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Silver nanoparticles embedded into silica functionalized with vitamins as biological active materials

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Abstract

The paper describes a rapid and simple method for preparing silver nanoparticles coated with tunable silica shell thickness and their further functionalization with vitamins. Monodispersed silver nanoparticles (Ag NPs) with a mean particle size of 10 nm were prepared by chemical reduction. Silica coating was carried out using the Stober method, by mixing the as prepared silver nanoparticles with tetramethoxysilane and 3-aminopropyltrimethoxysilane.

These core–shell nanoparticles were further functionalized with B vitamins in order to facilitate their rapid functionalization to a wide range of end applications. Characterization of the newly synthesized materials was made by UV–visible absorption spectroscopy, transmission electron microscopy (TEM), Fourier transform infrared (FTIR) spectroscopy, dynamic light scattering (DLS) and thermal analysis (TG). Their antibacterial activity against Gram-positive and Gram-negative bacterial strains was investigated and the results of our study showed that the linked vitamins on silver nanoparticles coated with silica lead to an increased antimicrobial activity at lower concentrations against planktonic bacterial cells and microbial biofilms. The present study can be useful for future development of different types of biological active materials.

Keywords: Silver nanoparticles; B vitamins; Transmission electron microscopy (TEM); Microbiological evaluation

1. Introduction

Functionalization of biomedically important metal nanoparticles (NPs) on the surface of dielectric material (silica) to obtain composite structures is motivated by interdisciplinary application in nanoscience [1–3]. Hybrid nanostructure of metals and non-metal, silica has proven applicability in biomolecular detection [4], surface enhanced Raman spectroscopy [5], photocatalysis [6], magnetic nanomaterials [7], photonics [8], biocatalysis [9] and optoelectronics [10]. Especially, silver nanoparticles (Ag NPs) have attracted biomedical interests and are widely used to modify silica surface for pronounced anti-microbial activity.

Recently, the use of Ag NPs as antimicrobial reagents in anti-infective applications was revived, due on one hand to the emergence of microbial resistance correlated with the very limited number of new antimicrobial agents that are in development [11], and on the other hand, to technical advances in the fabrication of Ag NPs [12].

The synthesis of Ag NPs involves reduction of silver ions in aqueous solution, yielding colloidal silver with particle diameter of several nanometers. Initially, the reduction of various complexes will lead to the formation of silver atoms, which is followed by agglomeration into oligometric clusters [13]. These clusters eventually lead to the formation of colloidal Ag NPs. When the colloidal particles are much smaller than the wavelength of visible light, the solutions have a yellow colour, with an intense band in the 380–400 nm range and other less intense bands at a longer wavelength in the absorption spectrum [14–16].

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However, for practical biomedical applications, Ag NPs usually have to be integrated with other materials that act as a stabilizing matrix, in order to avoid undesired coagulation and/or oxidation, which would degrade or even abolish their antimicrobial efficacy [13,16]. Vast investigations have been devoted to silica (SiO_2) as a matrix for stabilizing Ag NPs, due to its relative ease of preparation [17,18].

There are several advantages using silica shells instead of organic stabilizers. Silica is chemically inert and does not affect reactions at the core surface, except through physical blocking of the surface [19,20]. Second, the silica shell is optically transparent, so that chemical reactions can be monitored spectroscopically. The shell can also be used to modulate the position and intensity of colloidal metal surface plasmon absorption bands, which relates to the color of the metal sol [19]. Finally, and most obviously, the shell prevents coagulation during chemical reactions so that concentrated dispersions of nanosized semiconducting, magnetic or metallic materials can be created [21].

Such core–shell particles may be further functionalized, enabling their incorporation into non-polar solvents, glasses, or polymeric matrixes. An added advantage is that silica is well-known to form ordered colloids crystals, so silica coating may be a useful precursor to the creation of 2D and 3D arrays of any type of nanoparticles system [22,23].

