Chapter 13
Colloidal Bio-nanoparticles in Polymer Fibers: Current Trends and Future Prospects

Zuzana Konvičková, Ondrej Laššák, Gabriela Kratošová, Kateřina Škrlová, and Veronika Holišová

Abstract Biotechnology and bio-nanotechnology are emerging fields that inspire vast scientific and engineering inquiry. Bio-nanotechnology is relatively new and dynamic, applying biological principles to produce new systems and materials at nanoscale level. Eco-friendly nanomaterial development and production by biosynthesis have an interesting niche, where metallic and functionally diverse biosynthesized nanoparticles (bio-NPs) are prepared by exploiting both biological processes in microorganisms and biochemical reactions in plant extracts and other biomass. The major advantage of this approach is one-step chemical reduction and stabilization, with the two principal components providing toxic-free intermediates in the bio-NP genesis. This heralds exciting possibilities for inexpensive NP production and consequent rapid and wide adoption of novel applications, such as incorporation of bio-NPs to augment polymer nanofiber properties.

This chapter presents an overview of critical aspects of the composite materials' design and development. The recognized mechanics of bio-NP formation is followed by idiosyncrasies in choice of the core material and the "host" environment where synthesis occurs and the physical and chemical characterization of resultant bio-NPs. Application potential is then outlined, and highly biocompatible polymers are highlighted in a major review of nanofiber production. Finally, future prospects in bio-NP and nanofiber composition are investigated.

Keywords Metallic nanoparticles • Biosynthesis • Phytosynthesis • Polymer fibers • Electrospinning • Colloids

Z. Konvičková (✉) • G. Kratošová • K. Škrlová • V. Holišová
Nanotechnology Centre, VŠB - Technical University of Ostrava,
17. listopadu 15/2172, Ostrava, Poruba 708 33, Czech Republic
e-mail: konvickova.zuzana@gmail.com

O. Laššák
4 Medical Innovations CBTD, Dr. Slabihoudka 6232/11,
Ostrava, Poruba 708 52, Czech Republic

M. Rai, R. Shegokar (eds.), *Metal Nanoparticles in Pharma*,
DOI 10.1007/978-3-319-63790-7_13

Nomenclature

Ag	Silver
Au	Gold
CM	Carboxy-methyl
CuO	Copper oxide
DLS	Dynamic light scattering
Fe_2O_3	Iron (III) oxide
FTIR	Fourier transform infrared spectroscopy
MEMS	Microelectromechanical systems
NP	Nanoparticle
PCL	Poly(ε-caprolacton)
Pd	Palladium
PGA	Poly(glycolic acid)
PLA	Poly(lactic acid)
PLGA	Poly(lactic-co-lactic acid)
Pt	Platinum
PVA	Poly(vinyl alcohol)
PVP	Polyvinylpyrrolidone
SEM	Scanning electron microscopy
TEM	Transmission electron microscopy
XRD	X-ray diffraction
ZnO	Zinc oxide
ZrO_2	Zirconia oxide

13.1 Introduction

Nanotechnology explores strategies for engineering, manipulating matter and energy on atomic and molecular levels. This technology creates nanosystems, assembles them in functional systems, and converts them to devices which facilitate novel applications. It provides access to their unusual properties which are emerging from the quantum realm. As the dimensions shrink to the nanoscale level, the quantum aspect dominates and defines a wide range of properties, including chemical, optical, electrical, mechanical, and thermal capacity (Narayanan and Sakthivel 2010; Krahne et al. 2011; Díez-Pascual et al. 2012; Son et al. 2012).

The two basic approaches in producing nanoscale materials and structures are top-down and bottom-up strategies (Narayanan and Sakthivel 2010). Top-down procedures reduce macro- and mesoscale materials to nanodimensions. Although photolithographic processes play a dominant role in nanofabrication, these are burdened by excessive cost and focus on fixed-bulk substrate nanostructures with very strict requirements for precision and accuracy. Expedient examples include specific conditions such as production of integrated circuits, MEMS, and quantum optics; and this method is unsuitable for mass production of colloidal nanoparticles (NPs).

Further application is ball milling. This is a mechanical method for NP production with long processing time, low level of control over NP parameters, impurities, and common defects in crystal structure (Yadav et al. 2012), but these can be minimized, and ball milling remains a preferred method for some types of materials and applications, such as gas sensing (Pentimalli et al. 2015).

Although the bottom-up approach appears most effective for NP production because it forms nanostructures by assembling single atoms and molecules, combining the bottom-up and top-down procedures offers an optimal strategy for some applications, and their use together also provides the sole solution to some NP production problems (Choi et al. 2008; Pinna et al. 2013; Hu et al. 2014).

An alternative dichotomy discerns between physical and chemical approaches and additive and subtractive methods (Engstrom et al. 2014). An example of a physical approach that also fits the bottom-up and additive categories is atomic force lithography where single atoms are manipulated under high control. However, there is a wide range of chemical methods to prepare nanomaterials in material science and nanotechnology. For example (a) sol-gel is used to fabricate silicon and TiO_2 metal oxides, and a general feature here is the homogenization of metal alkoxides in the solution and their transition to gel, (b) precipitation produces solid material from solution, and (c) synthesis using microwave radiation can be applied to chemical reactions (Nguyen et al. 2010; Junlabhut et al. 2014; Omri et al. 2015).

Biosynthesis fits the combined chemical, additive, and bottom-up approach, and this is further explored throughout the text because this specialized chemical method has emancipated into an individual research field. The application of biological reactions and processes in living organisms contributes to the formation of nanomaterials, especially metal NPs (Castro-Longoria et al. 2011; Schröfel et al. 2011; Zhang et al. 2011). In biosynthesis, an inorganic precursor plays the simple role of metal donor to the biological system. A further example occurs in herbal leachate extract. Although herbs lack living entities, added metal precursors such as tetrachloroauric acid ($HAuCl_4$) are reduced by the active phytochemical leachate in the extract into capped and stable bio-NPs. Although this process in living bio-matter results from an active and complex effort to neutralize and eliminate exogenous elements, it is expected to be similar to that in inanimate species, and while the precise mechanism in both processes remains undetermined, biosynthesis retains a great potential for efficient NP production from different precursors in a scalable and environmentally friendly manner.

