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Physical Chemistry*

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Serbia*

*in co-operation
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STRUCTURAL CHARACTERISTICS OF Ag NANOPARTICLES SYNTHESIZED *in situ* WITHIN PNiPAAm HYDROGEL BY γ -IRRADIATION

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ABSTRACT

In this work, silver nanoparticles (AgNPs) are synthesized within thermo-responsive poly(N-isopropylacrylamide) (PNiPAAm) hydrogels of different concentrations, by γ -irradiation. The UV-Vis plasmon absorption characterization of AgNPs and its modeling using Mie theory showed that their diameters are less than 20 nm. The X-ray diffraction (XRD) data are consistent with the face centered cubic (FCC) crystal structure of bulk metallic Ag. The negative lattice strain (lattice contraction) was observed for the samples where the AgNPs are incorporated in the xerogel solid matrix of highest polymer concentration (15 wt.% PNiPAAm). The lattice parameter values are found to be higher than the bulk lattice parameter of Ag for larger nanoparticles formed in 5 wt.% PNiPAAm, whereas the crystallites were under tensile stress. On the other hand, for smaller nanoparticles formed in 15 wt.% PNiPAAm, crystallites were under compression stress (negative stress) whereby the lattice is contracted.

INTRODUCTION

The realization of potential application of metal nanoparticles in the fields such as optic, photonic, catalysis or in biomedicine, has led to the need to produce samples of well defined metal clusters stabilized in protective matrices. It is important because trends in the crystallite size/strain are related to the properties of the nanoparticles and consequently to the properties of the resulting nanocomposites [1].

The aim of this research was to investigate the influence of the concentration of the crosslinked polymer matrix of PNiPAAm in the form of hydrogel/xerogel as nanoreactor template on the structural characteristics of AgNPs synthesized *in situ* by γ -irradiation. Therefore, using the XRD structural analysis the various crystalline properties of these nanoparticles such as lattice parameter, size, strain and stress have been calculated.

Moreover, the UV-Vis plasmon absorption characterization of AgNPs and its modeling using Mie theory is performed [2]. The SEM analysis is used to investigate the morphology of PNiPAAm networks.

EXPERIMENTAL

Aqueous solutions of NiPAAm (5, 10 and 15 wt.%) (bubbled with Ar) were exposed to γ -irradiation, at room temperature, and at a dose rate of 0.5 kGy/h (total absorbed dose of 25 kGy) to induce crosslinking. The weight fraction of gel (ratio of the water-insoluble fraction to the feed monomer) was 95.5 (for 5 wt.% PNiPAAm), 97.3 (for 10 wt.% PNiPAAm) and 96.8 (for 15 wt.% PNiPAAm). The hydrogel samples were equilibrated in the solutions containing 1×10^{-2} M AgNO_3 and 0.2 M 2-propanol, and exposed to γ -irradiation (dose rate 12.3 kGy/h, total absorbed dose 18 kGy). Characterization of the as prepared AgNPs was carried out using Thermo Fisher Scientific Evolution 600 UV-Vis spectrophotometer. The surface morphology of the samples was observed using JEOL JSM-6610LV SEM. The XRD measurements were performed on Bruker D8 Advance Diffractometer (Cu $K_{\alpha 1}$ radiation, $\lambda = 0.1541$ nm).

RESULTS AND DISCUSSION

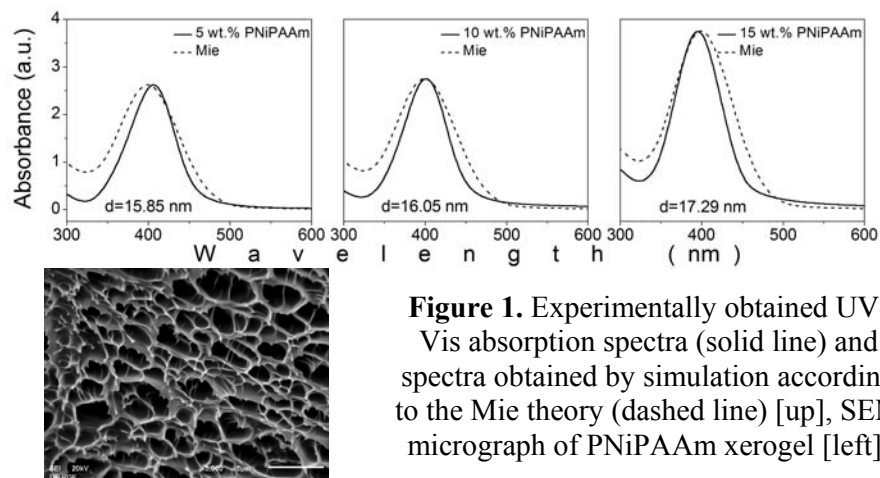


Figure 1. Experimentally obtained UV-Vis absorption spectra (solid line) and spectra obtained by simulation according to the Mie theory (dashed line) [up], SEM micrograph of PNiPAAm xerogel [left].

