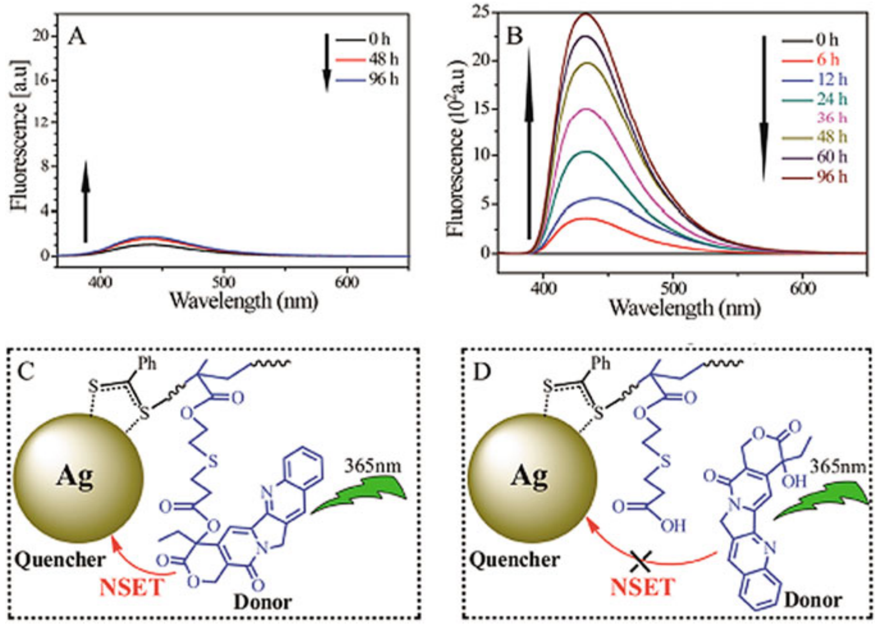


Fig. 14 Principle of NSET "on" and "off" for the P(HEO2MA-co-MACCPT) @AgNPs. Fluorescence spectra of the hybrid AgNPs after incubation in PBS solution at pH = 7.4 **A** and at pH = 5.0 **B** for different times. Schematic diagram of NSET "on" **C** and NSET "off" **D** for the P (HEO2MA-co-MACCPT) @AgNPs. Reused with permission Qiu et al. (2017)

with P(HEO$_2$MA-co-MACPT)@AgNPs, the relative cell viability was sharply decreased with the drug concentration increased. Therefore, P (HEO$_2$MA-co-MACPT)@AgNPs is a potential efficient drug delivery system for cancer therapy and a useful approach to investigate the mechanism of drug release in the living cells.

Drug delivery nanocarriers can lead to improved drug solubility, reduced side effects, enhanced tumor targeting efficiency, increased drug half-life in the body, and therefore to a more effective cancer therapy. Polymer/AgNPs are highly interesting structures since they synergistically combine the excellent physical-chemical properties of both polymeric and inorganic components, providing superior functionality to the final material. Another important field in nanomedicine is the detection and diagnosis of cancer at early stages. Polymer/AgNPs may be a promising candidate for cancer theranostics, which combine therapeutic and diagnostic capabilities into a single platform to enable more specific and individualized therapies for various diseases and damages

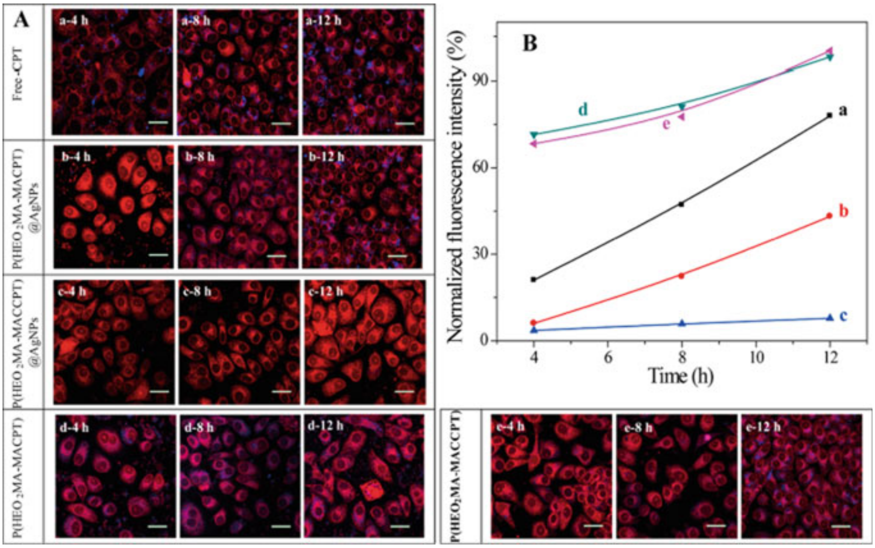


Fig. 15 **A** Drug release from the hybrid AgNPs in the living HeLa cells. **B** Relationship between normalized fluorescence intensities of the HeLa cells with incubation time. The scale bar is 20 μm. Reused with permission Qiu et al. (2017)

5 AgNPs/Polymer Nanocomposite for Antiviral Application

The viruses seriously threaten the safety of human life. Due to its frequent mutation and rapid spread, serious individuals directly lead to death, the more serious of which is HIV. According to the statistics of the World Health Organization (WHO), HIV infection has caused nearly 33 million deaths so far. In recent years, there have been no important breakthroughs in vaccines against Acquired Immune Deficiency Syndrome (AIDS), chemicals remain the mainstay of treatment. The use of chemical drugs has effectively improved the dilemma of treating the virus, but with the widespread use of drugs, the emergence of drug resistance in the virus leads to the decline of the treatment effect, so it is urgent to find safe and effective method. Due to the advantages of small size and simple synthesis, nanomaterials have been widely concerned by scientists, and the use of nanomaterials as drug carriers has become a hot research. Ancient people realized that the antimicrobial effect of silver is widely used as tableware, with the development of times, now AgNPs as a representative of the metal nanomaterials has been applied for the antiviral application to achieved better results, but the AgNPs can spontaneous release of silver ions in the cell environment damage mitochondria, and thus cell toxicity. Scientists began to modify some biological macromolecules or polymers on nanosilver particles to reduce cytotoxicity.

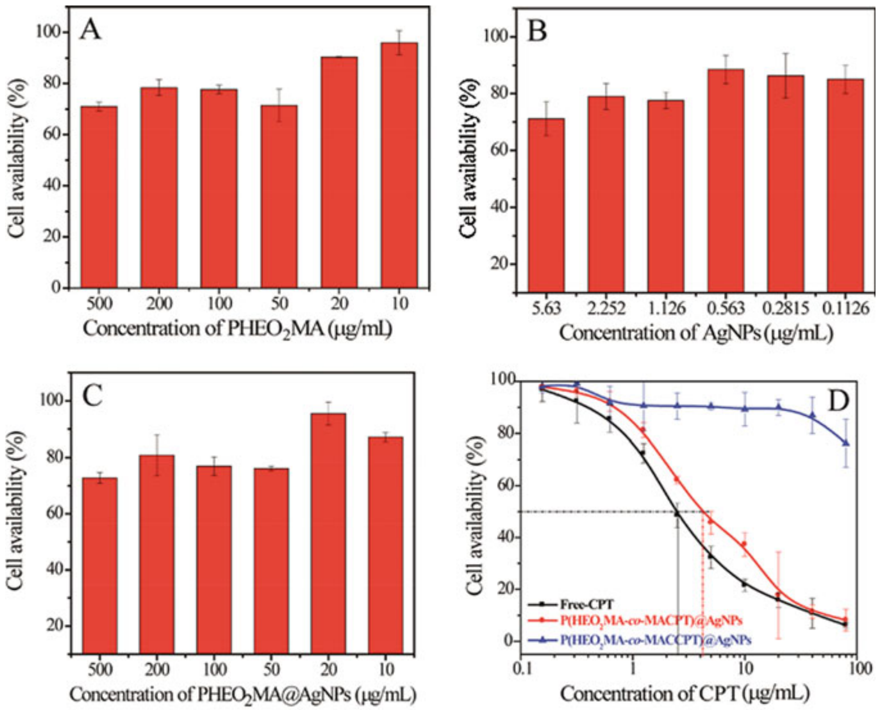
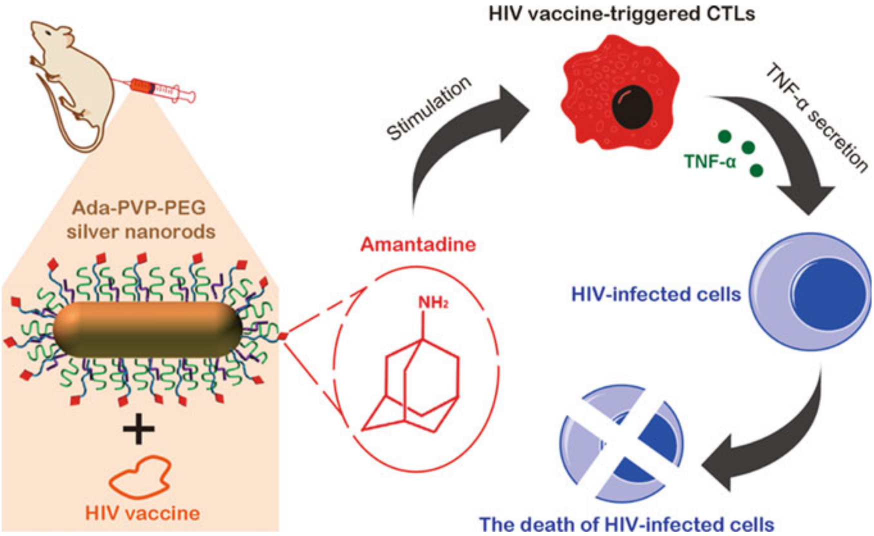


Fig. 16 Relative cell viability of HeLa cells evaluated by MTT assay after incubation with the pH = 7.4 solutions of **A** P(HEO2MA); **B** AgNPs; **C** P(HEO2MA)@AgNPs; and **D** free CPT, P (HEO2MA-co-MACPT)@AgNPs, and P(HEO2MA-co-MACCPT)@AgNPs, at their different concentrations. Incubating temperature: 37 °C; time: 48 h. Reused with permission Qiu et al. (2017)

Li's group modified PVP-PEG coated silver nanorods with Amantadine (Scheme 5), (Li et al. 2018). It enhanced HIV vaccine-triggered cytotoxic lymphocytes(CTLs) to get more than eightfold stronger tumor necrosis factor alpha (TNF-α) in vivo, which made the death of HIV cell greatly and reduced the HIV recurrence rate more than sixfold simultaneously. This work highlights how modifying the surface of the silver nanorods could greatly improve the efficiency of HIV treatment.

In the work, the effect of Ada–PVP–PEG silver nanorods on regulating HIV vaccine-triggered CTLs to produce TNF-α was investigated in vivo (Fig. 17). The CD3$^+$CD4$^+$ T cells/T helper cells and CD3$^+$CD8$^+$ T cells/CTLs are two major subgroups of T cells, and these two T cells can produce HIV-specific TNF-α. Then, the flow cytometry assay was used to quantify the percentage of the two T cells. The percentage of CTLs in groups 2, and 3 was 0.127% and 0.076%, respectively. However, the CTLs produced HIV-specific TNF-α in group 1 was 0.581%, which was significantly higher than the percentage of CTLs in group 2 and group 3. The



Scheme 5 Outmost modification of Ada on silver nanorods facilitates HIV vaccine-triggered CTLs to produce stronger TNF-α to kill HIV-infected cells. Reused with permission Li et al. (2018)

results demonstrated that Ada modification predominantly enhanced HIV vaccine-triggered CTLs, instead of T helper cells, to produce TNF-α.

The effect of ada surface-modified silver nanorods on the immunotherapy of HIV vaccine against HIV-infected cells was studied (Fig. 18). From the Fig. 18B, we can got the group 1 made more histone production by use enzyme-linked immunosorbent assay (ELISA). Figure 18C showed that $1 * 10^5$ CTLs are enough to induce the death of $1 * 10^4$ cells and proved that histones are mainly from dead HIV-infected cells not from CTLs. Figure 18D proved that the TNF-α mAbs reduced the death of HIV-infected cells effectively. Figure 18E suggested modified Ag nanorods can cause more death of HIV cells. Figure 18F and 18G suggested that introducing Ada–PVP–PEG silver nanorods can effectively reduce HIV regeneration through the death of HIV cells. From the Fig. 19, Immunohistochemical analysis of tissues and organs in mice showed no confirmed cell infiltration and tissue necrosis, these results proved that this is a reasonable category to construct Ada–PVP–PEG silver nanorods.

Sofy' group in situ prepared stabilize AgNPs through using POP-based oligo-chitosans(PQPOCs) (Scheme 6), (Sofy et al. 2019) which act as synergistic reductant and encapsulating agents, suggested that PQPOCs has the greatest antiviral activity against feline calicivirus (FCV), hepatitis A virus (HAV), and coxsackievirus B4 (CoxB4). It can got the greatest antiviral efficiency when the condition at pH 4.

