Chapter 10
Role of Nanomaterials in Food Preservation

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10.1 Introduction

Foods are composed of carbohydrates, proteins, fats, fiber, vitamins, minerals, and water, thus making them more susceptible to microbial and chemical changes. Microbial contamination of food is often via air, water, soil, and raw materials used as food. Microbial enzymes secreted during their multiplication split complex components like carbohydrate, protein, and fat to different undesirable products like various organic acids, amino acids, H_2S, NH_3, and free fatty acids. These chemical/enzymatic reactions change the color, flavor, texture, taste, nutrient value, and shelf life of the food products. Food quality is also affected in the presence of light, oxygen, etc. Rancidity is an outcome of similar hydrolytic reaction of fats. Unsaturated fat is oxidized to peroxide compounds in the presence of oxygen and oxidizing agents. This phenomenon is restricted in the presence of antioxidant, e-donating agents, and reducing agents.

Some of the spoilage-causing microbes may be pathogenic, which produce different toxins or cellular components detrimental to human health. Thus an effective strategy of food preservation could be by impeding microbial contamination and their action. Microorganisms may be eliminated by different physical and chemical methods. Best physical method is heat treatment. But excessive heat may change the nutritional quality of the foods. So, recently hurdle technology is used to combat this problem. Different selective nanoparticles are able to kill the microorganisms

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and have reducing properties, thereby demonstrating the plausibility of their application for preservation of the quality of food. Hence nanoparticles may be used for preservation of foods.

Nanotechnology in food industry is a less-experimented area. Few studies that have already been carried out illustrate that nanotechnology has a potential impact on food system, particularly in food safety, molecular synthesis of food products, etc. As nanomaterials exhibit phenomena different from their bulk counterpart depending on their size and shape, so use of nanomaterials in the food chain impedes size- and shape-guided biological processes on food systems, particularly in processed food products and food packaging. Briefly, ingredients of living organisms such as proteins, DNA, amino acids, hormones, etc., consist of hierarchical organization of atoms and molecules at nanoscale; hence their tuning or modification becomes easy by nanomaterials due to dimension matching.

Presently, nanomaterials of metal (e.g., Ag, Fe, Ca, Se, etc.), metal oxides (viz., ZnO, MgO, TiO_2, CeO_2, etc.), polymer (chitosan, polypyrrole, polyamide, etc.), and organic materials (lipid, protein, carbohydrate, etc.) are being used in different food sections. In short, it may be stated that nanotechnology opens the door of new array of next-generation food products having good quality and high security. For example, fresh fruit, vegetables, meat, poultry products, and fish seem to be potential vehicles for transmission of pathogenic microbes that leads to foodborne diseases. Here, nanomaterials have rescued us due to their antimicrobial activity. Suitable nanomaterials are either mixed directly to foods or used in packaging system.

Utility of nanotechnology as a tool in the food industry includes (1) increased security of manufacturing, processing, and shipping of food products through sensors for pathogen and contaminant detection, (2) devices to maintain historical environmental records of a particular product and tracking of individual shipments, (3) systems that provide integration of sensing, localization, reporting, and remote control of food products (smart/intelligent systems) and that can increase efficacy and security of food processing and transportation, and (4) encapsulation and delivery systems that carry, protect, and deliver functional food ingredients to their specific site of action. Nanodispersions and nanocapsules are available for delivery of the functional ingredients of drugs, vitamins, antimicrobials, antioxidants, flavorings, colorants, and preservatives. Association colloids, i.e., surfactant micelles, vesicles, bilayers, reverse micelles, and liquid crystals, are used to encapsulate and deliver polar, nonpolar, and/or amphiphilic functional ingredients as depicted in Figs. 10.1 and 10.2, respectively. Nanotechnology is directed for food applications by two different approaches as "bottom up" (deals with building and growing of larger structures from atoms and molecules) and "top down" (is based on a physical processing of the food materials).

10.2 Nanotechnology in Food Quality

Nanotechnology is being significantly used to improve food qualities such as color, flavor, nutrition value, and flow character or to reduce detrimental effect of excess fat, sugar, salt, etc., of the food products.

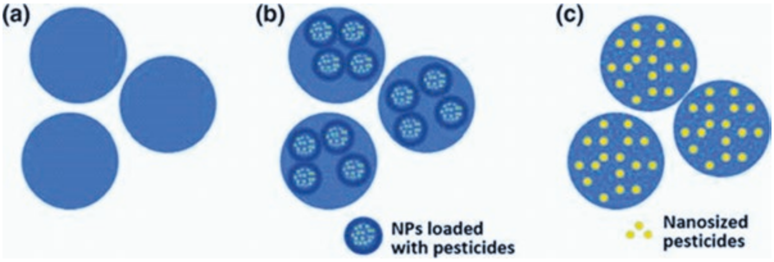


Fig. 10.1 Types of nano-loaded products

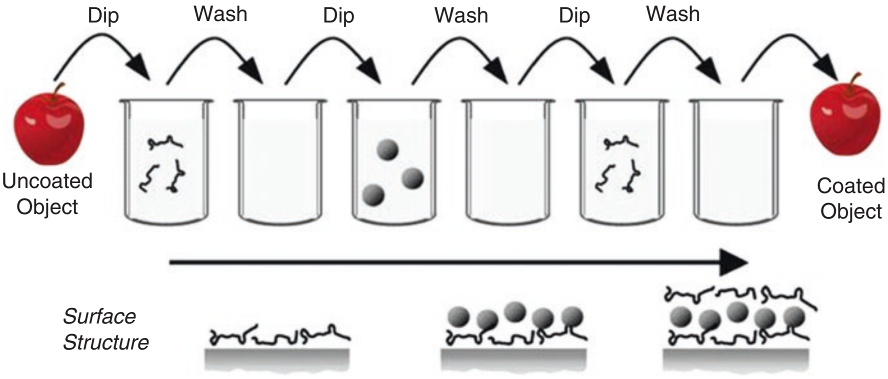


Fig. 10.2 Formulation of nanocoated products

- As an example, triacylglycerol immobilization onto functionalized SiO_2 nanoparticles has been observed to hydrolyze olive oil; hence adaptation and stability of the food get increased significantly (Bai et al. 2006).
- Ceramic nanoparticles exhibit catalytic activity that limits thermal polymerization of oil and results in crisper deep-fried food with longer shelf life.
- Often, enzymes are used to improve flavor and nutritional quality of food. Few enzymes are insoluble in water; hence their effects get decreased due to nonuniform dispersion in food matrix. However, nanotechnology has offered certain nanomaterials on which enzymes can be immobilized, thereby increasing dispersion in food matrix and enhancing enzyme activity.
- Nano-supplements, nano-additives, and nano-delivery system are other important developments of nanotechnology to improve quality of the food products. For example, nano-supplements, added to food stuffs, increase taste and texture of food products along with minimization of fat of the food, yielding healthier food.
- Nano-textured mayonnaise, spread over ice cream as nano-supplement, reduces fat while imparts creaminess of the ice cream.

- The use of beta-carotenes and phytosterol functionalized nanoparticles in food system helps to prevent cholesterol accumulation (Mozafari et al. 2008). Additives of Ag, Fe, Mg, Ca, Se, etc., used for coloration and preservation or to increase flavor and taste, are often found to be insoluble or not well dispersed in water in macroscopic form; thus their efficiency gets reduced. To increase dispersion, functionalization with surfactant or emulsification is required. Alternative is synthesis in nano-dimension, wherein dispersion increases and consequently activity gets enhanced.
- Functional ingredients like vitamins, antioxidants, flavors, preservatives, bioactive peptides, probiotics, etc., offer improvement of quality of processed foods. They are used as a part of a delivery system, rather than in pure form, that cause instability under processing conditions (temperature, moisture, gases (O_2, CO_2, etc.), light, pH, etc.). Generally, ingredients are classified according to their molecular and physical forms such as polarities (amphiphilic/polar/nonpolar), molecular weights (low/high), physical states (gas, liquid, solid), etc., and depending on biochemical characteristics of these ingredients, several strategies like immobilization, nanodispersion, association colloids, and nanoencapsulation have been developed to protect them from harsh chemical or biological environment causing degradation and to deliver them to desired sites keeping taste and texture the same.
- Nano-colloidal strategy is adopted for encapsulation and delivery of polar, nonpolar, and amphiphilic ingredients.
- Nano-micelle process is employed to encapsulate nonpolar bioactive ingredients like lipid, vitamin (A, C, E, Q_{10}, etc.), antioxidant, flavorants, etc.
- Sustained release of ingredient at target sites is another feature of delivery system that has to be considered for the development of efficient delivery system wherein sustained release is achieved on the basis of biological environment like pH, temperature, etc. Different biopolymers and copolymers are used here. For example, cochleate which is a multilayer structure of lipid bilayer in spiral form can encapsulate bioactive materials with poor water solubility, hydrophilic molecules, drug, peptide, protein, etc., and exhibits its strong potency in nanoscale. Biopolymer matrices like chitosan nanoparticles and nanofibers show potency for this purpose. Nowadays, graphene and metal chalcogenide nanoparticles are used as durable and efficient carrier of antioxidants, antibrowning agents, and enzymes, to extend shelf life (Vargas et al. 2008).
- Lipid, protein, and carbohydrate nanoparticles in next-generation delivery system.

Very recently, it has been investigated that nanomaterials of lipid, protein, and carbohydrate can be used to develop efficient delivery system of food ingredient. Main advantage lies with easy digestion in gastrointestinal tract. For example, nanocolloidal delivery system has been developed using lipid nanoparticles for hydrophobic bioactive ingredients of color, flavor, nutrients, nutraceuticals, antioxidant, etc. The major advantage of using lipid nanoparticles is that they also act as source of functional ingredient, thus helping to improve delivery process. There exist few optically transparent lipid nanoparticles, desirable for clear food products and beverage. Lipids, used here, are neutral lipids such as triacylglycerol, diacylglycerols, monoacylglycerols, terpene, etc., or polar lipids like surfactant, phospholipid, free fatty acid, etc. Depending on ingredients to be delivered, neutral or polar lipids with size ranging from few nanometers to few hundred nanometers are employed. In this case, it may be stated that the strategy of surfactant micelle-based delivery is suitable for small-sized nanoparticle, while oil droplet or solid is preferred for others.

