COMPLEX FORMATION BETWEEN Co-METALLOPORPHYRIN AND SILVER COLLOID IN ACIDIC MEDIA

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Abstract
Large flower sized nanoparticles of silver were synthesized and hybrid colloids with porphyrins were obtained. Daisy-like round aggregates generated from triangular-shaped silver nanoparticles can be observed, evenly distributed. The complexation of these particles with organic dyes was the main purpose of this work in order to achieve nanomaterials exhibiting wide absorption bands.
The formation of a complex between an acidified Co(II) 5,10,15,20-meso-tetra(3-hydroxyphenyl) porphyrin (**Co-3OHPP**) solution in THF and the silver colloid negatively charged at the surface was proven by analyzing the UV-vis spectra during the experiment.

Introduction
The obtaining ofsilver nanoparticles using non-polluting natural materials is a new trend in science today and thereforevarious natural extracts were used to stabilize the nanosized metal. The reduction with banana peel extract [1] aqueous extract of *Solanum torvum* fruit [2] ora mixture of ascorbic acid and starch were also tested with promising results [3]. In order to prevent the colloids from coagulating, poly(vinyl alcohol), poly(vinylpyrrolidone) or sodium dodecyl sulfate are used to obtain a narrow size distribution of particles [4]. Silver colloids stabilized by cellulose, glass, and quartz supports can be stable for more than 3 weeks [5].
The oxygen-binding behavior of cobalt(II) porphyrin complexes strongly depends on the nature of substituents linked to the porphyrin ring [6].
Our work focuses on obtaining large sized nanoparticles of silver and on forming hybrid materials containing these silver colloids and porphyrins, in order to enhance their optical and biological properties.

Experimental
The method chosen for the obtaining of a sustainable plasmon was adapted from literature [7]. The Co(II) 5,10,15,20-meso-tetra(3-hydroxyphenyl) porphyrin was synthetized as previously mentioned in literature [8].
The silver salt ($AgNO_3$), poly(vinylpirrolidone) (PVP) (Mw=360000), ascorbic acid ($C_6H_8O_6$) and tetrahydrofurane (THF) were purchased from Merck or Sigma-Aldrich and were used without further purification. The water was previously distilled and the ethanol was p.a. grade.
The procedure of obtaining the silver colloid: aqueous solution of $AgNO_3$ (0.6 mL 1M) and poly(vinylpirrolidone) (PVP, Mw=360000, 6 mL, 1% w/w) were added under intense stirring in 30 mL distilled water at room temperature. Ascorbic acid (0.6 mL, 1M) solution was poured at once over the mixture and the stirring was maintained until the solution turned grey. The colloid was investigated by means of UV-vis spectroscopy and AFM measurements.
UV-visible spectra were recorded on a JASCO UV-visible spectrometer, V-650 model (Japan). The surface imaging investigations were done in ambient conditions on a Nanosurf® EasyScan 2 Advanced Research AFM (Switzerland), with samples deposited onto pure silica

plates by slow evaporation of the water. AFM images were obtained in contact mode and are quantitative on all three dimensions.

Results and discussions

The purpose of introducing a large molecular mass polymer into the solution of freshly prepared silver nanoparticles is to prevent them to aggregate and to allow the generation of nanoparticles with various shapes other than spherical, thus enhancing the average surface. Another advantage is that the polymer has no influence upon the light absorption domain and is biocompatible.

As can be observed from the UV-vis spectrum of the colloidal solution of silver nanoparticles (Figure 1), the absorption maximum is located at 424 nm, thus offering information about particle size. It can be estimated that the particles range from 66 to 82 nm[9].

