Poly(amidehydroxyurethane) Templated Fe_3O_4 and Ag Nanoparticles Galvanostatic Assay Synthesis

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Water soluble polymers can play an important role with regard to the formation and stabilization of particles with diameters in a range from hundred to a few nanometers. Combining the tunability of poly(amidehydroxyurethane) PAmHU as template with the electrochemical reduction of metal precursor in a galvanostatic process have been obtained magnetite and silver nanoparticles with the dimensions varying from 17 to 20 nm and 19 to 21 nm respectively. The analysis of synthesized nanoparticles evidenced that the nanosystems are organized into a coreshell with an inner-core formed from unit cells of metal.

Keywords: magnetite and silver nanoparticles, galvanostatic assay synthesis, poly(amidehydroxyurethane) as template, nanomorphological analysis

Metal nanoparticles display novel physical and chemical properties due to the competition between surface and bulk atoms, the first being majority in the surface effect [1]. These novel properties have put metal nanoparticles to play an interesting role in materials technology [2-5], biomedicines [6-8], catalysis [9-11], etc. The properties of metal nanoparticles are highly influenced by the preparation methods and conditions, which result in particles of various sizes; shape and surface stabilization [12-14] often, the surface/interface interactions having their signatures in the properties investigated [15, 16].

In the last time, different wet chemical methods have been used for the synthesis of nanoparticles, the most common the synthesis by nucleation process involving the use of excess reducing agents [17]. Nanoparticles formation in template phases was inspired from biological processes [18]. In essence, template phases are used for the formation of well-defined nanoparticles with a narrow size distribution. Amphiphilic block copolymers provide a large number of microstructures that can be used to prepare inorganic nanoparticles [19]. The self-assembly of block copolymers leads to a broad variety of morphologies e.g., micelles of various shapes, lamellae, ordered cylinders, or bicontinuous structures. The ability to control the different micelles morphologies consist in the regulation of the hydrophilic/hydrophobic balance. In order to use block copolymers as templates for the nanoparticles formation, the inorganic precursors are first loaded into the template, meaning into the micellar cores or the bulk block copolymer microphases. For a size-controlled synthesis of nanoparticles it is necessary to control the size of the microcompartment.

A special feature is presented in the case of water – soluble polyelectrolytes, due to the possibility of bearing dissociated groups. Combining the tunability of PAmHU with the electrochemical reduction of [M^{n+}] metal ions in a galvanostatic process; the H^+ proton source being the hydrogen releasing by cathode electrolysis process there is the possibility of obtaining nanoparticles from reactions that lead to reduced metal [20-23]. This route has the major advantages that the selection of the particles size is done by controlling the current of galvanostatic process which controls the restricted reduction reaction, and the water soluble polymer that acts as restricted capping agent controlling the size of the microcompartment room and diffusion processes in it as dependence with the aqua polymer composition, pH and temperature.

In this paper is presented the electrochemical method for magnetite (Fe_3O_4) and metal Ag nanoparticles capped with PAmHU water soluble polymer. The obtained nanoparticles have an excellent water-solubility, stability and biocompatibility.

Materials and methods

The synthesis of magnetite and silver nanoparticles was performed in a simple two-electrode cell. In case of magnetite nanoparticles synthesis as working electrode (WE) was used a coiled iron wire with 130 mm long and 0.57 mm diameter, and in case of silver nanoparticles synthesis a coiled silver wire with 170 mm long and 1.2 mm diameter. In both cases, the counter electrode (CE) was a coiled platinum wire with 140 mm length and 1mm diameter. The electrolysis was carried out in the galvanostatic regime at room temperature under strong stirring and nitrogen atmosphere. The synthesis time was 30 min for magnetite nanoparticles and 15 min for silver nanoparticles. The electrolytic solutions for obtaining magnetite nanoparticles consisted of $Na_2S_2O_3$ (0,02M) and a water – soluble polymer, (PAmHU) (0.1% *w/w*) that was *p*H adjusted at 10 with 1% *w/w* NaOH. In the case of silver nanoparticles, $AgClO_4$ (10^{-4}M) and PAmHU (0.1% *w/w*) were used. The synthesis and physico - chemical characterizations of PAmHU in film and in aqua were reported elsewhere [24-26]. The silver perchlorate was obtained in laboratory from silver nitrate (Merck) solution treated with sodium carbonate (Na_2CO_3) and with perchloric acid, $HClO_4$ (Merck) [27]. The solution used in electrolytic process was obtained by silver perchlorat dissolution in water. For obtaining a *p*H = 10, in this solution was added a sodium carbonate and bicarbonate mixture.

