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Two completely different biomimetic reactions mediated by the same matrix producing inorganic/organic/inorganic hybrid nanoparticles

Michael Arkas [a,*], G. Kithreoti [a], N. Boukos [a], I. Kitsou [b], F. Petrakli [b], K. Panagiotaki [a]

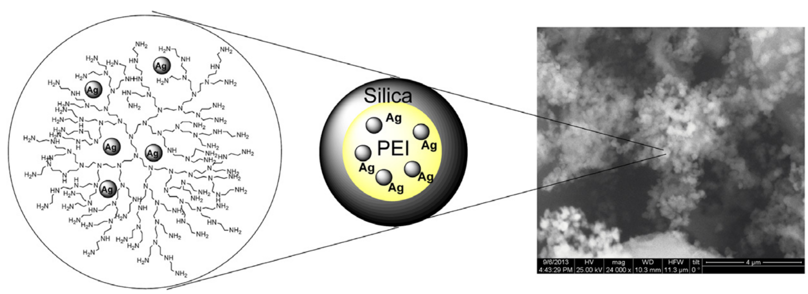
[a] *Institute of Nanoscience and Nanotechnology, NCSR "Demokritos", 15310 Aghia Paraskevi, Attiki, Greece*

[b] *National Technical University of Athens, School of Mining Engineering and Metallurgy, Iroon Polytechneiou 9, 15780, Athens, Greece*

HIGHLIGHTS

- A novel method to obtain doped-core/shell hybrid nanoparticles is introduced.
- Two reactions in one pot are mediated biomimetically by the same dendritic polymer.
- Silica/hyperbranched polyethylene imine (PEI)/silver nanoparticles are produced.
- Drastic compounds of these systems retain release and overall chemical properties.
- Possible applications of bactericide complexes in textiles and water purification.

GRAPHICAL ABSTRACT



An environment friendly procedure for the preparation of inorganic/organic/inorganic i.e. silica/hyperbranched polyethylene imine (PEI)/silver antibacterial nanoparticles employing two biomimetic reactions.

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ABSTRACT

An environment friendly procedure for the preparation of inorganic/organic/inorganic i.e. silica/hyperbranched poly(ethyleneimine) (PEI)/silver nanoparticles employing two biomimetic reactions is described. Silver ions can be absorbed into the hyperbranched PEI cavities and undergo reduction without employing a reducing agent. This is a process mimicking biomineralization, realized by specific proteins in some microorganisms. Dendritic poly(ethyleneimine) possesses size and functions that are similar to proteins and thus presents an ideal alternative to their role by mimicking their catalytic activity. At the periphery of PEI another procedure mimicking biosilicification can also be performed due to the presence of amino groups mimicking another category of proteins. To our knowledge this is the first example of a combination of two different biomimetic reactions performed by a single molecule in one pot synthesis procedure. The resulting hybrid nanoparticles are characterized by spectroscopy (FTIR, visible), thermogravimetry (TG), scanning electron microscopy (SEM), dynamic light scattering (DLS) X-ray diffraction, Energy-dispersive X-ray spectroscopy. Their antibacterial activity was assessed towards *Escherichia coli, Pseudomonas aeruginosa* and *Staphylococcus aureus*.

1. Introduction

Nowadays there is growing interest in biological methods for the production of tailor made inorganic materials. These methods are referred to as 'green chemistry', and considered to be environmentally friendly approaches as they involve natural processes

* Corresponding author.

E-mail address: m.arkas@inn.demokritos.gr (M. Arkas).

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that take place in living systems in ambient temperature without implementation of solvents or other toxic compounds nor generation of hazardous by-products. Numerous microorganisms are capable of synthesizing inorganic-based materials with amazing diversity of nanostructure frameworks through a process called biomineralization [1,2]. Biomineralizing organisms use organic molecules mainly proteins to generate species-specific mineral patterns. In this context aqueous extracts of Rhizophora Mangle [3], bacteria such as *Pseudomonas stutzeri* A259 [4] *Lactobacillus A09* [5] *B. subtilis ATCC* 6633 [6] and *Aeromonas sp. SH10* [7] form silver nanoparticles from Ag^{+} ions. Eukaryotic fungi such as *Fusarium oxysporum* [8,9] *Hormoconis resinae* [10] and *Aspergillus flavus* [11] have also been reported as Ag nanoparticle producers. It has been proposed that the reduction of Ag+ ions to silver is attributed to a number of enzymes, such as hydrogenase and NADH-dependent reductase [8,12].

Biogenic silica nanoparticles on the other hand are formed by many eukaryotic, unicellular algae as diatoms *Thalassiosira pseudonana*, *Cylindrotheca fusiformis* and *Stephanopyxis turris* and some sponges. This process known as biosilicification proceeds rapidly in water under mild conditions, at ambient temperatures, pressures and pH values [13,14]. The formation of networks of silica nanoparticles from silicic acid ($Si(OH)_4$), which is the main form of silica in aqueous environments, is attributed to enriched in charged polycationic peptides silica transporter proteins (SIT) for example silaffins located in the specific silica deposited vesicles (SDV) [13,15] and the R5 peptide [16].

