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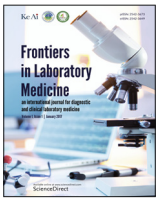

Synthesis and characterization of Ag-Protoporphyrin nano structures using mixed co-polymer method

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ABSTRACT

In this paper, we report the synthesis of hybrid silver nanostructures (AgNPs) based on an effective mixing of polyols with Polyvinylpyrrolidone (PVP) and Porphyrin molecules, in particular Protoporphyrin IX (PP). The combination of PVP and PP, which act as co-directing agents and favour the anisotropic growth of nanostructures, yields to very stable complexes for six months. The resulting hybrid silver nanoparticles have been further characterized by polarization modulation-infrared reflection-adsorption spectroscopy (PM-IRRAS), UV–Visible spectroscopy, X-ray diffraction (XRD), transmission electron microscopy (TEM) and scanning electron microscopy (SEM), revealing that the main role of Porphyrin molecules in the formation of silver nanostructures.

Introduction

Recently, the development of hybrid metal nanoparticles (NPs) with organic and biological components has gained enormous attention than ever before due to the possibility of tailored shape, size and novel properties.[1–4] Among others, silver NPs (Ag-NPs) are commonly used in biomedical devices due to antimicrobial properties;[5–11] in solar cells[12] and conductive adhesives[13] due to electrical conductivity; and in many other technological applications such as catalysis,[14] memory devices,[15] and inkjet printing.[16] In literature there are many synthesis processes that have been reported to prepare Ag-NPs, namely bio-synthesis,[17–21] ultrasonic spray pyrolysis,[22] laser ablation,[23] green synthesis,[24] microwave plasma,[25,26] reduction method,[27] colloidal or solvo-thermal synthesis.[28,29] One of the most frequently used protective agents in metal nanoparticles synthesis is poly(N-vinyl-2-pyrrolidone) (PVP). This water-soluble polymer has been extensively exploited as protecting agent against agglomeration of metal colloids in the well-known polyols-based process.[9,17] In this synthetic procedure, the alcohol (normally ethylene glycol (EG)) works contemporary as solvent and as reducing agent of the metal ions. PVP has also been used in the reduction of silver and gold in water or ethylene glycol/water mixtures.[18]

In most of the papers about the synthesis of nanoparticles, the PVP polymer plays the role of stabilizer or protecting agent against particles sticking and agglomeration, which is still a challenge to be fixed in most of the synthesis methods proposed for the preparation of Ag-NPs, mainly due to its light sensitivity. Many surfactants and protecting agents have been used such as poly ethylene glycol (PEG),[12–14] Triton X-100,[15] citrate,[16] water-soluble bifunctional surfactant.[3] Leading works in the synthesis of AgNPs have focused on the shape control of silver nanocrystals via different approaches. Wiley et al. [30] controlled the shape of silver nanocrystals by varying reaction condition such as the precursor concentration molar ratio of the surfactant and silver ions. In the polyols-based process, PVP helps in the control of the shape. Chou et al. [31] compared the ability of PVP to stabilize silver colloids in the presence of NaOH or Na_2CO_3. Liu et al. [32] also proposed that the crystal structure shape was related to the capping modes between PVP with different molecular weights (MWs) and silver nanocrystals. On the other hand, Protoporphyrin IX (PP) (its structure is reported in Scheme 1) is a tetrapyrrole macrocycle, produced in heme biosynthesis of biological systems; which has attracted considerable attention due to its efficiency in photodynamic therapy of skin tumors.[33] PP shows 22π electrons and two propionic groups in the same direction, perpendicular to the porphyrin plane. Some authors have demonstrates the effect of

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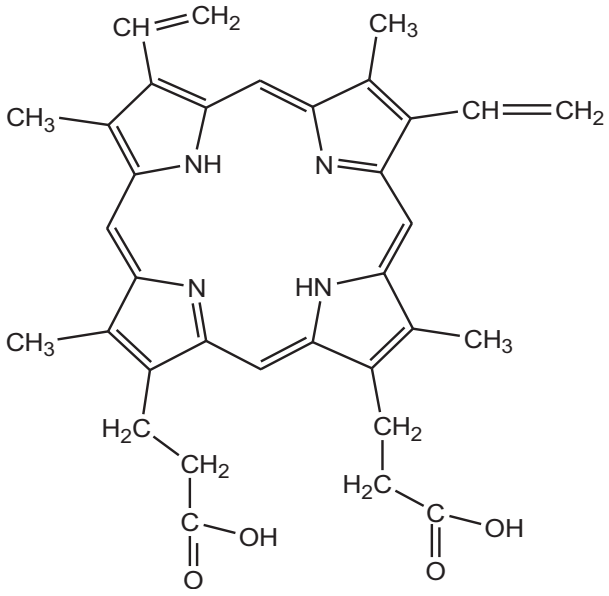

Scheme 1. Schematic representation of Protoporphyrin IX (PP).

