

Methods of ZnO nanoparticles synthesis

KAMILA ŹELECHOWSKA

Gdansk University of Technology, Faculty of Applied Physics and Mathematics, Gdańsk, Poland

e-mail: kzelechowska@mif.pg.gda.pl

Abstract

Zinc oxide nanostructures are interesting nanomaterials with a wide range of applications. Since the physical and chemical properties of ZnO nanoparticles are influenced both by their shape and size, a control of morphology of ZnO structures is needed for their commercial usage. Different chemical, physical, and biological methods used to produce ZnO nanostructures can be found in the literature. The production of ZnO nanoparticles using so-called green methods, using, for example, plant extracts or living organisms, is being investigated as these methods are environmentally friendly and of low-cost. This review also discusses the trends in the biological synthesis of semiconducting nanoparticles.

Key words: biotemplating, green chemistry, ZnO nanoparticles, nanostructures, modified microorganisms, bioremediation

Introduction

Zinc oxide nanoparticles (ZnO NPs) are one of the most studied materials. They are generally of low toxicity. However, they may pose a significant risk to the environmental biota at higher concentrations (Ma, 2013; Lopes et al., 2014; Sarkar et al., 2014). On the other hand, ZnO NPs possess several favorable properties such as good transparency, strong room-temperature luminescence, high electron mobility, wide bandgap, chemical and photochemical stability, etc. (Vaseem, 2010). These properties make them an interesting material for use in new light-emitting devices, solar cells, biosensors, and photocatalysts (Fan and Lu, 2006; Vaseem, 2010). In the applications of ZnO NPs, controlling the size and the shape of growing nanoparticles is the main problem. There is an evidence that the shape and size of the ZnO NPs influence their physical properties. Simplicity, high speed, and low cost of their production are some other aspects that should be considered. ZnO NPs can be prepared by several methods, resulting in nanostructures of different shapes. The most popular methods are wet chemical methods performed in water (Lee et al., 2009; Medina et al., 2012; Mehta et al., 2012), organic solvents (Spanhel, 1991; Meulenkamp, 1998; Mezni et al., 2012), ionic liquids (Zhu, 2006; Singh, 2012; Gandhi et al., 2013), or microemulsions (Hingorani et al., 1993; Singhal et al., 1997). Sonochemical- (Jung et al., 2008; Ya-

dav, 2008; Jia et al., 2010) and microwave- (Ambrožič, 2011; Nehru, 2012) assisted synthesis of ZnO NPs was reported. Various methods such as electrochemical deposition (Kim, 2009), evaporation-condensation (Kong, 2003), and chemical vapor deposition (Fujita et al., 2004) were also used to produce ZnO nanostructures. These are, however, expensive and require specific equipment. The recently proposed biogenic synthesis of ZnO NPs using plant extracts and biotemplates, including macromolecules, bacteria, and bacteriophages, has also been described in this review.

Synthesis using plants, algae, and fungi

In the literature, there are numerous examples of ZnO NPs synthesis using plants. Extracts were obtained using different parts of plants, including leaves, roots, fruit, as well as plant's secretions. In this review, the usage of plants producing milky sap, such as, for example, *Aloe vera* or *Calotropis gigantea*, and soapberry family plants, such as rambutan or *Sapindus rarak*, as well as examples of ZnO NPs synthesis using plants belonging to Rutaceae family such as *Poncirus trifoliata* or *Citrus aurantifolia* have been presented (references given below). Other plants that are highly utilized in the synthesis of ZnO NPs, mainly due to their accessibility and known source of phytochemicals, include herbaceous plants which are also used in medicine. Examples

include *Coriandrum sativum*, *Ocimum basilicum* or *Rhizoma coptidis*, and others. Although this topic is gaining increasing interest, there is almost no information on the mechanism of ZnO NP synthesis in the presence of plant extracts. Thus, this topic needs more detailed studies.

Biosynthesis of ZnO NPs using plants such as *Aloe vera* was reported and their optical and antimicrobial properties were tested (Sangeetha et al., 2011, 2012). In a typical procedure, aloe extracts at different concentrations (5-50%) were prepared with distilled water, and zinc nitrate was dissolved in this aloe extract solution. The obtained particles were found to be predominantly spherical. The size of the particle, controlled by varying the concentrations of aloe extract, was 25-40 nm, as determined by a transmission electron microscopy (TEM) analysis. The X-ray diffraction (XRD) patterns of the products confirmed wurtzite crystal structure for all samples; no diffraction peaks from other species were detected. The mechanism by which nanoparticles are formed in the biosynthesis procedure is still not clear. Overall observations prove the existence of some phenolic compounds, terpenoids or proteins that are bound to the surface of ZnO. The stability of ZnO NPs may be due to the free amino and carboxylic groups that interacted with their surface.

Calotropis procera is a plant that produces milky sap, which is a mixture of chemicals including proteins, amino acids, carbohydrates, lipids, vitamins, alkaloids, resins, and tannins. Singh et al. (2011) used sap from *Calotropis procera* and zinc acetate to produce nearly spherical ZnO NPs with average size between 5 and 40 nm. According to the authors, ZnO NPs are stabilized by alkaloids and proteins present in the used sap. Heating aqueous solution of zinc nitrate aqueous solution and leaves extract of another plant of genus *Calotropis* (*Calotropis gigantea*) produced ZnO nanocrystallites, as described by Vidya et al. (2013). Nanoparticles were spherical in shape, with size in the range of 30-35 nm as confirmed by scanning electron microscopy (SEM) and XRD analysis. ZnO NPs were also synthesized from the so-called gum tragacanth, which can be extracted from the dried sap obtained from the roots and stems of *As-tragalus gummifer* (Darroudi et al., 2013). Here, zinc nitrate solution was used as a metal source. TEM imaging showed that the size of the majority of the obtained nanoparticles was less than 50 nm. Other plant species