13.2 Biosynthesis: A Simple Method for Metallic Nanoparticles Preparation

Processes involved in NP biosynthesis occur in living organisms such as bacteria, yeasts, algae, and/or in their immediate surroundings containing bioactive agents originating from the organisms. Other possible milieu is a biomass completely free of living organisms such as plant extracts. All aforementioned systems are capable of producing nanostructures and nanoparticles via the processes described below. Microorganism/plant extract and metallic precursor are mixed together in a single step, and NP formation starts after mutual contact.

13.2.1 Formation of Nanoparticles

Biomasses contain large amounts of organic compounds composed of positively and negatively charged functional groups. Examples of negatively charged include hydroxyl (−OH), amino ($-NH_2$), and carboxyl (−COOH) groups, and metal ions are reduced to the zero valent (or oxide) form when the biomass and a metal salt precursor are mixed (Vijayaraghavan et al. 2011). NP growth based on thermodynamic models is observed simultaneously with their stabilization by organic compounds. Although NP nuclei are generated homogeneously at the same time, growth and nucleation are discrete processes, and NPs subsequently grow without additional nucleation. Here, the La Mer model with its modifications is the commonly accepted model describing the general mechanism of NP formation, but this describes only the nucleation process followed by growth of the stable nuclei, and it cannot predict or characterize the evolution of NPs' size distribution (Polte 2015). The complex nature of microorganisms and higher plants makes very difficult to determine the organic compounds responsible for NP biosynthesis and stabilization. For example, it was shown that NP biosynthesis can be initiated by enzymes present in live bacteria. Examples include the mechanism of intracellular biosynthesis using nitrate reductase and NP biosynthesis using *Escherichia coli* (Gurunathan et al. 2009) or *Bacillus licheniformis* (Duran et al. 2011). Flavonoids in fruit extracts also play a major role in NP biosynthesis, where *Syzygium cumini* fruit extract, for example, has been successfully utilized in Ag NP biosynthesis (Mittal et al. 2014).

While the stabilizing agent is an organic component from the microorganism or plant extract encasing the NP, the precise stabilization period depends on temperature changes denaturing the protein or acidic/alkaline pH fluctuations (Thatoi et al. 2016; Yuan et al. 2017).

Different biosynthetic processes enable preparation of a wide spectrum of NPs including Ag, Au, Pd, Pt, and the oxidic ZnO, ZrO_2, and Fe_2O_3 NPs. For example, NPs can be synthesized on cell body or plant substrate matrices or directly in colloidal systems, depending on the type of organism involved. NP type and concentration also strongly depend on the following: capping agents, thermodynamic size control, and kinetic and stoichiometric influences. Different NP shapes can be due to organisms' complex nature; while most NPs are spherical, others can be triangular, hexagonal, or rods.

NP synthesis is generally accompanied by color change of the final metal colloid solution (Fig. 13.1a, b) or biomass (Fig. 13.1c, d).For example, Au NPs change the color of the solution to dark red or purple (Fig. 13.1a) and Ag NPs to orange or brown (Fig. 13.1b). NP size also influences sample appearance.

Despite great biosynthetic ability of different organisms and plants and interesting catalytic and antibacterial properties of NPs, not all types of organisms have subsequent nanoparticle application potential. Bio-NPs can be attached to some parts of organism (scales, frustules, scaffolds, husks, etc.) or cellular parts; their separation may be an obstacle for further application (Fig. 13.2). In contrast, metallic NPs embedded on matrices could be easily dried to powder forming so-called bionanocomposite and can be resuspended in different solvents, including water and ethanol (Schröfel et al. 2011; Konvičková et al. 2016; Konvičková et al. 2017; Holišová et al. 2017).

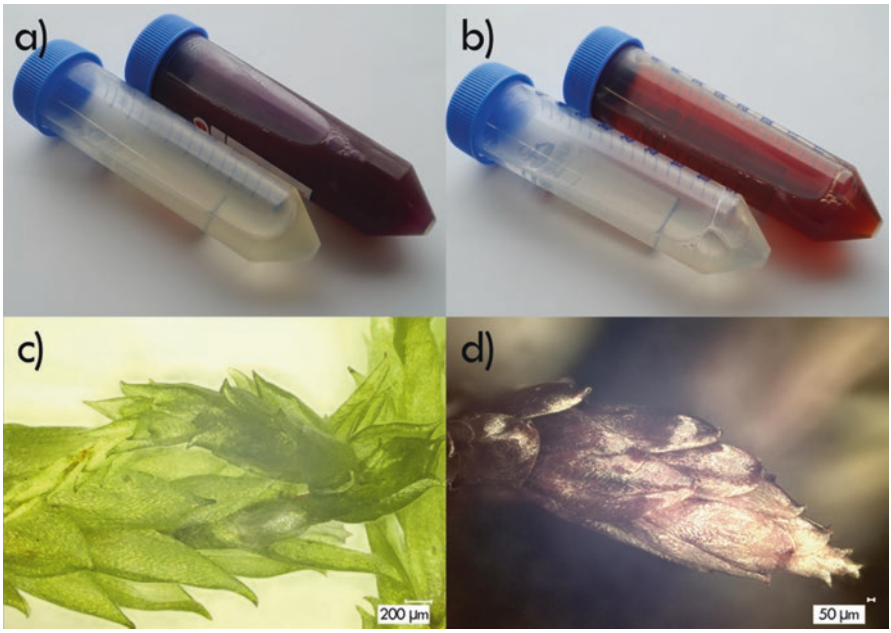

Fig. 13.1 Biosynthesis protocols with different biomass. Colloidal solutions of Au (**a**) and Ag NPs (**b**) are prepared by linden extract. Color change is clearly visible due to reduction of metal precursor and subsequent stabilization by organic compounds in the extract. Another biosynthesis of Au NPs using parts of a moss is presented. Optical microscopy images show a color change between pure biomass (**c**) and the moss with sorbed Au NPs (**d**)