- Natural protein nanoparticles in the form of casein micelle, found in bovine milk and other dairy products, are being widely consumed by us starting from ancient time. Similar to lipid, protein nanoparticles are also used in delivery system for color, flavor, preservatives, vitamins, minerals, etc. Protein nanoparticles of different sizes ranging from few nanometers (globular protein) to several nanometers (micelle, zein, gliadin, whey protein, etc.) are prepared from protein molecules by physical interactions like hydrophobic, van der Waals, hydrogen bonding, and electrostatic interaction or covalent bonding according to requirement. Physical bond primarily depends on reaction conditions, determined by nature, pH, ionic strength of solvent, etc., while covalent bond gets formed only at a particular physicochemical condition. Generally, protein nanoparticles are prepared in spherical shape, but in some cases fibrous structure is required to develop delivery system. Fate of the protein nanoparticles in gastrointestinal tract significantly depends on their shape, size, and surface charge.
- Digestible or indigestible carbohydrate nanoparticle which is defined as assembled structure of polysaccharides has been successfully adopted to develop delivery system of functional ingredient. These are synthesized from starch, cellulose, pectin, xanthan, etc. Carbohydrate nanoparticles can be prepared either by top-down approach by breaking larger structured polysaccharides such as starch, cellulose fibril, chitosan fibril, etc., or bottom-up approach starting from polysaccharide molecules. In general the former strategy leads to formation of spherical nanoparticles, whereas the latter one gives both spherical and fibrous nanostructures. It has been studied that the digestion of the carbohydrate nanoparticles significantly depends on source from which it has been derived. For example, certain type of starch-derived carbohydrate readily gets hydrolyzed by amylases in upper gastrointestinal tract, but there also exists polysaccharide-derived carbohydrate, those that don't get digested in upper gastrointestinal tract; rather they are fermented in lower gastrointestinal tract in the presence of enzymes.

10.3 Nanotechnology in Food Packaging

10.3.1 Freestanding Packaging

Food packaging is another essential aspect of food industry which needs care, since good packaging can only protect food from degradation retaining food quality, increasing shelf life, providing nutritional information to consumers, etc. In addition, packaging materials must have high mechanical strength, stability, temperature resistivity, etc. Earlier, various degradable copolymers, viz., ethylene vinyl alcohol, polyimides, polyethylene terephthalate, etc., or biopolymers, viz., polylactic acid, polystyrene, etc., were used as packaging materials (Mahendra 2017).

With global change in environment, these packaging materials are found to be not very suitable to protect food from bacterial contamination, global warming, O_2, CO_2-induced degradation, etc. Nanotechnology has helped to develop next-generation packaging system. Nanocomposite polymers like polymer silicate nanocomposite developed with the help of nanotechnology offer improved gas barrier property, heat resistance, etc.; potato starch and calcium carbonate-based nanocomposite system exhibits higher thermal stability and biodegradability and is likely to replace polystyrene-based packaging system, used for fast food (Moraru et al. 2003). Strategically, earlier polymer matrices, used as packaging materials, are now mixed with various organic and inorganic nanoparticles (silica, inorganic clay, organic clay, carbon nanotube, graphene, polysaccharide, chitosan, cellulose, ZnO, TiO_2, etc.) of different shape and size to prepare more reliable and versatile packaging material. As guided by nanotechnology, the ratio of largest to smallest filler material plays a crucial role in determining the efficiency of nanocomposites as packaging material. Among them, silicate nanoplate-based montmorillonite has gained attention as filler material due to formation of octahedral sheets of $Al(OH)_3$ between silica tetrahedral bilayers (Weiss et al. 2006). Also cellulose nanofibers have been identified as an attractive reinforcement material, since their incorporation into polymer matrix improves strength, moisture barrier, and thermal resistance of base matrices along with their support for the growth of other nanomaterials (Podsiadlo et al. 2005). Another study reveals that cellulose-starch nanocomposite can lead higher thermomechanical property and biodegradability in addition to reduced water sensitivity (Sharma et al. 2017). In the development of plastic or for glass bottles and cartons, impermeable to gases like CO_2, O_2, etc., nanoclay-based materials have got a lot of attention and are being readily used in the market as packaging material of meat, fruit, etc. Here, nanoclay material having ability to block gases, moisture, etc., is dispersed in plastic matrix such as Durethan. In some cases, clay-ethylene-vinyl-alcohol copolymer-polylactic acid biopolymer nanocomposite has been developed with improved oxygen barrier property, to increase shelf life of food products. Therefore, it can be stated that these newly developed packaging systems have multifunctional characteristics and can be divided into the following categories:

10.3.1.1 Improved Packaging

Nanoparticle and polymer-based nanocomposites are used as packaging material with improved gas, moisture barrier properties, as well as heat resistance ability. Packaging materials come in direct contact with food. The main strategy is to prevent food by maintaining inert and low-oxygen environment that inhibits microbial growth and spoilage. Nanomaterials, used as filler to the packaging polymer matrix, act as an impermeability barrier, and the impermeable property gets increased significantly due to larger surface area of the nanomaterials. Nanoclay which is the polymer nanocomposite with complex metallic ores, obtained from volcanic ash as montmorillonite, provides very good barrier to gas permeability. Different polymers such as nylons, polyolefin, PET, epoxy resin, and poly methane are found suitable here. As studied by Park et al., thermoplastic starch/clay nanocomposite with higher tensile strength and lower water vapor permeability in contrast to bare thermoplastic starch is being widely used in food industry (Park et al. 2003).

10.3.1.2 Active Packaging

The active packaging provides the inert barrier between the food product and outside environment and reacts with the food product for extension of the shelf life and good conditions (Grumezescu 2017). Components of the active packaging for food include (1) nanocomposites (metal ions of silver, copper, and gold and metal oxides of TiO_2 and MgO), (2) antimicrobial films (antibacterial/antifungal compounds like sodium benzoate and benomyl, acid, silicate, ethanol, zinc, elements (Si, Na, Al, S, Cl, Ca, Mg, Fe, Pd, and Ti), edible clove, pepper, cinnamon, coffee, chitosan, antimicrobial lysozyme, and bacteriophages), and (3) gas scavengers [TiO_2, iron powder, silicates, sulfites, chlorides, polymeric scavengers, elements (Fe, Si, Ca, Al, Na, Cl, K, Mg, S, Mn, Ti, Co, V, Cr, and P)] (Ahvenainen 2003; Brockgreitens and Abbas 2016). Enzymatic oxygen scavenging is achieved by the chemical reaction between alcohols generated in the food product and the alcohol oxidase enzyme**.**

Nanoclay-polymer composites were used for improving of gas barrier properties of food packages. The most often used one is montmorillonite (also called as bentonite), with natural nanoscalar layered structure that can restrict the permeation of gases when incorporated into a polymer.

Here, polymer and inorganic material (Ag, TiO_2, MgO, CuO, etc.) nanocomposites are used in packaging system. Ag nanoparticles have potency of antimicrobial activity and anti-odorant efficiency and are being widely used as health supplements and food packaging. Due to biocompatibility, SiO_2 nanoparticles are used in direct food contact applications, packaging, in the clearing of beers and wines. Nanosized TiO_2 are often incorporated into the packaging materials for photocatalytic sterilization. Other important achievements of nanotechnology are the incorporation of efficient nanosensor into the packaging system to detect food spoilage due to oxygen and moisture (Lagarón et al. 2005). Nanocomposite of oxide nanoparticles and food-grade polypeptide is being widely used as oil packaging system that protects oil from oxidation due to their antioxidant property (Scheffler et al. 2010). Composite of silica gels and thiosulfate is being used as packaging material due to their long-lasting antibacterial activity (Gupta and Silver 1998). Silver zeolite, made from alkaline earth metal, aluminosilicate, followed by partial replacement by silver ions, shows antimicrobial activity in nano-form, ascribed to reactive oxygen species (ROS) generation. Silver zeolite is being used to various products, viz., food preservation, disinfections of medical products, etc., as antimicrobial coating of food (Kawahara et al. 2000; Matsumura et al. 2003). In this context, different noble metal and metal oxide-based antimicrobial materials, carbon nanotubes having improved mechanical barrier, have been developed as waxy nano-coating materials to extend shelf life of foods. Among various antimicrobial nanomaterial agents, TiO_2 and Ag have gained attraction as they highly generate ROS preventing foodborne pathogens and food spoilage. For example, Ag/TiO_2 and Ag/carbon nanotube nanocomposites show significantly enhanced antimicrobial activity against *E. coli* and *Bacillus cereus* spores exhibiting their importance as packaging materials (Krishna et al. 2005). Ag-doped TiO_2 nanoparticles exhibit antimicrobial activity against *Bacillus cereus* spores on aluminum and polyester coating surfaces and also destroy several airborne bacteria (Vohra et al. 2006). Sodium dodecyl sulfate (SDS) and polyvinylpyrrolidone (PVP)-stabilized Ag nanoparticles show enhanced antimicrobial activity against *E. coli* and *Staphylococcus aureus*.

10.3.1.3 Smart Packaging

Smart packaging can be defined as small and inexpensive labels or tags attached onto primary packaging such as pouches, trays, and bottles or more often onto secondary packaging such as shipping containers to facilitate communication throughout the supply chain (Yam et al. 2005). Carbon dioxide absorbers and generators can be used in sachet or label form to reduce the respiration rate, and eliminate or minimize the oxygen concentration, which can cause quality deterioration of fruits and vegetables. Modified atmospheric packaging (MAP) is applied to extend the shelf life by removing or replacing the air surrounding food products, altering the amounts of carbon dioxide (CO_2) and nitrogen (N_2), and eliminating extension of the postharvest life, thus prolonging the primary fresh conditions of food products (vegetables, fruits, meat, and fish). However, use of some components in the food packages and preservative manufacture such as silver, surfactant, lipid, protein, carbohydrate nanoparticles, and carbon nanotubes in emulsified form caused health impairments.

These types of packaging systems include sensor to detect any internal or external biochemical and microbial changes in food product and packaging materials, thus helping to take necessary initiative in food security. For example, nanosensor, used in plastic packaging system, changes its color in the presence of gases in food when it gets spoiled. Several types of nanomaterial-based sensor, electronic nose, biosensor, and nano-test strip have been developed by researchers for smart packaging. For example, Mills et al. have developed nanosensor where oxygen gets employed as an indicator to monitor uncooked bacon under CO_2 environment (Mill 2005). Nanosensor based on carbon nanotube functionalized with *Salmonella* antibody is used to detect pathogenic infection on the surface of food such as chicken (Villamizar et al. 2008)). Chemical sensors, developed on the basis of xanthine and hypoxanthine, are being successfully used to monitor freshness of canned tuna (Çubukçua et al. 2007). Companies like Nestle, Monoprix supermarket, and British Airways are already using colorimetric chemical sensors to identify food spoilage that significantly improves food transportation (Pehanich 2006).

10.3.1.4 Intelligent and Responsive Packaging

Intelligent packaging is capable of carrying out detecting, sensing, recording, tracing, communicating, and applying scientific logic to extend shelf life, enhance safety, improve quality, provide information, and warn about possible problems (Yam 2009). The components of the intelligent packages are (1) indicators (methylene blue, acid, antioxidants, mineral oil and sugar, elements (Na, K, Ca, Si, Al, and Mg). Responsive packaging technologies are based on the integration of a sensor or sensing interface on the packaging film in real-time and continuous quality monitoring by implementing three important design features: prevention of cross-contamination, selection of the target analytes, and choice of the transduction system. The components of responsive packages are stimuli-responsive materials, hydrogels, surfaces, particles, and supramolecules (Brockgreitens and Abbas 2016). Oxygen scavengers used in the intelligent packaging prevent microbial growth, off flavors and off odors development, color changes and nutritional losses, and reduction in the shelf life of foods based on the following mechanism of iron oxidation.