tested were *Sapindus rarak* and *Nephelium lappaceum* belonging to Sapindaceae family, also known as soapberry family. The use of an aqueous extract of *Sapindus rarak* as a medium in the synthesis of ZnO particles by the hydrothermal method was performed by Maryanti et al. (2014). Depending on the concentration of aqueous extract of *S. Rarak*, ZnO particles of different shapes and crystallinity were obtained; however, the obtained particles were in micro-sizes rather than nano-sizes. A biosynthesis of zinc oxide nanocrystals employing *Nephelium lappaceum* L. (rambutan) peel extract as a natural ligation agent and zinc nitrate as a source of metal was reported by Yuvakkumar et al. (2014). The utilized rambutan peel extracts are a rich source of active ingredients such as polyphenols, alkaloids, flavonoids, and vitamins, of which especially polyphenols such as ellagic acid, corilagin, and geranin are present as major extract components. According to authors, polyphenolic compounds, for example, ellagic acid, can form complexes with metal cations (Fig. 1), which gives white solid of ZnO NPs after calcination at 450 °C. SEM and XRD employed to study the morphology and size of the prepared ZnO structures showed that needle-like structures with average size of ~440 nm comprised wurtzite-type nanocrystals with an average size of ~50 nm.

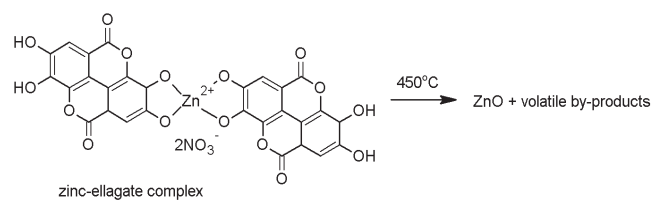


Fig. 1. Possible structure of zinc-ellagate complex (after Yuvakkumar et al., 2014)

Citrus fruits, a rich source of polyphenols and organic acids, were used in the synthesis of ZnO NPs as well. Synthesis of ZnO NPs using orange juice was reported by Jha et al. (2011). The synthesis was performed at near-room temperature, using diluted orange juice and ZnCl₂ aqueous solution. X-ray and TEM analyses were performed to ascertain the formation of ZnO NPs. Crystalline, well-dispersed ZnO NPs of sizes between 9 and 25 nm were formed. The orange juice, along with reducing carbohydrates, contains an oxidoreductively labile ascorbic acid, citric acid, and polyphenols (as for example hesperidin), that might have played a major role in ZnO NP synthesis. However, the mechanism of ZnO

biosynthesis requires more detailed studies in this case. Later, the biosynthesis of ZnO NPs using another citrus fruit, *Citrus aurantifolia* (lime), was reported (Samat and Nor, 2013). Spherical ZnO NPs with sizes in the range of 50-200 nm were produced using different concentrations of zinc acetate as the metal source.

The trifoliolate orange (*Poncirus trifoliata*), a member of the family Rutaceae closely related to citrus, was also shown to be useful in the synthesis of ZnO NPs (Nagajyothi et al., 2013). Nanoparticles synthesized using fruit extract of this plant and zinc nitrate solution were spherical in shape and their sizes were between 8 and 36 nm. The mean size of ZnO NPs was 21 nm, and they showed wurtzite crystallinity.

As mentioned above, herbs extracts are also frequently used in the biogenic synthesis of ZnO NPs. Gnanasangeetha and Thambavani used leaves extracts of *Coriandrum sativum* (2013a) and *Acalypha indica* (2013b) to synthesize ZnO NPs, taking zinc acetate dihydrate as the metal source. The XRD study confirmed the wurtzite-type structure of ZnO NPs with average size of ~66 nm in case of synthesis using *Coriandrum sativum* extract, and 80 nm, when *Acalypha indica* extract was used. Fourier transform infrared spectroscopy (FTIR) studies of ZnO NPs obtained by both methods revealed the presence of hydroxyl and carbonyl groups, amines and aromatics, confirming the presence of phytocompounds on their surface.

Green synthesis of hexagonal (wurtzite) phase ZnO NPs of about 50 nm was achieved by Salam et al. (2014) using leaf extract of *O. basilicum* L. var. *purpurascens* Benth and zinc nitrate solution. In this case, presence of linalool, a naturally occurring terpene alcohol in *O. basilicum*, was found to facilitate the ZnO NP formation. The spherical and rod-shaped ZnO NPs (size 3-25 nm) were also synthesized by treating the zinc nitrate solution with *Rhizoma coptidis* extract (Nagajyothi et al., 2014). The presence of different classes of organic compounds (amines, aromatics, alkynes, nitro groups and alkyl halides) in this extract involved in the formation of ZnO NPs was confirmed by FTIR analysis. Similarly, ZnO NPs were biologically synthesized using the leaf extract of *Plectranthus amboinicus* (Vijayakumar et al., 2014). TEM analysis of ZnO NPs showed their average size to be in the range of about 20-50 nm. According to authors, phytocompounds from plant extract chemisorb on the surfaces of ZnO NPs, and such nanoparticles have a spe-

cific odor caused by the adsorbed compounds due to which they can be used as potential mosquito repellents.

The liquid fraction of palm oil, which is highly mono-saturated and rich in oleic acids called palm olein, was used as a medium in the synthesis of ZnO nanostructures (Ramimoghdam et al., 2013). Zinc acetate and NaOH water solutions were mixed to produce colloid suspension, which was followed by adding different volumes of palm olein. The solution was transferred to an autoclave and hydrothermal growth was conducted. Particles of different morphology including flake-, flower- and three-dimensional starlike structures were obtained. The physicochemical properties of the resulting ZnO particles can be tuned changing the ratio of palm olein to Zn cation. Further, the mechanism of ZnO starlike nanoparticle formation was proposed. According to the authors it could be summarized in three steps. First, the fatty acids of palm olein form a spherical micelle. In the second step, zinc acetate aggregates over the micelle in a regularly ordered array to form zinc hydroxide crystals, leading to the formation of nucleation sites of ZnO. Thus, during the reaction time, together with increasing quantity of the reactant, the ZnO nuclei will subsequently grow and conglomerate to finally form three-dimensional starlike particles. In the last step, the organic templates are removed, resulting in phase-pure ZnO nanostructures. This method is described as being environmentally friendly and of low cost, and is, essentially, a combination of sol-gel and hydrothermal methods, but using a rather high temperature of reaction. Thus, this method is not very beneficial when compared to other methods described in this review. Lately, Shekhawat et al., (2014) prepared aqueous extracts from various parts of *Passiflora foetida* L., including leaves, stem, roots, and flowers as well as immature and mature fruit, to be used in the biogenic synthesis of ZnO NPs. However, in this case, the authors gave no convincing evidence of the formation of ZnO NPs, showing no data concerning their morphology or crystallographic nature.