In case of magnetite, the reactions are:

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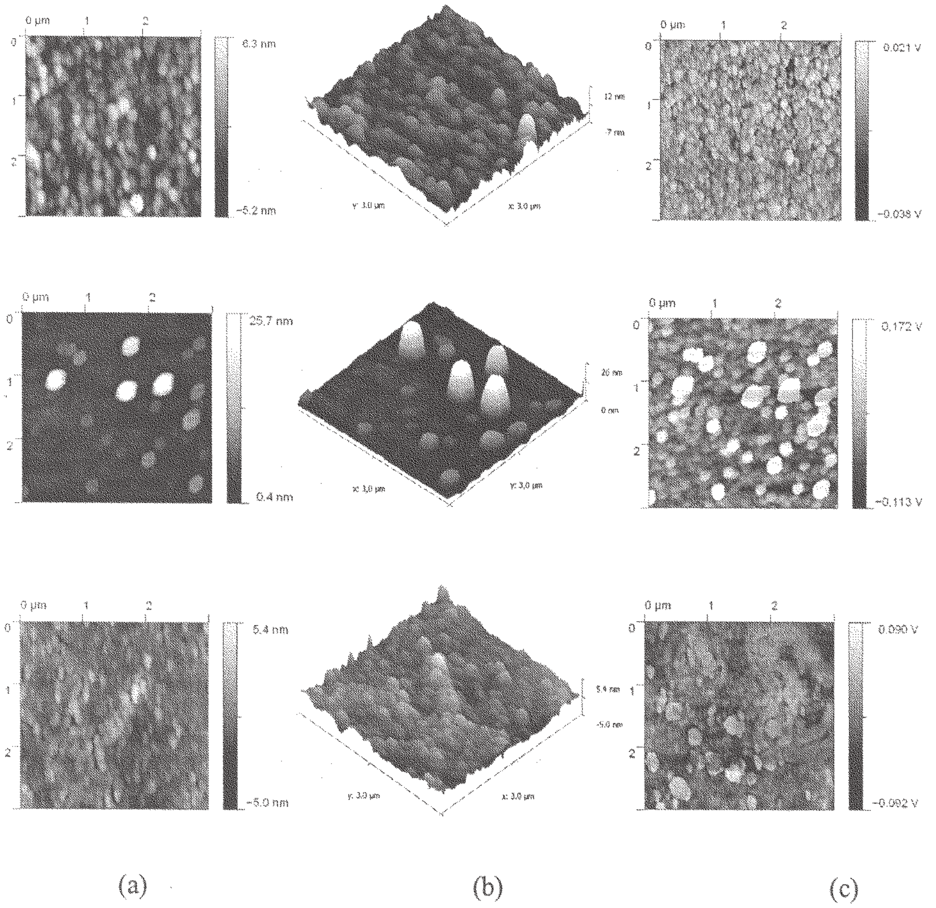

(a) (b) (c)

Fig. 1. The 2D (a) and 3D (b) topographies, and phase contrast (c) of PAmHU film (top), magnetite nanoparticles (middle), silver nanoparticles (bottom); the scale of square area is 3 . 3µm^2

Anode: $Fe + 3OH^- \rightarrow \gamma\text{-}FeOOH + H_2O + 3e^-$ (oxidation)

Cathode: $H_2O + e^- \rightarrow 1/2H_2 + OH^-$ (reduction)

Solution: $3\gamma\text{-}FeOOH + 1/2H_2 \rightarrow Fe_3O_4 + 2H_2O$

Balance: $6Fe + 8H_2O \rightarrow 2Fe_3O_4 + 8H_2$

By passing an electrical current through silver perchlorat solution, the following electrochemical processes take place:

Anode: $Ag \rightarrow Ag^+ + e^-$(oxidation)

$HO^- \rightarrow HO^{\cdot} + e^-$

$2\ HO^{\cdot} \rightarrow H_2O + [O]$

Cathode: $H_2O + e^- \rightarrow 1/2H_2 + OH^-$ (reduction)

