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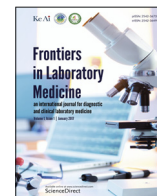
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Synthesis and characterization of Ag-Protoporphyrin nano structures using mixed co-polymer method

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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.

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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 cells¹² and conductive adhesives¹³ 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 Na₂CO₃. 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 demonstrated the effect of

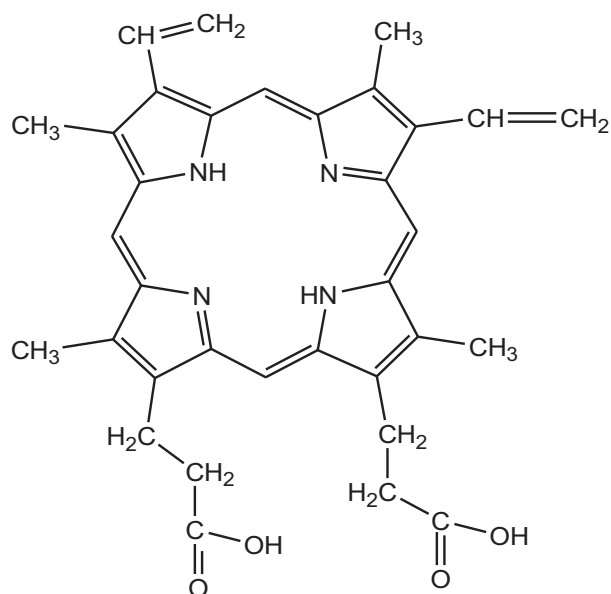
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Scheme 1. Schematic representation of Protoporphyrin IX (PP).

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 Polyvinylpyrrolidone-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_2O 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 synthesized 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 Polyvinylpyrrolidone-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 $\text{Cu K}\alpha$ 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.

Polarization modulation-infrared reflection-adsorption spectroscopy (PM-IRRAS)

PM-IRRAS spectra were acquired by a Thermo Nexus spectrometer (Les Ulis, France). The external beam was focused on the sample with a mirror, at an optimal incident angle of 80°. A ZnSe grid polarizer and a ZnSe photoelastic modulator, modulating the incident beam between *p*- and *s*-polarizations (HINDS Instruments-Thermo scientific-France, PEM 90, modulation frequency = 37 kHz), were placed prior to the sample. The light reflected at the sample was then focused onto a nitrogen-cooled MCT detector. The presented spectra result from the sum of 128 scans recorded with an 8 cm⁻¹ resolution.

Results and discussion

Formation and characterization of AgNPs with and without PP molecules

In the present study, the influence of PP and PVP-PP molecules in the formation of the silver nanostructures was first investigated and characterized (Scheme 2). PP molecules were expected to be involved in the nucleation process and could, thus, influence the final shape and size of nanoparticles. Sun et al. reported that PVP could passivate the side surface of the silver nanoparticles, determining the final shape.³⁰ As described by other authors,³¹ during the AgNPs formation process, the PVP could be adsorbed on the (100) facets of silver nanocrystals (see Scheme 3). We expected a similar effect, in case of PP molecules, on the formation of Ag-PP-NPs, due to both chemical adsorption and steric hindrance. That could tune nucleation and growth. It could be hypothesized that propionic groups, which contemporary stabilized the metallic nuclei's particles, firstly reduced Ag⁺ ions. In a second time, the complete reduction with NaBH₄ induced the final formation of nanoparticles with a characteristic shape and size and the consequently change of color of the solution.