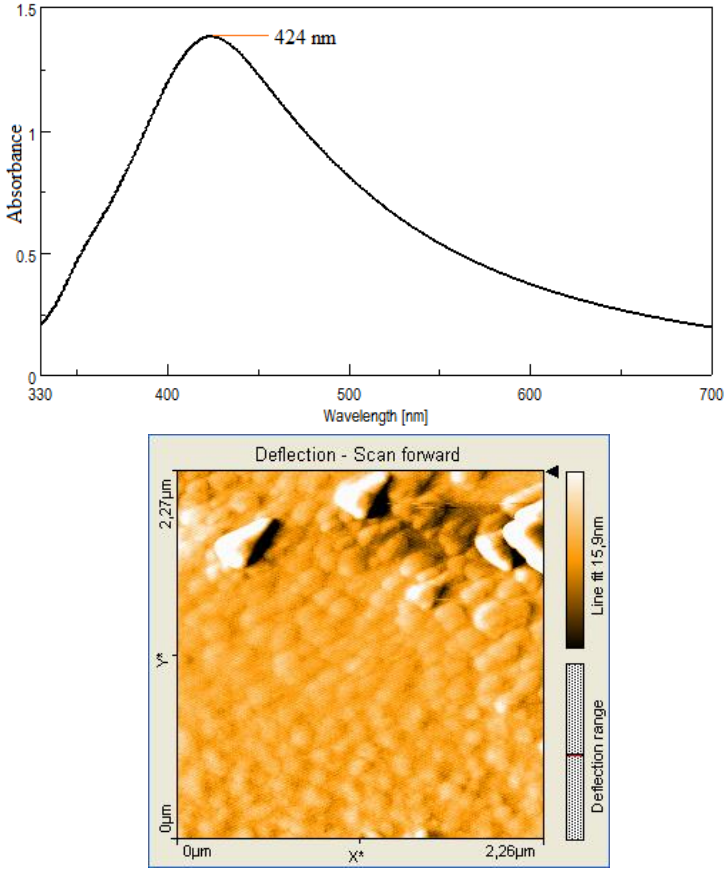

Figure 1. The UV-vis spectrum and 2D AFM imageof water solution of silver nanoparticles

The most conclusive analysis of particle size can be provided by AFM studies. The solution of silver particlesreveals various sizes of nanoparticles, ranging in dimensions from 79 to 290 nm (Figure 1). The formation of larger aggregates by stacking of triangular-shaped particles is also visible (Figure 2).

3D AFM imaging for 2 and 9 µm respectively (Figure 2) reveals the beautiful round flower-like assemblies of silver particles obtained in an environmentally friendly manner.

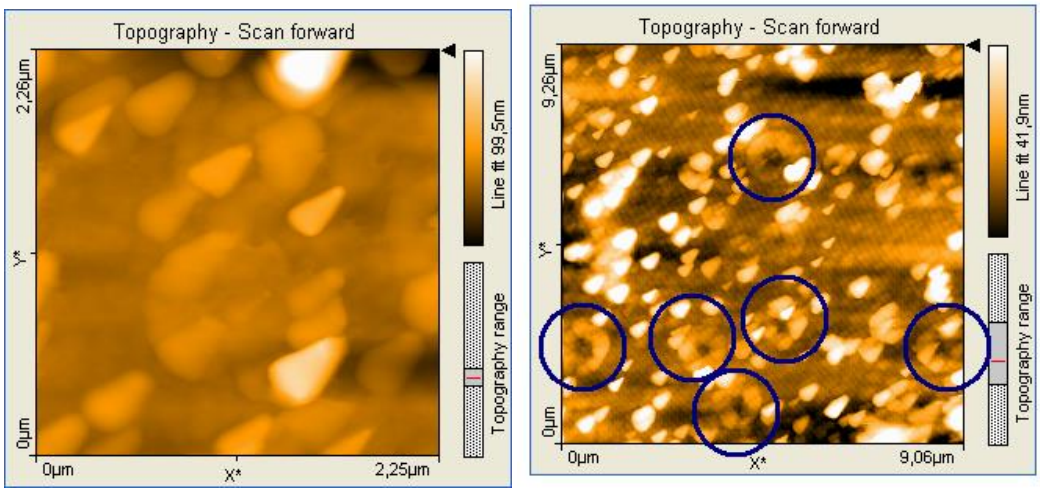

Figure 2. 3D-AFM images of 2 and 9 µm areas of samples measured from water extract of silver colloid

The formation of a complex between these large silver nanoparticles and the Co-porphyrin was attempted as follows: a quantity of 0.18 mg ($2.447x10^{-7}$ mole)Co(II) 5,10,15,20-meso-tetra(3-hydroxyphenyl) porphyrin (**Co-3OHPP**) (M_w=735,65 g/mol)was added to 5 mLTHF and the solution ($c=0.323x10^{-6}$M) was acidified by adding HCl solution (37% wt) until the pH reached 2.This initial solution was added dropwise to 3 mL silver colloid, as follows: 20 µLporphyrin solution in the first ten determinations; then 50 µLporphyrin solution for the next eight determinations. The colloid concentration used in the experiments was $9.375x10^{-5}$M.
After succesive adding of acidified **Co-3OHPP** solution to the silver colloid it can be observed that the intensity of the plasmonic band of the colloid decreases with the increase in porphyrin concentration (Figure 3)as opposed to the case of gold plasmon, where a hyperchromic effect on the Soret band of the **Co-3OHPP-nAu** hybridcan be observed with increasing Co-porphyrin concentration [8].