From the Fig. 20, the antiviral effect of the NBC1 against HAV showed a highly significant reduction. This article got the better antiviral efficiency can be concluded

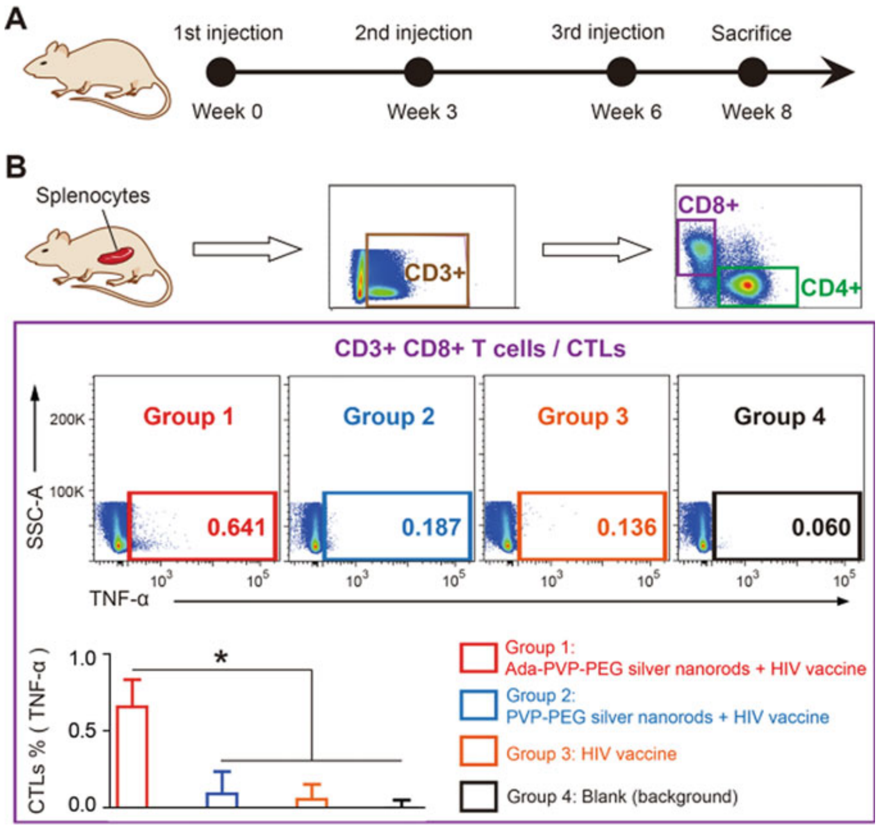


Fig. 17 HIV-specific CTL-derived TNF-α in mice. **A** Vaccination scheme: each mouse receives three intradermal vaccinations with an interval time of three weeks. **B** We design four mouse groups (six mice per each group). Group 1 (red): each mouse receives 50 μg HIV DNA vaccine and 10 μg Ada–PVP–PEG silver nanorods. Group 2 (blue): each mouse receives 50 μg HIV DNA vaccine and 10 μg PVP–PEG silver nanorods. Group 3 (orange): each mouse receives 50 μg HIV DNA vaccine. Group 4 (blank): mice do not receive any vaccination. We use flow cytometry analysis to gate HIV vaccine-triggered CTLs ($CD3^+CD8^+$ T cells) from $CD3^+$ splenocytes and quantify the percentage of CTLs that produce HIV-specific TNF-α. The corrected value of CTLs % (TNF-α) = the original value of CTLs % (TNF-α) − the background value of CTLs % (TNF-α) (the value in group 4). The corrected value of CTLs % (TNF-α) > 0.05 is defined as positive. * means $p < 0.05$. Reused with permission Li et al. (2018)

that The interaction between the active site of the virus particle and the silver nanoparticles prevents the attachment and penetration of the virus and the CS backbone further prevents its transcription and translation by inducing ribonuclease to degrade viral RNA.

The AgNPs/polymer hybrid nanocomposite has emerged as one of the most promising system on account of its ability to deal with the viral diseases in a more efficient manner, addressing the limitations of the traditional antiviral drugs. It has

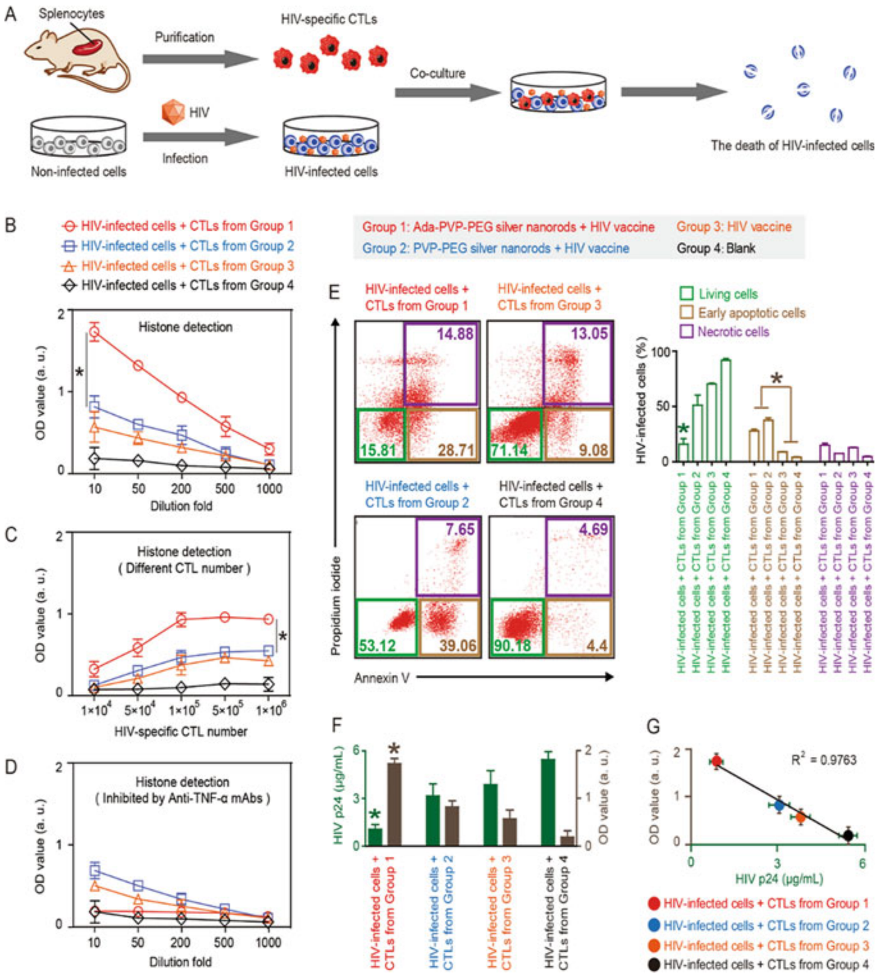


Fig. 18 Death of HIV-infected cells caused by HIV vaccine-triggered CTLs. **A** HIV-infected TZM-BL cells are co-cultured with CTLs isolated from mouse splenocytes. Forty-eight hours later, the death of HIV-infected cells is evaluated via quantifying histone (ELISA) or staining Annexin V/propidium iodide (flow cytometry). **B** 1 × 104 HIV-infected cells are co-cultured with 1 × 104 CTLs from groups 1, 2, 3, or 4 for 48 h. Histone in cell culture medium is quantified using ELISA. **C** 1 × 104 HIV-infected cells are co-cultured with different numbers of CTLs (1 × 104, 5 × 104, 1 × 105, 5 × 105, 1 × 106 cells) from groups 1, 2, 3, or 4 for 48 h. Histone in cell culture medium is quantified using ELISA. **D** Anti-TNF-α monoclone antibody (5 μg/mL) is added into the co-cultured system of HIV-infected cells (1 × 104 cells) and CTLs (1 × 104 cells) from groups 1, 2, 3, or 4 for 48 h. Histone in cell culture medium is quantified using ELISA. **E** Cells in co-cultured system of HIV-infected cells (1 × 104 cells) and CTLs (1 × 104 cells) from groups 1, 2, 3, and 4 are stained by Annexin V and propidium iodide. Flow cytometry analyzes the percentage of cells that are stained by either Annexin V alone or dual Annexin V-propidium iodide. **F** HIV-infected cells (1 × 104 cells) are co-cultured with CTLs (1 × 104 cells) from groups 1, 2, 3, or 4 for 48 h. HIV p24 antigen, an indicator for HIV production, is quantified using ELISA (dark green). Histone is detected using ELISA (dark brown). **G** Correlation analysis between HIV p24 production and histone leak. * means $p < 0.05$. Reused with permission Li et al. (2018)

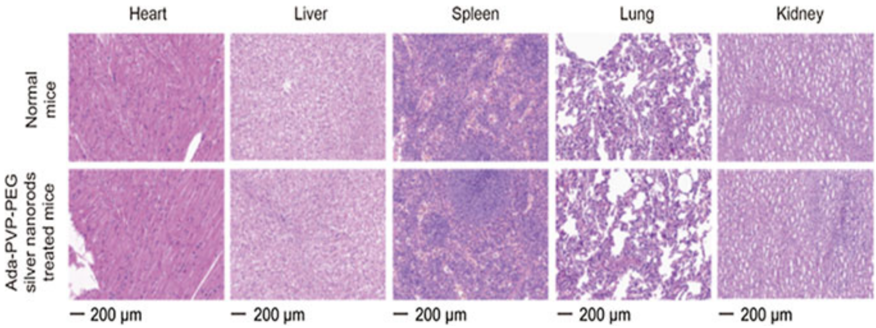
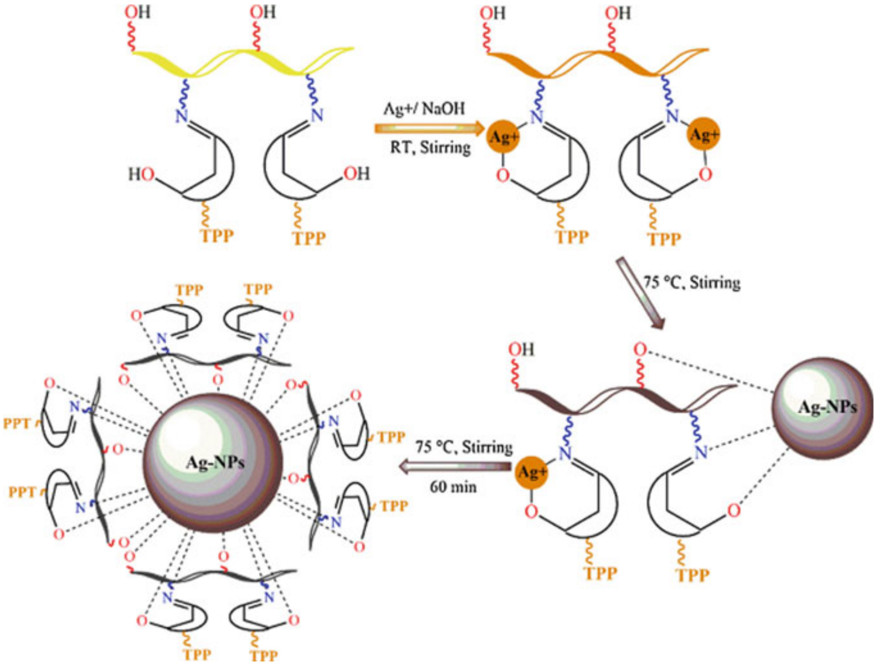


Fig. 19 10 μg Ada–PVP–PEG silver nanorods are injected into one mouse. 30 days later, pathological sections (H&E staining) from heart, liver, spleen, lung, and kidney are observed. Reused with permission Li et al. (2018)



Scheme 6 Proposed mechanism for formation of AgNPs mediated by PQPOCs as synergistically capping and reducing agents Reused with permission Sofy et al. (2019)

not only helped us to overcome the problems related to the solubility and toxicity of drugs, but also imparted unique properties to the antiviral system, which in turn has enhanced their potency and selectivity toward the viral cells against the host cells.

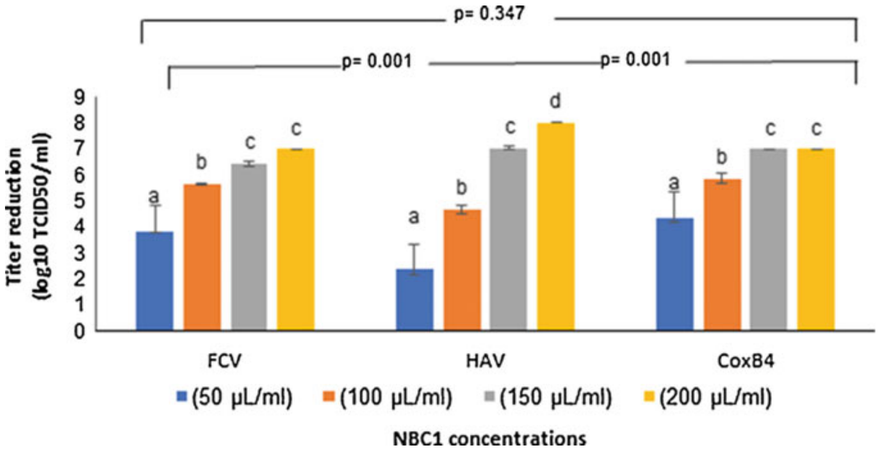


Fig. 20 Infectious titer reduction of FCV, HAV, and CoxB4 after treatment with different concentrations (50, 100, 150, and 200 μL/mL) of NBC1, as detected by log10 TCID50/mL (where letters (a, b, c, d) to show which bars are significantly different). Reused with permission Sofy et al. (2019)

6 Conclusion

This chapter is a summarization of a variety of AgNPs/polymer hybrid nanocomposites that have the future to be used as biomaterials for antibacterial,wound dressing, tissue engineering, anticancer, and antiviral application. AgNPs, one of the predominant nanomaterials, have been extensively investigated as biomaterials due to its surface plasmon resonance effect and toxicity. It's well known that the biological effect of Ag is related to the particle size of silver. However, when the radius of AgNPs decrease, the surface energy dramatically enlarge, and the AgNPs is easier to agglomerate in the solution medium, which limits its biological applications. Biocompatible polymers such as dextran, poly(vinylpyrrolidone) (PVP), poly(ethylene-glycol) (PEG), chitin, soluble starch, chitosan, dextrose, carboxymethyl cellulose, as well as synthetic polymer PLGA, etc. have been widely used for the stabilize the AgNPs. However, the mechanisms and biological interactions behind these AgNPs/polymer hybrid nanocomposites are not fully understood. Therefore, there is a pressing need to fully study the mechanisms concerning the efficacy and toxicity of AgNPs/polymer hybrid nanocomposites before widespread medical application can occur.