In this work we have tried to obtain nanosystems with enhanced biological activity, due to the nanoassemblies formed from silver nanoparticles coated with silica and functionalized with B vitamins, having thus multiple possible benefits on human health.

The vitamins B, such as niacin, biotin and pantothenic acid are necessary for cellular growth, lipid and protein metabolism and the production of fatty acids. Moreover, vitamins B are implicated in the anti-infectious immunity, as demonstrated in individuals with genetic disorders exhibiting increased susceptibility to bacterial and fungal infections, and with a more severe clinical risk towards infections, such as dermatitis and conjunctivitis [24].

Therefore, taking into account the importance of an appropriate immune response in infectious diseases, we tried to find out how these nanosystems (formed from silver nanoparticles embedded into silica and functionalized with B vitamins-known for their imunostimulatory activity) are responding from a pharmacological point of view. The global emergence of multiple-drug, extended-drug and pan-drug resistance of pathogenic bacterial strains current antibiotics, as well as the poor perspectives in the development of novel antimicrobial drugs, led to the research of alternative antimicrobial strategies. A great potential in this direction involves the application of metal nanocomposites to control resistant pathogens [25–30].

The objectives of this paper are the coating of colloidal silver nanoparticles with silica and the covalent immobilization of three vitamins (biotin, nicotinic acid and pantothenic acid) on the modified silica surface with 3-aminopropyltrimethoxysilane (APTMS), through amide bond formation between the amino and carboxyl groups [24]. The last part of this study involves the biological evaluation of these newly synthesized materials.

We expect that the addition of vitamins will improve the antimicrobial activity of the Ag NPs embedded in silica and will enlarge the range of medical applications, therefore the obtained nanosystems should be more beneficial to the host organism than the unfunctionalized silver nanoparticles.

2. Materials and methods

2.1. Materials

Silver nitrate 99%, polyvinylpyrrolidone, sodium borohydride granular 10–40 mesh, 98%, tetramethoxysilan 98%, (3-aminopropyl)trimethoxysilan 98%, D-pantothenic acid hemicalcium salt were purchased from Sigma-Aldrich. Other reagents namely, ethyl 2-ethoxy-1,2-dihydro-1-quinoline-carboxylate, nicotinic acid and D-(+)-biotin, were purchased from Merck.

2.2. Synthesis of silver nanoparticles

Silver nanoparticles (Ag NPs) were prepared by chemical reduction according to the literature [31]. Typically, an aqueous solution containing 17 mg of silver nitrate and 100 mg polyvinylpirrolidone (PVP) in 20 mL of deionised water was added dropwise over an aqueous solution of 18 mg of sodium borohydride in 20 mL deionised water, under stirring, at room temperature. The final solution was allowed to stand for 1 h at room temperature in darkness.

2.3. Ag NPs embedded in silica

Silver nanoparticles (Ag NPs) obtained as above were suspended in 20 mL isopropanol under stirring. Separately, to 5 mL methanol were added 50 μL of 3-aminopropyltrimethoxysilane (APTMS) and 100 μL of tetramethoxysilane (TMOS). Finally, 1 mL of this mixture was added to the solution of the Ag NPs suspended in isopropanol, under stirring at room temperature for 3 h, after which the silica coated nanoparticles were separated by centrifugation and washed with methanol for three times.

2.4. Immobilization of the vitamins (nicotinic acid, pantothenic acid and biotin) on the surface of APTMS-modified Ag NPs

To 20 mL dimethylformamide (DMF) were added 50 mg of Ag–SiO_2 nanoparticles and the suspension was stirred until a uniform dispersion was observed. Under stirring were added 60 mg of biotin or 30 mg of nicotinic acid. For each reaction we used 25 mg of *N*-ethoxycarbonyl-2-ethoxy-1,2-dihydroquinoline (EEDQ) as coupling agent. The reactions were continued at room temperature for a few days. After this period, the nanoparticles were separated by centrifugation and washed with methanol, then left to dry.