Given the extent of morphological variations encountered in biology systems their application in the production of inorganic nanomaterials presents great interest. They are generally, biocompatible, nontoxic, and eco-friendly. However, biogenic methods also have some drawbacks, such as cultivation of microorganisms, which is an expensive, tedious and time-consuming procedure. Microorganisms are fragile and susceptible to the variation of environmental conditions, such as temperature, light, and pH. The control of the shape, size, and crystallinity of the materials generated via these methods presents difficulties.

The formation of nanocomposites having complex morphologies need not be restricted to the biological methods employed by microorganisms and the conditions encountered in nature. Several studies performed during the past decade have identified that the proteins from these organisms involved in biomineralization reactions in vivo can also be used as enzymes or templates for the assembly of nanostructured inorganic components into hierarchical structures leading to the synthesis of inorganic materials in vitro. In addition purely synthetic compounds can adopt conformations very similar to the active centers of these proteins, and generate inorganic materials with morphologies that are every bit as remarkable as those of their counterparts produced by natural methods. A variety of approaches using synthetic compounds having recognition and nucleation capabilities that mimic the role of the biomolecules has thus been developed giving rise to biomimetic chemistry.

Among the most interesting candidates for biomimetic template synthesis of silica nanoparticles are a variety of homopeptides such as poly(arginine) and poly(lysine), [17] a combination of triethanolamine and cetyltrimethylammonium chloride, [18] poly(ethyleneimine) or amine-terminated dendrimers [19]. The latter are symmetric molecules with shapes reminiscent of the branches of a tree, their non symmetric analogues hyperbranched polymers bear functional primary secondary and tertiary amino groups and have dimensions, molecular weight distributions and chemical structures similar to proteins and polypeptides. Due to this reason they exhibit biomimetic properties and are often referred to as ''artificial proteins'' [20–24]. They can react as templates and yield silica nanoparticles with specific round morphologies called nanospheres with distinct distribution which depends on the amino group concentration. The dendritic polymeric matrices encapsulate into silica and precipitate from water solution as their biological analogues the bioactive peptides.

Biomimetic chemistry can also be implemented in the field of biomineralization [25] Stone et al. demonstrated biomimetic synthesis of polyhedral silver nanoparticles using silver-binding peptides identified from a combinatorial phage display peptide library [26]. Dendritic polymers are established as unimolecular nanoreactors possessing cavities in their interior that allow the pre-organization of metal ions into nanoparticles [27,28]. Dendrimers have also been implemented to produce metal nanoparticles upon reduction of metal ions trapped by stereochemical interactions or complex formation. Such examples include Au, Ag, Cu, Pt and Pd nanoparicles into polyamido amine (PAMAM) dendrimers [29–37] and Cu and Au nanoparticles into poly(propylene imine) (DAB), dendrimers [38,39]. Randomly branched non-symmetric hyperbranched poly(ethyleneimine) (PEI) polymers have been also successfully used as templates for the stabilization of Ag, Au, Cu and Pt metal nanoparticles [40,41].

Silver is known since antiquity as a broad-spectrum agent exhibiting therapeutic properties against a broad range of microorganisms such as bacteria and viruses [42]. It was been used in antimicrobial coatings, [43] as an additive in textiles [44] in order to fight against infections and in food packaging to prevent spoilage [45].

There is a debate on the mechanism of this activity against microorganisms. Many researchers conclude that silver's toxicity functions through the slow release of silver ions from nanoparticles to the environment. [46–56] In contrast, others believe that the toxicity is attributed to the contact of the nanosilver particles themselves with the microorganisms [57] whereas a third point of view relates it to the combination of the two aforementioned factors [58,59]. In any case Balogh et al. confirmed that PAMAM dendrimer–silver nanocomposites displayed antimicrobial activity comparable or better to those of silver nitrate solutions and reaction of those nanocomposites with chloride and sulfate ions neither blocks the diffusion of the silver nor the activity against *S. aureus, Ps. aeruginosa and E. coli* [60].

The control over the size of the nanosilver particles, and Ag^{+} release rate [28] presents great scientific interest. Both can be achieved through the elegant synthesis of hybrid organic/inorganic nanocomposites containing silver nanoparticles templated using dendritic materials and their immobilization on an inert, nanostructured support in the form of silica nanoparticles. These hybrid materials have applications, among others in the fields of textile industry [61] and water decontamination [62]. Moreover, silica coating increases biocompatibility and allows further surface modification [63].

Therefore, the scope of the present work is to examine if the combination of two completely different biomimetic reactions by employing only one hyperbranched compound i.e. hyperbranched poly(ethyleneimine) as bio-matrix in one pot synthesis procedure is possible. To introduce thus a novel method for the production of doped-core/shell inorganic/organic/inorganic complex hybrid materials having a periphery made from ceramic material and an organic dendrimeric core bearing metal nanoparticles. There is no reason the applications of this synthetic strategy to be restricted only in metals. In contrast it can be adapted to any compound capable to be absorbed into dendritic cavities.

The feasibility of applying the above mentioned biomimetic methods in order to obtain these materials and avoiding the previously employed techniques resides to the environmentally friendly conditions used for the integration of dendritic polymers in silica and the reduction of silver cations into metallic silver. More specifically the hybrid dendritic-silica composites were produced by functionalization of the polymers and cross-linking reactions, [64,65] or by impregnation [66,67] into silica. All these