Not only plant extracts but living plants were also found to produce ZnO nanostructures (Qu, 2011). *Physalis alkekengi* L. (Fig. 2A) plants grew healthily in soils highly contaminated with zinc. It was confirmed that *P. alkekengi* could be used for the remediation of zinc-contaminated soils, simultaneously synthesizing ZnO NPs. The XRD pattern and EDS (energy dispersive spectroscopy) spectrum clearly showed that crystalline ZnO

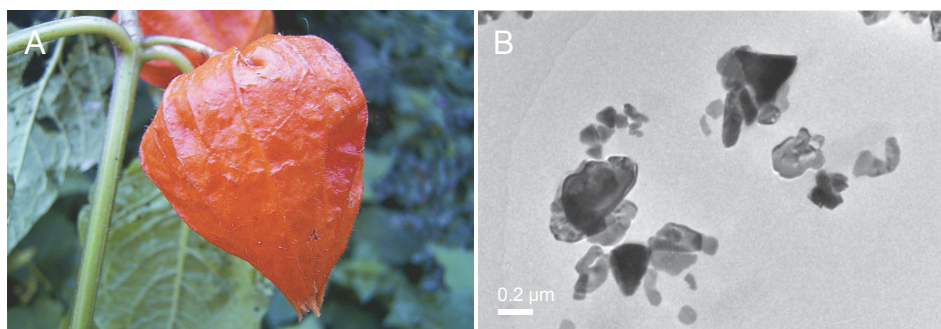


Fig. 2. A) Photograph of *Physalis alkekengi* L. and B) TEM image of ZnO NPs synthesized with *P. Alkekengi* (Qu, 2011, with permission from Elsevier, Copyright © 2011)

structures were synthesized; however, some synthesized ZnO particles were amorphous. In addition, TEM images demonstrated that ZnO NPs were polydispersed and had a mean size of 72 nm (Fig. 2B).

Algae and fungi were also utilized in ZnO NP synthesis; however, there are only few literature examples, which are summarized in the following. So far extracts of seaweeds such as green *Caulerpa peltata*, red *Hypnea Valencia*, and brown *Sargassum myriocystum* (Nagarajan and Kuppusamy, 2013) or brown *Sargassum muticum* (Azizi, 2014) were used for the synthesis of ZnO NPs. The effects of concentration of zinc ions, concentration of seaweed extract and the type of seaweeds, temperature, pH, and the time of reaction were studied (Nagarajan et al., 2013). The results showed that only *S. myriocystum* extracts were able to synthesize ZnO NPs (of 36 nm average size). According to authors, it was the fucoidan water soluble pigment present in *S. myriocystum* leaf extract that was responsible for the formation and stabilization of ZnO NPs. Similarly, an aqueous extract of brown *Sargassum muticum* was shown to be able to transform zinc acetate into ZnO NPs (Azizi, 2014). In this case, the data obtained by the XRD method confirmed a hexagonal wurtzite-type structure of these nanoparticles and the calculated average nanoparticle size was ~42 nm, as additionally confirmed by the SEM analysis. Also, culture filtrate of fungi *Alternaria alternata* was used to synthesize ZnO NPs from zinc sulfate solution (Sarkar et al., 2014). The ZnO NPs showed distinct polydispersity and the particle size ranged from 45 to 150 nm, with an average size of 75 nm. The FTIR characterization confirmed the presence of proteins on the nanoparticle surface, important as a stabilizing agent.

Synthesis using biotemplates

Biotemplating can be described as seeking to either replicate the morphological characteristics and the functionality of a biological species or use the biological structure to guide the assembly of inorganic materials (Kelley, 2012). In the latter case, biotemplate is removed giving a pure-phase material with the required morphology. For the synthesis of ZnO NPs some biotemplates such as proteins (e.g., albumen-egg white, casein, gelatin) (Gan et al., 2010; Sabbaghan, 2012; Prakash et al., 2013), biopolymers (cyclodextrins, cellulose, silk) (Han et al., 2012; Cai, 2012; Sabbaghan, 2012), eggshell membrane (Dong et al., 2008), and different types of microorganisms (Hussein, 2005, 2009; Zhou, 2007; Jayaseelan et al., 2012) were used.

Macromolecules

Peanut-like (Fig. 3) and flower-like ZnO 3D architectures were synthesized *via* a facile biomimetic process using gelatin as a matrix. Zinc nitrate and ammonia were mixed with gelatin at room temperature (30 min) and then incubated at 30°C (24 h). The XRD patterns proved that as-prepared products indexed to the wurtzite (hexagonal) structure of ZnO and were well crystallized (Gan et al., 2010). Similarly, the fabrication of spherical nanoparticles by sol-gel method using gelatin as a stabilizer was described (Darroudi et al., 2014). Silk fibroin fibers (SFF) were also introduced to obtain spherical ZnO nanoparticles. By taking SFF as the reactive substrates, ZnO could be *in situ* synthesized and partially stabilized on SFF. Thus, the crystals growth was restrained, and most nano-ZnO displayed a spherical shape of ~13 nm diameter (Han et al., 2012).