10.3.2 Nanolaminates

Nanolaminate which consists of chemically or physically bounded few layers of nanomaterials like proteins, polysaccharides, lipid, etc., is the new strategic concept that has been added to packaging system as edible packaging material for fruit, meats, clothes, chocolate, candies, etc. Due to its extreme low thickness, it is better to be coated on food materials, rather than use as freestanding packaging materials. Nanolaminates also offer higher moisture, gas, and lipid barrier along with textural properties (Morillon Vet al. 2002; Phan et al. 2008). Continuous use of earlier non-degradable packaging materials is contaminating our environment and becoming a main threat globally. In contrast, nanolaminates have been developed from biodegradable nanoparticles like proteins, carbohydrates, and lipids, obtained from plant and renewable resources. But these natural nanoparticle layers have their own advantage and disadvantage. For example, lipid layer has high barrier to moisture, but suffers from mechanical strength and other gas impermeability. On the other hand, polysaccharide and protein nanoparticles are effective to gas barrier, but not to moisture. In this context, nanotechnology has helped to develop efficient nanolaminating material out of these. For example, cellulose nanoparticle, obtained from corn, when added with nanoclay exhibits excellent mechanical, stability, and gas barrier property suitable for nanolaminates.

10.4 Types of Nanoparticles Applied in Food Systems

10.4.1 Inorganic Nanoparticles

Many types of nanoparticles used in foods are mainly composed of inorganic materials, such as silver, iron oxide, titanium dioxide, silicon dioxide, or zinc oxide. These particles are either crystalline or amorphous solids at ambient temperature, which may be spherical or non-spherical, have different surface characteristics, and come in different sizes depending on the initial materials and preparation conditions used in their fabrication. Inorganic nanoparticles also vary in their tendency to dissolve under different solution conditions (such as pH and ionic strength) and in their chemical reactivities, which has a major impact on their GIT fate and toxicity.

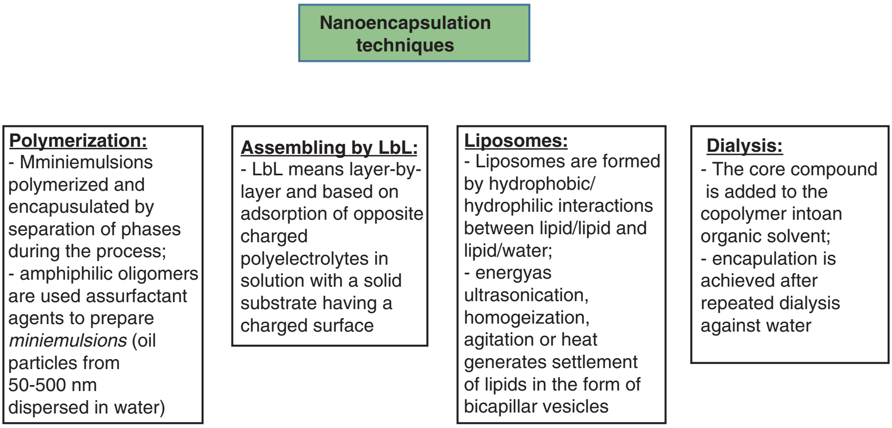
10.4.2 Organic Nanoparticles

This type of nanoparticle is primarily composed of organic substances, such as lipids, proteins, and/or carbohydrates. These substances tend to be liquid, semisolid (gelled), or solid (crystalline or amorphous) at ambient temperatures depending on their composition and processing conditions. Most organic nanoparticles commonly used in foods are spherical, but they may be non-spherical under some circumstances (e.g., nanofibers). Organic materials vary considerably in their behaviors within different regions of the human GIT, e.g., they may dissolve, precipitate, aggregate, or be digested in the mouth, stomach, small intestine, or colon depending on their compositions and structures. In general, it is thought that organic nanoparticles are less toxic than inorganic ones, because they are often fully digested within the human GIT and are not bio-persistent. Nevertheless, there may be certain circumstances where they could cause toxicity.

10.5 Types of Nanoformulations

10.5.1 Nanoencapsulation

Nanoencapsulation in food processing is defined as technology to pack substances in miniature at the nanoscale and also improve food rehydration; edible coatings are used on fruits, vegetables, meats, chocolate, candies, and bakery products, by serving as moisture, lipid, and gas barriers. Nanoencapsulation is applied for manufacturing of confectionary products, pharmacological and dietary supplements, and nanocarrier food systems (Ezhilarasi et al. 2013). Nanoencapsulation can be achieved by using three methodologies as explained in Fig. 10.3: (1) physical processes based on spray drying-coating, extrusion, and spray drying, (2)



Polymerization:
- Mminiemulsions polymerized and encapusulated by separation of phases during the process;
- amphiphilic oligomers are used assurfactant agents to prepare *miniemulsions* (oil particles from 50-500 nm dispersed in water)

Assembling by LbL:
- LbL means layer-by-layer and based on adsorption of opposite charged polyelectrolytes in solution with a solid substrate having a charged surface

Liposomes:
- Liposomes are formed by hydrophobic/ hydrophilic interactions between lipid/lipid and lipid/water;
- energyas ultrasonication, homogeization, agitation or heat generates settlement of lipids in the form of bicapillar vesicles

Dialysis:
- The core compound is added to the copolymer intoan organic solvent;
- encapulation is achieved after repeated dialysis against water

Fig. 10.3 Nanoencapsulation techniques

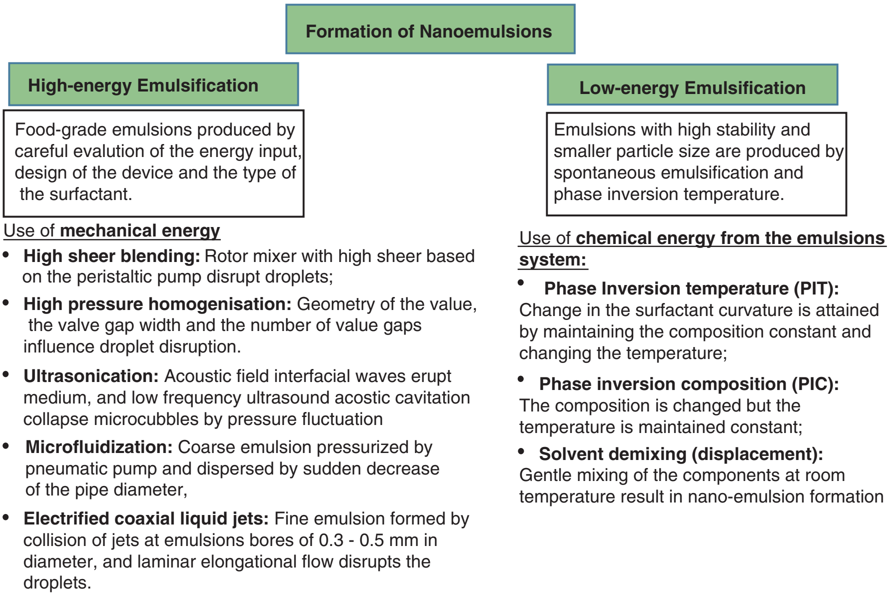
physiochemical processes based on the simple or complex coacervation and entrapment into liposomes, and (3) chemical processes based on interfacial polymerization and molecular inclusion (Quintanilla-Carvajal et al. 2010).

Three types of nanosystems as wall materials used in nanoencapsulation of food ingredients are as follows: (1) lipid-based nanosystems including nanoliposomes, nanocochleates, colloidosomes, solid lipid NPs, and archeosomes; (2) polymeric-type nanosystems including nanofibers, carbohydrate-based NPs, starch, cellulose, pectin, guar gum, alginate, chitosan, and dextran; and (3) protein-based nanosystems including corn protein or zein ultrafine fibers and milk protein nanotubes.

10.5.2 Nanoemulsification

Nanoemulsification in food processing is preparation of nanoemulsions by using techniques specified in Fig. 10.4, such as “phase inversion composition, high-pressure homogenization, ultrasonication and microfluidization” (Quintanilla-Carvajal et al. 2010). Nanoscale delivery systems such as microemulsions, emulsions, nanoemulsions, multiple emulsions, multilayer emulsions, solid lipid nanoparticles, liposomes, biopolymer nanoparticles, and microgels need to be selected for particular application in food industry based on the following criteria: (1) safety, (2) commercial viability and food matrix compatibility, (4) robustness, (5) performance, and (6) labeling requirements (McClements et al. 2015).

Hydrocolloid proteins derived from milk, egg, soy, collagen, and gelatin are most commonly used as emulsifiers in food emulsions.



Formation of Nanoemulsions

High-energy Emulsification

Food-grade emulsions produced by careful evalution of the energy input, design of the device and the type of the surfactant.

Use of **mechanical energy**

- **High sheer blending:** Rotor mixer with high sheer based on the peristaltic pump disrupt droplets;
- **High pressure homogenisation:** Geometry of the value, the valve gap width and the number of value gaps influence droplet disruption.
- **Ultrasonication:** Acoustic field interfacial waves erupt medium, and low frequency ultrasound acostic cavitation collapse microcubbles by pressure fluctuation
- **Microfluidization:** Coarse emulsion pressurized by pneumatic pump and dispersed by sudden decrease of the pipe diameter,
- **Electrified coaxial liquid jets:** Fine emulsion formed by collision of jets at emulsions bores of 0.3 - 0.5 mm in diameter, and laminar elongational flow disrupts the droplets.

Low-energy Emulsification

Emulsions with high stability and smaller particle size are produced by spontaneous emulsification and phase inversion temperature.

Use of **chemical energy from the emulsions system:**

- **Phase Inversion temperature (PIT):** Change in the surfactant curvature is attained by maintaining the composition constant and changing the temperature;
- **Phase inversion composition (PIC):** The composition is changed but the temperature is maintained constant;
- **Solvent demixing (displacement):** Gentle mixing of the components at room temperature result in nano-emulsion formation

Fig. 10.4 Methods of formation of nanoemulsions

10.6 Characteristic Parameters of Nanoparticles for Application in Food Systems

The nanoparticles found in food and beverage products vary considerably in their physiochemical and structural properties, which determines their GIT fate and propensity to cause toxicity (Fig. 10.5).