porphyrins molecules and their assemblies onto silver nanoparticles in surface enhanced Raman scattering.[34] In this paper, we propose an alternative route to the synthesis of hybrid AgNPs, on basis of the simultaneous presence of the organic substances (i.e. the polymer PVP and the macromolecule PP) and their combinations. In particular, PP with three side chains, such as methyl, propionic acid and vinyl, enhances the stabilization of AgNPs. We have investigated the role of PP molecules also in the nucleation solution, with the aim to examine and discuss the possible involvement of PP molecules in the synthesis process, as surfactant, reducing and shape-modulating agent. The obtained hybrid Ag-PP, Ag-PVP and Ag-PP-PVP nanoparticles have been fully characterized by means of spectroscopic measurements, such as PM-IRRAS, UV–Visible, X-ray diffraction (XRD), transmission electron microscopy (TEM) and scanning electron microscopy (SEM), revealing how the main intrinsic properties of organic molecules influence on the formation of silver nanostructures, in terms of particles stability and biocompatibility.

Experimental

Chemicals

Protoporphyrin IX (PP), sodium borohydride ($NaBH_4$), Silver nitrate ($AgNO_3$), Poly vinyl pyrrolidone with MW equal to 10.000 (PVP), ethanol, and Milli Q water were used throughout the experiments. All chemicals and reagents were of analytical grade, purchased from Sigma–Aldrich and used without any further purification.

Synthesis procedure

The synthesis of silver nanoparticles was performed following the modification of established procedure, in the presence of polymers (PVP) and macromolecules (PP),[35] as briefly described in the following.

Synthesis of Polyvinylpyrrrolidone-silver nanoparticles (Ag-PVP-NPs)

0.067 g of PVP was dissolved in 100 ml ethanol, and then stirred under 70 °C for 2–3 h. An aqueous solution of $AgNO_3$ (0.007 M, 100 ml) was prepared. 5 ml of PVP solution previously prepared was added drop wise into 25 ml of $AgNO_3$ solution. Then 1 ml of $NaBH_4$ (9.2×10^{-3} M) was added to the $AgNO_3$-PVP solution and the content was stirred thoroughly for 5 min. The colour of mixed solution changed from dark to yellow due to the reduction of AgNPs.[5,6] Finally, these aliquots were checked for UV–vis absorption spectra and TEM to verify the formation of Ag-NPs.

Synthesis of Protoporphyrin-silver nanoparticles (Ag-PP-NPs)

50 ml of PP solution ($EtOH/H_20$ 30:20; 3.0×10^{-5} M), 50 ml of aqueous $AgNO_3$ solution (3.9×10^{-4} M), and 10 ml of $NaBH_4$ (9.2×10^{-3} M) were prepared separately. Ag-PP-NPs were synthetized using the following method: 15 ml of $AgNO_3$ was placed in the vigorous stirring at room temperature; after this time, 10 ml of PP was added into $AgNO_3$ solution under the same conditions. Finally 2.5 ml of $NaBH_4$ was added drop wise until change of colors from dark to purple due to occurred reduction of silver and consequent formation of PP silver nanoparticles.

Synthesis of Polyvinylpyrrrolidone-Protoporphyrin silver nanoparticles (Ag-PP-PVPNPs)

PVP-PP coated AgNPs were synthesized followed this procedure: 100 ml of ethanol solution composed by PP and PVP (4.0×10^{-5} M), was prepared under stirring conditions for 1 h at room temperature. 10 ml of PVP-PP solution was added drop wise into 15 ml of $AgNO_3$ solution under stirring condition for 10 min. After this time, 2.5 ml of $NaBH_4$ was added until complete reduction and formation of Ag-PVP-PP NPs.

UV–vis spectroscopy

All the absorption spectra reported in this work have been recorded by using a double-beam Varian Cary 500 UV–vis spectrophotometer. UV absorption spectra of the solution of silver nanoparticles (AgNP) and hybrid silver nanoparticles were recorded in the 400–1000 nm spectral range.

Transmission electron microscopy (TEM)

Transmission electron microscopy measurements were performed with a JEOL JEM 1011 microscope operating at an accelerating voltage of 100 kV. The TEM graphs were taken after separating the surfactant from the metal particles by centrifugation. Typically 1 ml of the sample was centrifuged for 21 min at a speed of 11,000 rpm. The upper part of the colourless solution was removed and the solid fraction was re-dispersed in 1 ml of water. 2 μl of this re-dispersed particle suspension was placed on a carbon-coated copper grid and dried at room temperature.

Scanning electron microscopy (SEM)

SEM images were obtained using a SEM FEG Hitachi SU-70 scanning electron microscope with a low voltage of 1 kV, and distance of 1.5–2 mm; the secondary electron detector "in Lens" was used. 50 μl of the nanoparticles colloidal solution was deposited onto a clean gold substrate and dried at room temperature for the SEM images.

X-rays diffraction (XRD)

The XRD spectra of AgNPs powder samples were recorded by means of a Siemens D500 diffractometer and a Bruker D8 diffractometer (France) using Cu Kα radiation (1.5418 Å). This analysis was carried out at 40 kV and 100 mA, the scan step size was set at 0.0500° and the scan step time was 10 s. Theoretical diffraction patterns of silver, polymers and macromolecules components were extrapolated from the literature data for the corresponding crystal structures.

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