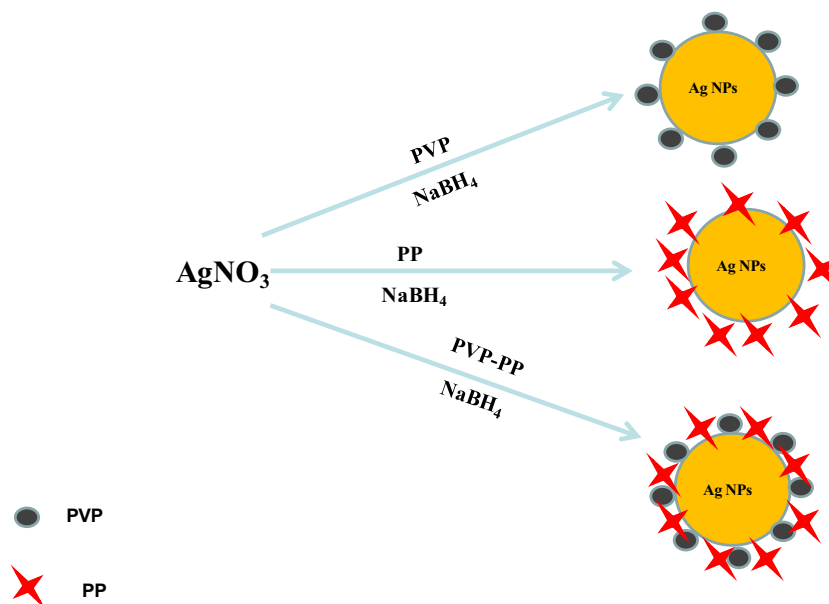
When PVP and PP molecules were mixed, during the NPs synthesis, an ionic interaction between their functional groups produced a complex PVP-PP that was adsorbed onto (100) facets of silver seeds, thus influencing the resulting nanoparticles (Ag-PP-PVP-NPs). The

steric competition between PVP and PP, determined by different MWs, was responsible for preferential dimer complexes and the aggregation of nanoparticles through the so-called depletion-flocculation mechanism.