Phytosynthesis is a biosynthetic protocol used by many scientific teams. This involves the preparation of metallic NPs from selected plant extracts and eluates (Velmurugan et al. 2015; Yallappa et al. 2015). It is necessary to consider whether extract preparation or the use of nutritionally significant product fits appropriately with the concept of environmentally and economically friendly biological synthesis. Considerations must also include the nanomaterials' intended use, how often is it to be used, and in what quantities. The use of waste biomass from agriculture and food industries has therefore been intensively studied and tested for bioreduction potential in NP preparation (Yang et al. 2014). The focus should be on wastes which have no further use and are landfilled and on those which are not primarily toxic and used in secondary raw materials.

13.2.2 Phytosynthesized NPs and Their Stabilization

One of the most important aspects of NPs preparation is their stabilization in the dispersal medium. Nanoscale particles are unstable and tend to agglomerate because of short inter-particle distance and their attraction by van der Waals electrostatic

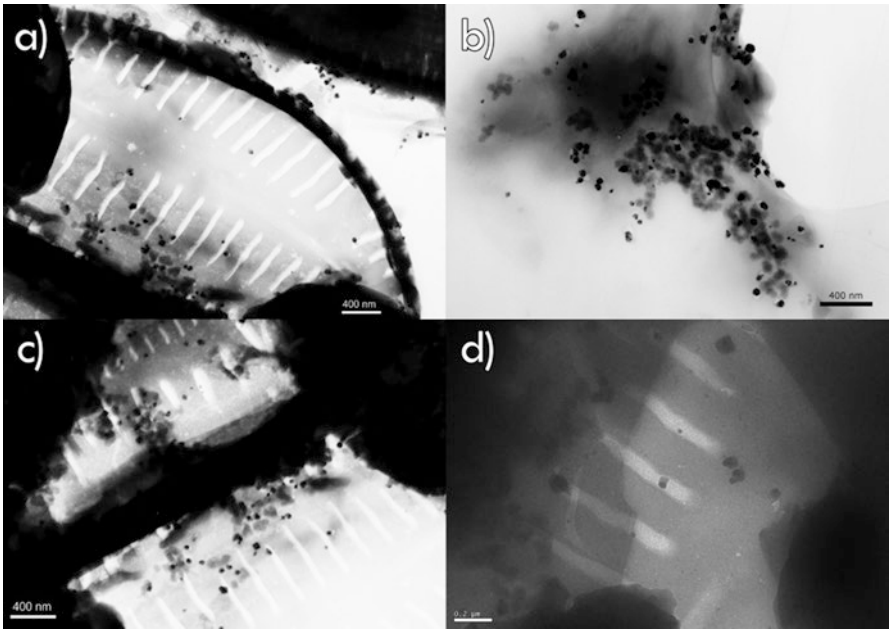

Fig. 13.2 TEM micrographs of Ag NPS on biosilica surface. NPs are synthesized on the diatom silica frustules (**a**). NPs are synthesized on the biosilica surface (**b**) where reduction of metal ions and stabilization of metal NPs occur. Diatoms are unicellular microorganisms with typical ornate frustules with pores on biosilica surface (**a**, **c**, **d**)

forces. Aggregation, agglomeration, and coalescence proceed in the absence of counteractive repellent forces. In contrast, electrostatically stabilized NPs have at least one electric double layer due to surface charging, with the resultant Coulomb forces between the particles decaying exponentially with distance between particles. Particle coagulation is prevented when this repulsion is sufficiently strong. The most commonly used stabilizing agents in chemical synthesis are sodium citrate, cetrimonium bromide, and thiols (Polte 2015). In phytosynthesis, the stabilization is mainly provided by phytochemicals released during biosynthesis process.

13.2.3 Preparation of Phytosynthesized NPs and Their Characterization

As outlined above, many NP types can be produced by biosynthesis including Ag NPs, Au NPs, zirconia oxide (ZrO_2 NPs), copper oxide (CuO NPs), and platinum (Pt NPs). The simplest method of extract preparation is a biomass immersion in cold or hot distilled water. For example, this method provides rapid plant extract preparation in up to 30 min, with the final extract obtained by filtering through a strainer. The pure extract is then mixed with the metal precursor, and concentration ranges from 10^{-2} to 10^{-4} mol/dm^{-3} to synthesize NPs.

UV/VIS spectroscopy verifies NP presence in colloidal solutions via absorption of atomic and molecular electron transitions from ground to excited states. Resultant peaks determine NP size, where narrow, sharp peaks estimate the size in tens of nanometers (Baset et al. 2011).

The dynamic light scattering method (DLS) determines the particle size in a colloidal solution via laser beam illuminating the particles and analyzing the scattered light intensity fluctuations. These fluctuations are associated with light interference in unsteady dispersed phase particles. An electrical double layer exists around each particle, and mV potential between this layer and the outer region is the ζ-potential. ζ-potential determination is suitable for colloidal system study because net charge development at the particle surface affects ion distribution at the interface, resulting in increased concentration of "counterions" with opposite charge to that of the particle. The magnitude of the ζ-potential indicates the potential stability of the colloidal system. When the suspension has a highly positive value above +30 mV or highly negative below −30 mV, the system provides no tendency for aggregation. In contrast, when the ζ-potential approaches 0 mV, there is no force to prevent particles conglomerating. However, pH is a determining factor in ζ-potential; addition of alkali to the suspension increases particle negative charge, and this negative charge is neutralized if acid is added, and surfeit of acid causes positive charge. The ζ-potential and pH therefore have a strong relationship; ζ-potential will be positive at low pH and lower or negative at high pH (Bhattacharjee 2016).