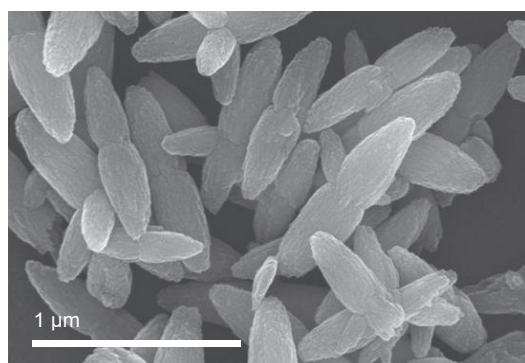


Fig. 3. SEM image of the peanut-like ZnO particles synthesized in gelatin matrix (Gan et al., 2010, with permission from Yong Gan et al., Copyright © 2010)

Micro/nanostructures of ZnO with different morphologies were successfully prepared using zinc acetate, ethanolic NaOH solution, and β -cyclodextrin (β -CD) at relatively mild conditions (Cai, 2012). The effect of the reaction time and cyclodextrin concentration, which acted as a crystallization modifier, was evaluated. It was found that the cavities of β -CD molecules are important because their participation in the formation of hierarchical flower-like ZnO structures. ZnO nanostructures with a diversity of morphologies such as nanoparticles, nanocauliflower, nanorod-like, and nanosheet-like were successfully obtained from the reaction of $\text{Zn}(\text{AcO})_2 \cdot 2\text{H}_2\text{O}$ and NaOH using different templates. In these experiments, sucrose, methyl cellulose, sodium dodecylsulfate (SDS), and casein were examined as templates (Sabbaghan, 2012).

Recently, ZnO NPs were synthesized through isothermal evaporation using zinc nitrate and NaOH solution in the presence of albumen as a biotemplate (Prakasha et al., 2013). Albumen, a protein with a long chain of amino acids, is present in hen's egg. Single-crystal ZnO NPs with particle sizes in the range between 10 nm and 30 nm were obtained. The mechanism of nanocrystals formation in the presence of albumen is still not fully understood. It was assumed that albumen, which has a high affinity to metal ions, can form organic-inorganic complexes, stabilizing the created nanoparticles. Similarly, the applicability of the metalloenzyme, a diamine oxidase, for a shape and size-selective synthesis of ZnO nanostructures was also demonstrated (Murugappan and Parthasarathy, 2014). The morphology of ZnO nanostructures changed from hexagonal plates to spherical particles when the pH of the medium was changed from acidic to basic. It was concluded that the electrostatic

charge, the overall conformation, and the redox activity of the enzyme, all together, affect the nanoscale morphology.

Natural scaffolds

Natural materials, which may have numerous biological structures, provide novel platforms for the construction and organization of new materials.

An eggshell membrane was used to produce ZnO nanoarchitectures (Dong et al., 2008). In this case, the membrane was separated from egg shell, dried, and then immersed into $\text{Zn}(\text{NO}_3)_2$ ethanol solution (RT). After drying at room temperature, it was calcined at 700°C to obtain ZnO hierarchical nanostructures. The obtained sample presents a network comprising interconnected ZnO porous fibers (Fig. 4). ZnO three-dimensional structures were also produced using the wings of an *Ideopsis similis* butterfly as templates and zinc nitrate water-ethanol solution as a precursor (Zhang et al., 2006). The XRD data of the calcined replica revealed that the sample possessed a zincite hexagonal structure of high crystallinity. The average crystallite size of the replicas was 13 nm. The biomorphic 3D porous structures maintained the structural features of the original butterfly wing. Even the microstructure details were faithfully represented in the ZnO replica.

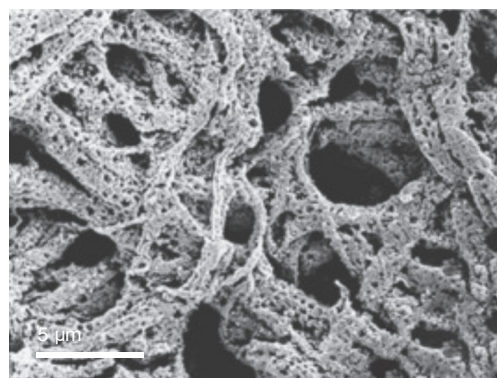


Fig. 4. Typical SEM image showing interwoven ZnO hierarchy prepared at pH 2 and 700°C (Dong et al., 2008, with permission from Elsevier, Copyright © 2008)

Bacteria

Bacteria of different sizes and shapes can be used as biotemplates for inorganic material synthesis. They can act as bio-scaffold for mineralization, or take an active part in nanoparticle synthesis (Hussein, 2005, 2009; Zhou, 2007; Jayaseelan et al., 2012). Hussein et al. (2015) sho-

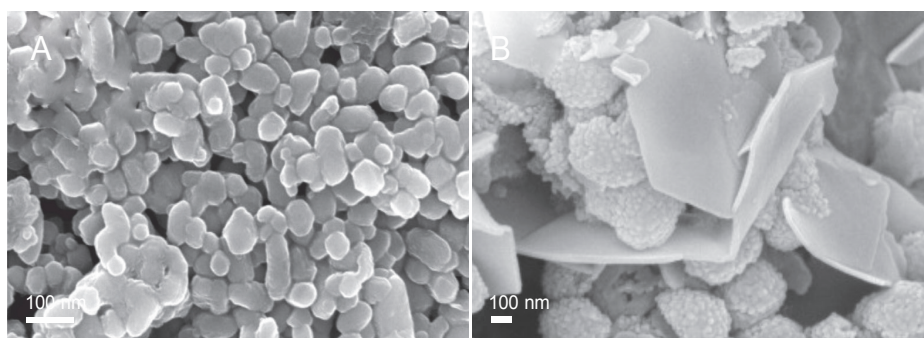


Fig. 5. Field-emission SEM micrographs showing: A) raspberry- and plate-like ZnO structures synthesized using *Bacillus cereus* as biotemplate (Hussein, 2009, with permission from Elsevier, Copyright © 2009); B) ZnO nanostructures synthesized using *Aeromonas hydrophila* as biotemplate (Jayaseelan et al., 2012 with permission from Elsevier, Copyright © 2012)

