Digest Journal of Nanomaterials and Biostructures Vol. 5, No 4, October-December 2010, p. 1035 – 1040

BIOGENIC PRODUCTION OF NANOPARTICLES

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Nanoparticles of interest in nanotechnology (design of nanodevices) and medicine (controlled-release of drugs) can be produced both by anorganic and organic synthesis. The biogenetic production is now of high interest due to simplicity of the procedures and their versatility. Several species of bacteria and plants are able to synthesize nanoparticles or to help in the process of their production. The paper gives an overview on the biogenetic production of nanomaterials.

(Received November 10, 2010; accepted November 15, 2010)

Keywords: Biogenic production; Nanoparticles; Nanomaterials; Bacteria

1. Introduction

It is quite surprising that from simple microbes and bacteria up to more evolved plants it is possible to get nanoparticles [1]. The production of nanoparticles is environmentally friendly because this involves natural phenomena that take place in the biological systems. Moreover, the biologically fabricated nanostructures offer substantially different properties: good adhesion, tribologically good properties, optical and electrical properties of high interest in optoelectronics. Up today, several procedures have been used for silver, gold and other nanoparticle production and applications [2-12]. In the last decades numerous enrichment and pure cultures isolated from a variety of environments have been shown to enzimatically reduce many dissolved heavy metals, metalloids and radionuclides to insoluble nano and microparticles. Although the potential application of biologically manufactured selenium and sulphur nanoparticles has been pointed out in a few studies, the biotechnological utilization of microbial nano-synthesis has thus not been explored. In this note we show how bacteria and vegetables are able to give rise of nanomaterials of interest in science and technology. Biologically synthesized of e.g. silver nanoparticles could have many applications such as spectrally selective coating for solar energy absorption and intercalation material for electrical batteries [13] as optical receivers, catalysts, biolabelling etc…

Last but not least the nanoparticles could be successfully used in the cancer diagnosis and treatment [14].

2. The mechanism of nanoparticle production using the biogenic way

Unicellular organisms such as Diatoms (brown algae) are able to carefully design and control natural nanostructures formation. They have a silica exoskeleton named Frustules, that consists of well organized SiO_2 nanoparticles (size 50-100 nm). The nanoparticles are formed from naturally occurring precursors, within a few hours near or below the room temperatures.

Let's take the silicon as basical component of simplest nanoparticles. Silicic acid ($Si(OH)_4$) is a precursor of silica in aqueous environment. It is transported into the cell through specific trans-membrane protein named SET (silicic acid transporter) and can be accumulated at very high concentrations. These silicon precursors can be transported into specific vesicles named silicon deposition vesicle (SDV) located at the vicinity of cytoplasmic membrane. The first isolated silicic acid transporter (SIT) was from diatom species Cylindrotheca Fusiformis [15]. It was shown that some proteins are involved in the Si polymerization process. Diatoms shells when treated with magnesium vapors at high temperature, lead to Mg-Si oxide replica. The process was shown to be compatible with other metals and this is a significant step towards application of diatoms in nanotechnology.

Several natural molecules are able to activate silica formation in the conditions found in the intracellular compartment of the living organisms.

3. Nanoparticles produced by bacteria

Gold nanoparticles could be precipitated within the bacterial cells by incubation of the cells with Au^{3+} ions [16]. It was shown by Klaus et al. [17], that bacteria Pseudomonis stuzeri AG 259 isolated from silver mine form silver nanoparticles when placed in silver nitrate solution.

Silver nanoparticles of well defined morphology and size are formed within the periplasmic space of the bacteria.

The magnetotactic bacteria such as Magnetosirillium magneticum have been reported to produce magnetic nanoparticles [17]. Magnetosomes are membrane-enclosed inorganic crystals consisting either of magnetite or minerals as (Fe_3O_4) or greigite (Fe_3S_4). The particles are usually arranged along the cell axis in one or multiple chains which are oriented with the (111) easy magnetization axis along the chain direction and are organized along a cytoskeletal filamentous structure. Particle size is typically 35-120 nm which is situated within a single magnetic-domain size for these minerals [18].

Sulphate reducing bacterium Desulfovibrio desulfuricans NCIMB 8307 has been shown to produce palladicum nanoparticles of interest in catalysis [19]. Mandal et al. [20] have observed spherical aggregates of 2-5 nm of sphalerite ZnS nanoparticles by the sulphate reducing bacteria under the anaerobic conditions. Clostridicum thermoaceticum and Klebsiella aerogens were used to form CdS nanoparticles [20].

Gold nanowires were reported by synthesis from the extract of Rhodopseudomonas capsulate [21]. Such synthesis of the nanoparticles offers a control of the shape of nanogold particles when $HAuCl_4$ is used in different concentrations.

A major biomolecule, a protein is probably involved in the bioreduction and synthesis of Au nanoparticles.