Fourier transform infrared spectroscopy (FTIR) is widely applied in biosynthetic protocols. This is based on the absorption of infrared radiation passing through the sample and changing molecule vibrational energy levels according to changes in the molecule's dipole moment. FTIR is thought to determine the specific functional groups such as -OH and -COOH responsible for bioreduction. Other spectroscopic methods useful for bio-NP characterization are also atomic emission (or absorption) spectroscopy, X-ray diffraction, or Raman spectroscopy.

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) are also integral parts of characterization. Here, the TEM micrographs determine particle size, shape, crystallinity, and chemical composition. The combined analytic capabilities of such methods are most important for identification and further characterization of metal NPs used as antibacterial agents, in catalysis, for enzyme immobilization, drug delivery, sensing, detection, etc. Moreover, metallic bio-NPs can be incorporated in substrates, such as polymer fibers, dependent on their determined properties. For these purposes, biosynthesis and especially *phytosynthesis* are the most simple, rapid, and successful methods of preparing functional metallic NPs.

13.3 Fibers as Matrix for Bio-NPs

New fiber and nanofiber protocols have been developed for the following important applications: material engineering (Chronakis 2005), medicine (Sebe et al. 2013), or biotechnology (Nair and Laurencin 2007). Polymers are large molecules

composed of repetitive monomers (McMurry 2004), and initial polymer solutions, copolymers, and melts significantly control the chemical and physical properties of final fibers (Lukáš et al. 2009). Polymer nanofibers can range from tens of nanometers to 1 μm in diameter.

13.3.1 Brief History of Fiber Spinning

Spinning in an electrostatic field has been known since the sixteenth century, and the first paper on fine-fiber spinning was published by William J. Morton at the beginning of twentieth century (Morton 1902). This was then followed by crucial work on modern capillary electrospinning by John Zelený who designed capillary apparatus to study liquid point electrical discharge (Zeleny 1914). Unfortunately, this advance had insufficient industrial application and development terminated, most likely due to lack of optical and analytical instruments to study at the nanometer level, and it was also unnecessary to focus on this topic because of the limited number of applications. Although the first electron microscope prototype was designed in 1931 (Ruska 1980), it was not until the 1980s that application for its use emerged. The unique technique Nanospider™ patented by Czech scientist Oldřich Jirsák at the Technical University in Liberec heralded an important impetus in the field of polymer fiber preparation. Nanospider™ changed the spinning technique from needle-use to the new needleless innovation, producing fibers in the 200–500 nm diameter range (Jirsak et al. 2009).

13.3.2 Fiber Preparation via Spinning Techniques

Electrospinning is a nonmechanical, electrostatic technique using a high-voltage electrostatic field to charge the surface of liquid solutions, especially polymers. The electric field is applied between the polymer solution and a grounded collector, polymer drops are drawn, and the charged jet is ejected when the electric field overcomes liquid surface tension. The path of the charged jet is controlled by the electric field (Fig. 13.3). Electrospinning technology is divided into "capillary" and "needleless" categories, depending on the place where the fibers are extracted. While capillary electrospinning is limited by the amount of injected polymer, the needleless technique has high fiber production from the free surface of the polymer via self-organization (Lukáš et al. 2009).

Electrospinning covers a wide range of physical phenomena in the field of electrohydrodynamics, including electrophoresis, electro-diffusion, and electroosmosis. The liquid in electrospinning acquires surface tension from short intermolecular forces without influence from the external electrostatic field, but this can only occur when the liquid surface thickness lies within the range of the intermolecular forces. The external electrostatic field then acts on the liquid surface and charge is induced (Lukáš et al. 2009).

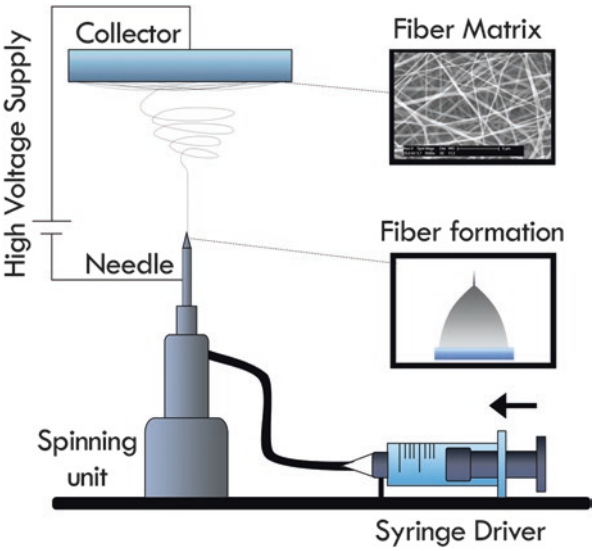

Fig. 13.3 Preparation of polymer fibers by capillary electrospinning. The polymer is pressed from the syringe to the spinning unit and injected during the spinning process. After applied voltage, the polymer jets are taken out and fall on the collector. The jet path is accompanied by solvent evaporation and solid fiber formation

Important technical parameters for polymer fiber preparation include polymer molecular weight and concentration, voltage and conductivity, viscosity, surface tension, flow velocity, distance between the spinneret and collector, and laboratory temperature and humidity (Lukáš et al. 2009). Polymer concentration is important because the fibrous sample becomes a mixture of fibers and defects when the concentration reaches a limiting value. Higher voltages and consequent higher Coulomb forces in the jet induce greater stretching of the polymer solution, leading to fiber diameter decrease and rapid evaporation of solvent from the fibers.

Centrifugal spinning is an alternate technique for fiber preparation, also called rotary-jet or force spinning, because it uses centrifugal force to extrude fibers from the spinning unit. The spinneret rotates around its axis, and a viscous jet is ejected as fibers onto a metal collector under maximized rotation speed (Mellado et al. 2011). Replacement of electrostatics by centrifugal force initiated increase in conductive fiber-spinning materials, and the application of heat near the spinning unit enhanced the melting and spinning of solid materials, thus negating chemical preparation (Sarkar et al. 2010). Centrifugal spinning also enables fiber preparation from solutions with higher concentrations than possible with electrostatic spinning (Lu et al. 2013).