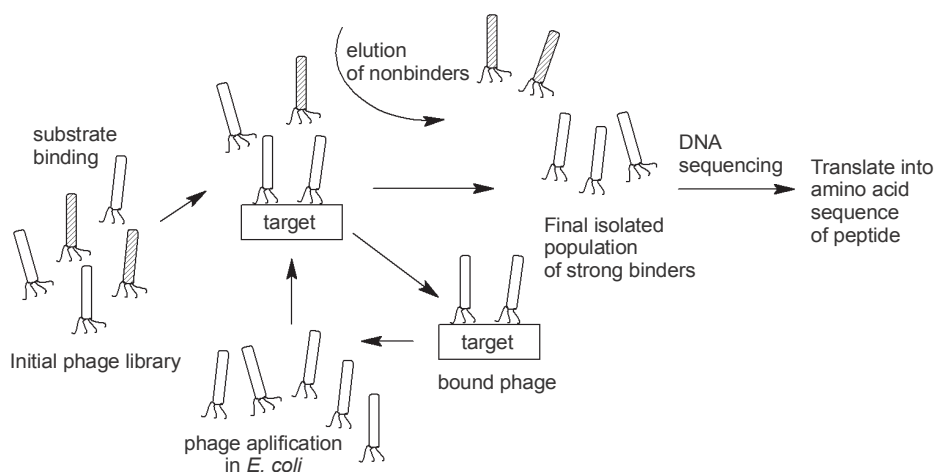


Fig. 6. Procedure for the isolation of peptides possessing high affinity for an inorganic material from a phage-displayed library

wed that ZnO can be prepared through a hydrolysis of zinc acetate in the presence of *Acetobacter xylenium*, a type of cellulose-producing bacterium. The XRD pattern of a synthesized ZnO showed that a relatively pure phase could be obtained. The thread-like and the bottle-like shapes of ZnO nanostructures were observed. In another experiment, using zinc acetate and triethanolamine solution and spherobacterium *Streptococcus thermophilus* as a natural biotemplate under hydrothermal conditions resulted in the formation of ZnO hollow spheres (Zhou, 2007). The obtained bacteria/ZnO core-shell structures were spherical, their diameters ranging from 1.2 μm to 1.5 μm . The thickness of a ZnO shell was estimated to be about 200-400 nm. Careful observations showed that the surfaces of these spheres were constructed by nanoparticles with diameters ranging from 20 nm to 40 nm. After calcination at 600°C, the bacteria were removed

from the interior, leaving hollow spheres. Another one, rod-shaped bacterium *Bacillus cereus* was reported by Hussein (2009) to be a biotemplating agent for the formation of ZnO NPs with raspberry- and plate-like structures. In this case, nanostructures were obtained through a simple thermal decomposition of zinc acetate in the presence of a biomaterial. A possible mechanism of the nanostructure formation was proposed based on the surface chemistry and biochemistry processes involving organic-inorganic interactions between ZnO and the microbial cells. The produced ZnO nanostructures are presented in Fig. 5A. In turn, Jayaseelan et al. (2012) presented a low-cost and simple procedure for the biosynthesis of ZnO NPs using reproducible bacteria *Aeromonas hydrophila*. Synthesized ZnO NPs were smooth and spherical in shape, with an average size of 50-60 nm (Fig. 5B). Later, E. Selvarajan and V. Mohanasrinivasan

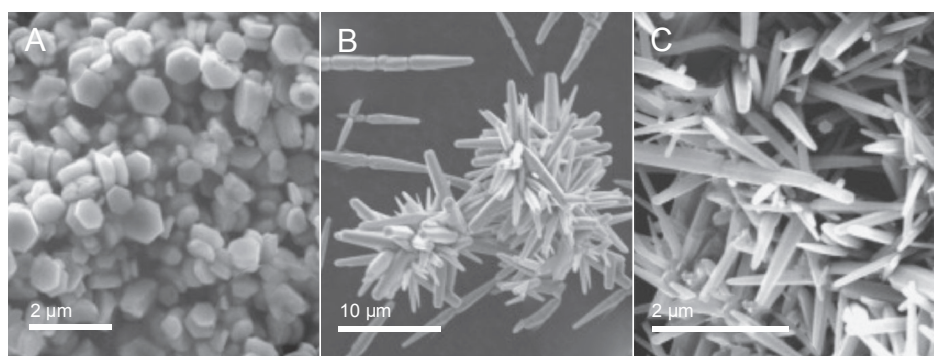


Fig. 7. SEM micrographs of ZnO crystals obtained by biomineralization using ZnO-binding peptide: A) using 0.5 mg/ml ZnO-binding peptide + equimolar concentrations of $\text{Zn}(\text{NO}_3)_2$ and urotropin; B) equimolar concentrations of $\text{Zn}(\text{NO}_3)_2$ and urotropin (no peptide); C) control reaction containing 0.5 mg/ml of bovine serum albumin (Tomczak et al., 2009 with permission from Elsevier, Copyright © 2008)

(2013) described a synthesis of small ZnO particles using probiotic bacteria *Lactobacillus plantarum* VITES07 and ZnSO_4 as a source of metal. The XRD, SEM, and TEM analyses revealed that obtained nanoparticles were in a hexagonal phase, polydispersed, nearly spherical in shape, with diameters ranging from 7 to 17 nm. Moreover, it was found that the size of nanoparticles could be controlled by the reaction time. Lately, ZnO NPs were rapidly synthesized from zinc sulfate solution at room temperature using actinobacteria *Rhodococcus pyridinivorans* NT2 (Kundu et al., 2014). The produced nanoparticles were moderately stable, of hexagonal phase, roughly spherical, and with the average particle diameter in the range of 100-120 nm. The role of bacterial protein in the synthesis and stability of nanoparticles was proved.

Peptides

The wide use of ZnO NPs has moved forward the search for compounds that may specifically bind such structures. Peptides and proteins were demonstrated to be particularly useful in this approach, even when used with substances not commonly found in biological systems as semiconductors. Much effort was focused on discovering new inorganic-binding peptides in order to build materials of interest from the bottom-up with nanoscale precision. The production of inorganic solids by biological systems is called biomineralization. Biomineralization attracted much attention in the field of bio-nanotechnology because biomineralization reactions proceed under milder conditions than conventional industrial methods. Several sequences within natural proteins were

identified as mineralizing motifs. Unfortunately, such systems mineralize only a limited set of inorganic materials, excluding semiconductors; thus, the naturally occurring peptides are not expected to be useful in the synthesis of ZnO. However, binders of materials that have not been encountered by living systems during their biological evolution can be created artificially (Whaley et al., 2000; Sarikaya, 2003; Umetsu et al., 2005; Dickerson, 2008; Tomczak et al., 2009; Seker and Demir, 2011).