- Based on their composition, the nanoparticles found in foods may consist of inorganic (e.g., silver, titanium dioxide, silicon dioxide, iron oxide, and zinc oxide) and/or organic components (e.g., lipids, proteins, and carbohydrates).
- The ability of inorganic nanoparticles to produce toxicity is often associated with their chemical reactivity, which depends on their composition. For example, some inorganic nanoparticles dissolve and release ions that promote undesirable chemical or biochemical reactions (e.g., silver nanoparticles), whereas others are relatively inert (e.g., titanium dioxide nanoparticles).
- Dimensionally, food nanoparticles vary considerably in their dimensions, ranging from a few nanometers (surfactant micelles) to a few hundred nanometers (lipid, protein, or carbohydrate nanoparticles), depending on the materials and processes used to create them.
- Nanoparticle dimensions influence their GIT fate and toxicity through a number of mechanisms. Smaller nanoparticles are usually dissolved or digested more

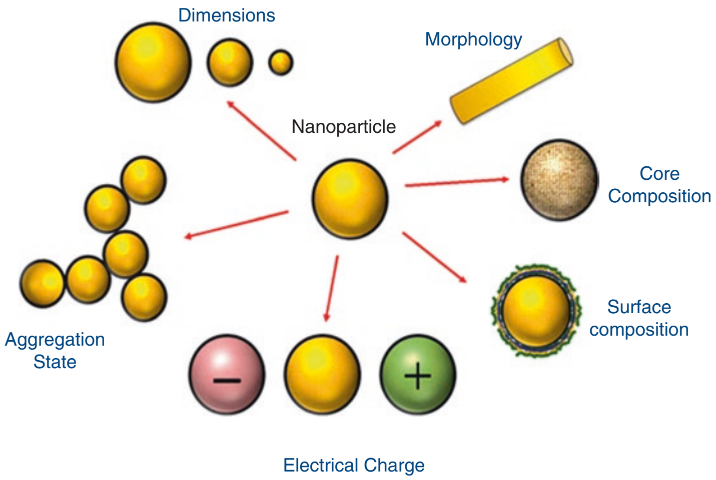


Fig. 10.5 Characteristics of nanoparticles

rapidly in GIT fluids and have higher interacting ability with GIT components (such as digestive enzymes, phospholipids, bile salts, or mineral ions), and consequently their penetration through the mucus layer coating epithelium cells usually increases as their size decreases.

- Interfacial properties of nanoparticles in foods and within the GIT are influenced typically by a surrounding coating of adsorbed substances (sometimes referred to as a "corona"), which determines the electrical charge, hydrophobicity, thickness, digestibility, and chemical reactivity of the interface. These surface properties will determine the behavior of the nanoparticles in the GIT.
- Food-grade nanoparticles may exist as isolated individual particles, or they may form clusters that vary in size, morphology, and strength. Typically, nanoparticles in clusters are held together by physical forces, such as Van der Waals, electrostatic, hydrogen bonding, and hydrophobic forces. The aggregation state of the nanoparticles is therefore often highly dependent on environmental conditions, such as pH, ionic strength, ingredient interactions, and mechanical forces. The dimensions of nanoparticle clusters may be much greater than the dimensions of the individual nanoparticles, which has a major impact on their GIT fate, such as their ability to move through the gastrointestinal fluids, mucus layer, or epithelium cells.
- A major factor that has been frequently ignored in the studies of the biological fate of ingested food nanoparticles is their interactions with various components within complex food matrices and GIT.
- Prior to ingestion, nanoparticles are typically dispersed within food matrices that vary considerably in their compositions, structures, and properties. Foods are assembled into different structural features (such as bulk phases, biological cells, polymers, droplets, bubbles, particles, and networks), and they are produced using various processing operations (such as mixing/separation, cooling/heating,

concentration/dilution, hydration/dehydration, and mechanical action). The physicochemical and structural properties of nanoparticles may therefore be changed considerably when they are dispersed in food products, which would play an important role in determining their subsequent GIT fate and toxicity.
- The interaction between these food components and nanoparticles may significantly alter the biological fate of these nanoparticles.

10.7 Synthesis of Nanomaterials

Nanoparticles, used in different section of the food chain, vary significantly in their physicochemical and structural properties determining their efficiencies in food system starting from processing to packaging and their fate in gastrointestinal tract. The variation of physicochemical and structural properties of the nanoparticles considerably depends on the shape and size of the nanomaterials, those that get tuned by their synthesis methods. Hence, for multipurpose uses of nanomaterials in food system, nanomaterials with suitable shape, size composition, and interfacial properties have to be designed properly, and experimentally it is only achieved by different synthesis processes. In general, nanomaterials, used in various sections of the food chain, can be divided into two categories, inorganic and organic, and primarily this is the factor on which fate of the nanoparticles in gastrointestinal tract depends.

Inorganic nanomaterials, viz., Ag, TiO_2, SiO_2, Fe_2O_3, ZnO, etc., either in amorphous or crystalline form, are already reported to be used in the food chain regularly, starting from active ingredient to gas-impermeable barrier to smart packaging materials having nanosensor. They are present in food system either in spherical or in non-spherical shape and different dimensions ranging from few nanometers to several nanometers. These nanoparticles are metal oxide (TiO_2, SiO_2, Fe_2O_3, ZnO, MgO, etc.) nanoparticles and noble metal, viz., Ag, nanoparticles.

10.7.1 Methods for Synthesis of Metal Oxide Nanoparticles

Among various metal oxide nanoparticles, used so far in the food chain, TiO_2 nanoparticles have gained much attention as functional ingredient of certain food product to increase their lightness and brightness. TiO_2 nanoparticles (<100 nm) are being widely used in chewing gum, candies, dessert, beverages, etc., as food colorant as well as UV-resistant food packaging material, and anatase phase is preferred in food application because of its less toxicity. Spherical and amorphous SiO_2 nanoparticles having size of 100–1000 nm (food grade: E551) are used in powdered foods as anticaking agents to increase flow properties including salt, spices, dried milk, icing sugar, etc. ZnO nanoparticles are being used as sources of Zn, in supplements and functional foods, since Zn is highly essential to maintain food and well-being. In food packaging Zn nanoparticles are used due to their antibacterial activity and UV absorption property. However, a recent study illustrates that high intake of ZnO nanoparticle causes adverse effect to human, and intake depends on the size of nanoparticles. Fe_2O_3 nanoparticles are significantly utilized as colorant and source of bioavailable Fe. Few of the synthesis strategies of metal oxide nanoparticles are briefly described below.

10.7.1.1 Coprecipitation Method

Coprecipitation is one of the most adopted strategies to synthesis of metal oxide nanoparticles since monodisperse particle could be easily prepared by this method along with scalability. The synthesis method involves coprecipitation of solids from aqueous/nonaqueous solutions followed by thermal decomposition of the precipitate. Nucleation and growth determining size distribution of the particles get tuned by reaction parameters such as precursors, sequence of reaction, solvent, etc. Slow-growth mode follows Oswald ripening process giving uniform size, while fast-growth mode generates nonuniform size and irregular shape. As the system, overall, would try to minimize energy, thus smaller-sized particle would diffuse into the solution and get adsorbed on the surface of the bigger-sized particles. Nanoparticles of ZnO, TiO_2, and Fe_2O_3, used in the food chain, have been synthesized by this process from respective chloride salt. Often, precipitate exists in amorphous form; thus subsequent heating or annealing is necessary for rendering crystallinity into them. As an example, TiO_2 nanoparticles (~40–100 nm) have been synthesized in aqueous medium by precipitating $TiCl_3$ in the presence of NH_4OH (Borse et al. 2002). Though aqueous medium is cost-effective, truly monodisperse nanoparticle can't be prepared by this technique. In contrast, nonaqueous medium offers higher control over size of the nanoparticles. However, nonaqueous medium requires significantly higher time (from several days to week) and involves more toxic solvents, but it is preferred in some cases for monodisperse size. For example, monodisperse Fe_3O_4 nanoparticles (~4 nm) have been prepared by mixing $Fe(acac)_3$ with oleylamine and diphenyl ether (Sun and Zeng 2002). Fe_2O_3 nanoparticles of this size range are very suitable for their utilization as bioavailable source of Fe, since Fe easily gets leached out from surfaces of these small-sized nanoparticles. Coprecipitation technique generally produces spherical nanoparticles, but anisotropic nanoparticle can also be synthesized in the presence of surfactant.

10.7.1.2 Sol-Gel Method

Sol-gel technique was adopted to synthesize metal oxide nanoparticles. The process consists of hydrolysis followed by condensation of a liquid precursor that leads to formation of solid-phase network finally giving nanoparticles. It can be divided into two distinct steps, sol and gel formation. Sol consists of stable colloid suspension of precursor in liquid phase or stable solution. When sol turns into a network structured porous semisolid diphasic system, it is termed as gel. Gel is then dried at elevated temperature to remove liquid for densification, followed by thermal decomposition or annealing to achieve crystalline nanoparticle. Hydrolysis and condensation affect the formation of sol and gel and consequently affect the size and composition of the nanoparticles. Hydrolysis and condensation, hence sol-gel formations, are controlled by reaction parameters such as precursor, solvent, pH, temperature, etc. Finding of suitable precursor and solvent (aqueous/nonaqueous) is the main key of this strategy to synthesize monodisperse nanoparticles. As an example, four-coordinated tetraethoxy [$M(OEt)_4$, M = Si, Ti, Zr] compound is generally preferred for the preparation of metal oxide nanoparticles. Partial charge on metal ion generally causes hydrolysis which subsequently controls the shape and size. Higher partial charge causes higher reaction rate preparing nanoparticles of irregular shape and size. To decrease reaction rate, often transitional metal ions are dispersed in the aqueous solution. Here, water molecules react with transitional metal ions by transferring electrons to empty "d" orbital of the transition metal ions forming $[M(OH)_x]^{Z+}$, where x and Z represent coordination number and charge of the transition metal ions; thus hydrolysis kinetics yielding $[M = O]^{(Z-2)+}$ gets to slow down. Sometimes, hydrolysis kinetic is also tuned by controlling the amount of water (in case of aqueous reaction) and organic solvent (in case of nonaqueous reaction). A larger variety of metal oxide including TiO_2, ZnO, MgO, CuO, Cu_2O, and SiO_2 nanoparticles having a wide range in size has been synthesized by this method using a wide variety of precursors like halides, acetylacetonates, alkoxides, etc. As an example, the following reaction has been assigned for the growth of TiO_2 using alkoxide as precursor (Andhariya et al. 2013):

$$\mathrm{Ti(OR)_3 + H_2O \rightarrow Ti(OH)_3 + R_2O}$$
$$\mathrm{Ti(OH)_3 \rightarrow TiO_2 + H_2O}$$

Here, "R" represents the alkoxide group. Apart from metal oxide with antimicrobial activity, sol-gel processing is also widely used to prepare SiO_2 nanoparticle which is used as carrier of functional ingredient in food system. Tetramethoxysilane (TMOS) and tetraethoxysilanes (TEOS) are mostly used as precursors for this purpose. When water is added to TMOS or TEOS, OR functional group of TMOS or TEOS is hydrolyzed by OH^- ions that can be described by the following reaction:

$$\mathrm{Si(OR)_4 + H_2O \rightarrow HO\text{-}Si(OR)_3 + R\text{-}OH}$$

After hydrolysis, condensation takes place according to the following reaction which subsequently reduces three-dimensional Si-O-Si network structure:

$$\mathrm{2HO\text{-}Si(OR)_3 \rightarrow (OR)_3\,Si\text{-}O\text{-}Si(OR)_3 + H_2O}$$

or

$$\mathrm{2OR\text{-}Si(OR)_3 + 2OH\text{-}Si(OR)_3 \rightarrow (OR)_3\,Si - O - Si(OR)_3 + R\text{-}OH}$$

The main disadvantage of the current strategy is the van der Waals force-induced aggregation which enhances size of the nanoparticles decreasing their efficiency as functional ingredient carrier. Increasing surface charge or incorporating steric hindrance by functionalization by reactive ligands is adopted to prevent aggregation. Depending on removal process of solvent, sol-gel strategy could be classified into "aerogel" and "xerogel" processes. When pore fluid of gel is removed in gaseous phase, a very low-density network forms at some hypercritical condition, and then it is defined as "aerogel." The characteristic feature of aerogel is that its shape remains unchanged and this process is very useful for the synthesis of assembled structures. When pore fluid is getting removed at ambient pressure at elevated temperature, network gets shrunk further into dense gel, and then it is called xerogels. Drying stress destroys monolithic gel bodies giving powder. Primary advantages of this technique are the versatility and flexible rheology that allows easy shaping and embedding. This method provides a significant homogeneity for multicomponent system, particularly suitable for laminating purpose.