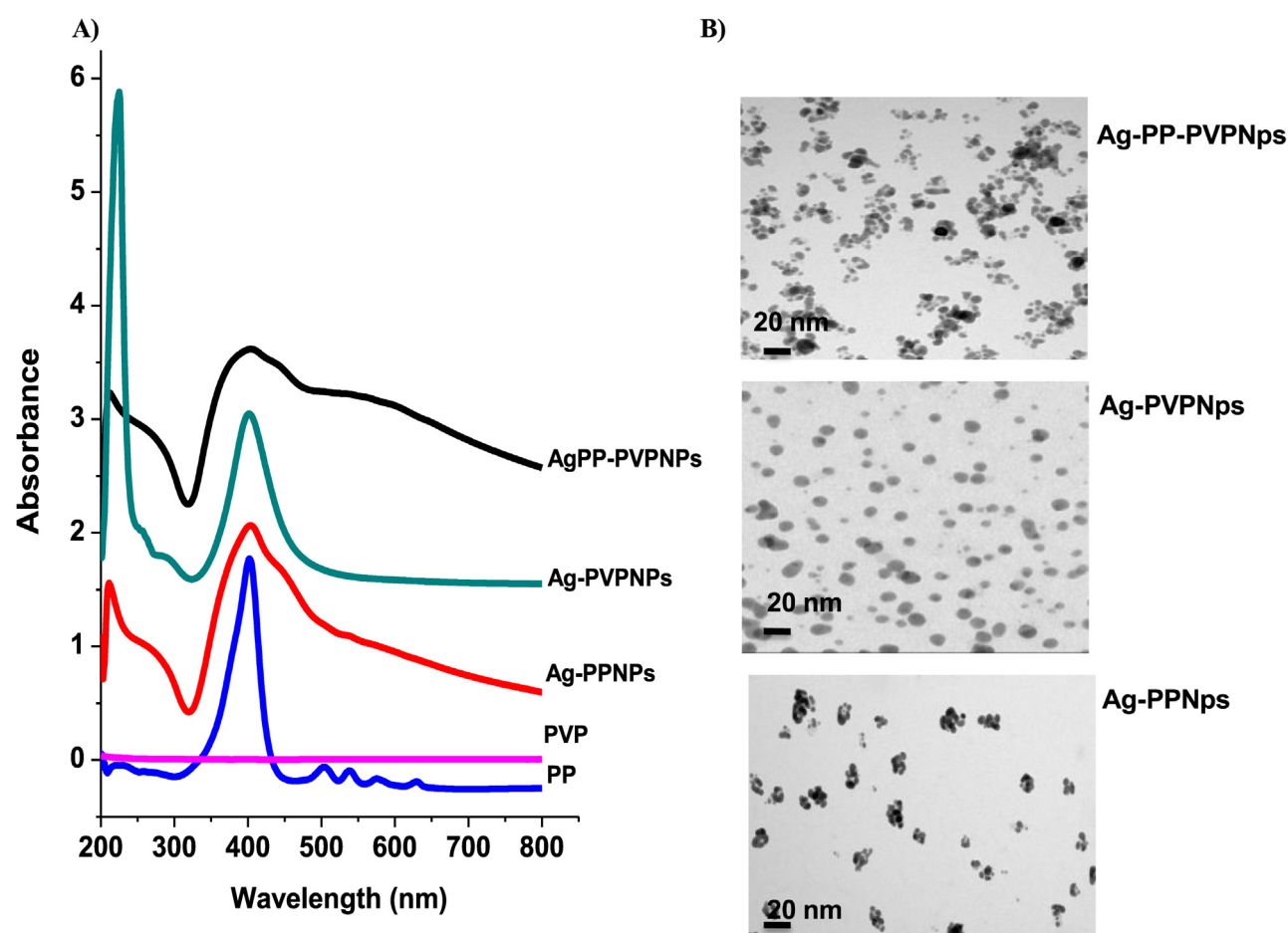
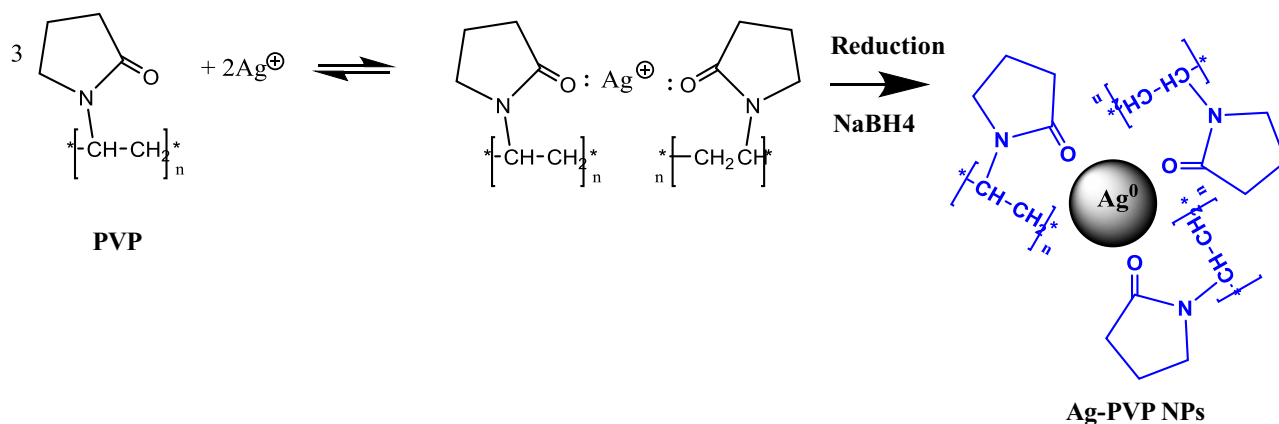
UV-vis adsorption and TEM imaging analysis