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Silver Nanoparticle as an Effective Antiviral Agent

Hiran Mayookh Lal, Arya Uthaman, and Sabu Thomas

Abstract The infections from viral pathogens pose a significant global health challenge. The emergence of viral strains resistant to conventional antiviruses and the adverse side effects due to their prolonged use slow down the application of many antiviral therapies. The silver nanoparticles are considered a potentially useful tool for preventing various pathogens. The silver nanoparticles have already proven its potential as an efficient antiviral agent offered by their unique physical and chemical properties. The silver nanoparticles provide an excellent opportunity for novel antiviral therapies as it can attack a broad range of viruses with a lower possibility for developing resistant antiviral strains compared to conventional antiviral drugs. This chapter discusses the application of silver nanoparticles as an efficient antiviral agent against human immunodeficiency virus, respiratory syncytial virus, hepatitis B virus, monkeypox virus. Furthermore, the effect of silver nanoparticles against coronaviruses and the development of silver nanoparticles on their application as an effective antiviral therapeutic agent against pathogenic viruses have been discussed in this chapter.

Keywords Silver nanoparticles · Virus infection · Antiviral therapy · Antivirus mechanism

1 Introduction

The viruses are sub microscopic infectious agents that replicate only inside the living cells of organisms. It can infect any type of living form that varies from plants and animals to microorganisms such as bacteria and archaea. The viruses constitute one of the prime causes of diseases and death worldwide. The vaccination programs are

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an effective way of preventing infections by viruses. The vaccinations could permanently disable numerous diseases that have killed many and others have been eradicated, such as smallpox in 1979. In the case of paralytic disease poliomyelitis, the development of vaccination programs greatly reduces the burden of disease. However, for some of today's critical viral pathogens, there is still no vaccine has been developed. The viruses contain genetic materials RNA or DNA, capsid proteins, and a lipid envelop. The viruses are classified as enveloped and non-enveloped viruses based on the presence or absence of a lipid envelope. The human pathogenic viruses such as Hepatitis C and B, Dengue, Yellow fever, Measles, Influenza, Ebola, Respiratory syncytial, and most recently of COVID-19 (1.12 million people have died so far from the COVID-19 outbreak as of October 21, 2020, 01:34 GMT) (WHO 2020) are enveloped viruses. Some of the viruses are capable to cause persistent infections that may lead to cancer or acquired immunodeficiency, for e.g. human immunodeficiency virus (HIV) and hepatitis (mainly HBV and HCV). Up-to-date a numerous effort has been expended in attempts for developing vaccination programs for these viruses. The new vaccines for viruses such as HIV, HCV, and some herpesviruses have been developed without appreciable success.

The development of vaccines against diseases can save millions of lives each year. If a human body is exposed to infection- causing viruses or bacteria later, the body is immediately ready to destroy them. The vaccines work by preparing the body's immune system (natural defense) to recognize and ruin the bacteria and viruses they target. The emerging and re-emerging of viruses are a threat to human health because of their ability to adapt their present host, to their transition to a new host, to undergo an evolution of various adaptive conditions, and to escape from different antiviral measures. The development of a new vaccine for viruses such as COVID-19, HIV, HCV, etc., seems likely to continue to be elusive. The field of development of a new vaccine is very promising even together with the risk of emerging and re-emerging of the viruses. Currently, technological advances have led to the discovery and characterization of molecules that are essential for the replication of viruses, so the development of new antiviral agents is possible to inhibit viral infections. Great progress has been achieved in the field of antiviral therapy, but still there exists a margin of ineffectiveness. The development of new antiviral agents is very much essential to continue the fight between the host responses and invading viruses.

The effects of viral infection are administrated by the interaction between the host cells and the virus. When a cell of an organism is exposed to a virus it first binds to the cells and then the virus or its genome gets penetrate into the cytoplasm. The genome is released from the capsid, and it is transcribed either in the nucleus or in the cytoplasm. The mRNA of the virus directs protein synthesis in a well-regulated manner. Finally, the virus goes through the genome replication and together with viral proteins get together and forms a new virus which is then released from the cell (Galdiero et al. 2011). The virus replication cycle is represented in Fig. 1, showing the HBV replication as an example (Zoulim 2004).

The development of drugs that target viral entrance or attachment and possibly inhibit viral infections have proven very difficult to invent. Due to the emerging and

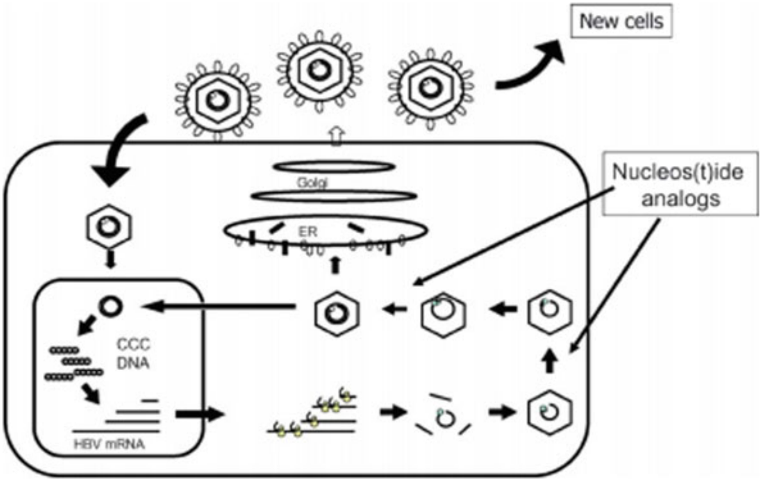

Fig. 1 Major steps involved in the HBV replication cycle. Reused with permission from Zoulim (2004)

re-emerging of diseases caused by various pathogenic viruses and the rising of antiviral resistance to conventional antivirus drugs, researchers and pharmaceutical companies are in search of the development of new effective antiviral drugs.

The introduction of nanotechnology widely for numerous biomedical applications has also extended their contributions to the development of antiviral drugs that act by preventing viral infections during the viral attachment and entry. Among nanoparticles, metal nanoparticles are a promising candidate for various biomedical applications due to their unique physicochemical properties. The dimension of nanoparticles is less than 100 nm and possess unique physical and chemical properties that are derived from the presence of a higher quantity of surface atoms and also the surface area to volume ratio. Among the metal nanoparticles, the silver nanoparticles (Ag NPs) are well known antimicrobial materials that are effective against numerous types of bacteria and fungi. The antimicrobial and antifungal activity of Ag NPs is mainly due to the obstruction of respiratory enzymes, electron transport component, and tampering the DNA function by released Ag+ ions. One of the main advantages of silver is the microorganisms are unlikely to evolve resistance against silver as compared to conventional antibiotics, as silver can fight against a broad range of targets in microbes. The application of Ag NPs in the biomedical field has been found in various forms such as wound dressing, silver-impregnated textile fabrics, coating for medical devices, etc. Ag NPs have received significant attention as antimicrobial agents and was proven their effectiveness against Gram-positive and Gram-negative bacteria. The biological interaction between the microbes and the host cells is multivalent that includes multiple copies of ligands and receptors that bind together in a coordinated manner. This multivalent bond enhances the efficiency and strength of such interactions that allow the microbes to invade cells under attack. Interfering these identified interactions between microbes and cells, and thus blocking the viral entry into the cell membranes is the promising strategy being perused for developing a new antiviral drug and preventive microbicides.

2 Ag NPs as an Emerging Antiviral Agent

Silver nanoparticles have been proven to be an excellent antimicrobial agent however, the antiviral properties of Ag NPs remain still undeveloped. Nowadays, viruses represent one of the leading causes of diseases and death worldwide. We have witnessed several examples occurring each year, and presently on October 2020, the world is suffering very seriously from the Coronavirus disease (COVID-19) pandemic which has already taken the life of 1.13 million human beings as reported by WHO (2020). The other known examples are SARS coronavirus, monkeypox virus, West Nile virus, Nipah virus, Chikungunya virus, Hantavirus, Influenza virus, etc. As we discussed earlier in this chapter, the emerging and re-emerging of viruses are a major threat for discovering a new antiviral drug. The changes to the ecosystem that disorder the balance between microbes and the host species cells, and the changes in human behaviour and increase in urbanization are some of the factors responsible for the outbreak of a pandemic. Therefore, there is a greater need for a new methodology for treatment with developed antiviral agents that can also overcome the problem of antiviral resistance.

Due to the potential antiviral properties of Ag NPs, they are emerging as one of the choices of action for the management of viral diseases. The significant application of Ag NPs in the treatment of viral infections that require maintenance of circulating drug concentration or long-lasting therapeutic regimens. Ag NPs are active against a broad range of viruses and, the possibility for the development of bacterial resistance is lower compared to traditional antiviral drugs (Rai et al. 2014). Ag NPs received considerable attraction as an antiviral drug due to their intrinsic properties since they have shown antiviral behavior against several viruses regardless of the specific family. There are only a limited amount of studies emerged to demonstrate that silver nanoparticles can apply as effective antiviral agents. Several studies have arisen since the last few years showing the effectiveness of Ag NPs as an excellent antiviral agent against the viruses such as HIV, respiratory syncytial virus, influenza virus, hepatitis B virus (HBV), hepatitis C virus (HCV), and monkeypox virus. Some of the studies showing the inhibitory effect of Ag NPs against each virus are mentioned in Table 1.

Considering the application of metal nanoparticles as an antiviral agent, the properties of each nanoparticle vary depending on their size, capping agents, level of dispersion, and shape. The available research data regarding the antiviral usage of nanoparticles are heterogeneous and difficult to categorize. From the various nanoparticles, Ag NPs are commonly used as an antiviral agent for a different type of viruses. So far, from the antiviral properties of silver three key aspects can be extrapolated.

Table 1 A review on antiviral properties of silver nanoparticles

Virus	Family	Ag NPs type/composition/size	References
HIV 1		PVP—Coated AgNPs (1–10 nm)	Elechiguerra et al. (2005) Sun et al. (2005) Lara et al. (2010a)
HIV 1	Retroviridae	Mangrove-mediated green synthesised AgNPs (12–28 nm)	Kumar et al. (2017)
HIV 1		Curcumin stabilized Ag NPs (45 nm)	Sharma et al. (2017)
HIV		NH_2*f*MWCNT with Ag NPs (10 nm) (anti-HIV drug RIL)	Aftab et al. (2019)
HIV 1		Ag NPs (0.92–2.48 nm)	Tsai et al. (2019)
RSV		PVP coated Ag NPs (69 ± 3 nm)	Lova et al. (2008)
RSV	Paramyxoviridae	Curcumin modified AgNPs	Yang et al. (2016)
RSV		PVP coated Ag NPs (8–12 nm)	Morris et al. (2019)
Influenza virus H1N1		Ag NPs solution (5–20 nm)	Xiang et al. (2011)
Influenza virus H3N2		Ag NPs solution (9.5 nm)	Xiang et al. (2013)
Influenza virus H1N1	Orthomyxoviridae	Amantadine modified AgNPs (3–2 nm)	Li et al. (2016a)
Influenza virus H1N1		Oseltamivir decorated AgNPs (3–2 nm)	Li et al. (2016b)
Monkey pox	Poxviridae	AgNPs and Polysaccharide coated AgNPs (10–80 nm)	Rogers et al. (2008)
HBV	Hepadnaviridae	Ag NPs (10–50 nm)	Lu et al. (2007)
HCV		Green synthesised Ag NPs from total extract and petroleum ether fraction of *Amphimedon* (8.22–14.30 nm)	Shady et al. (2020)

Expanded abbreviations from this Table, Human immunodeficiency virus (HIV), Respiratory sincitial virus (RSV), Hepatitis B virus (HBV), Hepatitis C virus (HCV), poly vinylpyrolidone (PVP)

(1) The Ag NPs used for the viral inhibition also depends on their size. From Table 1, it is clear that the average size of Ag NPs are generally less than 25 nm. The lower size of nanoparticles resulted in more effective antiviral infectivity inhibition.

(2) Ag NPs exhibits excellent antiviral properties against a large number of viruses infecting both eukaryotic and procotic organisms. Thus, Ag NPs could be considered a true broad-spectrum antiviral agent.

(3) The early infection might be the common time frame where Ag NPs exert their antiviral activity inhibiting the rest of the virus replication cycle.

3 Mechanism of Ag NPs Antiviral Activity

Several studies have been reported the excellence of Ag NPs as an antiviral agent inhibiting several bacterial infections. However, the exact stage of viral infection at which the silver exerts their antiviral property and the precise mechanism behind the antiviral activity of Ag NPs have yet to be determined. Comprising much literature; (Rai et al. 2014) demonstrated the possible mechanism behind the antiviral activity of Ag NPs and represented in Fig. 2.