The phage-display peptide library system is a simple tool for creating peptide binders of user-assigned targets. In 2000, Belcher's group first applied this system to select peptides with an affinity for the surfaces of semiconductors (Whaley et al., 2000). They initially incubated a phage peptide library with a semiconductor substrate under aqueous conditions, after which they collected the phage that bound to the surface of the substrate and identified the sequence motifs that had affinity for semiconductors (Fig. 6). Several (3-5) rounds of stringent washing and elution were used to remove the weakly binding peptides from the final screened phage population. The amino acid sequence of the displayed peptide was determined through the DNA sequencing of the final phage clones.

Peptide-directed growth of zinc nanostructures was reported for the first time in 2005. Umetsu and coworkers (2005) used a phage peptide display to identify a dodecamer peptide from a combinatorial library that bound specifically to ZnO crystals. The study concluded that the identified peptide not only revealed preferential immobilization of ZnO, but could also synthesize ZnO flo-

wer-like nanostructures at room temperature. The XRD pattern of the precipitated material indicated the formation of wurtzite ZnO, and the particle size, estimated from the width of the diffraction peaks, was 15-35 nm. More recently, the same group analyzed the influence of ZnO-binding peptides on the crystal growth of ZnO structures synthesized from zinc hydroxide and observed the formation of needle-like microstructures (Togashi et al., 2011). Naik's group also used the phage display technique to isolate peptides that bind to ZnO crystals. They identified a nearly identical peptide to the previously reported ones by Umetsu (Tomczak et al., 2009). ZnO-binding peptide was used to tailor ZnO NP growth. In this case, zinc nitrate and urotropin at different ratios were used as a stock solution for biomineralization reactions. As a result, a biodirected growth of twinned, hexagonal ZnO nanoplatelets of variable aspect ratio was observed (Fig. 7).

Conclusions

Biosynthesis of zinc oxide nanoparticles is an attractive alternative to other known methods, gaining an increasing interest in the development of bottom-up fabrication procedures of nanometer-scale devices. The ability of living matter to assemble nanoscale components into controlled and sophisticated structures can be used directly to produce different nanomaterials under mild conditions. However, more detailed studies are required to fully benefit from these natural manufactures.

References

- Ambrožič G., Orel Z.C., Iligon M. (2011) *Microwave-assisted non-aqueous synthesis of ZnO nanoparticles*. Mater. Technol. 45: 173-177.
- Azizi S., Ahmad M.B., Namiar F., Mohammad R. (2014) *Green biosynthesis and characterization of zinc oxide nanoparticles using Brown marine macroalga Sargassum muticum aqueous extract*. Mat. Lett. 116: 275-277.
- Cai A.-J., Wang Y.-L., Xing S.-T., Ma Z.-Ch. (2012) *Cavity of cyclodextrin, a useful tool for the morphological control of ZnO micro/nanostructures*. Ceram. Int. 38: 5265-5270.
- Darroudi M., Sabouri Z., Oskuee R.K., Zak A.K., Kargar H., Hamid M.H.N.A. (2013) *Sol-gel synthesis, characterization and neurotoxicity effect of zinc oxide nanoparticles using gum tragacanth*. Ceram. Int. 39: 9195-9199.
- Darroudi M., Sabouri Z., Oskuee R.K., Zak A.K., Kargar H., Hamid M.H.N.A. (2014) *Green chemistry approach for the synthesis of ZnO nano powders and their cytotoxic effects*. Ceram. Int. 40: 4827-4831.
- Dickerson M.B., Sandhage K.H., Naik R.R. (2008) *Protein- and peptide directed syntheses of inorganic materials*. Chem. Rev. 108: 4935-4978.
- Dong Q., Su H., Zhang Ch., Zhang D., Guo Q., Kiessling F. (2008) *Fabrication of hierarchical ZnO films with interwoven porous conformations by a bioinspired templating technique*. Chem. Eng. J. 137: 428-435.
- Fan Z., Lu L.G. (2006) *Nanostructured ZnO: building blocks for nanoscale devices*. Int. J. High Speed Electron. Syst. 16: 883-896.
- Fujita S., Kim S.-W., Ueda M., Fujita S. (2004) *Artificial control of ZnO nanostructures grown by metalorganic chemical vapor deposition*. J. Cryst. Growth 272: 138-142.
- Gan Y., Gu F., Han D., Wang Z., Guo G. (2010) *Biomimetic synthesis of zinc oxide 3D architectures with gelatin as matrix*. J. Nanomater. 2010: ID289173.
- Gandhi R.R., Gowri S., Suresh J., Sundarajan M. (2013) *Ionic liquids assisted synthesis of ZnO nanostructures: controlled size, morphology and antibacterial properties*. J. Mater. Sci. Technol. 29: 533-538.
- Gnanasangeetha D., Sarala Thambavani D. (2013a) *One pot synthesis of zinc oxide nanoparticles via chemical and green method*. Res. J. Material Sci. 1: 1-8.
- Gnanasangeetha D., Sarala Thambavani D. (2013b) *Biogenic production of zinc oxide nanoparticles using Acalypha Indica*. J. Chem. Bio. Phy. Sci. Sec. B. 4: 238-246.
- Han J., Su H., Xu J., Song W., Gu Y., Chen Y., Moon W.-J., Zhang D. (2012) *Silk-mediated synthesis and modification of photoluminescent ZnO nanoparticles*. J. Nanopart. Res. 14: 726.
- Hingorani S., Pillai V., Kumar P., Multani M.S., Shah D.O. (1993) *Microemulsion mediated synthesis of zinc oxide nanoparticles for varistor studies*. Mat. Res. Bull. 28: 1303-1310.
- Hussein M.Z., Yahaya A.H., Ling P.L., Long C.W. (2005) *Acetobacter xylenium as a shape-directing agent for the formation of nano-, micro-sized zinc oxide*. J. Mater. Sci. 40: 6325-6328.
- Hussein M.Z., Azmin W.H., Mustafa M., Yahaya A.H. (2009) *Bacillus cereus as a biotemplating agent for the synthesis of zinc oxide with raspberry- and plate-like structures*. J. Inorg. Biochem. 103: 1145-1150.
- Jayaseelan C., Rahuman A.A., Kirthi V., Marimuthu S., Santhoshkumar T., Bagavan A., Gaurav K., Karthik L., Rao K.V. (2012) *Novel microbial route to synthesize ZnO nanoparticles using Aeromonas hydrophila and their activity against pathogenic bacteria and fungi*. Spectrochim. Acta A 90: 78-84.
- Jha A.K., Kumar V., Prasad K. (2011) *Biosynthesis of metal and oxide nanoparticles using orange juice*. J. Bionanosci. 5: 162-166.
- Jia X., Fan H., Zhang F., Qin L. (2010) *Using sonochemistry for the fabrication of hollow ZnO microspheres*. Ultrason. Sonochem. 17: 284-287.
- Jung S.-H., Oh E., Lee K.-H., Yang Y., Park C.G., Park W., Jeong S.-H. (2008) *Sonochemical preparation of shape-selective ZnO nanostructures*. Cryst. Growth Des. 8: 265-269.