Fig. 1 showed TEM images and UV-vis absorption spectra of the Ag samples prepared with and without addition of PP in the reaction mixture. Fig. 1 panel A showed the absorption spectra of aqueous dispersion solutions of AgNPs was coated by the two mixed macromolecules. The UV-vis spectrum of PP molecules, as control, has also been reported for comparison (Fig. 1 panel A-green line). An intense band at 400 nm was called B-band or Soret band and four weaker bands, Q bands, at 626 nm (Q I), 574 nm (Q II), 536 nm (Q III) and 504 nm (Q IV), due to π - π^* electronic transitions associated with the pyrrole-porphyrin ring, in agreement with the optical characteristics of standard PPs are clearly visible.³² According to the existing literature, the Q-band transition can borrow intensity from the Soret-band transition in the so-called PP J-aggregates.³³ The clustering effect of PPs in aqueous solutions has been extensively investigated: PP-macro-complexes are formed at large PP concentrations,³³ on addition of inorganic salt,³⁴ on variation of pH,³⁵ with cationic surfactants,³⁶ or on binding to DNA.³⁷ Ag-PP-NPs showed UV-vis absorption spectrum (Fig. 1 panel A-red line) with an intense band at 400 nm, which could be identified as the Soret band; a broadening band at 447 nm due to a steric arrangement of PP molecules in silver seeds, corresponding to (Q I) band, as well as small bands at 540 nm which could be assigned to the (Q III) band. Variations of the peripheral substituents on the PP ring could be responsible for minor changes in the intensity and wave length of the absorption features, while protonation of two of the inner nitrogen atoms or the insertion of metal atoms in the macrocycle usually strongly changed the absorption spectrum. The Soret band was also well evident in case of Ag-PVP NPs (Fig. 1 panel A-blue line).

The presence of PVP-PP onto AgNPs (Fig. 1 panel A-black line) determined a broadening of both the Soret and Q bands due to the Wan der Waals interaction between PP-PVP during the nucleation and growth of particles. Based on previous published work,³⁸ it was suggested that the propionic acid tails of one PP unit formed



Scheme 2. Proposed mechanism of Ag NPs formation in the presence of PVP, PP and PVP-PP.



specific hydrogen bonded pairs with the tails of other PVP units in an alternate fashion. Typical TEM images of three as-synthesized products (Fig. 1 panel B), showed nanostructures in the ranges of 20–50 nm of diameter. Ag-PP NPs were around 50 nm and also clustered together, which determined the broadening of Soret band at 400 nm. Ag-PVP NPs appeared better separated and more regular in size around 20 nm, due to the steric arrangement of the polymer during reduction process. On adding PVP-PP mixed

solutions into the reaction system, some new nanostructure like small flowers appeared, due to both mixed polymers combination within the nano-scale range. From imaging analysis, PVP clearly protected the particles against agglomeration and acted as nucleation controller through electrostatic reactions.¹⁵ The use of an organic polymer could kinetically control the growth rates of various faces of crystalline structures.¹⁷ PP molecule also participated in the formation of hybrid nanomaterial structures.

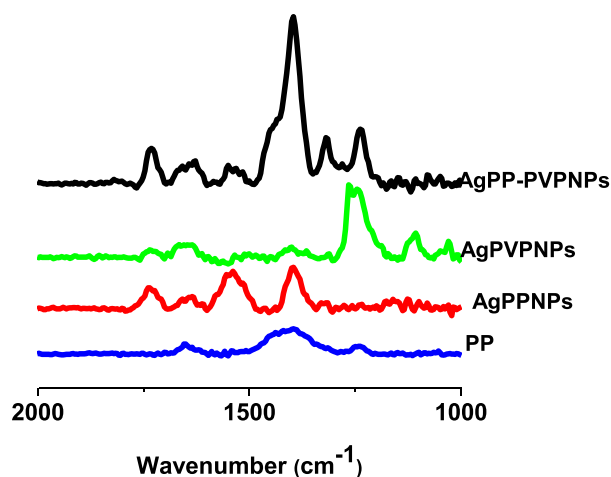


Fig. 2. PM-IRRAS spectra of PP molecules as control (blue line) and Ag NPs coated with PP (red line), PVP (green line) and PP-PVP (black-line) deposited onto gold surface.