Different studies based on the antiviral activity of Ag NPs without a capping agent revealed that it could inhibit several viruses. Lu et al. (2007) showed that the smaller particle size Ag NPs (10 and 50 nm) could effectively inhibit HBV due to

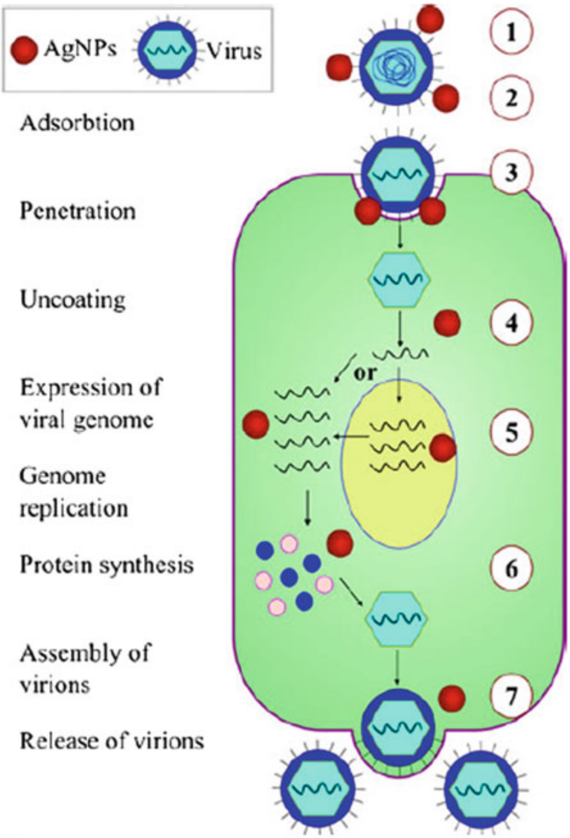

Fig. 2 Antiviral mechanism of silver on different stages of viral replication. 1—Bonding/interaction with viral surface, 2—Interference with viral attachments, 3—resisting the penetration of virus into host cell, 4—interaction with viral genome, 5—inhibition of genome replication, 6—inhibition of protein synthesis, 7—inhibition of viral assembly and release of virions. Reproduced from Ref. (Rai et al. 2014) with permission

the specific interaction between smaller size nanoparticles and DNA of HBV virus. Similarly, the Ag NPs with 10 and 50 nm showed a strong binding affinity with HBV virions and thus preventing the virions from entering the host cells than Ag NPs with 50 nm size. Larger nanoparticle size (800 nm) induced several cytotoxic effects in cell culture-based assays, but the smaller size Ag NPs showed less cytotoxic effects. The in vitro anti-HBV activities of the different sized Ag NPs are determined using the HepAD38 cell line that secretes HBV particles and exhibits a high level of HBV DNA to the surrounding medium. The authors explained feasible mechanisms for the anti-HBV effect of Ag NPs is due to their reduced size. The smaller size facilitates their higher possibility of interaction with other smaller molecules. The Ag NPs with 10 nm size might imide the RNA of the virus by directly binding or interacting with the HBV DNA, which serves as a template of RNA synthesis. Xiang et al. (2011) studied the inhibitory effect of Ag NPs (10 nm) against the influenza virus. The authors found that the virus presumed to be dependent on the soluble silver ions (Ag+ ions), which impede strongly the growth of pathogens via the suspension of electron transport components, respiratory enzymes, and interface with DNA function. Speshock et al. (2010) studied the inhibition effect of Ag NPs against Tacaribe virus (TCRV). The 10 nm size Ag NPs exhibited excellent anti-TCRV activity compared to 25 nm-sized Ag NPs. The authors demonstrated that the Ag NPs seem to interact with TCRV before the viral infection due to exposure of virus into host cells. The Ag NPs interfere with cellular receptors binding or the internalization of Ag NPs together with the virus and develop an inhibitory effect on viral replication interfering with virus RNA-dependent RNA polymerase.

Numerous researches have emerged in the last few years on the antiviral effect of modified Ag NPs and green synthesized Ag NPs. Lara et al. (2010a) demonstrated the PVP modified Ag NP exert anti-HIV activity at the early stage of viral replication. Ag NPs inhibited all strains of HIV 1 isolates include T-tropic, M-tropic, dual-tropic and resistant isolates. The anti-HIV mechanism of Ag NPS is based on the inhibition of the initial stage of the HIV-1 cycle that can be attributed to the inhibition of virus fusion or binding with the host cells. The Ag NPS inhibits the interaction between HIV-1 gp120 glycoprotein and the target cell membrane receptor. The Ag NPs might interact with disulfide bonds located in the carboxyl half of HIV-1, which has been implicated in binding to CD4 host cell receptors. Lara et al. (2010b) observed the PVP-coated Ag NPs could function as effective microbicides with virucidal properties, they are capable of inhibiting the transmission of HIV-1, and offers long-lasting protection of cervical tissue from infection for 48 h, authors observed no trace of cytotoxicity exists in the explants. From these studies, we can conclude that the precise mechanism of interaction between Ag NPs and HIV-1 still has to explore. However, various data points to direct interaction with HIV-1 glycoproteins and Ag NPs could interfere with the fusion of viral penetration into the host cell. Ag NPs can also inhibit the post-entry stages of infection by preventing other functional HIV-1 proteins or by decreasing reverse transcription or proviral transcription rates by directly interacting with the DNA or RNA molecules (Rai et al. 2014).

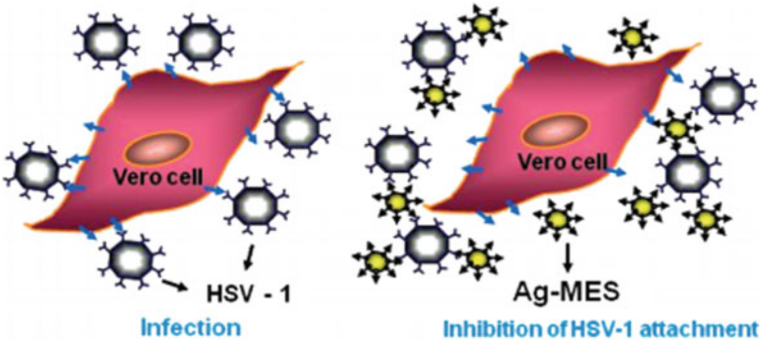

Fig. 3 Proposed mechanism of inhibition of HSV-1 by Ag NPs decorated with MES. Reproduced from Ref. (Baram-Pinto et al. 2009) with permission

The sulfonate capped Ag NPs (4 ± 1 nm) have been introduced as an anti-HSV-1 infection (Baram-Pinto et al. 2009). The authors used mercaptoethane sulphonate (MES) as a capping agent. The entry and attachment of HSV-1 into cells involve the bonding between the viral glycoprotein and cell surface heparan sulfate (HS). Ag NPs are expected to block the interaction between the virus and cells and thus prevents the virus from entering the cell and thus inhibit the cell-to-cell spread of the virus. The authors found that the Ag NPs capped with MES served as a multivalent inhibitor that mimics the HS of the host cell as shown in Fig. 3.

There are different studies reported demonstrating the Ag NPs alone and with their different compositions as an excellent antiviral agent. However, the precise mechanism behind the antiviral activity has yet to be determined. In this section, we have explained the antiviral activity of Ag NPs compiled from the available literature. The overall picture from the literature showed a tendency of smaller size Ag NPS is more incisive in inhibiting the infectivity of each virus regardless of the viral specious. The smaller particle exerts minor cytotoxicity. With our limited knowledge, we have tried our best to refer to various research studies in this chapter although, there have been many studies that we may not be able to include in this chapter regarding the mechanism of Ag NP's antiviral activity.

4 Ag NPs and Their Antiviral Activity

4.1 Retroviridae

A retrovirus family of virus inserts a copy of its RNA genome into the DNA of the host cell's cytoplasm that it invades. Once this virus entered the host cell's cytoplasm, it uses its reverse transcriptase to develop DNA from its RNA genome. The acquired immunodeficiency syndrome (AIDS) is the disease caused by HIV. The cure for HIV does not exist. The treatment of HIV involves taking medicine that slows down the progression of the virus inside the human body. Highly active antiretroviral therapy (HAART) is a treatment regimen that includes taking a cocktail of drugs that suppresses the HIV infection of an HIV infected patient. This treatment has significantly improved the life expectancy and quality of millions of HIV infected individuals.

The replication of HIV-1 is a complicated multistep process that is only dependent on both the virus and host cell factors. The entry of the virus into target cells is achieved via fusion of the viral lipid envelope and the cellular plasma membrane. The viral components glycoproteins composed of two subunits such as gp120 (binds to the cellular receptors), and gp41 (which is subunits bearing the transmembrane segments, and executes the fusion. After the fusion following gp120 binding to the CD4 (cellular receptor), and the following interaction with CXCR4 or CCR5 (co-receptors), a conformational change in gp41 leads to membrane fusion and delivery of capsid to the cytoplasm. Soon after the entry, RNA is reverse transcribed to a complimentary DNA that converted to a double stranded DNA, and integrated into the host cellular genome. The integrated viral DNA is transcribed to develop full-length progeny viral RNA and a number of spliced mRNA transcripts. This results in the synthesis of viral proteins together with progeny viral RNA are transported to the site of virus particle assembly at plasma membrane, which is the place where the virus gains access to extracellular milieu upon building events.

Elechiguerra et al. (2005) first demonstrated the size-dependent interaction of Ag NPs with HIV-1, with the Ag NPs size ranges of 1–10 nm attached to the virus. The authors suggested that the sulphur bearing residues of the virus glycoproteins are attractive sites for nanoparticle interaction with HIV-1 through preferential binding to gp120 glycoprotein knobs. In their investigation, they demonstrated the interaction of Ag NPs with capping agents opens the possibility for their physiochemical properties. For this reason, they used three different surface treatments of Ag NPs. (1) Foamy carbon, (2) poly (N-vinyl–2-pyrrolidone) (PVP), and (3) bovine serum albumin (BSA). The authors found the BSA and PVP coated AG NPS exhibits a slightly lower inhibition effect to HIV-1 may due to the Ag NP's surface are directly bond and encapsulated to those capping agents. The Ag NPs released from the carbon matrix observed a higher inhibitory effect because of the indispensably free surface area. Lara et al. (2010a) showed the Ag NPs coated with PVP were an effective antiviral agent against HIV-1. A luciferase-based assay showed an effective virucidal effect against cell-free virus including laboratory strains, clinical isolates T and M tropical strains, and resistant strains, and cell-associated virus. The authors observed the antiviral effect of Ag NPs is due to the nanoparticle itself, rather than just to the Ag ions present solution. The antimicrobial effect of Ag salts through Ag ions inhibited HIV-1 12 times lower than the one of Ag NPs. The mechanism of inhibition of HIV-1 is based on inhibiting the interaction between HIV-1 glycoprotein gp120– and host cell receptor CD4. Lara et al. (2010b) showed the PVP—coated Ag NPS as an excellent antiviral drug against HIV-1 using an in vitro human cervical tissue based organ that simulates in vivo conditions. Mohammed Fayaz et al. (2012) developed Ag NPs coated polyurethane condoms

(PUC). They demonstrated that the Ag NPs coated PUC could effectively inhibit and inactivate HIV-1 and HIV-2 on contact. It can also develop a defence line against other sexually transmitted infections.

Kumar et al. (2017) prepared green synthesized Ag NPs by aqueous leaf extract of mangrove *Rizophora lamarckii* with a size range from (12–28 nm). The Ag NPs showed high HIV-1 (RTase) reverse transcript inhibitory activity. The authors claimed the mangrove-synthesized Ag NPs is a promising candidate against HIV and other viruses.

Whiteley et al. (2016) investigated the interaction between HIV aspartic protease (PR) and AgNPs (2.12 nm) using molecular dynamic simulations. The interacting docking of Ag NPs and HIVPR is represented in Fig. 4. The authors found the Ag NPs coated with citrate molecules implied strongly anionic particles interacted with HIVPR through van der Waals forced of interaction. The naked Ag NPs with zero charges interacted with HIVPR via π π* hydrophobic-hydrophobic interactions with aromatic moieties of tryptophan, phenylalanine, or tyrosine residues via the side chain of amino acids including sulphur bearing residues of cysteine and methionine. The in silico investigations revealed the interaction of Ag NPs with Trp6, Trp42, Phe,53, and Cys95, as represented in Fig. 4.

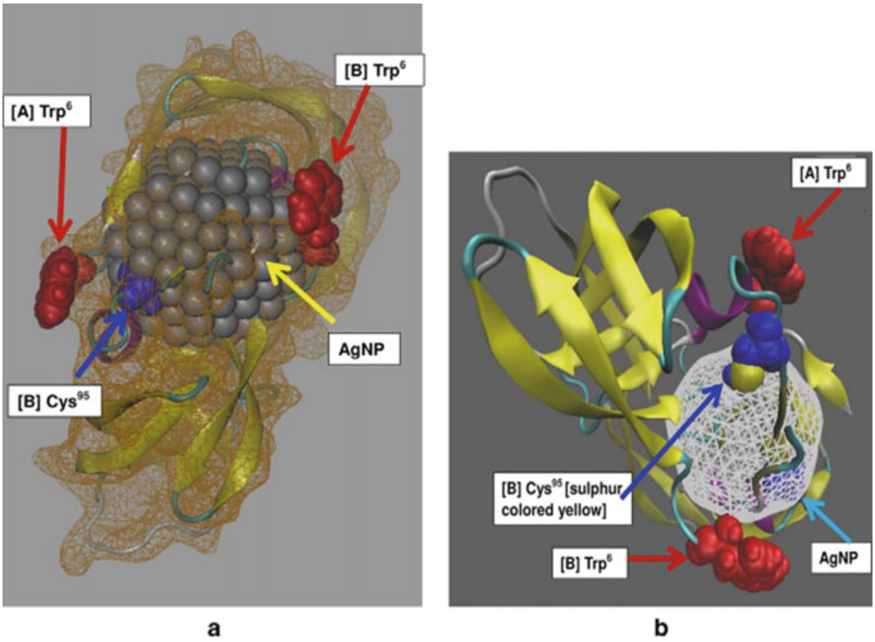

Fig. 4 HIVPR docked with Ag NPs: **a** HIVPR represented as an electron density map. **b** Ag NPs represented as an electron density map. Reproduced from Ref. (Whiteley et al. 2016) with permission

Tsai et al. (2019) demonstrated the interaction between Ag NPs (0.92–2.48 nm), HIV-1 protease (PR), and target peptides (synthesized). These interactions have been studied using three protocols: (1) Ag NPs + HIV-1 PR (24 h incubation) + peptides; (2) Ag NPS + peptides (24 h) + HIV-1 PR; (3) Ag NPs + peptides + HIV-1 PR. (Ag NPs, HIV-1 PR, and synthesized peptides were mixed inside HEPES buffer solution). The incubation of Ag NPs and HIV-1 PR allows the nanoparticles to attach on the surface of HIV-1 PR, and thus active sites of virus forming a HIVPR-Ag NPs complex as shown in Fig. 5. Further, the incubation of peptides with the Ag NPs allows Ag NPs to interact or bond with peptides to form a peptide*nanoparticle complex. This complex can protect the peptides from being cleaved by HIV-1 and let the peptide to remain intact. The HIV-1 PR and peptides interact faster than the Ag NPs interact with peptide. If the AG NPs, Peptides, and HIV-1 PR mixed, HIV-1 PR will cleave some of the initial peptides, and those peptides that remain intact will interact with Ag NPs. Thus, the authors demonstrated the late presence of Ag NPs would have no inhibition effect on HIV-1 PR activity.