$Ag^+ + e^- \rightarrow Ag^0$ (reduction)

The structural and morphological characterizations of nanoparticles-PAmHU systems were done in solution and as thin films. The thin film samples were prepared by spin coating method, using a WS-400B-6NPP/LITE spin coater, being deposited on microscope slide glass substrates with 25 . 25 mm^2 area. The glass substrates were cleaned by soaking them initially in a dish detergent solution, followed by a thorough rinsing with deionized water and 100% ethanol (Chemical Company). The substrates were sonicated (Sonoplus, Bandeline) for 10 min while immersed in a 2% RBS 35 detergent solution (Fluka), followed by a second rinse with ethanol and deionized water. Finally, the substrates were air dried.

The microphase structure was investigated by X-ray diffraction (XRD) performed on a DURON-2 diffractometer, employing nickel-filtered Cu Kα radiation (1.54182 Å) at 25 kV operational voltage. The particle size was determined from X-ray diffractograms according to Scherrer relationship [28]:

$$d = \frac{K\lambda}{\beta\cos\theta}. \qquad (1)$$

where d is the diameter of nanoparticle, K is a constant (0.89), β is the half maximum line width, θ is the diffraction angle and λ is the X-ray wavelength (in our case 1.54182 Å).

Atomic Force Microscopy (AFM) analyses were performed in tapping mode, with a standard silicone nitride tip (NSC21) and tips radius 10-20 nm.

The dimension of the particles coated with PAmHU polymer was determined by laser diffraction method with Shimadzu - SALD-7001 Laser Diffraction Particle Size Analyzer.

Results and discussions

The nanoparticles were synthesized with and without polymer and at different current intensities (5, 10, 20, 45 and 70 mA).

In the case of PAmHU free magnetite synthesis the obtained solutions are dark grey and after few hours the colloidal suspension precipitates and solutions become clear. On the other hand, the solutions obtained in PAmHU presence are clear and brown colored, the color becoming darker with increasing of preset current intensity value. During the synthesis process a quantity of flocculated magnetite was obtained at cathode, this quantity depending on current intensity value.

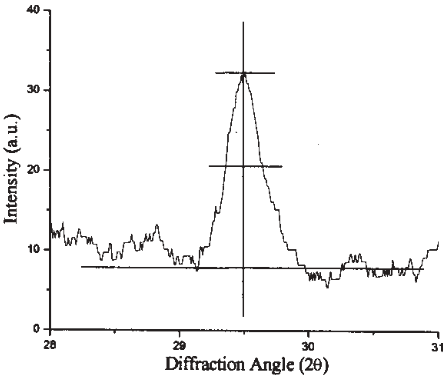

Fig. 2 Determination of half maximum line width for magnetite nanoparticles obtained at 45 mA in polymer presence

Table 1

THE DIMENSSIONS OF MAGNETITE AND SILVER NANOPARTICLES COMPUTED FROM XRD SPECTRA

Sample		Current intensity (mA)	2θ (degree)	Intensity (a.u.)	L (nm)
Magnetite nanoparticles	PAmHU free	25	35.60	36.16	19
	with PAmHU	20/precipitate	31.10	8.51	21
		20/volume	29.51	16.04	17
Silver nanoparticles	PAmHU free	25	38.42	109.81	140
	with PAmHU	25	38.07	133.93	18