Figure 1(up) shows the UV-Vis spectra of the Ag-PNiPAAm hydrogel nanocomposites, experimentally obtained (solid line), and obtained by simulation according to the Mie theory (dashed line). The diameter of AgNPs was determined by applying the program, “MiePlot v.3.4”. The SEM micrograph of polymer network is shown in Figure 1(left).

The obtained XRD data (Figure 2) are consistent with the face centered cubic (FCC) crystal structure of bulk silver (JCPDS FileNo. 04-0783). The diffraction maxima at 2θ angle values correspond to the Bragg's reflections

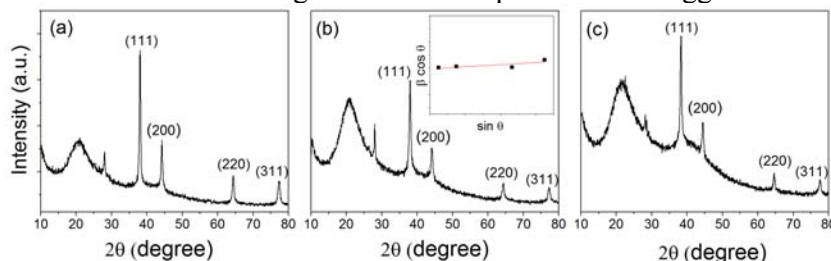


Figure 2. XRD patterns of AgNPs in PNiPAAm xerogel matrix (a) 5 wt.%, (b) 10 wt.% and (c) 15 wt.%.

from the crystal planes (111), (200), (220) and (311), ($d_0=0.236$ nm, $a_0=0.4086$ for the crystal plain (111)). To distinguish the effect of crystallite size induced broadening and lattice distortion induced broadening at full width at half maximum (FWHM) of XRD profile, Williamson-Hall plots [3] have been drawn for all the reflections of each sample (insert of Figure 2). Using the Eq. (1), the grain size and the lattice strain are determined from the intercept and the slope of line, respectively:

$$\beta \cos \theta = (k\lambda/D) + 4\varepsilon \sin \theta \quad (1)$$

where β is the FWHM in radian, θ is the diffraction angle, $k=0.9$ is a constant for cubic structure, $\lambda=0.1541$ nm is the X-ray wavelength, D is the grain size in nm, ε is the strain. Strain is defined by the relation $\varepsilon=\Delta d/d_0$ where d is the interplanar spacing [4]. The lattice strain thus obtained is from -0.001 to 0.002 (Figure 3(a)). Theoretical study predicts significant negative lattice strain (lattice contraction) for NPs smaller than 5 nm, but even for NPs of 30 nm the small lattice contraction is suggested [5]. The lattice contraction is caused by the bond-order loss and effective coordination number (CN) imperfection induced bond contraction at the surface shell. Here, lattice contraction was observed for the samples where the AgNPs are incorporated in the xerogel solid matrix of highest polymer concentration (15 wt.% PNiPAAm). The intrinsic stress (σ) is calculated on diffraction maxima (111), the most intense and well defined peak for FCC materials, using Eq. (2):

$$\sigma = (Y(a - a_0))/2\gamma a_0 \quad (2)$$

where a and a_0 are the lattice parameters of the prepared samples and bulk samples, respectively, while Y and γ are the Young's modulus and Poisson's

ratio of the bulk sample. The lattice parameter was calculated as $a = d_{hkl} (h^2 + k^2 + l^2)^{1/2}$ ($d = \lambda / 2 \sin \theta$ and h , k , and l are Miller indices) (Table 1).

Table 1. Summarized XRD data obtained for crystal plane (111).

PNiPAAm (wt.%)	2θ (degree)	β (degree)	a (nm)
5	38.1	0.38	0.4089
10	38.0	0.49	0.4099
15	38.3	0.53	0.4068

The lattice parameter values are found to be higher than the bulk lattice parameter of AgNPs for larger nanoparticles formed in 5 wt.% PNiPAAm, whereas the crystallites were under tensile stress (positive stress, as shown in Figure 3(b)). On the other hand, for smaller nanoparticles formed in 15 wt.% PNiPAAm crystallites were under compression stress (negative stress) whereby the lattice is contracted.

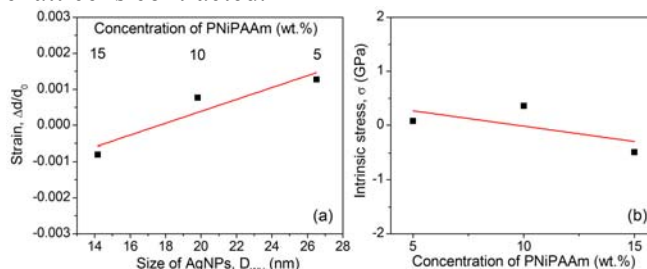


Figure 3. Lattice strain as a function of size of AgNPs (a) and lattice stress as a function concentration of PNiPAAm xerogel.

CONCLUSION

The changes of interplanar spacing and lattice parameter of crystalline AgNPs sensitively reflect their state of strain and stress depending on the formation conditions (the concentration of PNiPAAm hydrogel/xerogel matrix) and consequently on the diameter of AgNPs.

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