4.2 *Paramyxoviridae*

This family of viruses consists of large enveloped RNA viruses infecting mammals and birds or in some cases reptiles and fish. Many of the Paramyxoviridae such as a respiratory syncytial virus (RSV), measles virus, Nipah virus, measles virus, Hendra virus, and several parainfluenza viruses are pathogenic for humans.

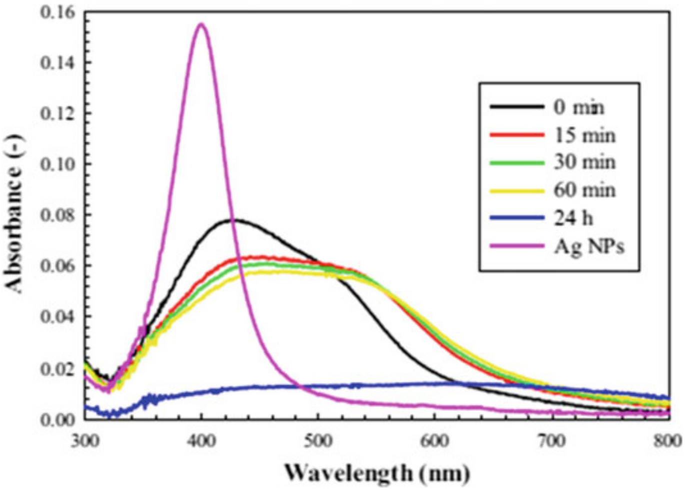

Fig. 5 UV-vis spectra of Ag NPs + HIV-1 PR. The peak at 393 nm for Ag NPs disappears with increase in incubation period. The shift of absorbance to broad band between 400 and 550 nm, and no clear peaks on 24 h contact shows the interaction of Ag NPs with the HIV-1 PR, and complete interaction at 24 h contact. Reproduced the image from Ref. (Tsai et al. 2019), with permission

RSV causes infections of the lungs and respiratory tract. This disease can cause severe infection in humans especially premature babies, infants, and adults with lung and heart diseases, or humans with a weak immune system. RSV genome consists of single RNA molecules of negative-sense RNA that encodes among others. The RSV viral envelope is exposed to two surface glycoproteins, which are (G) protein (serves as receptor binding proteins), and (F) proteins (responsible for fusion between the viral envelop and cell membrane. Following the infection of the host cell, the F protein is expressed on the surface of the cells and fuse to the adjacent cells, giving rise to syncytia development.

Sun et al. (2005) utilized Ag NPs conjugated to different proteins to analyse the inhibition of RSV infection in Hep-2 cell culture. The authors used three types of capping agents for Ag NPs such as BSA, PVP, and a recombinant F protein from RSV (RF 412). The interaction between the RSV and Ag NPs was characterized by utilizing transmission electron microscopy. The authors found that the PVP-coated Ag NPs were able to interact with the viral surface with a specific association or a regular spatial arrangement that possibly provides interactions with G proteins that are uniquely distributed on the envelope of the RSV virion. Ag NPS conjugated with BSA also interacted with RSV but without a spatial arrangement, while RF 412—conjugated Ag NPs appeared to be floating freely without any proof of regular interaction. The hypothesized interpretation for having good interaction of PVP coated Ag NPs with G proteins is because of the uniformity and smaller size of Ag NPs (4–8 nm) compared to those of RF 412 and BSA coated Ag NPs (3–38 nm). Since metal nanoparticles have to be regarded cytotoxic, especially intended for treating respiratory diseases such as RSV. Using the Trypan Blue Exclusion Assay the authors revealed the Ag NPs decorated with capping agents such as PVP, BSA, and RF 412 showed only less than 20% cytotoxicity up to a concentration of 100 μg/ml.

4.3 Hepadnaviridae

This family of the virus has a small genome of partially single-stranded, partially double-stranded circular DNA. The genome of this virus consists of two variable-length strands, a longer negative-sense strand, and a shorter positive-sense strand. These strands are arranged in such a way that the two ends of the long strand meet, and they are not covalently bonded. The shorter strand overlaps this divide and is connected to either side of the split of the longer strand through a direct repeat (DR) segment, which connects both strands. In the viral replication, the viral partially double-stranded and partially single-stranded DNA is converted into the host cell nucleus to covalently closed circular DNA formed by the viral polymerase.

There are eighteen viral species in the Hepadnaviridae family, Hepatitis-B virus is the commonly known species from this family. HBV is a partially double-stranded DNA virus that is provided with a lipid envelope. HBV consists of a string tropism for hepatocytes, and once it has penetrated the cell then the viral particles can enter into the nucleus where the HBV viral genome is completed to form a covalently closed circular DNA which, is a template for the viral mRNA transcription and the development of pre-genomic RNA (pg RNA). This pg RNA develop the template for reverse transcription by the viral encoded reverse transcriptase and develop new viral genomes. The antivirals drugs developed against HBV virus that includes nucleotide and nucleoside analogue inhibitors represent the approved pharmaceuticals exhibits excellent antiviral activity against HBV virus. However, it is well known that the effectiveness of these antiviral drugs is less due to the fast development of drug-resistant HBV strains. Lu et al. (2007) studied the inhibitory effect of Ag NPs against HBV replication. The Ag NPs used in their study are with mean diameters 10, 50, and 800 nm. The Ag NPs were prepared from AgNO3 in the HEPES buffer. The authors found that the Ag NPs with a diameter of 800 nm is highly toxic compared to the smaller size Ag NPs. Ag NPs with smaller sizes like 10 and 50 nm showed higher antiviral activity against HBV activities. The 10 nm Ag NPs can inhibit HBV of 38% for 5 μM and 80% for 50 μM, monodispersed Ag NPs solution. The authors concluded that the Ag NPs could inhibit the production of HBV RNA through the specific interaction between double-stranded DNA of HBV and the nanoparticles.

Shady et al. (2020) studied the antiviral inhibitory effect against HCV NS3 helicase and protease using green synthesized Ag NPs. The total extract and petroleum ether fraction of marine sponge (Amphimedon) were used for green synthesis of Ag NPs. The Ag NPs synthesized from Amphimedon total extract have particle size 8.22–14.30 nm, and those prepared from petroleum ether revealed particle size 8.22–9.97 nm. The authors found a diverse phytochemical class of natural products identified utilizing LCMS based metabolic investigations, followed by the reorganization of 14 known compounds through bioassay-guided isolation. The docking studies of those compounds suggested their mechanism of action, which were further proved by in vitro assays. The authors found that, among the Amphimedon sponge nakinadine B and 3,4-dihydro-6-hydroxymanzamine A, phytochemicals were found as an efficient anti-HCV drug candidate.

4.4 Orthomyxoviridae

The influenza viruses constitute the genus Orthomyxovirus, which are classified into three types of species: A, B, and C. These viruses are responsible to cause influenza, an acute respiratory disease. Type A viruses cause periodic worldwide epidemics/pandemics; both Type A and B are reported to cause recurring regional and local epidemics. These viruses are highly contagious pathogens that cause much fear among humans for its potential to develop new viruses that can jump to humans from various animal species and causing pandemics. Xiang et al. (2011) investigated the inhibitory effect of Ag NPs on the H1N1 influenza A virus. The Ag NPs with an average particle size of 10 nm were prepared and analyzed for the hemagglutination test, the embryo inoculation assay, MTT assay (Mosmann-based

3-(4,5-dimethylthiozol-2yl)-2,5-diphenyltetrazolium bromide), where these tests were utilized for investigating the inhibitory effect of Ag NPs against the H1N1 virus. The authors used MDCK cells as the infection model. The cytotoxicity of MDCK cells after 24 and 48 h exposure to Ag NPs revealed that the higher concentration Ag NPs can cause cytotoxicity, where toxicity at a silver concentration of 200 μg/ml exhibited severe toxicity than 100 μg/ml. The lower concentration of silver for e.g. 50 μg/ml exhibited a lower toxicity effect. The authors found the Ag NPs concentration between 12 and 100 μg/ml showed potential anti-H1N1 influenza A virus activity at both 72 and 96 h exposures. The 98% of cell viability was observed at a concentration of Ag NPs of 6.25, 12.5, and 25 μg/ml at 24 and 48 h. From the test conducted the authors concluded that Ag NPs could effectively inhibit the H1N1 influenza A virus. Xiang et al. (2013) investigated the inhibition of A/human/Hubei/32005 (H3N3) influenza virus by Ag NPs (9.05 nm) in vitro and in vivo. The authors demonstrated that the Ag NPs can effectively inhibit the growth of influenza virus in Mandin-Darby canine kidney cells via Hemagglutination assay. The H3N2 virus treated with Ag NPs interact with each other, resulting in the demolition of morphologic viral structures. The intranasal administration of Ag NPs in mice enhanced the survival of the mice after infected with the H3N2 virus. Also, the mice treated with Ag NPs have observed lower lung vital titer level and very small pathologic lesions inside lung tissue. The authors thus proved that the Ag Nps have a beneficial effect in inhibiting H3N2 influenza virus infection, and demonstrated that Ag NPs could be used as potential therapeutics for the prevention of outbreak of influenza virus. Li et al. (2016a) prepared Ag NPs decorated by Amantadine with antiviral properties. The authors developed the Ag NPS co-delivery of Amantadine to overcome the antiviral drug resistance. The results revealed that the Ag NPs decorated with Amantadine could inhibit H1N1 from infecting the host cell and prevent the DNA fragmentation, activity of capase-3, and chromatin condensation. Besides, this newly developed drug could prevent the accumulation of reactive oxygen species and reversed virus-induced apoptosis by the H1N1 influenza virus. Li et al. (2016b) introduced surface decoration of Ag NPs using oseltamivir (Ag@OTV) with antiviral properties to inhibit the activity of the H1N1 influenza virus. The newly developed Ag@OTV co-delivery system remarkably inhibited the accumulation of reactive oxygen species by the H1N1 influenza virus and activation of AKT and P53 phosphorylation. The authors found that this silver-based co-delivery system of oseltamivir could effectively inhibit the activity of the H1N1 influenza virus.

4.5 Coronaviridae

Coronaviride is a family of viruses enveloped, positive-strand RNA viruses with a crown-like morphology (corona is a Latin term for crown). This family of the virus includes subfamilies Letovirinae and Orthocoronavirinae. The coronaviruses belong to the subfamily of Orthocoronavirinae. The members of this family can cause respiratory, hepatic, enteric, and neurological diseases in various animals including mammals, birds, and amphibians. Up-to-date there are seven human coronaviruses (CoVs) are reported to be capable of infecting humans, in which some of them are identified in the mid-1960s, and others were detected in the new millennium. The common coronavirus (CoV) that could affect humans are HCoV-229E, and HCoV-NL63 (alphaCoVs), HCoV-OC43, and HCoV-HKU1 (betaCoVs). These types of coronavirus can cause common colds and can cause upper respiratory infections by self-limiting immunocompetent individuals. The other CoVs that affect humans includes severe acute respiratory syndrome coronavirus (SARS-CoV) (from 2002 to 2003), the Middle East respiratory syndrome coronavirus (MERS CoV) (identified in Saudi Arbia 2012), and the coronavirus disease 2019 pandemic or known as COVID-19 is caused by SARS-CoV-2 (detected in Wuhan, China). It has been reported that 1.12 million people have died so far from the COVID-19 outbreak as of October 21, 2020, 01:34 GMT (WHO 2020). Currently, there is no specific antiviral treatments are recommended for COVID-19, and no vaccines are still available. Jeremiah et al. (2020) demonstrated the effect of Ag NPs against COVID-19. The diameter of Ag NPs $\approx$ 10 nm was found effective in inhibiting extracellular SARS-CoV-2 at a concentration between 1 and 10 ppm. However, the authors observed a cytotoxic effect at a concentration of 20 ppm. The Luciferase-based pseudovirus entry assay test revealed that the Ag NPs could prevent viral entry by disrupting viral entry. The Ag NPs can interact with the proteins on the surfaces of the extracellular viruses to prevent infection at the early stage of viral entry or viral attachment by damaging the surface proteins that affect the structural integrity of the virus. Du et al. (2020) developed Au/Ag nanorods (Au@Ag NRs) to inhibit porcine epidemic diarrhea virus (PEDV), a member of the coronaviradae family. Au@Ag NRs were synthesized by coating Au nanorods with silver. Viral titer analysis showed that the developed Au@Ag NRs could effectively inhibit the PEDV infection by a magnitude of 4 orders (at a non-toxic concentration of 0.04 μM) at 12 h post-infection. The mechanism of action of Au@Ag NRs against PEDV demonstrated that the inhibition of the virus at its entry stage and thus prevented the apoptosis induced by a viral infection. The Au@AgNRs decreased the potential of mitochondrial membrane and caspase 3 activity. The authors demonstrated that a large amount of virus proliferation causes the generation of reactive oxygen species in the cells and released Ag+ ions and the exposure to Au NRs from Ag@AuNRs after the stimulation of reactive oxygen species has a higher-level of antiviral activity that is capable for long term inhibition of PEDV replication cycle. The authors suggested that the Au@AgNRs could be further improved and effectively applied as a potential treatment strategy to inhibit the activity of all the other members of the coronavirus family such as SARS, MARS, and COVID-19. Chen et al. (2016) tested the antiviral activity of graphene oxide-AgNPs (GO-Ag) sheets against feline CoV and Infectious bursal disease virus (IBDV). The authors found the GO-Ag sheets could inhibit 25% of infection by feline CoV and 23% of infection by IBDV. The authors suggested that the application of GO-Ag could be considered for personal protection equipment (PPE) to reduce the transmission of viruses.