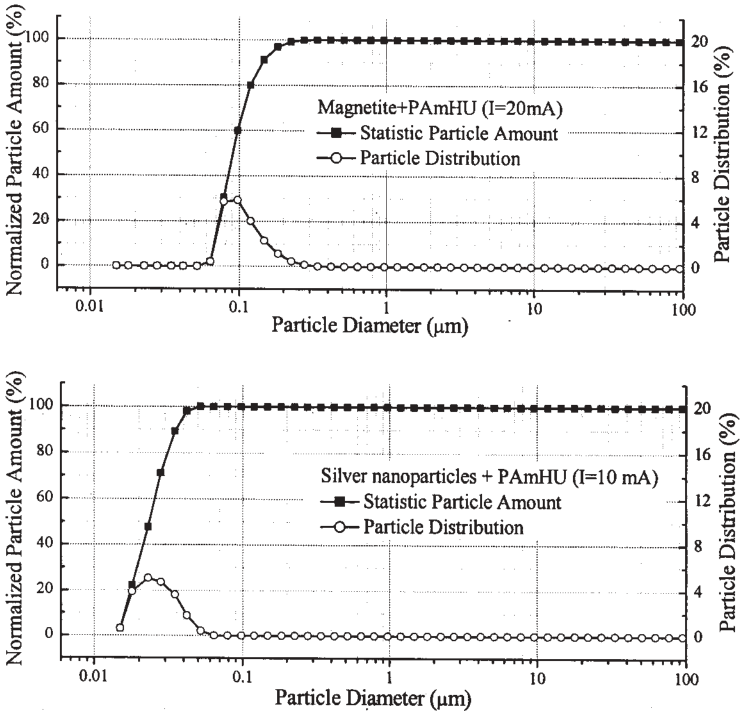

Fig. 3 DSL diagram of (a) magnetite nanoparticles (the value of average diameter of particles is 96 nm) and (b) silver nanoparticles (the value of average diameter of particles is 24 nm)

It was observed that magnetite nanoparticles obtained in polymer presence are more stable, maintaining in suspensions for months, while those obtained without polymer precipitate after few hours.

In the case of silver nanoparticles PAmHU free syntheses the resulted solutions initially are colorless in time becoming dark grey. For the synthesis with PAmHU the solution initially are green to yellow – brown colored, after 3 – 4 h become light blue, blue to dark blue, red to brown and brown to gray depending on the applied value of current intensity.

In figure 1 are shown the AFM 2D and 3D topographies, and phase contrast of PAmHU film, magnetite nanoparticles and silver nanoparticles. It is observed the homogeneity of the polymer film. In case of nanoparticles – polymer system films, from AFM analysis result the distribution dimension within tenth to hundred nanometers of nanoparticle entities.

It is known that the magnetite presents characteristics peaks at diffraction angles (2θ) of 18.30, 30.10 and 35.46 and intensities of 8.20, 28.21 and 100 and the silver at diffraction angles (2θ) of 38.117, 44.279 and 64.428 and intensities of 8.20, 28.21 and 100. Using Scherrer relationship (1) was calculated the nanoparticles size and the nanoparticles dimensions have been found less than in the AFM analysis, which suggests that nanoparticles were capped with PAmHU polymer (table 1). As example, in the calculus of magnetite nanoparticles dimension was used the peak at about 2θ = 30 degree (fig. 2) and were obtained sizes in the 17 to 20 nm range. In the case of silver nanoparticles the dimensions were within 19 – 21 nm.

In figure 3 is shown the diagram of particle distribution. From DSL studies, the dimensions of nanoparticles are larger then those obtained from XRD analysis; the maximum distribution being at 96 nm for magnetite nanoparticles and 24 nm for silver nanoparticles. This confirms the fact that nanoparticles are capped with polymer, suggested by AFM studies.

Conclusions

The proposed synthesis route combine the tuneability of PAmHU with the electrochemical reduction of metal ions in a galvanostatic process; the H^+ proton source being the hydrogen releasing by cathode electrolysis process. This route has the major advantages that the setting of the particles size can be done by current of galvanostatic process and the aqua polymer composition, pH and temperature.

By this method, the nanoparticles with dimension within 17-20 nm in the case of magnetite and 19 – 21 nm in the case of silver were obtained.

The water solubility and the stability of these nanoparticles are conferred by the PAmHU water – soluble polymer used as template.

From AFM and DLS studies results that nanoparticles are capped with biocompatible PAmHU polymer.

These nanoparticles are water soluble, stable and biocompatible due to the PAmHU polymer that capping them, being suitable for many biomedical applications.