13.3.3 Biocompatible Polymers Suitable for Fiber Formation via Electrospinning

Many materials are suitable for spinning natural polymers fibers with submicron diameters. These are extremely useful in tissue engineering, filtration membranes, and other biomedical fields. The natural collagen, gelatin, chitin, casein, cellulose acetate, and fibrinogen polymers have high biocompatibility and low immunogenicity

compared to synthetic polymers. For example, (1) collagen scaffolds are used in wound dressing and tissue engineering, as they mimic the native collagen network, (2) gelatin is a natural polymer widely used in medical and pharmaceutical applications because of its biocompatibility and biodegradability in physiological environments, and (3) in tissue engineering, chitosan has beneficial physicochemical properties derived from its solid-state structure. One drawback of naturally derived polymer fibers, however, is that they can undergo partial denaturation, leading to degradation of the initial material during spinning (Bhardwaj and Kundu 2010). A three-dimensional (3D) fiber network can be prepared naturally by living organisms. These include the *Acetobacter* bacterium which forms cellulose (Yamada 1983). Its 3D fibrous structures are similar to plant cellulose, characterized by high porosity, water absorbance, high chemical purity and biocompatibility, and they are therefore called bacteria cellulose (Hu et al. 2009). A further inspiration from nature is mimicry of the insect cuticle. The main components here are chitosan and fibrin, with biodegradable and biocompatible features approved for clinical products. In addition to medical application, it replaces plastics in consumer products (Fernandez and Ingber 2012).

In the case of synthetic polymers, frequently used polymers are group of polyesters such as poly(ε-caprolacton) PCL, poly(lactic acid) (PLA), or poly(glycolic acid) (PGA) and its copolymers. PCL is used in bone tissue engineering as its fibrous structure and high porosity provide viability, proliferation, and cell adhesion, and its large pores enhance cell growth and bone integration (Erben et al. 2015). The mixture of PCL with gelatin improves the final scaffold for enhanced cell migration to the PCL mesh (Zhang et al. 2005). Poly(lactic-co-lactic acid) (PLGA) is suitable for nonwoven scaffolds because their porosity is over 90% and their high surface area enables cellular attachment and fiber orientation. In addition, their subsequent impregnation with antibiotics reduces post-surgery adhesions (Bhardwaj and Kundu 2010).

Synthetic poly(vinyl alcohol) (PVA) combined with Ag NPs produces a nonwoven membrane which controls antibacterial properties (Jia et al. 2007). It is also advantageous in a wide range of biomedical applications through its water-solubility, biocompatibility, and hydrophilic nature. PVA and carboxy-methyl (CM) chitosan are also promising carriers of Ag NPs for biomedical application, and chitosan and its derivatives' biocompatibility and biodegradability make these the most widely used natural polysaccharides in biomedical applications (Nguyen et al. 2011).

13.4 Prospective Bio-NP Incorporation into the Polymer Fibers

Many types of colloidal NPs such as gold (Deniz et al. 2011), zinc (Virovska et al. 2014), titanium (Fathona and Yabuki 2014), or carbon nanotubes (Salalha et al. 2004) and other particulates (Hansen et al. 2005) can be incorporated into the

polymer fibers, polymer mixtures, or copolymers. NPs are usually obtained by chemical and/or thermal synthesis, dispersed in the polymer solution, inserted into the spinning unit, and spun into fibers with solvent evaporation (Reneker and Yarin 2008). However, this approach can result in nonhomogenous NP dispersion in the polymer matrix or aggregation which destroys uniform composite structure (He et al. 2009). Dissolution of the metallic precursor prior to polymer spinning may prevent these problems (Wang et al. 2005).

Examples of conventionally prepared NPs in polymer fibers include:

1. Chemically prepared ZnO is incorporated in a wide range of polymers including PEO, PVP, and PVA, and ZnO nanoparticles are incorporated in PLA fibers by combined electrospinning and electrospraying. This hybrid fibrous material combines the polymer and inorganic filler properties of biodegradability, photocatalytic, and antibacterial activity (Virovska et al. 2014).
2. TiO_2 NPs are also incorporated in polymer fibers, as in cellulose acetate electrospun fibers. While this composite enhances drug delivery systems, material template fabrication, and composite fibril fillers, high NP concentration causes aggregation inside the polymer (Fathona and Yabuki 2014).
3. Examination of chitosan/sericin/PVA fibers with incorporated Ag NPs highlights that chitosan is beneficial in filtration, drug delivery, tissue engineering, and wound dressings. Intermolecular interactions between chitosan and both sericin and PVA are through hydrogen bonding, and these compounds can reduce silver ions to Ag NPs. Impressively, these fibers completely inhibited bacterial growth, with 100% antibacterial activity against *E.coli* (Hadipour-Goudarzi et al. 2014).
4. PVA/Ag NPs and PVP/Ag NPs fibers were tested against *E.coli*, *Staphylococcus aureus*, and *Pseudomonas aeruginosa* in two NP preparation methods: thermal synthesis and chemical reduction of silver nitrate. The NPs are produced by these methods and then incorporated in PVA and PVP. Further antibacterial testing using disk diffusion formed a larger inhibition zone in PVA/Ag NPs than in PVP/Ag NPs (Pencheva et al. 2012).
5. Silver selenide nanoparticle incorporation in PVP fibers highlighted that selenide on the Ag NP surface effects a strong chemical interaction between NPs and the polymer. This hybrid nanocomposite's antibacterial activity emanates mainly from the Ag NPs, and it can also be applied as a filter membrane in systems removing heavy metals and bacteria from water (More et al. 2015).