10.7.1.3 Microemulsion Method

Here, a molecule with both hydrophilic and hydrophobic moiety, defined as amphiphilic surfactant molecule, is used as basis of this process. Due to this dual character, amphiphilic molecules get accumulated at water-air interface to reduce surface tension, and such accumulation results in a self-assembled order in bulk solution. In a mixture of organic solvent and water, amphiphilic molecules accumulate at their interface. In aqueous solution, hydrophobic tail of the surfactant molecule avoids contact with water and as surface concentration crosses a critical value, micelle gets formed. Micelles have the dimension ranging from few nanometers to micrometers depending on water, solvent ratio, and surfactant concentration. These micelles act as a reactor for the growth of metal oxide nanoparticles including ZnO, TiO_2, SiO_2, Fe_2O_3, etc. Addition of co-surfactant gives anisotropic micelle which results in non-spherical structure. Notably, unlike conventional emulsion technique, no shear condition is required for microemulsions. Depending on hydrophilic head, surfactants are divided into ionic and nonionic surfactant. There also exists another type of surfactant, named as zwitterionic surfactant, which contains both anionic and cationic hydrophilic head. Amphoteric surfactant has gained attention due to its ability to synthesize a wide varieties of nanostructures. This ability may be attributed to the change of its hydrophilic head from cationic and zwitterionic to anionic with increasing pH of the medium. Microemulsion process is classified into two categories, direct microemulsions in which organic solvent is dispersed in water and reverse microemulsions where water is dispersed in organic solvent.

10.7.1.4 Microwave Method

Here, electromagnetic energy is being converted into heat energy that is required to carry out chemical reaction. This technique is found to be more efficient in comparison to conventional heating process, as this produces heat homogeneously. Two mechanisms, dipolar polarization and conduction, are involved here for the conversion of energy. In polarization mechanism, dipole when irradiated to microwave generates heat, attributed to collision between dipoles in the presences of rapid oscillating electric field of microwave. Frequency of the microwave plays a crucial role for heat generation. There exists an optimum frequency which depends on the nature of solvent at which generation of heat is maximum. Conduction mechanism occurs when solvents have free charge carrion in the form of either electron or ion. Here, heat is being generated due to conventional Joule heating mechanism. Microwave can easily penetrate the material; thus heat is being generated throughout the volume of the system, defined as volumetric heating, which results in high reaction rate, smaller particle size, narrow distribution in particle size, high purity, enhanced physicochemical properties, etc. Temperature, generated in this process, significantly depends on the dipole moment of the solvent; the higher the dipole moment, the higher the temperature. With the advancement of microwave technology, it is possible to control synthesis parameters; thus monodisperse particles are easily being generated. Various metal oxide nanoparticles and structures, used in food industry, like ZnO, TiO_2, CuO, and MgO, have already been synthesized by this technique. For example, Komarneni et al. synthesized TiO_2 microsphere by this technique (Komarneni and Roy 1985).

10.7.1.5 Chemical and Reduction Method

Chemical reduction is largely utilized to synthesize noble metal, i.e., Ag nanoparticles, as size could be easily controlled by this method. Here, $AgNO_3$ salt is mostly used as precursor, while borohydride, citrate, elemental hydrogen, ethylene glycol, glucose, etc., are generally used as reducing agent. The main problem of this process is the agglomeration, but it has been taken care of by stabilizing agents like polyvinylpyrrolidone (PVP), oleylamine, sodium dodecyl sulfate, N,N-dimethylformamide (DMF), etc. Concentration of the reducing and stabilizing agents plays a crucial role to determine size of the nanoparticle. Later, solubility of the nuclei determines the stage at which nucleation would be stopped and agglomeration to take place.

10.7.1.6 Sonochemical Method

Sonochemical method utilizes ultrasound to cause chemical reaction and basic principle can be described as follows: when liquids is exposed to intense ultrasound, acoustic cavitation which is the combination of formation, growth, and implosive collapses of bubbles occurs and leads to chemical reaction. Ultrasonicator which consists of piezoelectric transducer is used to convert conventional electrical supply into mechanical vibrational energy (~100 W/cm^2, 20 kHz–1 MHz). When vibration is allowed to pass through liquid, liquid medium alternatively gets compressed and relaxed at this frequency resulting in formation of microscopic bubbles. These bubbles implode during compression and expand during decompression. During this oscillatory compression and expansion, bubbles grow, and after reaching a maximum size, they collapse that generates high pressure and temperature. When large number of such events occurs successively within few microseconds, high energy is being generated in the medium due to cumulative effect. In sonochemical process, this energy is utilized for chemical reduction, particularly for reduction of noble metals such as Ag. Briefly, OH^- ions, generated by ultrasound irradiation, reduce Ag^+ ions into Ag^0 which successively leads to formation of Ag nanoparticles. As an example, Gutierrez et al. reduced Ag^+ in aqueous solution using 1 MHz ultrasound in the year 1987. Later in 1992, Nagata et al. prepared Ag nanoparticles after reducing Ag^+ ions under Ar atmosphere by 200 kHz ultrasonicator (Nagata et al. 1992). Concentration of precursor, i.e., $AgNO_3$, plays a crucial role on the size of the nanoparticles, lower the concentration less the particle size. There is also some report on the synthesis of Ag nanoparticles in alcoholic medium. Alcoholic medium offers faster reaction kinetics due to enhanced generation of OH^-. It has been studied that length of alkyl group affects significantly on the size of the nanoparticle (Caruso et al. 2002). Surfactants and organic additives such as polyethylene glycol, sodium dodecyl sulfate, etc., are often used to control size and stabilize the nanoparticles (Mizukoshi et al. 2001). Recently, sonochemical synthesis has been tried out in different gaseous environments in order to investigate their effect on reduction, and the study illustrates the reduction in the following order $N_2 = He < Ne < Ar < Kr$ (Okitsu et al. 2002). The observed phenomena can be explained as follows: the higher the ratio of C_p/C_v (specific heat ratios), the lower the thermal conductivity of the purging gas within the liquid and then the higher the temperature of collapsing bubbles that results in higher reduction rate. In addition, higher solubility of the gas also enhances reaction rate. Temperature is another factor affecting reduction reaction. Initially rate increases with temperature and finally it decreases, i.e., there exists an optimum temperature to carry out the reduction process using this strategy. In general, reduction rate gets decreased with increasing ultrasound frequency. One of the major advantages of this process is that bimetallic nanoparticles can also be synthesized those that often exhibit advantage over single-phase nanoparticles. In addition to colloidal particles, thin film of Ag nanoparticle can also be synthesized by this technique. As an example, Ag nanoparticle thin film on glass slides has been prepared using water-ethylene glycol (10 volume %) solution and $AgNO_3$ (0.05 M) solution at ambient condition using ultrasonicator of 20 kHz of frequency and 600 W/cm^2 power (Perkas et al. 2008).

10.7.1.7 Radiolysis Method

Radiolytic reduction is another method to synthesize Ag nanoparticles where Ag^+ ions get reduced by ions and radicals instead of oxygen. Hydrated ions or radicals get produced by radiations (x-ray, γ-ray, UV ray) and electron beam in aqueous medium, and the reduction reaction can be written as follows:

$$
\begin{gathered}
H_2O \text{ or} \\
Ag^{+} + \rightarrow Ag^{0} \\
Ag^{+} + \rightarrow Ag^{0} + H^{+}
\end{gathered}
$$

Ag^0 acts as nucleation center and coalescence further forming nanoparticles. Sometimes dimers of Ag atoms also get formed ($Ag^0 + Ag^0 \rightarrow Ag_{2,}\, Ag^0 + Ag^+ \rightarrow Ag_2{}^+$) and contribute to the formation of Ag nanoparticles. Here size of nanoparticle is controlled by concentration of precursor ($AgNO_3$) and dose of radiation. Like other processes, this also suffers from agglomeration. To prevent agglomeration, electrostatic stabilizing agents such as $–NH_2$, –COOH, –OH, etc., are used. As they have high electron affinity, they easily form covalent bond with Ag nanoparticles; thus surface activity gets reduced. Recently, polyvinyl alcohol (PVA) that prevents agglomeration by steric hindrance method is being used. –OH group, present in PVA, is strongly capable to absorb Ag^+ by forming secondary bond; thus steric entrapment occurs and agglomeration gets reduced (Gautam et al. 2006). The reaction between PVA and Ag^+ could be written as $\text{R-OH} + Ag^+ \rightarrow \text{R-O-Ag} + H^+$; here R-OH represents PVA monomer. For example, Ag nanoparticles ~7 nm have been synthesized using $AgNO_3$ (concentration ~2×10^{-4} M) as precursor in alcoholic medium (2 propanol) and PVA [59]. In this context, it is to mention that PVA can also reduce Ag^+ ions into Ag^0 in the absence of any radical scavenger. Using this strategy, different nanostructure has also been achieved. For example, Wang et al. investigated that dendritic structure of Ag gets isotropic when they synthesized Ag in the presence of ethanol and $C_{12}H_{25}NaSO_4$ (Wang et al. 2000). Main advantage of this technique is that no side reaction is involved here.