4.6 Poxviridae

Poxviridae family of a virus is classified among 22 genera, and are further categorized into two subfamilies. Smallpox is a disease associated with this family of viruses. The Monkeypox virus (MPV) is an orthopoxvirus that is similar to the variola virus that could infect many species of non-human primates. However, MPV is also considered as human pathogens with their clinical representation similar to that of smallpox. Rogers et al. (2008) prepared silver-based nanoparticles to inhibit the infectivity induced by MPV. The authors evaluated the antiviral efficacy of various nanosized Ag NPS ranges from 10 to 80 nm with or without polysaccharide, and silver nitrate at a concentration of 12.5, 25, 50, and 100 μg/mL using a plaque reduction assay. Both the polysaccharide coated Ag NPs (25 nm) (Ag-PS-25) and non-coated Ag NPs (55 nm) (Ag-NP-55) exhibited a significant dose-dependent effect of the test compound concentration on the average number of PFU (plaque-forming unit). Besides, all concentrations of silver nitrate (excluding 100 μg/mL) and Ag-PS-10 exhibited a significant reduction in the number of PFU compared to untreated controls. The authors found no toxicity effect of silver by any test compounds except 100 μg/mL silver nitrate. The results demonstrated that the smaller-sized nanoparticle with a diameter of 10 nm was most effective at preventing MPV infection as showed by a statically significant decrease in MPV plaque formation. The possible mechanism behind the inhibition of MPV could be due to physical obstruction of interaction between the virus and the host cell. Also, there is a possibility for disruption of intercellular pathways that could diminish viral replication. The authors observed, some concentration of nanoparticle treatment led to an increase in MPV PFU that ranged from 1.04 to 1.8 fold above the control. The overall results demonstrated that Ag NPs of ≈10 nm could effectively inhibit MPV infection in vitro, and thus supporting the anti-viral therapeutic efficiency of Ag NPs.

4.7 Arenaviridae

This family of viruses composed of 18 various species of viruses and they are classified into two antigenic groups, the New World (Tacaribe complex) and the Old World group. The Tacaribe complex that mainly includes Tacaribe virus (TCRV), consists of the viral hemorrhagic fever inducing viruses such as Sabia, Guanaritio, Junin, and Mchupo. These virus groups have higher transmissibility from humans to humans through the respiratory route. TCRV is generally not a human pathogen, however, they exhibit a similar antigenic relationship with Guanarito and Junin viruses. Therefore, TCRV could serve as a model virus for Arenaviridae-derived diseases with adequate safety for laboratory analysis and without affecting humans. Speshock et al. (2010) analyzed the interaction of TCRV with Ag NPs. The authors demonstrated that the TCRV could interact with Ag NPs before the host cellular exposure and thus inhibit the viral infectivity. Two types of Ag NPs were used for this study polysaccharide coated Ag NPs (PS-Ag) and uncoated Ag NPs. They treated TCRV with different concentrations of Ag NPs such as 50, 25, and 10 μg/mL, in which the 10 nm size Ag NPs exhibited a significant reduction in the progeny of the virus. The PS-Ag was found not effective compared to the uncoated Ag NPs, however, the polysaccharide coating indeed protects the cell's toxicity of Ag NPs. Ag NPs interact with TCRV prior to the attachment of virus with the host cells resulting in reduced infectivity with 10–25 nm Ag NPs, suggested that the Ag NPs may bind to the viral glycoproteins. The TCRV glycoproteins contain cysteine residues, and the Ag NPs can interact with the thiol groups found in cysteine residues. This interaction with TCRV and Ag NPs can inhibit the internalization of the viral particle by interfering with host cellular receptor interaction with the virus. In addition, the other possible mechanism of action suggested as the Ag NPs could interact with the viral glycoprotein and inhibit the virus uncoating in the endosome. The authors concluded that the Ag NPs are effective for inhibiting a prototype arenavirus at their non-toxic concentration, the Ag NPs can inhibit arenavirus replication when administrated early after initial exposure to the virus or prior to viral infection. The authors suggested the mode of action of inhibition of virus by Ag NPs occurs during the early phase of viral replication.

5 Conclusions

The emergence of viral resistant drugs and the severe side effects of the continuous usage of drugs represents enormous obstacles that are very difficult to overcome. The introduction of nanotechnology has evolved empower to explore their biological properties of already known antimicrobial compounds, such as metals, by manipulating their sizes. In this chapter, we have analyzed the application of metal nanoparticles peculiarly silver nanoparticles, which have proved its antiviral efficiency against a broad-spectrum of viruses. In most of the causes, the mechanism of interaction is between the silver nanoparticles and viral glycoproteins could be demonstrated. However, the exact mechanism or exact site of interaction is an intriguing problem to be solved. Besides the direct interaction of Ag NPs and viral surface glycoprotein, the Ag NPs are expected to get direct access to the cell and capable to exert their antiviral activity through the interaction with the viral genome.

The research advances with the advanced medical uses of Ag, including nanocrystalline silver, have been growing very fast and numerous medical products marketed, especially due to their excellent antiviral, antimicrobial, and anti-inflammatory properties. Recently the new results pointing to the exceptional usage of Ag NPs and silver-based products in particular to prevent the infections caused by bacterial, viruses, and fungi are reported on a regular basis. The development of new low-cost antimicrobial, antiviral and antifungal products through the nanochemistry aspects of Ag NPs, their controlled synthesis routes, and tailored microencapsulation are purposeful topics to develop new lectures and laboratory research activities in renewed chemistry education curricula utilizing the recent research outcomes.

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Implementation of Novel Nanosilver Composites in Drinking Water Treatment

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Abstract Water source is an essential component for the existence of all living organisms on the surface earth. There is a necessity to protect the hygienic quality of drinking water from the pollutants to achieve the target of refining and preservative the human, animal, and plant health. To overwhelm the drawbacks of the conventional system of water purification through using common disinfection techniques. The exploitation of metal nanoparticles such as silver (Ag+) either embedded in nanocomposite membrane or the form of nanofilaments can efficiently and economically filter the contaminated water. Newly, evaluation of the nanocomposites effectiveness against bacterial pathogens and heavy metal pollutants in water supplies are proved its fatal effect on bacterial contaminants and led to avoid the most hygienic complications associated with water pollution and overcome the struggle problem of different pathogens to common disinfectants used in water treatment. This chapter discusses the mechanism of action of Nano-silver particles (Ag NPs) and its antimicrobial effect, assessment the efficiency of Ag NPs, and the potential uses of novel Nano-silver composites involving polymeric membranes, chitosan/Nano-silver composite (Chitosan/Ag NPs), rice husk-Nano-silver composite (rice husk/Ag NPs), sawdust-Nano-silver composite (sawdust/ Ag NPs), and calcium hypochlorite-Nano-silver composite ($Ca(OCl)_2$/Ag NPs) as a bactericidal filter paper for water purification.

Keywords Water purification · Antimicrobial efficiency of nano-silver · Applications · Membranes · Filters

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1 Introduction

Nowadays, the freshwater shortage and hygienic complications associated with water pollution have been increasingly growing worldwide (Hegab and Zou 2015). The expectation by 2025 estimated that two-thirds of the world's population may have difficulties accessing safe water (Ying et al. 2017). Annually, 1.7 million people worldwide are exposed to diarrheal death (which accounts for 3.1% of all deaths) due to poor water quality. It is recorded that 90% of this ratio is made up of children in developing countries (UNICEF and WHO 2015; Acharya et al. 2018; Komarulzaman et al. 2017; Morgan et al. 2017).

In developing nations, rural areas account for the highest percentages of waterborne diseases such as typhoid fever and cholera. Mostly, the prevalence rate of those diseases is due to the anthropogenic activities such as contamination or pollution through the releasing of toxic waste materials by mining industries without responsible waste treatment technique before discharge into different water sources. In addition to a lack of affordable and easy techniques to disinfect water sources prior to human consumption (WHO 2008). Using traditional filters is addressing water quality problems. These filters are made by mixing the clay materials and some combustible organic compounds (Halem 2006).

Nanosilver particles (Ag NPs) are used in a variety of applications, including pharmaceuticals, medical devices, water purification, cosmetics, food ware, clothing, and among others uses, due to their antimicrobial properties (Choi et al. 2008). Silver (Ag) is considered as an antimicrobial agent and known as a disinfectant in water treatment, also incorporated into ceramic pots (Momba et al. 2010). Furthermore, they highlighted the use of Ag NPs in water disinfection in ceramic/zeolite pot filters. There are literature studies reported that Ag NPs were effective in preventing the reproduction of microorganisms such as *Escherichia coli* (*E. coli*) (Brobbey et al. 2017), *Staphylococcus aureus* (*S. aureus*), *Aspergillus flavus* (*A. flavus*) (Morsi et al. 2017), *Enterococcus faecalis* (*E. faecalis*) and *Pseudomonas aeruginosa* (*P. aeruginosa*) (Fernández et al. 2016).

Recently, disinfectant products on Ag NPs are widely used to increasing their efficiency against isolated bacterial pathogens from different water sources and subsequently using the nanocomposites information of biocidal filter papers and/or sheets used for water purification (Mohammed 2018). Dankovich et al. (2016) revealed that Ag NPs paper sheets showed a slightly higher coliform bacteria reduction compared to Cu NPs papers ($\log^{10}$ 5.1 and $\log^{10}$ 4.8, respectively), and pointed to thin Ag NPs papers exhibited complete reduction (100%) of ~109 *E. coli* bacteria/ml. Praveena et al. (2016) proved that the efficiency of cellulose filter paper impregnated in Ag NPs could be removed *E. coli* from 99 to 100%.

Nanocomposite membranes are greatly effective for water treatment applications such as wastewater treatment, water purification, removal of microorganisms, chemical compounds, and heavy metals (Ursino et al. 2018). In this chapter, the author focused on the antimicrobial efficiency of Ag NPs, manufacturing, and applications of novel Ag/polymer nanocomposites for purification of drinking water.

2 Nanosilver Particles (Ag NPs)

Nanotechnology is defined as the understanding and control of matter at dimensions between (1 and 100 nm), where unique physical properties make possible of novel applications. In several industries, using nanoparticles (NPs) has led to many investigations. NPs exhibit dissimilar characteristics in comparison with their bulk metal states (Huwe and Fröba 2007). Ag has many applications in the fields of medicine, dentistry, clothing, catalysis, mirrors, optics, photography, electronics, and food industries (Rai et al. 2009). In addition to, the incorporation of NPs into other substrates results in a system with novel properties (Shameli et al. 2011). Rai et al. (2009) regarded Ag NPs as a new generation of antimicrobial material. They found that the bacteria did not demonstrate a resistance profile to the common antibiotics as compared to Ag NPs used. However, in some cases there exist a chance for developing bacterial resistance against Ag NPs with their continued usage (Khan et al. 2011).

3 Synthesis of Nanosilver (Ag NPs)

Ag NPs can be synthesized using various methods including various reductants such as chemical reduction (Shameli et al. 2011; Szczepanowicz et al. 2010) and photochemical reduction (Nersisyan et al. 2003), biologically synthesized Ag NPs (Sathishkumar et al. 2010), using different precursors, electrochemical techniques, and addition of capping agents that varies for various approaches (Sharma et al. 2009; Chaloupka et al. 2010). The most common method used is chemical reduction. There are many studies focused on green synthesis approaches of Ag NPs to avoid using hazardous materials whereas the Tollens method is also widely applied for the synthesis of Ag NPs. On considering the reaction to reduce Ag $(NH_3)2+$ complex that formed by reacting AgNO3 with ammonia for the synthesis of Ag NPs, both benign monosaccharides and polysaccharides are used with avoiding hazardous chemicals and the reaction is environmentally friendly. Regarding the size of synthesized Ag NPs some literature have reported that Ag NPs synthesized with the size ranges from 50 to 200 nm and silver hydrosols size ranges from 20 to 50 nm (Panacek et al. 2006; Saito et al. 2003). In general, the size of silver nanoparticles ranges from 1 to 100 nm (Chaloupka et al. 2010).

During the synthesis of Ag NPs, aggregation of particles can hinder the production of nanosilver with smaller and uniform sizes. This aggregation of synthesized nanosilver may reduce their antimicrobial activity for those intended for biological and antimicrobial application purposes (Morones et al. 2005; Zhang and Oyanedel-Craver 2012). In the manufacturing process of Ag NPs incorporating stabilizers could ensure their stability in aqueous solutions. Absorption of the stabilizing molecules onto the nanoparticle surface depends on the molecular weight, charge density, and ionization of the stabilizing molecules (Sharma et al. 2009; Panacek et al. 2006; Kvitek et al. 2008; Ren and Smith 2012).