In addition to chemically prepared particles, metallic bio-NPs, and especially their colloid suspensions, also have spinning potential. Their major advantage is that preparation, stabilization (through organic layer on the NP surface), and reduction can be achieved in one simple step, and since bio-NPs are usually prepared in aqueous medium, the polymer precursor can be dissolved directly in the bio-NP solution (Fig. 13.4).The dissolution can be conducted at ambient temperature, and while continuous heating is also effective, this can have negative effects. Polymers can be hydrophilic and hydrophobic, so prior to commencing the experiment, it is crucial to

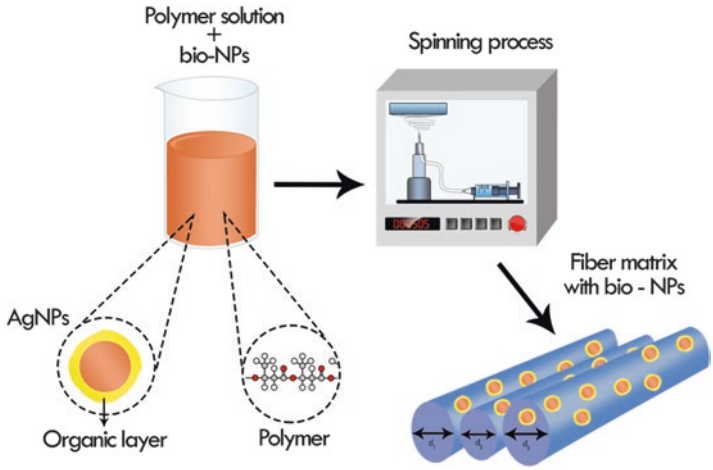

Fig. 13.4 Fiber preparation containing bio-Ag NPs: metallic NPs can be directly dispersed in polymer solution. The mixture is continuously batched to the spinning unit and fibers containing NPs are formed. Calculated diameters highlight that polymer fibers have nonuniform diameter

consider whether a water-soluble or oil-soluble solvent is appropriate for synthesis of chosen bio-NPs and also what type of biosynthesis is the most suitable.

13.5 Conclusions

Biosynthesis, and especially phytosynthesis, is a simple method for effective preparation of metallic nanoparticles suitable for a great variety of applications, most especially in antibacterial, medical, and chemical compound catalysis. This is proven in 4-nitrophenol, COx, and NOx (Schröfel et al. 2014; Holišová et al. 2017). The increasing trend of antibiotic and medicinal overuse has enabled bacteria to adapt in multidrug resistance to bacteriostatic and bactericidal agents, and nanoparticles may be quite effective in countering this problem. The preparation of new composite materials based on natural and synthetic polymers with active antibacterial particles heralds exciting possibilities for medical and pharmaceutical application.

Polymers must comply with exacting demands to satisfy these applications, especially biocompatibility, biodegradability, resistance to temperature changes, mechanical and chemical resistance, and chemical purity. This requires a new generation of active nanocomposites, where phytosynthesis-prepared nanoparticles incorporated in the fiber membranes release nano-sized killing agents against bacteria colonies. Finally, these prepared products can be widely used, especially in medical equipment coatings, antibacterial gels, and air-conditioning systems.

Acknowledgment This work was supported by Ministry of Education of the Czech Republic project No. SP2016/57, SP2017/70.

References

Baset S, Akbari H, Zeynali H, Shafie M. Size measurement of metal and semiconductor nanoparticles vis UV/VIS absorption spectra. Dig J Nanomater Biostruct. 2011;6(2):709–16.

Bhardwaj N, Kundu SC. Electrospinning: a fascinating fiber fabrication technique. Biotechnol Adv. 2010;28(3):325–47.

Bhattacharjee S. DLS and zeta potential – what they are and what they are not? J Control Release. 2016;235:337–51.

Castro-Longoria E, Vilchis-Nestor AR, Avalos-Borja M. Biosynthesis of silver, gold and bimetallic nanoparticles using the filamentous fungus Neurospora crassa. Colloids Surf B: Biointerfaces. 2011;83(1):42–8.

Choi WK, Liew TH, Chew HG, Zheng F, Thompson CV, Wang Y, Hong MH, Wang XD, Li L, Yun J. A combined top-down and bottom-up approach for precise placement of metal nanoparticles on silicon. Small. 2008;4(3):330–3.

Chronakis IS. Novel nanocomposites and nanoceramics based on polymer nanofibers using electrospinning process—a review. J Mater Process Technol. 2005;167(2–3):283–93.

Deniz AE, Vural HA, Ortaç B, Uyar T. Gold nanoparticle/polymer nanofibrous composites by laser ablation and electrospinning. Mater Lett. 2011;65(19–20):2941–3.

Díez-Pascual AM, Naffakh M, Marco C, Ellis G. Mechanical and electrical properties of carbon nanotube/poly(phenylene sulphide) composites incorporating polyetherimide and inorganic fullerene-like nanoparticles. Compos A: Appl Sci Manuf. 2012;43(4):603–12.

Duran N, Marcato PD, Duran M, Yadav A, Gade A, Rai M. Mechanistic aspects in the biogenic synthesis of extracellular metal nanoparticles by peptides, bacteria, fungi, and plants. Appl Microbiol Biotechnol. 2011;90(5):1609–24.

Engstrom DS, Porter B, Pacios M, Bhaskaran H. Additive nanomanufacturing – a review. J Mater Res. 2014;29(17):1792–816.

Erben J, Pilarova K, Sanetrnik F, Chvojka J, Jencova V, Blazkova L, Havlicek J, Novak O, Mikes P, Prosecka E, Lukas D, Kuzelova Kostakova E. The combination of meltblown and electrospinning for bone tissue engineering. Mater Lett. 2015;143(0):172–6.

Fathona IW, Yabuki A. Short electrospun composite nanofibers: effects of nanoparticle concentration and surface charge on fiber length. Curr Appl Phys. 2014;14(5):761–7.

Fernandez JG, Ingber DE. Unexpected strength and toughness in chitosan-fibroin laminates inspired by insect cuticle. Adv Mater. 2012;24(4):480–4.