10.7.1.8 Template and Hydrothermal-Assisted Method

One of the significant achievements of nanoscience and related technology is the synthesis of desire nanostructures in order to achieve required activity. It has been investigated that one-dimensional nanostructures like nanorod, nanowire, nanotube, and nanobelt exhibit better application opportunity due to their anisotropic structure rather than their isotropic spherical structure. One-dimensional structure is particularly very useful in sensor application in food monitoring. Template-assisted method is very much reliable to prepare these one-dimensional structures, and the size of the nanostructure is completely determined by pore size of the template. Templates are used as structural framework to grow nanostructures within its spatially confined space, followed by removal by calcination or chemical etching. Templates are divided into two categories: soft template such as peptide, lipid, polymer, liquid crystal, block copolymer, micelle, etc., and hard template such as anodic aluminum oxide (AAO), polycarbonate membrane, silica sphere, polymer latex, etc. As an example, ordered structure with Ag hollow sphere has been synthesized using AAO template (Chen et al. 2004). Though hard templates are robust, strong acid/base/high temperature is necessary to remove the template that diminishes the quality of the nanostructure (Lou et al. 2008). Compared with hard template, soft templates are easy to handle, making them more versatile. As an example, Zhang et al. synthesized hollow Ag sphere using PEO-b-PMAA-SDS complex micelle as soft template (Zhang et al. 2002). Spherical Ag nanoparticles with diameter ~11 nm have been prepared using poly(hydroxyethyl methacrylate) template (Salsamendi et al. 2013). Network structure consisting of cubic-shaped Ag nanoparticles has been synthesized by Chen et al. using PVP as template and ethanolic $AgNO_3$ solution (Chen et al. 2011). Recently few studies reveal that DNA can also be used as template to synthesize Ag nanoparticles (Nithyaja et al. 2012).

Template-assisted methods have limitation as few types of nanostructure are synthesized by these strategies. In contrast to template-assisted method, hydrothermal method offers to synthesize a large variety of nanostructures. Though this process was introduced by Sir Roderick Murchison more than 100 years ago, it has gained attention recently to prepare various nanostructures. Advantages of this technique are the ability to synthesize single crystalline nanostructure, nanocomposites, etc. Mechanistically, hydrothermal method has been developed on the basis of supercritical water or supercritical fluid technology. Though this technique is largely used, its chemistry is still under debate. As an example, Ag nanowires (diameter ~53 nm and length ~6 μm) have been synthesized using 100 μl of $AgNO_3$ (0.1 M) and 100 μl of sodium citrate solution (0.1 M) at 130 °C. Here, pH plays a key role; it is studied that with increasing pH, nanowire structure gets changed into nanosphere. Bari et al. (2016) have synthesized Ag nanowire (diameter ~45–65 nm and length 200 μm) using $AgNO_3$ (0.02 M, 15 ml), $_{D}$+ glucose (0.12 g, 5 ml) as reducing agent, and PVP (1 g, 5 ml) as surfactant. Here, hydrothermal reaction has been carried out at 60 °C for 22 h. The same group has also synthesized this film of Ag nanowire on PET substrate using hydrothermal technique. Two-dimensional arrays of Ag nanoparticles (diameter ~17 nm) have been grown by O. Ayyad et al. by this method. Here the reaction was carried out at 170 °C for 5 h, and $AgNO_3$ (0.4 g), $NaHCO_3$ (0.12 M), and PVP (2.5 g) were used as precursors (Cao et al. 2014). Here, hydrothermal reaction is carried out at 250 °C starting from $AgNO_3$, 1,2-benzenedicarboxylate (10 mM), and sodium stearate (10 mM) (Singh and Pandey 2011).

10.7.1.9 Green Synthesis

Various biological methods, known as green synthesis methods, have been developed on the basis of various microorganisms such as algae, fungi, etc., and plant extracts like leaf, fruit, flower, root, etc., in recent times. Mechanistically, Ag^+

ions get reduced by these biologically active extracts into metallic Ag which consequently forms Ag nanoparticles. These newly developed strategies offer several advantages such as their simplicity, low cost, eco-friendliness, and fast reaction rate. Some extracts also act as capping agents, so no surfactant is required to prevent agglomeration. In these methods, size of the nanoparticle is controlled by synthesis parameters like pH, temperature, reaction time, mixing ratio, etc. In addition, green synthesized Ag nanoparticles, particularly Ag nanoparticles prepared by medicinal plant extracts, are often found to be more pharmacologically active than chemically synthesized nanoparticles due to the presence of biologically active residue, attached to the nanoparticle's surface. As an example, Ag nanoparticles (~40 nm) have been synthesized by bio-reduction of aqueous Ag^+ using culture supernatant of nonpathogenic bacteria such as *Bacillus licheniformis*, *Klebsiella pneumoniae*, *Escherichia coli*, *Enterobacter cloacae*, etc. (Kalishwaralal 2008; Shahverdi 2007). Lactic acid present in bacteria-treated whey of buttermilk can also be used to grow silver nanoparticles (Korbekandi 2012). In order to increase synthesis yield, sometimes green synthesis is combined with other less expensive, less hazardous methods. For example, Saifuddin et al. have developed a process to prepare Ag nanoparticles by combining culture supernatant of *B. subtilis* and microwave irradiation technique in water (Saifuddin 2009). Like bacteria, various fungi have also been adopted for the synthesis of Ag nanoparticles. For example, Ag^+ gets bio-reduced into metallic Ag by an enzymatic reductive process which involves NADH of *F. oxysporum* (Ahmad 2003). In this context, Kumar et al. have demonstrated enzymatic synthesis of Ag nanoparticles of various sizes and morphologies, using α-NADPH-dependent nitrate reductase, purified from *F. oxysporum* and phytochelatin, in vitro (Kumar 2007; Prasad 2016, 2017; Prasad et al. 2018a). In this context, nonpathogenic fungi such as *Trichoderma asperellum* and *Trichoderma reesei* are found to be most suitable and are already being commercially used in food, animal feed, pharmaceutical, paper, and textile industries. Also the procurement and maintenance of the microorganism strain is difficult. This requires special culture and isolation techniques that increase the cost. The use of plant extract for the synthesis of Ag nanoparticles overcomes these problems. During recent past, significant research works have been performed on the green synthesis of Ag nanoparticles using plant extracts such as root, stem, leaves, flower, fruit, etc (Swamy and Prasad 2012; Prasad et al. 2012; Prasad and Swamy 2013; Prasad 2014; Joshi et al. 2018; Prasad et al. 2018b). Among different plant extracts, leaf extract exhibits significant potency as major bioactive molecules like glucose, fructose, chlorophyll, etc., causing reduction of Ag^+ into metallic Ag are present there. Several groups reported the green synthesis of silver nanoparticles from silver salts using leaf extract of parsley (*Petroselinum crispum*), celery, etc. Among fruit extracts, apple and cucumber extracts show potency for the synthesis of spherical Ag nanoparticles (~10 nm). It has been studied by our research group that underground root or stem extracts are rich source of bioactive reducing molecules like amino acid, protein, thiamine, ascorbic acid, etc.; thus they readily can be used to prepare Ag nanoparticles. Infusion of potato tuber seemed to be a good choice here. Amide and amino group, present in potato infusion, also act as capping agent and thus consequently help to stabilize the nanoparticles.

10.7.2 Methods for Synthesis of Organic Nanoparticles

Organic nanoparticles are manufactured for specific purposes such as encapsulation of nutrients to improve their bioavailability or mask undesirable taste or odor, etc. In general, they exist in three different forms: (1) monomer, i.e., single molecules; (ii) oligomer, i.e., monomer linkage in short chain; and (iii) polymer, i.e., monomer linkage in long chain and comes in direct contact of bloodstream via gastrointestinal tract. Depending on synthesis and composition, organic nanoparticles may exist in different forms such as liquid, semiliquid, and solid (crystalline/amorphous), significantly impacting activity. In comparison to inorganic nanoparticles, organic nanoparticles are less toxic and often get digested within human gastrointestinal tract.

10.7.2.1 Synthesis of Chitosan

Among various organic nanoparticles, chitosan is being widely utilized in the food chain to deliver and protect hydrophobic and hydrophilic function of bioactive ingredients (vitamin, probiotics, bioactive peptides, antioxidants, etc.) by the process of encapsulation or immobilization. Chitosan which is a partially deacetylated polymer of N-acetyl glucosamine containing β-(1,4)-linked-D-glucosamine residue with active amine group is generally synthesized from alkaline deacetylation of chitin monomer. A wide variety in application and functionality of chitosan is attributed to the presence of amine and –OH group. Chitosan, being very much bio-friendly, is being synthesized by various methods such as emulsion, ionic gelation, reverse micelle, self-assembly, etc. Among the methods, ionic gelation and reverse micelle are briefly discussed here, since these two methods only produce monodisperse chitosan nanoparticles over a wide range.

Chitosan nanoparticles are synthesized on the basis of interaction of two oppositely charged molecules. Nontoxic and multivalent tripolyphosphate, which helps gel formation by modifying ionic interaction, is generally utilized to prepare chitosan nanoparticles. In this context, it may be stated that reaction parameters such as pH, concentration, ratios of components, and mixing procedure considerably affect the size of the chitosan nanoparticles (Nasti et al. 2009). Multifunctional chitosan-Fe_2O_3 nanocomposite (50–100 nm), used as bioactive Fe source, has been synthesized by this ionic gelation method. It is achieved by cross-linking tripolyphosphate precipitate with NaOH, followed by oxidation by O_2 in HCl medium (Wu et al. 2009).

In reverse micellar process, a surfactant is dissolved in organic solvent to prepare reverse micelle, and then aqueous solution containing chitosan monomer is added to it with constant stirring. Here, the amount of the water plays a crucial role in determining the size of chitosan nanoparticles; more water gives larger-sized particles (Brunel et al. 2008). Reverse micelle strategy is found to be very much effective to prepare functionalized chitosan nanoparticles, viz., bovine serum albumin functionalized chitosan.

In addition to chitosan, other organic nanoparticles are synthesized by reprecipitation technique in which dilute solution of precursor in water-soluble media is directly injected into vigorously stirred water. Due to the sudden change of solubility of the precursor, the solute gets precipitated, forming a nanocrystal. As an example, nanoparticles of 1,3-diphenyl-5-(2-anthryl)-2-pyrazoline, used in the food chain in delivery system, are synthesized after injecting them from acetonitrile stock solution to water (Xiao et al. 2003). When acetonitrile is mixed with water, the dispersion property of the solute changes rapidly, leading to nucleation and growth of the nanoparticles. Here, size of the nanoparticles gets tuned by ripening process by regulating aging time. In this context, it may be stated that the nucleation of the nanoparticles gets initiated in the early-stage heterogeneous environment; thus broad distribution in size and shape is obtained. Recently, strategies have been developed that create homogeneous environment; thus size and shape control becomes easier. For example, perylene nanoparticles have been synthesized by reducing perylene perchlorate using bromine anions in acetonitrile solution. Here, size of the nanoparticles gets controlled by monomer concentration.