PM-IRRAS spectroscopy analysis

PM-IRRAS spectroscopy was used to analyse the interaction between the AgNPs with PVP, PP and their mixed polymeric systems (Fig. 2). In general, the interactions of such hydrophilic

groups, as the band positions of C=O and C–OH stretching vibrations as well as bending vibrations of C–O–H groups can be used to investigate their local interactions onto silver nanoparticles.³⁹ A characteristic PM-IRRAS spectrum of PP (Fig. 2 blue-line), as control, showed a band near 1600 cm^{-1} that could be interpreted as C–C vibration of the phenyl substituents.^{40,41} The predominant signals could be attributed to the carbonyl-stretching mode of the protonated heme propionates.⁴² The $\nu(\text{C}=\text{O})$ mode from metal was centered at 1683 cm^{-1} indicating the absence of the metal center due to the symmetry of the porphyrin ring.⁴⁰ The peaks at $1570/1562\text{ cm}^{-1}$, was assigned to the antisymmetric/symmetric $\nu(\text{COO}^-)$ vibration. The signal at 1410 cm^{-1} , also included ring vibrations. The $\nu(\text{C}=\text{O})$ vibrational mode of the protonated and the signals for the deprotonated form were only visible as a smaller shoulder.

The chemical interaction of PP onto silver nanostructure (Ag-PP-NPs) generated the red-line PM-IRRAS spectrum in Fig. 2. The signals, at $1392/1396\text{ cm}^{-1}$ (C–N vibration) were evident. The amide I band at 1650 cm^{-1} included signals from $\nu(\text{C}=\text{O})$ vibration. The amide II band, observable between 1570 and 1540 cm^{-1} included contributions from the coupled C–N/N–H vibration. The separated strong line at $1731\text{--}1733\text{ cm}^{-1}$ was related to the carbonyl group stretching of porphyrin dendrimers. In the spectra of Ag-PVP-NPs (Fig. 2 green line) strong peak at 1250 cm^{-1} was due to C–H deformation vibration. The absorption peaks located at