Gurunathan S, Kalishwaralal K, Vaidyanathan R, Venkataraman D, Pandian SR, Muniyandi J, Hariharan N, Eom SH. Biosynthesis, purification and characterization of silver nanoparticles using Escherichia coli. Colloids Surf B Biointerfaces. 2009;74(1):328–35.

Hadipour-Goudarzi E, Montazer M, Latifi M, Aghaji AAG. Electrospinning of chitosan/sericin/PVA nanofibers incorporated with in situ synthesis of nano silver. Carbohydr Polym. 2014;113(0):231–9.

Hansen LM, Smith DJ, Reneker DH, Kataphinan W. Water absorption and mechanical properties of electrospun structured hydrogels. J Appl Polym Sci. 2005;95(2):427–34.

He D, Hu B, Yao QF, Wang K, Yu SH. Large-scale synthesis of flexible free-standing SERS substrates with high sensitivity: electrospun PVA nanofibers embedded with controlled alignment of silver nanoparticles. ACS Nano. 2009;3(12):3993–4002.

Holišová V, Urban M, Kolenčík M, Němcová Y, Schröfel A, Peikertová P, Slabotinský J, Kratošová G. Biosilica-nanogold composite: Easy-to-prepare catalyst for soman degradation. Arab J Chem. 2017. in press, doi.org/10.1016/j.arabjc.2017.08.003.

Hu W, Chen S, Li X, Shi S, Shen W, Zhang X, Wang H. In situ synthesis of silver chloride nanoparticles into bacterial cellulose membranes. Mater Sci Eng C. 2009;29(4):1216–9.
Hu X, Chen X, Zhang L, Lin X, Zhang Y, Tang X, Wang Y. A combined bottom-up/top-down approach to prepare a sterile injectable nanosuspension. Int J Pharm. 2014;472(1–2):130–9.
Jia J, Duan Y-Y, Wang S-H, Zhang S-F, Wang Z-Y. Preparation and characterization of antibacterial silver-containing nanofibers for wound dressing applications. J US-China Med Sci. 2007;4(2):52–4.
Jirsak O, Sanetrnik F, Lukas D, Kotek V, Martinova L, Chaloupek J. Method of nanofibres production from a polymer solution using electrostatic spinning and a device for carrying out the method, Google Patents 2009;US 7,585,437 B2.
Junlabhut P, Mekprasart W, Noonuruk R, Chongsri K, Pecharapa W. Characterization of ZnO:Sn Nanopowders synthesized by co-precipitation method. Energy Procedia. 2014;56(0):560–5.
Krahne R, Morello G, Figuerola A, George C, Deka S, Manna L. Physical properties of elongated inorganic nanoparticles. Phys Rep. 2011;501(3–5):75–221.
Konvičková Z, Schröfel A, Kolenčík M, Dědková K, Peikertová P, Žídek M, Seidlerová J, Kratošová G. Antimicrobial bionanocomposite–from precursors to the functional material in one simple step. J Nanopart Res. 2016;18(12).
Konvičková Z, Schröfel A, Kolenčík M, Dědková K, Peikertová P, Žídek M, Seidlerová J, Kratošová G. Erratum to: Antimicrobial bionanocomposite–from precursors to the functional material in one simple step (Journal of Nanoparticle Research, (2016), 18, 12, (368), 10.1007/s11051-016-3664-y). J Nanopart Res. 2017;19(7).
Lu Y, Li Y, Zhang S, Xu G, Fu K, Lee H, Zhang X. Parameter study and characterization for polyacrylonitrile nanofibers fabricated via centrifugal spinning process. Eur Polym J. 2013;49(12):3834–45.
Lukáš D, Sarkar A, Martinová L, Vodsed'álková K, Lubasová D, Chaloupek J, Pokorný P, Mikeš P, Chvojka J, Komárek M. Physical principles of electrospinning (electrospinning as a nano-scale technology of the twenty-first century). Text Prog. 2009;41(2):59–140.
McMurry J. Organic chemistry. Belmont: Thomson-Brooks/Cole; 2004.
Mellado P, McIlwee HA, Badrossamay MR, Goss JA, Mahadevan L, Kit Parker K. A simple model for nanofiber formation by rotary jet-spinning. Appl Phys Lett. 2011;99(20): -.
Mittal AK, Bhaumik J, Kumar S, Banerjee UC. Biosynthesis of silver nanoparticles: elucidation of prospective mechanism and therapeutic potential. J Colloid Interface Sci. 2014;415(0):39–47.
More DS, Moloto MJ, Moloto N, Matabola KP. TOPO-capped silver selenide nanoparticles and their incorporation into polymer nanofibers using electrospinning technique. Mater Res Bull. 2015;65(0):14–22.
Morton WJ. Method of dispersing fluids, Google Patents. 1902;US 705,691.
Nair LS, Laurencin CT. Biodegradable polymers as biomaterials. Prog Polym Sci. 2007;32(8–9):762–98.
Narayanan KB, Sakthivel N. Biological synthesis of metal nanoparticles by microbes. Adv Colloid Interf Sci. 2010;156(1–2):1–13.
Nguyen T-H, Lee K-H, Lee B-T. Fabrication of Ag nanoparticles dispersed in PVA nanowire mats by microwave irradiation and electro-spinning. Mater Sci Eng C. 2010;30(7):944–50.
Nguyen TH, Kim YH, Song HY, Lee BT. Nano Ag loaded PVA nano-fibrous mats for skin applications. J Biomed Mater Res B Appl Biomater. 2011;96(2):225–33.
Omri A, Benzina M, Bennour F. Industrial application of photocatalysts prepared by hydrothermal and sol–gel methods. J Ind Eng Chem. 2015;21(0):356–62.
Pencheva D, Bryaskova R, Kantardjiev T. Polyvinyl alcohol/silver nanoparticles (PVA/AgNps) as a model for testing the biological activity of hybrid materials with included silver nanoparticles. Mater Sci Eng C. 2012;32(7):2048–51.
Pentimalli M, Bellusci M, Padella F. High-energy ball milling as a general tool for nanomaterials synthesis and processing. Handbook of mechanical nanostructuring, Wiley-VCH Verlag GmbH & Co. KGaA; 2015. pp. 663–679.