- Kelley S.O. (2012) *Biotemplated semiconductor nanocrystals*. *Compreh. Nanosci. Technol.* 5: 259-264.
- Kim H., Moon J.Y., Lee H.S. (2009) *Growth of ZnO nanorods on various substrates by electrodeposition*. *Electron. Mater. Lett.* 5: 135-138.
- Kong X.Y., Wang Z.L. (2003) *Spontaneous polarization-induced nanohelices, nanosprings, and nanorings of piezoelectric nanobelts*. *Nano. Lett.* 3: 1625-1631.
- Kundu D., Hazra Ch., Chatterjee A., Chaudhari A., Misra S. (2014) *Extracellular biosynthesis of zinc oxide nanoparticles using Rhodococcus pyridinivorans NT2: Multifunctional textile finishing, biosafety evaluation and in vitro drug delivery in colon carcinoma*. *J. Photochem. Photobiol. B: Biology* 140: 194-204.
- Lee J., Eastal A.J., Pal U., Bhattacharyya D. (2009) *Evolution of ZnO nanostructures in sol-gel synthesis*. *Curr. Appl. Phys.* 9: 792-796.
- Lopes S., Ribeiro F., Wojnarowicz J., Łojkowski W., Jurkschat K., Crossley A., Soares A.M.V.M., Loureiro S. (2014) *Zinc oxide nanoparticles toxicity to daphnia magna: size dependent effects and dissolution*. *Environ Toxicol Chem.* 1: 190-198.
- Ma H., Williams P.L., Diamond S.A. (2013) *Ecotoxicity of manufactured ZnO nanoparticles – a review*. *Environm. Poll.* 172: 76-85.
- Maryanti E., Damayanti D., Gustian I., Yudha S. (2014) *Synthesis of ZnO nanoparticles by hydrothermal method in aqueous rinds extracts of Sapindus rarak*. *Mater. Lett.* 118: 96-98.
- Medina A., Bejar L., Borjas S.E., Zarate J., Vargas R., Herrera G., Ruiz A. (2012) *Characterization of ZnO nanoparticles with short-bar shape produced by chemical precipitation*. *Mater. Lett.* 71: 81-83.
- Mehta S.K., Singh K., Umar A., Chaudhary G.R., Singh S. (2012) *Ultra-high sensitive hydrazine chemical sensor based on low-temperature grown ZnO nanoparticles*. *Electrochim. Acta* 69: 128-133.
- Meulenkamp E.A. (1998) *Synthesis and growth of ZnO nanoparticles*. *J. Phys. Chem. B* 102: 5566-5572.
- Mezni A., Kouki F., Romdhane S., Warot-Fonrose B., Joulié S., Mlayah A., Smiri L.S. (2012) *Facile synthesis of ZnO nanocrystals in polyol*. *Mater. Lett.* 86: 153-156.
- Nagarajan S., Kuppusamy A.K. (2013) *Extracellular synthesis of zinc oxide nanoparticle using seaweeds of gulf of Mannar, India*. *J. Nanobiotech.* 11: 39 (11).
- Nehru L.C., Swaminathan V., Sanjeeviraj C. (2012) *Rapid synthesis of nanocrystalline ZnO by a microwave-assisted combustion method*. *Powder Technol.* 226: 29-33.
- Murugappan G., Parthasarathy M. (2014) *Bio-inspired morphological evolution of zinc oxide nanostructures on a tunable enzyme platform*. *Enzym. Microb. Tech.* 61-62: 13-16.
- Nagajyothi P.C., Minh An T.N., Sreekanth T.V.M., Lee J., Lee D.J., Lee K.D. (2013) *Green route biosynthesis: characterization and catalytic activity of ZnO nanoparticles*. *Mater. Lett.* 108: 160-163.
- Nagajyothi P.C., Sreekanth T.V.M., Tettey C.O., Jun Y.I., Mook S.H. (2014) *Characterization, antibacterial, antioxidant, and cytotoxic activities of ZnO nanoparticles using Coptidis Rhizoma*. *Bioorg. Med. Chem. Lett.* doi: http://dx.doi.org/10.1016/j.bmcl.2014.07.023.
- Prakash T., Jayaprakash R., Sathya Raj D., Kumar S., Donato N., Spadaro D., Neri G. (2013) *Sensing properties of ZnO nanoparticles synthesized by using albumen as a biotemplate for acetic acid monitoring in aqueous mixture*. *Sens. Act. B* 176: 560-568.
- Qu L.J., Yuan X., Wang X., Shao P. (2011) *Zinc accumulation and synthesis of ZnO nanoparticles using Physalis alkekengi*. *Environ. Poll.* 159: 1783-1788.
- Ramimoghadam D., Hussein M.Z.B., Taufiq-Yap Y.H. (2013) *Synthesis and characterization of ZnO nanostructures using palm olein as biotemplate*. *Chem. Cent. J.* 7: 71-81.
- Sabbaghan M., Firooz A.A., Ahmadi V.J. (2012) *The effect of template on morphology, optical and photocatalytic properties of ZnO nanostructures*. *J. Mol. Liq.* 175: 135-140.
- Salam H.A., Sivaraj R., Venkatesh R. (2014) *Green synthesis and characterization of zinc oxide nanoparticles from Ocimum basilicum L. var. purpurascens Benth.-Lamiaceae leaf extract*. *Mater. Lett.* 131: 16-18.
- Samat N.A., Nor R.M. (2013) *Sol-gel synthesis of zinc oxide nanoparticles using Citrus aurantifolia extracts*. *Ceram. Int.* 39: S545-S548.
- Sangeetha G., Rajeshwari S., Venkatesh R. (2011) *Green synthesis of zinc oxide nanoparticles by aloe barbadensis miller leaf extract: Structure and optical properties*. *Mater. Res. Bull.* 46: 2560-2566.
- Sangeetha G., Rajeshwari S., Venkatesh R. (2012) *Green synthesized ZnO nanoparticles against bacterial and fungal pathogens*. *Prog. Nat. Sci.: Mater. Int.* 22: 693-700.
- Sarikaya M., Tamerler C., Jen A.K., Schulten K., Baneyx F. (2003) *Molecular biomimetics: nanotechnology through biology*. *Nature Mater.* 2: 577-585.
- Sarkar J., Ghosh M., Mukherjee A., Chattopadhyay D., Acharya (2014) *Biosynthesis and safety evaluation of ZnO nanoparticles*. *Bioprocess. Biosyst. Eng.* 37: 165-171.
- Seker U.O., Demir H.V. (2011) *Material binding peptides for nanotechnology*. *Molecules* 16: 1426-1451.
- Selvarajan E., Mohanasrinivasan V. (2013) *Biosynthesis and characterization of ZnO nanoparticles using Lactobacillus plantarum VITESO*. *Mat. Lett.* 112: 180-182.
- Shekhawat M.S., Ravindran C.P., Manokari M. (2014) *Biosynthesis of zinc oxide nanoparticles from Passiflora foetida L. extracts and their characterization*. *Int. J. Green Herb. Chem.* 3: 518-523.
- Singh R.P., Shukla V.K., Yadav R.S., Sharma P.K., Singh P.K., Pandey A.C. (2011) *Biological approach of zinc oxide nanoparticles formation and its characterization*. *Adv. Mat. Lett.* 2: 313-317.
- Singh T., Trivedi T.J., Kumar A. (2012) *Ionic liquid-assisted preparation of ZnO nanostructures*. *Nanomater. Energy* 1: 207-215.