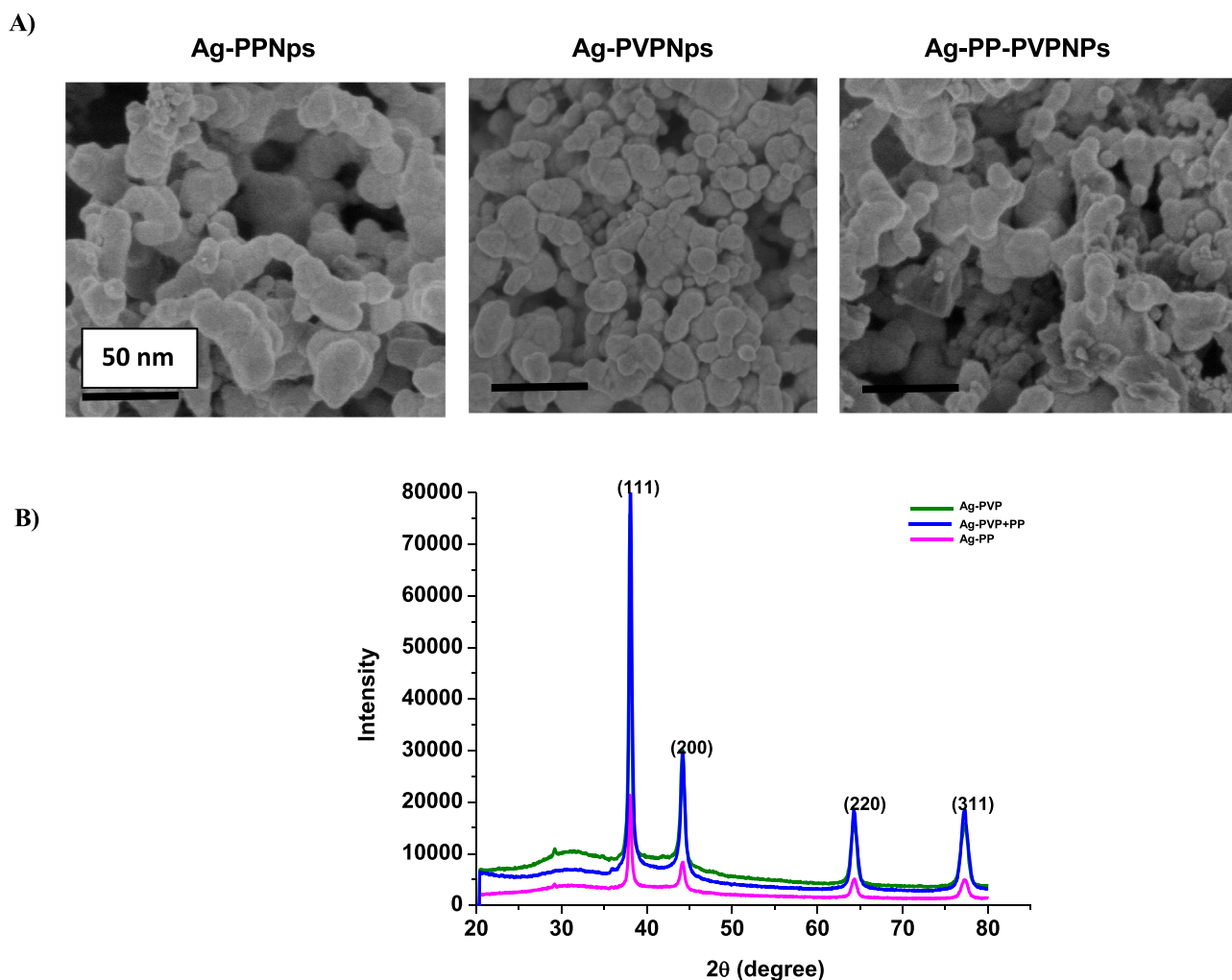


Fig. 3. (Panel A): SEM micrograph of Ag NPs synthesized in the presence of PP, PVP and PP-PVP respectively; (panel B): XRD diffraction patterns of the synthesised silver nanoparticles in the presence of PVP as protecting agent using PP and the mixed of them.

around 1649/1745 cm^{-1} , which was ascribed to the stretching vibration of C=O, and was slightly dependent on the coordination between Ag^+ ions and carbonyl oxygen, due to preferential adsorption of PVP on the (100) facets of silver nanocrystals. PP-PVP-AgNPs PM-IRRAS spectrum displayed a strong peak at 1396 cm^{-1} and a small band at 1434 cm^{-1} due to C–N vibrations and C–O deformation (Fig. 2 black line). A split from 1253 to 1237 cm^{-1} was due to the steric arrangement between propionic group of PP and C=O group of PVP during reduction from Ag^+ to Ag^0 in the final nanoparticles.

SEM microscopy and X-ray diffraction analysis

Fig. 3 (panel A) reports SEM images of silver nanoparticles obtained with PP and PVP respectively. Ag-PVP NPs revealed a mixed morphology between short nanorods and spherical nanoparticles, whereas in Ag-PP NPs and Ag-PP-PVP NPs prevailed a clustered structure that recalled those of carbon nanohorns. Anyway, by comparing the three SEM images, it was clear that the presence of PP, and the ionic interaction PP-PVP onto AgNPs, strongly influenced the effective final conformation. The formations of hybrid AgNPs were characterized by X-ray diffraction (XRD) pattern (Fig. 3, panel B) that reported intense peaks corresponding to the (111), (200), (220), and (311) diffraction peaks of AgNPs, conformal to the face centred cubic crystal (fcc) structure (Joint Committee for Powder Diffraction Standards (JCPDS), File No. 4-0783) of highly pure Ag.