Pinna A, Lasio B, Piccinini M, Marmiroli B, Amenitsch H, Falcaro P, Tokudome Y, Malfatti L, Innocenzi P. Combining top-down and bottom-up routes for fabrication of mesoporous Titania films containing ceria nanoparticles for free radical scavenging. ACS Appl Mater Interfaces. 2013;5(8):3168–75.

Polte J. Fundamental growth principles of colloidal metal nanoparticles – a new perspective. CrystEngComm. 2015;17(36):6809–30.

Reneker DH, Yarin AL. Electrospinning jets and polymer nanofibers. Polymer. 2008;49(10):2387–425.

Ruska E. The early development of electron lenses and electron microscopy. Stuttgart: Hirzel; 1980.

Salalha W, Dror Y, Khalfin RL, Cohen Y, Yarin AL, Zussman E. Single-walled carbon nanotubes embedded in oriented polymeric nanofibers by electrospinning. Langmuir. 2004;20(22):9852–5.

Sarkar K, Gomez C, Zambrano S, Ramirez M, de Hoyos E, Vasquez H, Lozano K. Electrospinning to Forcespinning™. Mater Today. 2010;13(11):12–4.

Schröfel A, Kratošová G, Bohunická M, Dobročka E, Vávra I. Biosynthesis of gold nanoparticles using diatoms—silica-gold and EPS-gold bionanocomposite formation. J Nanopart Res. 2011;13(8):3207–16.

Schröfel A, Kratošová G, Šafařík I, Šafaříková M, Raška I, Shor LM. Applications of biosynthesized metallic nanoparticles – a review. Acta Biomater. 2014;10(10):4023–42.

Sebe I, Szabó B, Nagy ZK, Szabó D, Zsidai L, Kocsis B, Zelkó R. Polymer structure and antimicrobial activity of polyvinylpyrrolidone-based iodine nanofibers prepared with high-speed rotary spinning technique. Int J Pharm. 2013;458(1):99–103.

Son Y, Yeo J, Ha CW, Lee J, Hong S, Nam KH, Yang D-Y, Ko SH. Application of the specific thermal properties of Ag nanoparticles to high-resolution metal patterning. Thermochim Acta. 2012;542:52–6.

Thatoi P, Kerry RG, Gouda S, Das G, Pramanik K, Thatoi H, Patra JK. Photo-mediated green synthesis of silver and zinc oxide nanoparticles using aqueous extracts of two mangrove plant species, Heritiera fomes and Sonneratia apetala and investigation of their biomedical applications. J Photochem Photobiol B Biol. 2016;163:311–8.

Velmurugan P, Cho M, Lim S-S, Seo S-K, Myung H, Bang K-S, Sivakumar S, Cho K-M, Oh B-T. Phytosynthesis of silver nanoparticles by Prunus yedoensis leaf extract and their antimicrobial activity. Mater Lett. 2015;138:272–5.

Vijayaraghavan K, Mahadevan A, Sathishkumar M, Pavagadhi S, Balasubramanian R. Biosynthesis of Au(0) from Au(III) via biosorption and bioreduction using brown marine alga Turbinaria conoides. Chem Eng J. 2011;167(1):5–5.

Virovska D, Paneva D, Manolova N, Rashkov I, Karashanova D. Electrospinning/electrospraying vs. electrospinning: a comparative study on the design of poly(l-lactide)/zinc oxide non-woven textile. Appl Surf Sci. 2014;311(0):842–50.

Wang Y, Yang Q, Shan G, Wang C, Du J, Wang S, Li Y, Chen X, Jing X, Wei Y. Preparation of silver nanoparticles dispersed in polyacrylonitrile nanofiber film spun by electrospinning. Mater Lett. 2005;59(24–25):3046–9.

Yadav TP, Yadav RM, Singh DP. Mechanical milling: a top down approach for the synthesis of nanomaterials and nanocomposites. Nanosci Nanotechnol. 2012;2(3):22–48.

Yallappa S, Manjanna J, Dhananjaya BL. Phytosynthesis of stable Au, Ag and Au–Ag alloy nanoparticles using J. Sambac leaves extract, and their enhanced antimicrobial activity in presence of organic antimicrobials. Spectrochim Acta A Mol Biomol Spectrosc. 2015;137(0):236–43.

Yamada Y. Acetobacter xylinus sp. nov., nom. rev., for the cellulose-forming and cellulose-less, acetate-oxidizing acetic acid bacteria with the Q-10 system. J Gen Appl Microbiol. 1983;29(5):417–20.

Yang N, WeiHong L, Hao L. Biosynthesis of Au nanoparticles using agricultural waste mango peel extract and its in vitro cytotoxic effect on two normal cells. Mater Lett. 2014;134:67–70.

Yuan C-G, Huo C, Yu S, Gui B. Biosynthesis of gold nanoparticles using Capsicum annuum var. grossum pulp extract and its catalytic activity. Physica E. 2017;85:19–26.

Zeleny J. The electrical discharge from liquid points, and a hydrostatic method of measuring the electric intensity at their surfaces. Phys Rev. 1914;3(2):69–91.

Zhang YZ, Venugopal J, Huang ZM, Lim CT, Ramakrishna S. Characterization of the surface biocompatibility of the electrospun PCL-collagen nanofibers using fibroblasts. Biomacromolecules. 2005;6(5):2583–9.

Zhang W, Chen Z, Liu H, Zhang L, Gao P, Li D. Biosynthesis and structural characteristics of selenium nanoparticles by pseudomonas alcaliphila. Colloids Surf B Biointerfaces. 2011;88(1):196–201.