The extracellular biosynthesis of silver nanoparticles using marine cyanobacterium oscillatory willei NTDMO1 which reduce silver ions and stabilizes the silver nanoparticles by a secreted protein was recently reported [43].

The use of cyanobacteria as a source of enzymes that can catalyze specific reactions leading to inorganic nanoparticles is a new rational biosynthesis strategy. Extracellular secretion of enzymes offers the advantage of getting large quantities of nanoparticles of size 100 – 200 nm in a relatively pure state, free from other cellular proteins. The further purification of nanoparticles is made successfully by filtering

4. Synthesis of As-S nanotubes by Shewanella sp. and of ZnS by Desulfobacteriaceae sp.

One of the most important optoelectronic nanoparticles is based on the alloy As-S. Different kind of morphology of nanoparticles has been modeled. We have demonstrated by modeling that long nanotubes (closed of not closed) can be constructed with low distortion of the As-S bands and high stability [22].

Recently it was published a report on the synthesis of long nanotubes by the Shewanella sp. Bacteria [23].

A number of bacterial strains have been shown to contribute to the formation of diverse arsenic minerals. If sulphide is present as a ligand for immobilization of arsenic As-S precipitates often are produced. It was already known that the dissimilatory arsenic-respiring bacterium

Desulfosporo sinus sinus auripigmenti can precipitate monodisperse, spherical, arsenic trisulfide particles (As_2S_3), both intra and extracellulary, under sulfate-reducing conditions [24] reported the microbial production of extracellular network filamentous arsenic sulphide (As-S) nanotubes by Shewanella sp. Strain HN-41 grown in the presence of As (V) and S_2O_3 under anaerobic conditions.

Nanotubes (As-S) have been obtained with 20-100 nm in diameter and ~ 3 μm in length. Initially amorphous As_2S_3 is avolved with increased incubation time toward polycrystalline phases of the minerals realgar As_xS_4) and duranusite (As_4S). The obtained nanotubes behave as metals or semiconductors and the semiconductors ones are photoconductive.

Jiang et al. [25] have recently shown that the formation of As-S nanotubes is widespread among Shewanella strains and is closely related to bacterial growth and the reduction rate of As (V) and thiosulfate.

Aside the important bioimplications, the biogenic formation of the one-dimensional As-S nanotubes will contribute to new, green, biosynthetic methods for the production of inorganic materials at nanoscale, which ultimately may find use in novel nano- and optoelctronic devices.

Biosynthesis of ZnS by sulphate-reducing Zinc sulphide is a very important electronic material and many efforts have been dedicated to the preparation and characterization of the non particles of ZnS [48-52]. It was shown by Labrenz et al. [26] that abundant micrometer-scale spherical aggregates of 2-5 nm in diameter of composition ZnS (sphaterite) are formed in natural biofilms. The articles are obtained with relatively aero-tolerant sulphate-reducing bacteria of the family Desulfobacteriaceae. The biofilm zinc concentration is $\sim 10^6$ times that of associated groundwater (0.09 to 1.1 ppm Zn). Sphalerite also concentrates arsenic (0.01 wt%) and selenium (0.004 wt%). The almost monominerallic product results from buffering of sulphite concentrations at low values by sphalerite precipitation.

These results show how microbes control metal concentration in ground water and wetland-based remediation systems and suggest biological routes for formation of some low-termperature ZnS deposits.

5. Nanoparticles produced by plants

5.1 Biosynthesis of Si-Ge-O nanocomposite by Diatom

Diatoms are single cells photosynthesizing eukariotic algae which produce intricately structured cell wall made of nano-patterned silica.

The incorporation of germanium into diatom cells has been achieved.

Ali et al. [27] have shown that the freshwater diatom, stauroneis sp. can be used to fabricate Silicon-Germanicum nanoparticles.

It was reported that silica from bioreactor cultured Nitzschia frustulum cells possess blue photo-luminescence. The luminescence intensity and wavelength are dependent on the change in frustules nanostructure as the cell culture moved from the exponential to the stationary phase of growth [28].

5.2 Biosynthesis of Au and Ag nanoparticles by different plant extracts

Sarnim et al. [29] reported the synthesis of gold and silver nanoparticles inaqueous medium using sun-dried peel of Citrus sinensis. Stable, monodispersed and predominantly spherical nano-particles of size 14 – 20 nm are obtained. The terpenoids with functional groups of alcohol, ketones, aldehyde and amines play an important role in the stability of the nanoparticles. These nanoparticles find applications in nanotechnology and medicine.

Several research groups synthesized different shapes and morphologies (nanotriangles, nanoprisms, octahedral gold particles using plant parts, such as tamarind leaves extract [30].

Pelargonium graveolens (geranium) leaves extract and its endophytic fungus colletra trichum sp [31] and Neem leaves extract (Azadirachta indica) [32], Hibiscus rosa sinensis [33], coriander leaf extract [34], Magnolia Kobus and Dyopiros Kaki leaf extracts [35], Emblica officinalis fruit extract [36], Phyllanthium [37,38], Aloe vera extract [39] mushroom extract [40] and even honey [41].