10.7.2.2 Synthesis of Polymer Fiber by Electrospinning and Electrospraying

Electrospinning and electrospraying are the two recently developed facile, cost-effective, and flexible techniques by which either fiber or structures ranging from few nanometers to several micrometers of any kind of polymer can be synthesized. Technically, the method has been developed which utilizes electrically charged jet of polymer solution to prepare fiber or particles, used for encapsulation, enzyme immobilization, food coating, laminating, etc. Mechanistically, in electrospinning or electrospraying processes, a polymer solution is spun or sprayed in the presence of high electric field to obtain a desired fiber or particle, respectively. Typically, the setup consists of a high DC voltage source (1–30 kV), a blunt ended needle or capillary of stainless steel, a syringe pump, and a flat or drum-shaped collector which is grounded. In case of electrospinning, polymer solution after gaining free charge from applied voltage when come at the tip of the capillary, a droplet forms on which two electrostatic forces, namely, repulsive force between like charges and Coulomb force due to external applied voltage, act. Due to these two electrostatic forces, droplet gets distorted into conical shape, known as Taylor cone. When electrostatic force counteracts surface tension, droplet gets injected from Taylor cone toward collector. Uneven distribution of charge on droplets causes whipping or bending motion of the jet and consequently elongation of jet, and raid evaporation of the solvent takes place, resulting in a solid thin fibrous structure on the collector as randomly oriented nonwoven mat. In contrast to electrospinning process, electrospraying technique relies on liquid atomization by electrical force. The parameters, by which final structure could be tuned, are molecular weight and microstructural features of the polymer, concentration of polymer, solvent, pH, conductivity, and viscosity surface tension of the solvent. Additionally, tip-collector distance, electric potential, and flow rate of solution affect fibrous structure.

10.8 Mechanism of Preservative Action

10.8.1 Protection Against Biological Deterioration

10.8.1.1 Antimicrobials

Microbial contamination has been leading to pathogenic infections and poor nutrition associated with weaning foods. Thus, dealing with bacterial deterioration is one of the most critical subjects in the production, processing, transport, and storing of food. Novel nanoantimicrobials have shown promising effects on safeguarding food deterioration, thereby extending the shelf life of food. A number of metal and metal oxide nanomaterials have long been suggested to be effective as antimicrobials. Their intrinsic physicochemical properties allow excessive formation of reactive oxygen species (ROS), leading to oxidative stress and subsequent cell damage. Furthermore, the release of metal ions outside the cell, at the cell surface, or within the cell can alter cellular structure or function (Prasad et al. 2016; Rajpal et al. 2016). Thus, metal/metal oxide-based nanocomposites have been utilized in food packaging and coating or even as ingredients. Silver nanoparticles and nanocomposites are one of the most widely used nanomaterials, as antimicrobials, in the food industry. Silver nanoparticles likely serve as a source of Ag ions, binding to membrane proteins, forming pits, causing other morphological changes, and catalyzing the generation of ROS in bacterial cells, subsequently leading to cell death through oxidative stress (Aziz et al. 2014, 2015, 2016, 2019). Nevertheless, multiple latest research studies suggested that silver nanocomposites are safe for food packaging, with no detectable or insignificant levels of silver nanoparticles that are released and migrated from impregnated containers into real food samples and food simulants. Nanocomposites offer added stability, which is important for sustaining antimicrobial activity and reducing the likelihood of migration of metal ions into stored foods. Polymers are largely engineered to form nanocomposites with metal/metal oxide nanomaterials for food application. Earlier, chitosan, polystyrene, polyvinylpyrrolidone, and poly(vinyl chloride) have also been reported as nanocomposite films that bind to Cu or ZnO nanomaterials to inactivate food pathogens.

10.8.2 Protection Against Chemical Ingredients

10.8.2.1 Antioxidants

Although some metal/metal oxide nanomaterials are known to cause oxidative stress via formation of ROS, less reactive nanomaterials are developed to act as antioxidant carriers. Polymeric nanoparticles are suggested to be suitable for the encapsulation of bioactive compounds (e.g., flavonoids and vitamins) and to release them in acidic environments (i.e., stomach). Furthermore, application of antioxidant treatments in association with edible coating is the most common way to control browning of fresh-cut fruits. It is well-known that browning of fresh-cut fruits is an undesirable effect brought by the conversion of phenolic compounds into dark-colored pigments in the presence of O_2, during storage and marketing. However, there are only a few applications of nanomaterials directly as antibrowning agents. Nano-ZnO-coated active packaging has been reported to be a viable alternative to common technologies for improving the shelf life properties of apples as a fresh-cut product.

10.8.2.2 Flavors

Nanoencapsulation techniques have widely been used to improve flavor release and flavor retention and to deliver culinary balance. It has also been shown that SiO_2 nanomaterials can act as carriers of fragrances or flavors in food and nonfood products.

10.8.2.3 Anticaking Agents

SiO_2 is used mainly to thicken pastes, as an anticaking agent to maintain flow properties in powdered products and as a carrier of fragrances or flavors in food and nonfood products. Recent research showed that in powdered food materials, at least a part of the SiO2 is in the nanosize range.

10.8.2.4 Others

In addition to the abovementioned benefits, nanomaterials have also been constantly developed to enhance the physical and mechanical properties of packaging in terms of tensile strength, rigidity, gas permeability, water resistance, flame resistance, etc. Aimed at providing those aforementioned properties, polymer nanocomposites are the latest materials with a huge potential for application in the active food packaging industry. Polymer nanocomposites with layered silicates were introduced in the 1990s. As these new polymer nanomaterials are much stronger, more flame resistant, as well as having a potential role in UV shielding applications, they are widely reported to have the potential to completely transform the food packaging industry.

10.9 Fate of Nanomaterials Within Human Systems

The nanoparticles found in foods may consist of inorganic and/or organic components. Nanoparticle composition plays a major role in determining their GIT fate as has been summarized in Table 10.1. Lipids, proteins, and starches can be digested by proteases, lipases, and amylases in the mouth, stomach, small intestine, or colon.

Table 10.1 Nanoformulations and their impact on human health

Nanoemulsion	Component	Health hazards
Nondigestible inorganic nanoparticles	Silver nanoparticles	Reducing ATP content Increasing ROS Production Damaging mitochondria and DNA chromosomal aberration Genotoxic Cytotoxic Carcinogenic
Digestible organic nanoparticles	Surfactants	Bioaccumulation
	Lipids, proteins, and carbohydrates	Cellular damage Degradation of proteins Cardiovascular diseases
	Carbon nanotubes	Obesity
		Cause skin and lung disease

However, some organic substances used to fabricate food nanoparticles (such as dietary fibers and mineral oils) may not be digested in the upper GIT. Inorganic nanoparticles are also not digested in the GIT, but some of them may be fully or partially dissolved as a result of alterations in pH or dilution. Any nanoparticles that are not digested or absorbed in the upper GIT will reach the lower GIT where they may alter the microbiome. The ability of inorganic nanoparticles to produce toxicity is often associated with their chemical reactivity, which depends on their composition. Nanoparticle dimensions influence their GIT fate and toxicity through a number of mechanisms. The GIT fate of food-grade nanoparticles, and therefore their potential to have adverse health effects, is often influenced by their interfacial characteristics. Food-grade nanoparticles may exist as isolated individual particles, or they may form clusters that vary in size, morphology, and strength. Typically, nanoparticles in clusters are held together by physical forces, such as Van der Waals, electrostatic, hydrogen bonding, and hydrophobic forces. The aggregation state of the nanoparticles is therefore often highly dependent on environmental conditions, such as pH, ionic strength, ingredient interactions, and mechanical forces. The dimensions of nanoparticle clusters may be much greater than the dimensions of the individual nanoparticles, which has a major impact on their GIT fate, such as their ability to move through the gastrointestinal fluids, mucus layer, or epithelium cells. Consequently, it is always important to determine the actual effective dimensions of the nanoparticles at the site of actions, rather than the dimensions of the original nanoparticles added in foods.

10.10 Conclusion

Embracing the development of nanotechnology and its application in food industry specifically for preserving the food quality attributes is likely to witness both success like in other fields and also certain implications of concern if used indiscriminately. Although the fate and potential toxicity of nanomaterials are not fully understood at this time, it is evident that there have been significant advances in the application of novel nanotechnology in the food industry. Application of nanotechnology can also assist in the detection of pesticides, pathogens, and toxins, serving in the food quality tracking-tracing-monitoring chain. Furthermore, nanotechnology has the potential to bring in a radical transformation in future food packaging systems. However, the challenges to develop a healthy and sustainable food industry remain with the personnel and organizations applying this nanotechnology taking precautions with respect to associated health, safety, and environmental impacts be addressed and regulated at the forefront. To be successful in the long run, proper education of the public is also paramount in the introduction and development of nanotechnology in food system.

References

Ahmad AMP (2003) Extracellular biosynthesis of silver nanoparticles using the fungus *Fusarium oxysporum*. Colloid Surf B Biointerfaces 28:313–318

Andhariya CN, Pandey OP, Chudasama B (2013) A growth kinetic study of ultrafine monodispersed silver nanoparticles. RSC Adv 3:1127–1136

Aziz N, Fatma T, Varma A, Prasad R (2014) Biogenic synthesis of silver nanoparticles using Scenedesmus abundans and evaluation of their antibacterial activity. J Nanopart:689419. https://doi.org/10.1155/2014/689419

Aziz N, Faraz M, Pandey R, Sakir M, Fatma T, Varma A, Barman I, Prasad R (2015) Facile algae-derived route to biogenic silver nanoparticles: synthesis, antibacterial and photocatalytic properties. Langmuir 31:11605−11612. https://doi.org/10.1021/acs.langmuir.5b03081

Aziz N, Pandey R, Barman I, Prasad R (2016) Leveraging the attributes of *Mucor hiemalis*-derived silver nanoparticles for a synergistic broad-spectrum antimicrobial platform. Front Microbiol 7:1984. https://doi.org/10.3389/fmicb.2016.01984

Aziz N, Faraz M, Sherwani MA, Fatma T, Prasad R (2019) Illuminating the anticancerous efficacy of a new fungal chassis for silver nanoparticle synthesis. Front Chem 7:65. https://doi.org/10.3389/fchem.2019.00065

Bai YX, Li YF, Yang Y, Yi LX (2006) Covalent immobilization of triacylglycerol lipase onto functionalized nanoscale SiO_2 spheres. Process Biochem 41:770–777

Bari B, Lee J, Jang T, Won P, Ko SH, Alamgir K, Arshad M, Guo LJ (2016) Simple hydrothermal synthesis of very-long and thin silver nanowires and their application in high quality transparent electrodes. J Mater Chem A 29. https://doi.org/10.1039/c6ta03308c

Brockgreitens J, Abbas A (2016) Responsive food packaging: recent progress and technological prospects. Compr Rev Food Sci Food Saf 15(1):3–15

Brunel F, Veron L, David L, Domard A, Delair T (2008) A novel synthesis of chitosan nanoparticles in reverse emulsion. Langmuir 24:11370–11377

Cao J, Zhao D, Lei X, Liu Y, Mao Q (2014) One-pot hydrothermal synthesis of silver nanoplates on optical fiber tip for surface-enhanced Raman scattering. Appl Phys Lett 104:201906

Caruso RA, Kumar MA, Grieser F (2002) Sonochemical formation of gold sols. Langmuir 18:7831–7836

Chen Z, Zhan P, Wang Z, Zhang J, Zhang W, Ming N, Chan C, Sheng P (2004) Two and three dimensional ordered structures of hollow silver sphere prepared by colloidal crystal templating. Adv Mater 16:417–422