4 Characterization of Nanosilver (Ag NPs)

The characterization of Ag NPs is important to evaluate the functional aspects of the synthesized particles. Characterization is performed by a variety of analytical techniques, including UV-vis spectroscopy, Fourier transform infrared spectroscopy (FTIR), X-ray diffractometry (XRD), X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), dynamic light scattering (DLS), scanning electron microscopy (SEM), and atomic force microscopy (AFM) (Zhang et al. 2016). SEM methods provide surface images, that are associated with sample properties such as porosity, homogeneity, roughness. SEM images are used to get information about lattice mismatch and compatibility. They are indispensable in characterizing PNCs. The AFM uses a sharp tip to scan across the sample and appropriate to evaluate the roughness of morphology (Magonov and Reneker 1997; Wan et al. 2015). Meanwhile, TEM image allows a qualitative understanding of the internal structure, spatial distribution of the various phases. XRD pattern provides the crystallinity and lattice structure of nanocomposite. Small-angle X-ray scattering (SAXS) is typically used to observe structures of the order of 10 Å or larger. Figure 1 clarified the morphological shape of Ag NPs that characterized utilizing TEM.

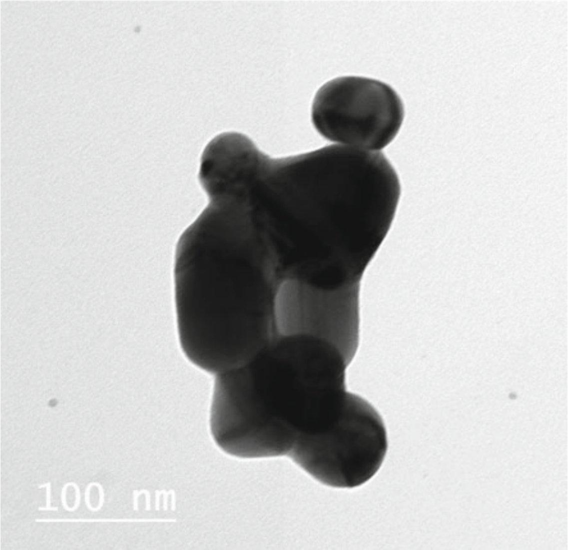

Fig. 1 Transmission electron microscopy (TEM) of silver nanoparticles (Ag NPs)

5 Mechanisms of Antimicrobial Efficiency of Ag NPs

Antimicrobial ability is a well-known property of Ag NPs. The broad spectrum of microorganisms can be inactivated by Ag NPs. There are three mechanisms of the antimicrobial properties of Ag NPs proposed in Fig. (2): 1. Could attach to the cell wall and disrupt the permeability and respiration functions of the cell membrane and thus kill the cells (Morones et al. 2005; Sondi and Salopek-Sondi 2004; Park et al. 2011), 2. Reactive oxygen species (ROS) can be generated on the surface of nanoparticles and cause DNA damage through exerting oxidative stress (Feng et al. 2000); 3. Ag+ released from Ag NPs can also cause disruption of ATP production and DNA replication (Cumberland and Lead 2009; Kittler et al. 2010). Recently, the antibacterial activity of Ag NPs has been discussed by López-Heras et al. (2015). Their activity depends on several physicochemical properties of the particles, including shape, their size, and chemistry. Ag NPs mitigate the bacterial activity due to a synergistic effect between direct particle specific biological effects and the release of Ag+ ions. Moreover, Ag NPs can stick to the bacterial cell wall that negatively influences the permeability and respiration of the bacteria, while particles affect the cell membrane resulting in lysis of the cell. In this way, the Ag particles can go through the cytoplasm of bacteria, causing DNA damage (Wei et al. 2015; Koseoglu-Imer and Koyuncu 2017).

The toxicity of Ag NPs toward different microorganisms was evaluated in aquatic systems. Gao et al. (2009) reported that the LC50 (µg/L) of Ag NPs against *Escherichia coli* (*E. coli*) and *Ceriodaphnia dubia* (*C. dubia*) is less than 112.14 and 6.18 µg/L, respectively. Furthermore, the toxicity of Ag NPs against other

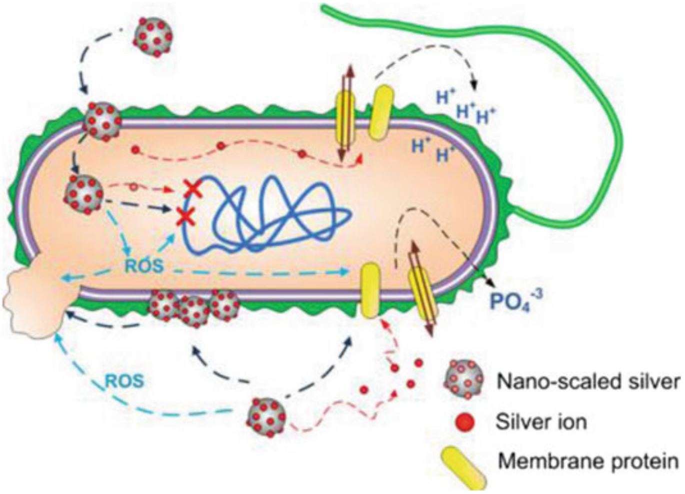

Fig. 2 Mechanisms of interaction between Ag NPs and bacterial cells (Marambio-Jones and Hoek 2010)

microorganisms was also reported such as *Leuconostoc mesenteroides* (Vertelov et al. 2008), *Staphylococcus aureus* (Kim 2007), *Bacillus subtilis* (Yoon et al. 2008), and *Pseudomonas aeruginosa* (Balogh et al. 2001). However, the inactivation of bacteria depended on the type of bacterial cell as well as the water hardness and alkalinity of the synthetic media.

The antimicrobial performance of Ag NPs affected by natural organic matters. Authors in previous studies (Zhang et al. 2012; Zhang and Oyanedel-Craver 2012; Gao et al. 2009; Fabrega et al. 2009) found that, the organic matters can adsorb on the surface of Nano-silver and mitigate the physical contact between the bacterial cell wall and Ag NPs. In the organic matter, adsorption can also inhibit their dissolution, resulting in a decreasing antimicrobial property (Liu and Hurt 2010).

6 Application of Nanosilver in Purification of Drinking Water

Currently, in the world according to WHO/UNICEF, there are 783 million people do not have access to safe drinking water (WHO/UNICEF 2012). Boschi-Pinto et al. (2008) reported that approximately, 1.87 million childhood deaths are occurred due to water-borne diseases (Boschi-Pinto et al. 2008). Furthermore, the conventional system of water treatment and delivery approaches are considered unfeasible in these under-developed districts because they need high capital investments, a high quantity of water source, a high cost of maintenance, and these require users to pay for the treated water (Van Halem 2006).

A ceramic water filter (CWF) is a simple device that can eliminate water-borne pathogens. This filter is manufactured using pressing and firing a mixture of clay and a burnable organic material such as flour, rice husks, and/or sawdust before treatment with Ag NPs (Oyanedel-Craver and Smith 2008). The filter is formed using a filter press, after which it is air-dried and fired in a kiln. This forms the ceramic material and burns off the sawdust, flour, or rice husk in the filters, making it porous and permeable to water. CWFs are highly effective in removing 90–99.99% of bacteria and more than 99% of protozoa from drinking water (Brown and Sobsey 2010; van Halem et al. 2009; Lantagne 2001). The mechanism of action of CWFs are two mechanisms include (a) removing of microorganisms by size exclusion or adsorption; (b) the presence of Ag NPs or Ag+ inside of filter can inactivate pathogens (Bielefeldt et al. 2009). Figure 3 showed the pathogenic bacteria was trapped inside of CWFs impregnated with Ag NPs (Table 1).

The previous studies have addressed the pathogen reduction of silver-coated CWFs manufactured with different clay materials that may affect the performance of CWFs. When applying silver on CWFs, a variety of water sources is used at factories to prepare silver solutions, from untreated surface water to treated water. Water properties at the filter users also vary with location. Various studies have reported a reduction in antibacterial properties of Ag NPs with an increased size of

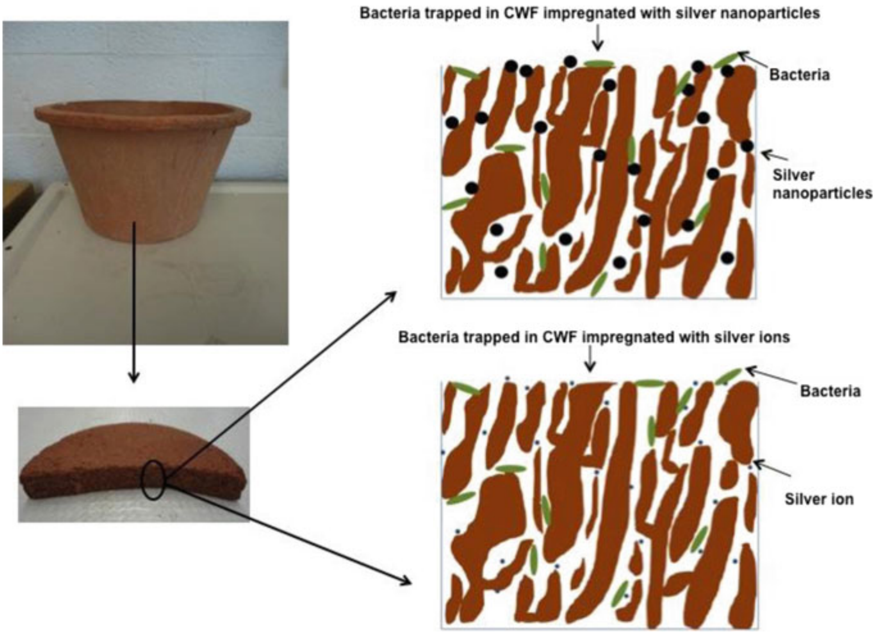

Fig. 3 Bacteria trapped in CWF impregnated with nanosilver (Ag NPs) (Zhang 2013)

Table 1 The performance of silver coated CWFs manufactured with different clay materials for removal of bacterial pathogens (Zhang 2013)

Clay type	Nanoparticles	Pathogenic bacteria	Reduction performance of pathogen (LRV %)	References
Nicaraguan	Ag NPs Ag NPs	*E. coli* *Clostridium*	2.9 3.3–7.9	Fahlin (2003) Van Halem (2006)
Guatem lan, Redart, and Mexican	Ag NPs	*E. coli*	>97.8	Oyanedel-Craver and Smith (2008)
Cambodian	Ag+	*E. coli*, bacteriophage	90–99	Brown and Sobsey (2010)
Guatemalan	Ag NPs	*E. coli*	4.56	Kallman et al. (2011)

NP clusters due to aggregation in the presence of divalent ions such as Ca^{2+} and Mg^{2+} (Zhang et al. 2012).

The different chemical parameter of water quality has an impact on the disinfection performance of nanosilver in the aqueous solutions (Zhang and Oyanedel-Craver 2012), these parameters have not been evaluated on CWFs either in the field or in laboratory tests. Due to the application of silver, desorption of silver from coated CWFs has been reported during the first flushes of water. Using a phosphate buffer as an influent solution reported a decrease in silver concentration in effluent from Ag NPs impregnated CWFs to below the Environmental Protection Agency (EPA) maximum permissible level (MPL) for silver in drinking water (0.1 mg/L) within few flushes, suggested by (the United States Environmental Protection Agency; USEPA).

7 Assessing of the Disinfection Efficiency of Nanosilver

The disinfectant properties of Ag NPs have been widely studied. Momba et al. (2010) clarified the disinfection properties Ag NPs and assessing their effectiveness. They found that disinfection efficiency depends on the size and shape of the NPs besides its dose, and the target organisms. The most susceptible organism was Gram-negative bacteria such as *E. coli* compared to Gram-positive species such as *S. aureus*, possibly because of differences in the structure of their cell walls. Moreover, Gram-negative bacteria have a 2–3 nm layer of peptidoglycan between the cytoplasmic membrane and outer membrane whereas Gram-positive bacteria have no outer membrane, but it has a 30 nm thick peptidoglycan layer. Morones et al. (2005) examined both the exterior and interior walls of Gram-negative bacteria (*E. coli, P. aeruginosa*, *S. typhus,* and *V. cholerae*) after treatment with Ag NPs suspensions, using Scanning Electron Microscopy (SEM).

8 Implementation of Novel Silver Nanocomposites for Water Treatment

Silver nanoparticles can be utilized in the manufacturing of novel nanocomposite membranes for water treatment applications (Prince et al. 2014). Recently, new types of nanocomposite membranes have been commercialized for a variety of filtration applications. Membranes containing nanosilver are used for Reverse Osmosis (RO) as recorded by Sterlitech (2018) and for water filtration by Lenntech (2018) and LG Chem (NanoH_2O composite membranes, 2018) (Hofs et al. 2013).

The silver nanocomposites due to their antimicrobial properties that give potential for numerous applications such as disinfection of medical devices, biomaterials, and water treatment, etc. In fact, Ag NPs are commonly used for antimicrobial applications. Zapata et al. (2016) reported the preparation of silver nanofibers in polyethylene for antimicrobial medical applications. While applying silver nanocomposites for water treatment, the human toxicity aspects of silver are of great concern. When the silver is released from the polymeric membrane, it must be investigated to avoid the health and environmental consequences. For drinking water, the World Health Organization's (WHO) guidelines reported that Ag salts can be used as bacteriostatic agents; according to the WHO guidelines the daily intake of silver from drinking water that only levels up to 0.1 mg/L, and it could be tolerated without any health risk (Gorchev and Ozolins 2008).

The development of nanocomposites is essential for improving the efficiency and mechanical properties of the materials that are used as a major component for various application purposes. In the field of nanotechnology, the challenges are associated with the development of nanocomposites and their application area from structural to functional and multifunctional composites (Ranđelović et al. 2012). In this way, a great improvement of composite materials based on using Ag NPs with different capping agents through processing for enabling the development of nanocomposites can be used in various application such as electrical, cosmetics, thermal, and water purification, that are relevant to current technological needs (Chung 2010; Ranđelović et al. 2012). Application of most nanocomposite materials is intended for long-term and outdoor usage. This is an important aspect of the need for nanocomposites stability (Allen et al. 1998).