Conclusion

In summary, we present a simple polymeric route to prepare hybrid AgNPs by using PVP, PP and a mix of the two polymers as stabilizing and protecting agents. UV-vis and Infrared spectroscopy clearly demonstrate that the obtained particles are hybrid in nature and the organic molecules present their characteristic fingerprints. This method is an innovative approach for controlling nanomaterials size and forming new nanostructures. Furthermore, the size and shape of AgNPs decorated by polymeric surfaces can be simply tuned by mixing the polymers in proper ratios. We believe that these polymeric NPs could have great potential bioanalytical applications, and this technique can be extended for drug formulation and biosensing.

References

- Politi J, Spadavecchia J, Iodice M, De Stefano L. Oligopeptide-heavy metal interaction monitoring by hybrid gold nanoparticles based assay. *Analyst*. 2015;140:149–155. <http://dx.doi.org/10.1039/C4AN01491J>.
- Politi J, De Stefano L, Longobardi S, et al. The amphiphilic hydrophobin Vmh2 plays a key role in one step synthesis of hybrid protein-gold nanoparticles. *Colloids Surf., B*. 2015;136:214–221.
- Politi J, Stefano LD, Casale S, Spadavecchia J. Original covalent approach for gold nanorods immobilization onto acid-terminated-cysteamine self-assembled monolayers for ft-spr biosensor applications. *J. Biosens. Bioelectron.* 2015;6:167. <http://dx.doi.org/10.4172/2155-6210.1000167>.
- Politi Jane, De Stefano Luca, Rea Ilaria, et al. One-pot synthesis of gold nanoparticles-Vmh2 hydrophobin nanobiocomplex for glucose monitoring. *Nanotechnology*. 2016;27:195701. <http://dx.doi.org/10.1088/0957-4484/27/19/195701>. 9pp.
- Sun Y, Yin Y, Mayers BT, Herricks T, Xia Y. *Chem. Mater.* 2002;14:4736–4745.
- Montazer M, Shamei A, Alimohammadi F. *Prog. Org. Coat.* 2012;75:379–385.
- Jovanovic Z, Radosavljevic A, Siljegovic M, Bibic N, Miskovic-Stankovic V, Kacarevic-Popovic Z. *Radiat. Phys. Chem.* 2012;81:1720–1728.
- Zhu Yu-P, Wang Xi-K, Guo Wei-L, Wang J-G, Wang C. *Ultrason. Sonochem.* 2010;17:675–679.
- Wiley B, Herricks T, Sun Y, Xia Y. *Nano Lett.* 2004;4(9).
- Crespo J, García-Barrasa J, López-de-Luzuriaga JM, et al. *J. Nanopart. Res.* 2012;14:1281.
- Pal Angshuman, Shah Sunil, Devi Surekha. Microwave-assisted synthesis of silver nanoparticles using ethanol as a reducing agent. *Mater. Chem. Phys.* 2009;114:530–532.
- Shameli Kamyar, Ahmad Mansor Bin, Jazayeri Seyed Davoud, et al. Synthesis and characterization of polyethylene glycol mediated silver nanoparticles by the green method. *Int. J. Mol. Sci.* 2012;13:6639–6650.
- Popa M, Pradell T, Crespo D, Calderon-Moreno JM. *Colloids Surf., A*. 2007;303:184–190.