References

1. TOSHIMA, N., in LIZ-MARZAN, L. M. and KAMAT, P. V. (Ed.), Nanoscale Materials, Kluwer Academi Pub., London, 2003, p. 79
2. JACAK, L., HAWRYLAK, P. and WOJS, A., Quantum Dots, Springer, 1998
3. BAWENDI, M. G., Science, **290,** 2000, p. 314
4. COLVIN, V., SCHLAMP, M., ALIVISATOS, A., Nature**, 370,** 1994, p. 354
5. ZEMEL, J. N., J. Franklin Inst., **296**, 1973, p. 475
6. BERGEMANN C., D. MULLER-SCHULTE, J. OSTER, L. A' BRASSARD, A. S. LUBBE, J. Magn. Magn. Mater., **194**, 1999, p. 45
7. KNAUTH, M., EGELHOF, T., ROTH, S.U., WIRTZ, C.R., SARTOR, K, Am. J. Neuroradiol. **22**, 2001, p. 99
8. MYKHAYLYK, O., CHERCHENKO, A., ILKIN, A., DUDCHENKO, N., RUDITSA, V., NOVOSELETZ, M., ZOZULYA, Y., J. Magn. Magn. Mater., **225**, 2001, p. 241
9. PETO, G., MOLNAR, G. L., PASZTI, Z., GESZTI, O., BECK, A., GUCZI, L., Mater. Sci. Eng., **C 19,** 2002, p. 95
10. STOEVA, S. I., HUO, F. W., LEE, J. S., MIRKIN, C. A., J. Am.Chem. Soc. **127,** 2005, p. 15362
11. PHADTARE, S., KUMAR, A., VINOD, V. P., DASH, C., PALASKAR, D. V., RAO, M., SHUKLA, P. G., SIVARAM, S., SASTRY, M., Chem. Mater., **15**, nr. 10, 2003, p. 1944
12. EDELSTEIN, A. S., CAMMARATA, R. C. Nanomaterials: Synthesis, Properties and Applications, IOP Pub., London, 1996
13. KREIBIG, U., VOLLMER, M., Optical Properties of Metal Clusters, Springer, Berlin, 1995
14. CISMARU, L., HAMAIDE, T., POPA, M., Mat. Plast., **44**, nr. 3, 2007, p. 243
15. HILGER, A., GUPPERS, N., TENFELDE, H., KREIBIG, U., Eur. Phys. J. D, **10**, 2000, p. 115
16. BURDA, C., CHEN, X., NARAYANA, R., EL-SAYED, M. A., Chem. Rev., **105**, 2005, p.1025
17. HINES, M. A., GUYOT-SIONNEST, P., J. Phys. Chem. **100,** 1996, p. 468
18. DUJARDIN, E., MANN, S., Adv. Mater, **11**, 2004, p. 14
19. KOETZ, J., KOSMELLA, S., Polyelectrolytes and Nanoparticles, Ed. Springer – Berlin - Heidelberg - New York, 2007
20. OBREJA, L., DOROHOI, D. O., MELNIG, V., FOCA, N., NASTUTA, A., Proceeding of the 1st International Conference on Polymers Processing in Engineering "PPE 2007", 25 – 26 October 2007, Galati, Romania, p. 163
21. MELNIG, V., DOROHOI, D. O., Nanoparticles Mild Synthesis by Using Water Soluble Polymers as Template, The 1st International Conference on Polymers Processing in Engineering "PPE 2007", 25 – 26 October 2007, Galati, Romania, (keynote presentation)
22. OBREJA, L., MELNIG, V., FOCA, N., DOROHOI, D., Poly(amidhydroxyurethane) Stabilized Magnetite Nanoparticles Synthesis and Characterization, The 6th National Biomaterials Symposium, "Biomaterials & Medical-Surgical Applications" 18-20 October 2007, Cluj-Napoca (oral presentation)
23. OBREJA, L., MELNIG, V., FOCA, N., DOROHOI, D., Characterisation of Silver Nanoparticles Obtained by Electrochemical Reduction, The 6th National Biomaterials Symposium, "Biomaterials & Medical-Surgical Applications" 18-20 October 2007, Cluj-Napoca (oral presentation)
24. APOSTU, M., MELNIG, V., J Optoelectron Adv Mater, **8**, nr. 3, 2006, p. 1044
25. MELNIG, V., CIOBANU, C., J Optoelectron Adv Mater, **7**, nr. 6, 2005, p. 2809
26. MELNIG, V., POHOATA, V., OBREJA, L. et al., J Optoelectron Adv Mater, **8,** nr. 3, 2006, p. 1040
27. TANG, S., TANG, Y., GAO, F., LIU, Z., MENG, X., Nanotechnolog, **18**, 2007, p. 295607 (6pp)
28. SCHERRER, P., Göttinger Nachr, .**2,** 1918, p. 98

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