- Singhal M., Chhabra V., Kang P., Shah D.O. (1997) *Synthesis of ZnO nanoparticles for varistor application using Zn-substituted aerosol OT microemulsion*. Mater. Res. Bull. 32: 239-247.
- Spanhel L., Anderson M.A. (1991) *Semiconductor clusters in the sol-gel process: quantized aggregation, gelation, and crystal growth in concentrated ZnO colloids*. J. Am. Chem. Soc. 113: 2826-2833.
- Tomczak M.M., Gupta M.K., Drummy L.F., Rozenzhak S.M., Naik R.R. (2009) *Morphological control and assembly of zinc oxide using a biotemplate*. Acta Biomaterialia 5: 876-882.
- Togashi T., Yokoo N., Umetsu M., Ohara S., Naka T., Takami S., Abe H., Kumagai I., Adschiri T. (2011) *Material-binding peptide application – ZnO crystal structure control by means of a ZnO-binding peptide*. J. Biosci. Bioengineer. 111: 140-145.
- Umetsu M., Mizuta M., Tsumoto K., Ohara S., Takami S., Watanabe H., Kumagai I., Adschiri T. (2005) *Bioassisted room-temperature immobilization and mineralization of zinc oxide – the structural ordering of ZnO nanoparticles into a flower-type morphology*. Adv. Mater. 17: 2571-2575.
- Vaseem M., Umar A., Hahn Y.-B. (2010) *ZnO nanoparticles: growth, properties, and applications in metal oxide nanostructures and their applications*, ed. Umar A., Hahn Y.-B., vol. 5: 1-36.
- Vidya C., Hiremath S., Chandraprabha M.N., Lourdu Antonyraj M.A., Gopal I.V., Jain A., Bansala K. (2013) *Green synthesis of ZnO nanoparticles by Calotropis Gigantea*. Int. J. Curr. Engineer. Tech. Special Issue 1: 118-120.
- Vijayakumar S., Vinoj G., Malaikozhundan B., Shanthi S., Vaseeharan B. (2015) *Plectranthus amboinicus leaf extract mediated synthesis of zinc oxide nanoparticles and its control of methicillin resistant Staphylococcus aureus biofilm and blood sucking mosquito larvae*. Spectrochim. Acta Part A: Mol. Biomol. Spectrosc. 137: 886-891.
- Whaley S.R., English D.S., Hu E.L., Barbara P.F., Belcher A.M. (2000) *Selection of peptides with semiconductor binding specificity for directed nanocrystal assembly*. Nature 405: 665-668.
- Yadav R.S., Mishra P., Pandey A.C. (2008) *Growth mechanism and optical property of ZnO nanoparticles synthesized by sonochemical method*. Ultrason. Sonochem. 15: 863-868.
- Yuvakkumar R., Suresh J., Nathanael A.J., Sundrarajan M., Hong S.I. (2014) *Novel green synthetic strategy to prepare ZnO nanocrystals using rambutan (Nephelium lappaceum L.) peel extract and its antibacterial applications*. Mater. Sci. Engineer. C 41: 17-27.
- Zhang W., Zhang D., Fan T., Ding J., Gu J., Guo Q., Ogawa H. (2006) *Biomimetic zinc oxide replica with structural color using butterfly (Ideopsis similis) wings as templates*. Bioinsp. Biomim. 1: 89-95.
- Zhou H., Fan T., Zhang D. (2007) *Hydrothermal synthesis of ZnO hollow spheres using spherobacterium as biotemplates*. Micropor. Mesopor. Mater. 100: 322-327.
- Zhu H., Huang J.-F., Pan Z., Dai S. (2006) *Ionothermal synthesis of hierarchical ZnO nanostructures from ionic-liquid precursors*. Chem. Mater. 18: 4473.