- Shkilnyy A, Souc M, Dubois P, Warmont F, Saboungib M-L, Chourpa I. *Analyst*. 2009;134:1868–1872.
- Mandala A, Medaa V, Zhanga WJ, Farhanb KM, Gnanamanic A. *Colloids Surf., B*. 2012;90:191–196.
- Prasad BLV, Arumugam Sujatha K, Bala Tanushree, Sastry Murali. Solvent-adaptable silver nanoparticles. *Langmuir*. 2005;21:822–826.
- Zhao T, Sun R, Yu S, et al. *Colloids Surf., A*. 2010;366:197–202.
- Sun Y, Xia Y. *Science*. 2002;298:2176.
- Anandhakumar S, Mahalakshmi V, Raichur Ashok M. Silver nanoparticles modified nanocapsules for ultrasonically activated drug delivery. *Mater. Sci. Eng., C*. 2012;32:2349–2355.
- Hu J-Q, Chen Q, Xie Z-X, et al. *Adv. Funct. Mater.* 2004;14(2):183–189.
- Liu Fu-Ken, Huang Pei-Wen, Chang Yu-Cheng, Ko Chu-Jung, Ko Fu-Hsiang, Chu Tieh-Chi. *J. Cryst. Growth*. 2005;273:439–445.
- Wilson Mick et al. *Nanotechnology*. 2005.
- Pillai ZS, Kamat PV. *J. Phys. Chem. B*. 2004;108:945.
- Yanfei Xu, Liu Zhibo, Zhang Xiaoliang, et al. *Adv. Mater.* 2009;21:1275–1279.
- Myles Andrew J, Gorodetsky Brian, Branda Neil R. *Adv. Mater.* 2004;16(11).
- Song Yujiang, Yang Yi, Medforth Craig J, et al. *J. Am. Chem. Soc.* 2004;126:635–645.
- Kojima Takahiko, Harada Ryosuke, Nakanishi Tatsuaki, Kaneko Kenji, Fukuzumi Shunichi. *Chem. Mater.* 2007;19(1).
- Wiley B, Sun YG, Mayers B, Xia YN. Shape controlled synthesis of metal nanostructures: the case of silver. *Chemistry*. 2005;11:454–463.
- Chou KS, Lai YS. Effect of polyvinyl pyrrolidone molecular weights on the formation of nanosize silver colloids. *Mater. Chem. Phys.* 2004;83:82–88.
- Liu XH, Zhang F, Huang R, Pan CF, Zhu S. Capping modes in PVP-directed silver nanocrystals growth: multi twinned nanorods versus single crystalline nanohexapods. *Cryst. Growth Des.* 2008;8:1916–1923.
- Shkilnyy A, Souc M, Dubois P, Warmont F, Saboungi M-L, Chourpa I. *Analyst*. 2009;134:1868–1872.
- Chen X, Hui L, Foster DA, Drain CM. *Biochemistry*. 2004;43:10918–10929.
- Sun Y, Xia Y. *Adv. Mater.* 2002;14:833–837.
- Jun Song Y, Wang M, Zhang X-Z, Wu Y-Z, Zhang T. *Nanoscale Res. Lett.* 2014;9:17.
- Dean ML, Miller TA, Brückner C. *J. Chem. Educ.* 2011;88:788–792.
- Guerrero-Martínez Andrés, Pérez-Juste J, Carbó-Argibay Enrique, Tardajos Luis M, Liz-Marzán Luis M. *Angew. Chem. Int. Ed.* 2009;48:9484–9488.
- Maiti NC, Mazumdar S, Periasamy N. *J. Phys. Chem. B*. 1998;102:1528–1538.
- Jana NR. *Small*. 2005;1:875–882.
- Hu M, Chen J, Li Z-Y, et al. *Chem. Soc. Rev.* 2006;35:11.
- Ohyama J, Hitomi Y, Higuchi Y, et al. *Chem. Commun.* 2008;47:6300–6302.
- Spadavecchia J, Casale S, Landoulsi J, Pradier C-M. *Chem. Phys. Lett.* 2014;609:134–141. Elsevier.
- Seo Jongcheol, Jang Jinhyeong, Warnke Stephan, Gewinner Sandy, Schöllkopf Gert, von Helden Gert. *J. Am. Chem. Soc.* 2016;138(50):16315–16321.