9 Nanosilver Composite Membranes for Water Treatment

Generally, membrane operations such as microfiltration, nano-filtration and reverse osmosis are commonly applied in a wide range of water treatment applications such as in potable water production, water recycling in aerospace, pharmaceutical, biological and food industries. The microfiltration (MF) is a pressure-driven process that applies a membrane to separate particles from the aqueous solution. The contaminated fluid when passes through the specially designed pore-sized membrane the microorganisms and other suspended contaminant particles are separated. The filters used for this process are designed specially to prevent bacteria, protozoa, algae, and other sediments. The nanofiltration (NF) membrane filtration technique utilizes the nanometre-sized pores of the membranes. The pore size of NF membranes (1–10 nm) are smaller than MF (0.1–10 μm), but the NF membrane pore sizes are larger than those used in the reverse osmosis technique. The specific applications of NF membranes include the removal of heavy metals from process streams for reuse of water, reduction of salt content in water, softening of hard water. On other hand, the RO process is utilized as a partially permeable membrane for extracting unwanted molecules ions and even larger particles from drinking water. In this process, pressure is applied to overcome the osmotic pressure. This method is applied in drinking water purification, wastewater, and water treatment, reverse osmosis water purification and food industries, etc.

The preparation of nanosilver composites membranes has been reported by several works of literature (Gorchev and Ozolins 2008; Sile-Yuksel et al. 2014; López-Heras et al. 2015) being cellulose acetate (CA), polyacrylonitrile (PAN), chitosan, and polysulfone (PSF) are the most commonly used polymeric materials for the preparation of silver nanocomposite membranes. Sile-Yuksel et al. (2014) showed the effect of Ag NPs location in different types of polymer matrices. The authors clarify how the location of Ag NPs changed depending on the type of polymer in Fig. (4) and subsequently, this location influences the antibacterial activities of the nanocomposite membranes. There are three different polymers such as polyether sulfones (PES), PSF, and CA, was used to fabricate nanocomposite membranes at three different ratios of Ag NPs (0.03, 0.06, and 0.09 w/w). The authors found that Ag NPs are homogeneously located along with the membrane matrix, but they protruded along the top surface of the PSF and PES membranes. Oppositely, the increase of Ag NPs/polymer ratio tended to increase water permeability in PSF (200 > 215 > 225 > 235 L/m^2 h bar) while it comparatively decreased using PES and CA polymers (360 < 325 < 250 < 220 and 80 < 67 < 46 < 40 L/m^2 h bar).

Results in Table 2 showed the main uses of these membranes are for water treatment. Furthermore, the generated nanocomposite membranes are described, as well as an overview concerning the type of membrane technology where the membranes were applied. The silver nanofillers in polymeric membrane preparation used for water treatment are described and the antifouling and antibacterial properties of nanocomposite membranes are reported.

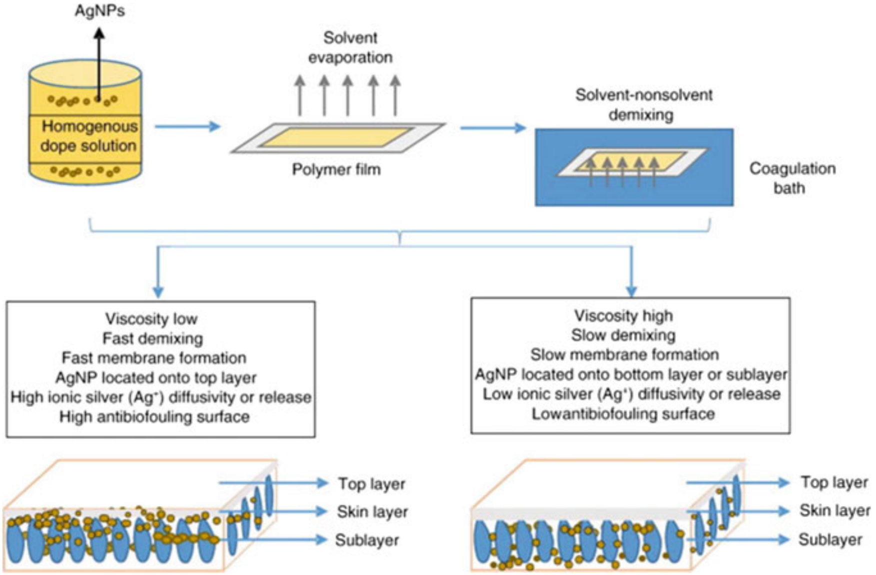

Fig. 4 Description of the location of Ag NPs in the nanocomposite membranes developed by Sile-Yuksel et al. (2014)

Table 2 Application of Nano-silver (Ag NPs) into polymeric membranes for water treatment prepared by Ursino et al. (2018)

Nanoparticle	Membrane process	Application	Polymer matrix	Concentration of Ag NPs	References
Ag NPs	(UF)	Water purification	PES	0–0.32–0.64 wt%	Ahmad Rehan et al. (2016)
		Evaluation of antifouling and antibacterial properties in composite membranes for water treatment. Model bacteria: *E. coli*	PES, PSF, CA	0.03–0.06–0.09 wt%	Sile-Yuksel et al. (2014)
		Evaluation of antifouling and antibacterial properties in composite membranes for water treatment. Model bacteria: *E. coli*. Mixture model: BSA and dextran solution	PES	0.25–0.5–1.0 wt%	Koseoglu-Imer et al. (2013)
		Evaluation of antifouling and antibacterial properties in composite membranes for water treatment. Model bacteria: *P. putida*. Mixture model: BSA	PES	3.6 gr	Hoek et al. (2011)
		Evaluation of antifouling properties in composite membranes for water treatment Mixture model: polyethylene glycol (PEG) and Dextran solutions	PES	0–0.1–0.4 wt%	Escobar and van der Bruggen (2015)

(continued)

Table 2 (continued)

Nanoparticle	Membrane process	Application	Polymer matrix	Concentration of Ag NPs	References
	(NF)	Evaluation of antibacterial properties in composite membranes for water treatment Model bacteria: *E. coli, S. aureus*	CA	0.5–1–2 wt%	Andrade et al. (2015)
		Evaluation of antibacterial properties and removal of salt (Na_2SO_4). Model bacteria: *E. coli*	PVA	10 Ml	Zhang et al. (2016)

10 Calcium Hypochlorite—Silver Nanocomposite ($Ca(OCl)_2$/Ag-NPs)

The sensitivity of *E. coli* strains isolated from water to chlorine [both calcium hypochlorite ($Ca(OCl)_2$) and sodium hypochlorite (NaOCl)] were evaluated at the different concentrations and exposure times. *E. coli* isolates when exposed to three concentrations of chlorine (6, 9, and 12 mg/L) for a contact time of 120 min. The author found that *E. coli* strains were highly sensitive to chlorine disinfection (Bester 2015). The chlorine concentration used for effective water disinfection dependent on certain characteristics such as chemical oxygen demand (COD) and total suspended solids (TSS) may limit effective chlorine as a disinfectant (Van Haute et al. 2013). The organic content of the water source may react with chlorine and lowers the amount of available chlorine for microorganisms. However, *E. coli* bacteria were greatly affected by the COD load in water during the disinfection process (Van Haute et al. 2013).

Increasing the disinfectant potent of the common disinfectants such as calcium hypochlorite used for water treatment is recently studied by Mohammed (2018), the author found that the efficiency of calcium hypochlorite loaded on silver nanoparticles ($Ca(OCl)_2$/Ag-NPs) was strongly lethal (100%) to the different bacteria (*E. coli*, *K. pneumoniae, and S. aureus*) isolated from drinking water supplies after 180 min of exposure. In addition to $Ca(OCl)_2$/Ag-NPs could be used as antimicrobial filter sheets for water purification that are suitable for removal of bacterial contaminants such as total coliforms, and fecal coliforms bacteria as shown in Fig. 5.

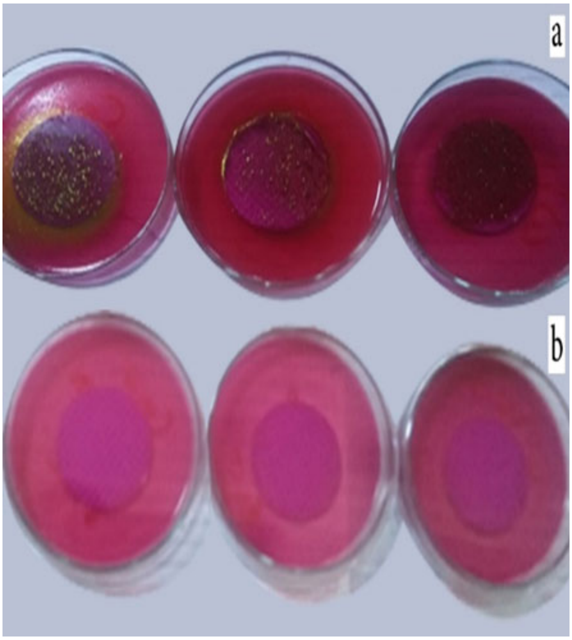

Fig. 5 The morphological shape of indicator coliforms bacteria on M les endo agar media **a** before and **b** after using the bactericidal filter paper impregnated in Ca $(OCl)_2$ disinfectant loaded with Ag-NPs, absence of bacterial growth was clarified

11 Rice Husk and Sawdust Loaded on Nano-Silver Composite (Rice Husk/Ag NPs and Sawdust/Ag NPs)

Rice husk is one of the low-value agricultural waste materials which have been used as a bio-adsorbent especially to heavy metals. Various studies have found that rice husk was capable to absorb heavy metals such as lead, mercury, selenium, cadmium, copper, and zinc in the water. Furthermore, using chemically modified rice husks showed higher absorption capacity than unmodified rice husks (Noor Syuhadah and Rohasliney 2012). As well, there are studies clarified that sawdust and risk husk are promising efficient adsorbent material for the removal of heavy metals from water source (Naiya et al. 2009). Investigation of risk husk/Ag NPs composite as a bio-adsorbent material are studied recently for the removal of heavy metals (Pb and Cd) from a water source and improving the physicochemical properties of water quality. Abdou et al. (2018) clarified that rice husk loaded on Nano-silver composite was highly effective as a bio-adsorbent material for improving water quality parameters and decreasing heavy metal concentrations in water supplies compared to sawdust/Ag NPs composited. Furthermore, water quality parameter (physio-chemical) values were gradually decreased after using rice husk and/or it loaded on Ag NPs compared to sawdust and sawdust/Ag NPs composite.

12 Chitosan-Silver Nanocomposite (Chitosan/Ag NPs)

Chitosan is derived from chitin and originated from many sources such as (crab shell, shrimp, and prawn) and it is the second most plentiful natural biopolymer and is relatively cheap (Gu et al. 2003). It has attracted considerable interest due to its biological properties, such as antimicrobial activity, antitumor activity, and immune-enhancing effect. The mechanism of action is binding to the negatively charged bacterial cell wall, and consequent destabilization of the cell envelope and altered permeability, followed by attachment to DNA with inhibition of its replication (Dutta et al. 2011). The antibacterial activity of chitosan is influenced by several factors, including concentration, pH, bacteria species, solvent, and molecular mass (Helander et al. 2001). Enhancement of antimicrobial properties of chitosan by loading it on various metals. Among all antimicrobial metals, silver (Ag) is well known for its strong antimicrobial agent to a wide range of microorganisms in addition to some processing advantages such as low volatility and high-temperature stability (Kumar and Münstedt 2005). The antimicrobial efficacy of chitosan/silver nanocomposites against *S. aureus* and *E. coli* bacteria was studied by Ali et al. (2010) and Cao et al. (2010). Kaur et al. (2013) found that chitosan/Ag NPs composite has a greater inhibitory effect against *S. aureus*, *P. aeruginosa* and *S. entrica* compared to chitosan alone. Furthermore, Saifuddin et al. (2011) prepared nanosilver particles embedded in chitosan that is a biodegradable natural polymer for the removal of pesticides from water using microwave irradiation. Naima et al. (2017) showed that Ag NPs destroy the *E. coli* bacteria completely in both filter paper and cellulose acetate (CA) membrane that is prepared after mixing the chitosan with Ag NPs. Bahrami et al. (2019) and Youssef et al. (2014) confirmed that adding a higher percentage of Ag NPs to biopolymer cause greater inhibition zones diameter against tested microorganisms. It is imperative to note that the antimicrobial effect in these applications is related to the release of nanoparticles from polymer nanocomposites and their interaction with microorganisms by direct contact (Cushen et al. 2013). In addition, Mohammed (2020) pointed to evaluating the potential impacts of nanocomposite on the surrounding environment should be applied besides positive effects in different fields of applications.

13 Conclusions

The improvement of drinking water quality (micropollutants, the physiochemical properties, and removal of heavy metal contaminants) is achieved by using water purification technologies. Different nanotechnologies are used that afford the properties of ideal nanoparticles for developing a technology of rapid drinking water treatment. Nanoparticles used may remove organic compounds, metal ions, and microorganisms. Among these technologies of water purification, Nano-adsorbents, nanomembranes, and disinfectants/nanocomposites are most promising.

There are different types of disinfectants that are commonly used for purification of water in addition to frequently using some of these disinfectants led to the presence of resistant bacteria that highly resist disinfectants used. Recently using disinfectant products loaded on Ag NPs is used to increase their efficiency against pathogenic bacteria isolated from different water sources and subsequently using the nanocomposites information of biocidal filter papers and/or sheets used for water purification.

The measurement of the long-term effects of available new technologies in water purification should be investigated. Furthermore, the commercialization of these technologies is possible only by knowledge of their long-term performance in the water treatment. As well, the adoption of an innovative technology strongly depends on the cost-effectiveness and potential hazards. The potential hazards of Nanomaterials used in water treatment should be studies on lab animals to examine the cytotoxicity of those materials before their applications.

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