Chen B, Jiao X, Chen D (2011) Fabrication of hollow cubic Ag microboxes with net-like nanofiber structures and their surface plasmon resonance. CrystEngComm 13:204–211

Çubukçua M, Timurb S, Anik U (2007) Examination of performance of glassy carbon paste electrode modified with gold nanoparticle and xanthine oxidase for xanthine and hypoxanthine detection. Talanta 74:434–439

Ezhilarasi PN, Karthik P, Chhanwal N, Anandharamakrishnan C (2013) Nanoencapsulation techniques for food bioactive components: a review. Food Bioproc Tech 6(3):628–647

Gautam A, Tripathy P, Ram S (2006) Microstructure, topology and X-ray diffraction in Ag-metal reinforced polymer of polyvinyl alcohol of thin laminates. J Mater Sci 41:3007–3016

Gupta A, Silver S (1998) Molecular genetics: silver as a biocide: will resistance become a problem? Nat Biotechnol 16:888

Joshi N, Jain N, Pathak A, Singh J, Prasad R, Upadhyaya CP (2018) Biosynthesis of silver nanoparticles using *Carissa carandas* berries and its potential antibacterial activities. J Sol-Gel Sci Technol 86(3):682–689. https://doi.org/10.1007/s10971-018-4666-2

Kalishwaralal KDV (2008) Extracellular biosynthesis of silver nanoparticles by the culture supernatant of *Bacillus licheniformis*. Mater Lett 62:4411–4413

Kawahara K, Tsuruda K, Morishita M, Uchida M (2000) Antibacterial effect of silver zeolite on oral bacteria under anaerobic condition. Dent Mater 16:452–455

Komarneni S, Roy R (1985) Titania gel spheres by a new sol-gel process. Mater Lett 3:165–167

Korbekandi HIS (2012) Optimization of biological synthesis of silver nanoparticles using *Lactobacillus casei subsp. casei*. J Chem Technol Biotechnol 87(7):932–937

Krishna V, Pumprueg S, Lee SH, Zhao J, Sigmund W, Koopman B, Moudgil BM (2005) Photocatalytic disinfection with titanium dioxide coated multi- wall carbon nanotubes. Process Safety Environ Protect 83:393–397

Kumar SA (2007) Nitrate reductase-mediated synthesis of silver nanoparticles from $AgNO_3$. Biotechnol Lett 29(3):439–445

Lagarón JM, Cabedo L, Cava D, Feijoo JL, Gavara R, Gimenez E (2005) Improving packaged food quality and safety. Part 2: nanocomposites. Food Addit Contam 22:994–998

Lou X, Archer LA, Yang Z (2008) Hollow micro/nanostructure: synthesis and applications. Adv Mater 20:3987–4019

Mahendra P (2017) Nanotechnology: a new approach in food packaging. J Food Microbiol Saf Hyg 2:120–121

Matsumura Y, Yoshikata K, Kunisaki SI, Tsuchido T (2003) Mode of bactericidal action of silver zeolite and its comparison with that of silver nitrate. Appl Environ Microbiol 69(7):4278–4281

McClements DJ, Hu K, Huang X, Gao Y, Huang X, Xiao H (2015) Core–shell biopolymer nanoparticle delivery systems: synthesis and characterization of curcumin fortified zein–pectin nanoparticles. Food Chem 182:275–281

Mills A (2005) Oxygen indicator and intelligent inks for packaging food. Chem Soc Rev 34:1003–1011

Mizukoshi Y, Takagi E, Okuno H, Oshima R, Maeda Y, Nagata Y (2001) Preparation of platinum nanoparticles by sonochemical reduction of the Pt(IV) ions: role of surfactants. Ultrason Sonochem 8:1–6

Morillon V, Debeaufort F, Blond G, Capelle M, Voilley A (2002) Factors affecting the moisture permeability of lipid-based edible films: a review. Crti Rev Food Sci Nutr 42:67–89

Mozafari MR, Johnson C, Hatziantoniou S, Demetzos C (2008) Nano-liposomes and their applications in food nanotechnology. J Liposome Res 18(4):309–327

Nagata Y, Watanabe Y, Fujita S, Dohmaru T, Taniguchi S (1992) Formation of colloidal silver in water by ultrasonic irradiation. J Chem Soc Chem Commun (21):1620–1622

Nasti A, Zaki NM, Leonardis PD, Ungphaiboon S, Sansongsak P, Rimoli MG, Tirelli N (2009) Chitosan/TPP and chitosan/TPP-hyaluronic acid nanoparticles: systematic optimization of the preparative process and preliminary biological evaluation. Pharm Res 26:1918–1930

Nithyaja B, Misha H, Nampoori VPN (2012) Synthesis of silver nanoparticles in DNA template and its influence on nonlinear optical properties. Nanosci Nanotechnol 2(4):99–103

Okitsu K, Yue A, Tanabe S, Matsumoto H, Yobiko Y, Yoo Y (2002) Sonolytic control of rate of Gold(III) reduction and size of formed gold nanoparticles: relation between reduction rates and sizes of formed nanoparticles. Bull Chem Soc Jpn 75(10):2289

Park HM, Lee WK, Park CY, Cho WJ, Ha CS (2003) Environmentally friendly polymer hybrids: part I: mechanical, thermal, and barrier properties of the thermoplastic starch/clay nanocomposites. J Mater Sci 38:909–915

Pehanich M (2006) Small gains in processing and packaging. Food Process 11:46–48

Perkas N, Amirian G, Applerot G, Efendiev E, Kaganovskii Y, Ghule AB, Chen BJ, Ling YC, Gedanken A (2008) Depositing silver nanoparticles on/in a glass slide by the sonochemical method. Nanotechnology 19(43):5604

Phan The D, Debeaufort F, Luu D, Voilley A (2008) Moisture barrier, wetting and mechanical properties of shellac/agar or shellac/cassava starch bilayer bio-membrane for food applications. J Membr Sci 325:277–283

Podsiadlo P, Choi SY, Shim B, Lee J, Cuddihy M, Kotov NA (2005) Molecularly engineered nanocomposites: layer-by-layer assembly of cellulose nanocrystals. Biomacromolecules 6:2914–2918

Prasad R (2014) Synthesis of silver nanoparticles in photosynthetic plants. J Nanopart:963961. https://doi.org/10.1155/2014/963961

Prasad R (2016) Advances and applications through fungal Nanobiotechnology. Springer International Publishing, Switzerland. isbn:978-3-319-42989-2

Prasad R (2017) Fungal nanotechnology: applications in agriculture, industry, and medicine. Springer Nature, Singapore. isbn:978-3-319-68423-9

Prasad R, Swamy VS (2013) Antibacterial activity of silver nanoparticles synthesized by bark extract of *Syzygium cumini*. J Nanopart. https://doi.org/10.1155/2013/431218

Prasad R, Swamy VS, Varma A (2012) Biogenic synthesis of silver nanoparticles from the leaf extract of *Syzygium cumini* (L.) and its antibacterial activity. Int J Pharma Bio Sci 3(4):745–752

Prasad R, Pandey R, Barman I (2016) Engineering tailored nanoparticles with microbes: quo vadis. Wiley Interdiscip Rev Nanomed Nanobiotechnol 8:316–330. https://doi.org/10.1002/wnan.1363

Prasad R, Kumar V, Kumar M, Wang S (2018a) Fungal nanobionics: principles and applications. Springer Nature, Singapore. https://www.springer.com/gb/book/9789811086656. isbn:978-981-10-8666-3

Prasad R, Jha A, Prasad K (2018b) Exploring the realms of nature for nanosynthesis. Springer International Publishing. https://www.springer.com/978-3-319-99570-0. isbn:978-3-319-99570-0

Quintanilla-Carvajal MX, Camacho-Díaz BH, Meraz-Torres LS, Chanona-Pérez JJ, Alamilla-Beltrán L, Jimenéz-Aparicio A, Gutiérrez-López GF (2010) Nanoencapsulation: a new trend in food engineering processing. Food Eng Rev 2(1):39–50

Rajpal K, Aziz N, Prasad R, Varma RG, Varma A (2016) Evaluating bionanoparticle infused fungal metabolites as a novel antimicrobial agent. J Adv Pharm Technol Res 7(3):42–46

Saifuddin NWC (2009) Rapid biosynthesis of silver nanoparticles using culture supernatant of bacteria with microwave irradiation. E-J Chem 6:61–70

Salsamendi M, Cormack AGP, Graham D (2013) Template-directed synthesis of uniformly-sized silver nanoparticles with high colloidal stability. New J Chem 37:3591–3594

Scheffler SL, Wang X, Huang L, Gonzalez FS, Yao Y (2010) Phytoglycogen octenyl succinate, an amphiphilic carbohydrate nanoparticle, and -polylysine to improve lipid oxidative stability of emulsions. J Agric Food Chem 58:660–667

Shahverdi AR (2007) Rapid synthesis of silver nanoparticles using culture supernatants of Enterobacteria: a novel biological approach. Process Biochem 42(5):919–923

Sharma C, Dhiman R, Rokana N, Panwar H (2017) Nanotechnology: an untapped resource for food packaging. Front Microbiol 8:1735

Singh RP, Pandey AC (2011) Silver nanosieve using 1,2-benzenedicarboxylic acid: a sensor for detection of hydrogen peroxide. Anal Methods 3:586–592

Sun S, Zeng H (2002) Size-controlled synthesis of magnetite nanoparticles. J Am Chem Soc 124:8204–8205

Swamy VS, Prasad R (2012) Green synthesis of silver nanoparticles from the leaf extract of Santalum album and its antimicrobial activity. J Optoelectron Biomed Mater 4(3):53–59

Vargas M, Pastor C, Chiralt A, McClements DJ, Gonzalez-Martinez (2008) Recent advances in edible coatings for fresh and minimally processed fruits. Crit Rev Food Sci Nutr 48:496–511
Villamizar R, Maroto A, Xavier RF, Inza RF, Figueras I (2008) Fast detection of Salmonella Infantis with carbon analytical nanotechnology for food analysis 17 nanotube field effect transistors. Biosens Bioelectron 24:279–283
Vohra A, Goswami DY, Deshpande DA, Block SS (2006) Enhanced photocatalytic disinfection of indoor air. Appl Catal B Environ 64:57–65
Weiss J, Takhistov P, Mc Clements DJ (2006) Functional materials in food nanotechnology. J Food Sci 71:107–116
Wu Y, Wang YJ, Luo GS, Dai YY (2009) In situ preparation of magnetic chitosan nanoparticles for lipase immobilization by cross-linking and oxidation in aqueous solution. Bioresour Technol 100:3459–3464
Xiao D, Xi L, Yang W, Fu H, Shuai Z, Fang Y, Yao J (2003) Size-tunable emission from 1,3-Diphenyl-5-(2-anthryl)-2-pyrazoline nanoparticles. J Am Chem Soc 125:6740–6745
Zhang D, Qi L, Ma J, Cheng H (2002) Synthesis of submicrometer sized hollow silver spheres in mixed polymer–surfactant solutions. Adv Mater 14:1499–1502