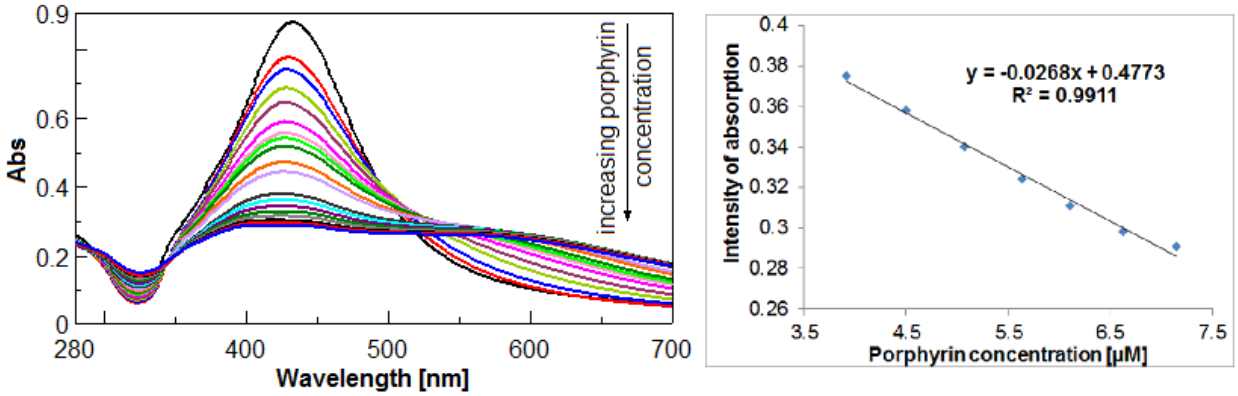

Figure 3. UV-vis spectra of the successive adding of Co-3OHPP to silver colloidand the linear dependence of the intensity of absorption of the nano-silver plasmonic band and the increasing porphyrin concentration

The presence of two isosbestic points, at 350 nm and 570 nm (Figure 3) proves the formation of a complex between the Co-porphyrin and the silver colloidal nanoparticles, indicating at least two equilibrium processes. It can also be observed that the plasmonic band is enlarged having the aspect of a plateau and covers a wide absorption domain with the increase in Co-3OHPP concentration, but the intensity of the absorption is low.

As can be seen in Figure 3, the linear dependence of the intensity of absorption of the nano-silver plasmonic band and the increasing porphyrin concentration can be detected only for a narrow domain of Co-3OHPP concentration, proving that the silver colloid is able to detect with high acuracy only minute quantities of the metalated porphyrin. Co-porphyrins are relevant for human physiology and their trace detection can offer medical information in early diagnosis.

Conclusions

Obtaining large flower sized nanoparticles of silver able to form hybrid colloids with porphyrins was performed. Thus daisy-like round aggregates of triangular-shaped nanoparticles can be observed, evenly distributed in different depths of the colloid. The surface area of these particles is considerable, allowing their use in several technical applications.

The formation of a complex between acidified Co(II) 5,10,15,20-meso-tetra(3-hydroxyphenyl) porphyrin solution in THF and the silver colloid negatively charged at the surface was confirmed by analyzing the UV-vis spectra during the experiment.

References

[1] A. Bankar, B. Joshi, A.R. Kumar, S. Zinjarde, Colloid Surface A: Physicochem. Eng. Aspects 368 (2010)58.
[2] C.H. Ramamurthy, M. Padma, I.D. Samadanam, R. Mareswaran, A. Suyavaran, M.S. Kumar, K. Premkumar, C. Thirunavukkarasu, Colloid Surface B: Biointerfaces 102(2013) 808.
[3] Z. Khan, T. Singh, J.I. Hussain, A.Y. Obaid, S.A. Al-Thabarti, E.H. El-Mossalamy, Colloid Surface B Biointerfaces 102(2013) 578.
[4] G. Carotenuto, G.P. Pepe, L. Nicolais, Eur. Phys. J. B 16(2000) 11.
[5] T. Vo-Dinh, Trends in analytical chemistry 17(1998) 557.
[6] J. Yang, P. Huang, Chem. Mater.12(2000) 2693.
[7] H. Liang, Z. Li, W. Wang, Y. Wu, H. Xu, Adv. Mater. 21 (2009) 1.
[8] E. Fagadar-Cosma, I.Sebarchievici, A.Lascu, I.Creanga, A.Palade, M.Birdeanu, B.Taranu, G.Fagadar-Cosma, J. Alloys Compds, 686 (2016) 896.
[9] A. Slistan-Grijalva, R. Herrera-Urbina, J.F. Rivas-Silva, M. Avalos-Borja, F.F. Castillon-Barraza, A. Posada-Amarillas, Physica E 27(2005) 104.