5.3 The use of yeast and fungi in nanoparticles synthesis

Yeast has been used successfully in the synthesis of CdS and PbS nanoparticles. Kowshik et al. [42] have shown that Torilopsis species is able to synthesize nanoscale PbS (intracellularly) when exposed to aqueous Pb^{2+} ions. Kowshik et al. observed the CdS Quantum dots, formed in Schizosacharomyces pombe yeast cells.

Recently, high quantity of Ag nanoparticles obtained by using silver tolerant yeast strains MKY3 has been reported [42].

Fungi are efficient candidates in the synthesis of metal and metal sulphide nanoparticles. Two types of fungi (Verticillium sp. and Fusarium oxysporum) are efficient. In the case of Verticillium sp., the reduction of the metal ions occurred extracellularly, leading to the formation of gold and silver nanoparticles of size 5-20 nm.

The production of bioactive nanoparticles from lichen fungi (Usneea longissima) in the culture conditions has been reported [44].

A novel biological method for synthesis of silver nanoparticles using Vericillum was proposed as a two-step mechanism. The first step involves trapping of Ag^{+} ions at the surface of the fungal cells. In the second step, enzymes present in the cell reduce silver ions. The extracellular production of metal nanoparticles by several strains of the fungus Fusarium oxysporum has been reported [45]. The presence of hydrogenase in the F. oxysporum has been demonstrated. This extracellular enzyme shows excellent redox properties and it can act as an electron shuttle in metal reduction. The electron shuttle or other reducing agents (e.g. hydrochinones) released by microorganisms are capable of reducing ions to nanoparticles.

The fungi Aspergillus flavus, Aspergillus furnigatus and Phanerochaete chrysoparium as well as white-rot fungus C. versicolar [46, 47] produce stable silver nanoparticles when challenged with silver nitrate in aqueous medium.

Silver nanoparticles obtained by use of Pleurotus sajor caju and their antimicrobial activity have been recently reported [45].

6. Discussion

One of the most intriguing examples of microbial interactions with rocks is the use of minerals for respiration. How bacteria interacts, e.g. with As minerals is still challenging. Respiration is the process of harvesting energy by transferring electrons from an electron donor to an electron acceptor. Typically the transfer occurs down a respiratory chain embedded in the cell membrane. Specific molecules hand electrons from one end to the other, thereby generating a potential across the membrane that can be harnessed to do work (such as storing chemical energy in the form of adenosine triphosphate).

For respiring to succeed a terminal electron acceptor, such as oxygen must exist to receive the electrons. Most terminal electron acceptors that bacteria use for respiration, such as oxygen, nitrate and sulfate, are soluble. They can thus make the way to the cell to receive electrons from the membrane-bound molecules of the respiratory chain. Which is the strategy of bacteria to transfer electrons to minerals during respiration?

Firstly, the bacteria must solubilize the minerals by producing chelating molecules. The bacteria may use soluble sulphides to transfer electrons from the cell to the mineral. These sulphides must be exogenous or produced by the organism itself. The outer membrane may be responsible for this electron transfer. The mechanism is dependent on area of the mineral, composition and microinhomogeneities. E.G. As-S minerals may exhibit microzones enriched in As and micro enzimes enriched in sulphur. The bacteria catch sulphur as sulfate ions and the electron transfer from arsenic to cell is achieved on the surface of the mineral grains, by use of the microvoltaic cells formed within the chelating electrolyte. Thus by a kind of electrolysis the Arsenic is metabolized and, as a final process of disassimilation, new As-S particles including nanotube configurations do appear.

The reduction process of metallic ions into metallic particles is strongly influenced by temperature, pH, etc. Gold nanotriangular particles are favored at low temperatures and pH=3. The presence of ions like Cl, Br, I in plants affect the nanoparticle formation. The presence Cl ions during synthesis promotes the growth of nanotriangles while the presence of iodide ions (I^-) distorts the nanotriangle morphology and induces the formation of aggregated spherical nanoparticles [53]. The biogenic method for nanoparticle production is simple, eco-friendly and allows for getting controlled nanoparticles which can be used as catalysts with specific composition, which cannot be synthesized by classical methods. Applications in sensors and medicine are envisaged. The nanoparticles synthesized in the bacteria can be used against the human pathogens and there are hopes to produce nanoparticles in the plant cells (e.g. Ag) that can be used to treat various human diseases.

7. Conclusions

The biogenic way of nanoparticle production is of great interest due to possible application in catalysis medicine and nano-optoelectronics. The field is still in its infancy but recent successes in preparation warrant its bright future.

Acknowledgement

The authors thank to CNCSIS-UEFISCSU for the support of this work in the frame of the Project IDEI 1249/2008 under Contract No. 673/2009.

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