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# AFM, X-RAY AND ELECTRON MICROSCOPY STUDY OF SILVER NANOPARTICLES STABILIZED BY AMPHIPHILIC POLYMERS

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## Introduction

Metal nanoparticles stabilized by organic molecules or polymers are now creating a novel class of materials different from both conventional bulk materials and atoms. In such materials, nanoparticles exhibit unique properties which differ from their bulk properties owing to the quantum size effects and the large number of unsaturated surface atoms. The polymeric matrix provides additional qualities, such as the processability, the solubility or the thermal stability of the systems and play important roles in not only protecting nanoparticles but also controlling functions. Metal/polymer materials offer tremendous scientific and technological promise because of their applications in a wide variety of fields ranging from catalysis, photonics, optoelectronic to biological nanotechnology, etc. [1–3].

In order to develop new nanocompositions exhibiting especially specific bactericide and bacteriostatic properties, with better efficiency and safety, our study was focused on synthesis, processes of formation, and combined AFM/WAXD/ASAXS/TEM/SEM and electron diffraction (ED) study of structure and morphology in combination with UV-vis absorption spectrophotometry for a large series of nanosystems based on zero-valence silver (Ag<sup>0</sup>) nanoparticles, stabilized by amphiphilic water-soluble polymers [4–7]. Particle shape, average size, size distributions and crystallinity of Ag<sup>0</sup>/polymer nanosystems were determined.

#### **Experimental**

Materials. Zero-valence silver nanoparticles stable to aggregation were prepared from the silver nitrate during the chemical reduction of silver ions by ethanol in an aqueous solution in the presence of polymer [4, 5]. The reaction solutions colored from light yellow to green or deep brown and displayed a broad plasmon bands, indicating the formation of silver nanoparticles.

Poly(vinyl pyrrolidone) (PVP) with different molecular weights ( $M_w = 8000-400000$ ) and poly(N-vinylformamide) (PVFA,  $M_w = 30000-60000$ ) were used for synthesis of Ag<sup>0</sup>/polymer nanosystems as a dual functional reductants and stabilizers. By varying the concentration of reactants, the molar ratio between Ag and the repeating unit of a polymer and synthesis conditions, nanocompositions with silver content from 4 to 70 mass. % and Ag<sup>0</sup>/PVFA with silver content from 2 to 16 mass. % were obtained. The reduction was accompanied by the formation of fast (high-temperature spray drying) or slowly dried dispersions (liophylic drying for 3 days).

Instrumentation. Atomic force microscopy (AFM) study of the  $Ag^0$ /polymer nanosystems were performed using the Nanotop NT-206 microscope ("Microtestmashines", Belarus) in the contact mode.

Wide angle X-ray diffraction (WAXD) measurements of the nanocrystalline hybrid materials were performed on a wide angle goniometer of a SEIFERT 3003TT X-ray diffractometer (GE, Germany). X-ray wavelength CuK $\alpha$  (0.154 nm) was selected using a graphite crystal primary monochromator. The small angular step of  $2\theta = 0.05$  and the fixed counting time of 8s were taken to measure the intensity of the Bragg reflections. WAXD experiments were performed on air.

The Ag"<sup>0</sup> nanoparticles were structurally characterized by means of powder X-ray diffraction. It is known that the diffraction pattern of nanocrystalline materials differ significantly from those of coarse-grained polycrystalline materials, e.g. in positions, values of integrated intensities, and profiles of diffraction lines. The X-ray line broadening, which is produced by the small crystalline particle size, stacking faults, and/or microstrain, has been used to estimate the crystallite sizes, too. The crystallite size D was calculated from the breath B of the peak corrected for the instrumental broadening using the Scherrer equation.

The ASAXS measurements were carried out at the JUSIFA beamline at HASYLAB, DESY Hamburg in the energy range of the K absorption edge of Ag at 25514 eV. Measurements were made with a two dimensional detector at three energies (24630, 25479 and 25512 eV) with the aim to apply an experimental technique to separate the pure-resonant scattering contribution of the Ag component in the hybrid materials, the q-range covered was from about 0.014 to 0.44 Å-1;  $q = 4\pi \sin\theta/\lambda$ , where 2 $\theta$  is the scattering angle and  $\lambda$  is the wavelength of X-rays, respectively. For X-ray studies the powdered samples were pressed then into pellets.

TEM and ED investigations were performed using the transmission electron microscope Phillips 200C operating in bright field mode at 200 kV. TEM specimens for each sample were prepared by evaporating the nanoparticle solution at room temperature onto a 400-mesh gold TEM grid.

### **Results and Discussion**

AFM images show that depending on the stabilizing polymer different morphologies can be obtained.

Investigation of the nanostructures using AFM indicates that enlarged particles aggregates are neither spherical nor cylindrical, but rather have a highly complex shape were obtained (Figure 1).



Fig. 1. AFM images of Ag0/PVP (a, b) and Ag<sup>0</sup>/PVFA (c, d) nanosystems with silver cotent of 8 wt. %. See next page



Fig.1. Ending. See beginning of fig. 1 on previsious page

In the case of PVP, the interconnected silver particle clusters were prepared (Figure 1, a, b), whereas AFM imaged show that the nanoparticles were non-agglomerated and well dispersed over a wide area when PVFA was used as a stabilizing agent (Figure 1, c, d).

TEM images of  $Ag^0$ /polymer nanosystems allowed estimate size distributions and shapes of nanoparticles in samples. Dominantly hexagonal shaped triangular and twinned nanoparticles with sizes of 5–100 nm and relatively large amount of small clusters (< 4 nm) were observed for system  $Ag^0$ /PVP after high-temperature spray drying (Figure 2, *a*, *b*). The powder diffraction pattern recorded for the nanocrystalline  $Ag^0$  is shown in Figure 2, *c*. It was confirmed from the crystallographic analysis of electron diffraction patterns that the polygons was hexagonal close packing single crystal whereas the crystal structure of spherical nanoparticles was face centered cubic (fcc).



Fig. 2. TEM (*a*, *b*, *d*), AFM (*e*) images and WAXD spectras (*c*, *f*) of  $Ag^{0}/PVP(a-c)$  and  $Ag^{0}/PVFA(d-f)$  nanocomposite thin films with silver content of 8 wt. %; the insets show the diffraction patterns obtained from the selected areas of Ag nanocrystals with the [111] (*a*) and [110] (*b*) zone axis. See next page



Fig. 2. Ending. See beginning of fig. 2 on previsious page

The powder diffraction patterns recorded for the nanocrystalline Ag0 is shown in Figure 2, c. ED patterns (Figure 2, a, b) and WAXD diffractogram (Figure 2, c) showed the facecentered cubic structure of silver. Under the slow rate drying conditions, the larger particles of various morphologies were found. Contrary, dominantly small spherical or rod-like nanoparticles with sizes of 1–30 nm and a narrow unimodal size distribution were observed in  $Ag^0/PVFA$  nanosystems even for slowly dried dispersions, as evidenced by TEM and AFM (Figure 2, d, e).

The application of ASAXS provides an opportunity for determining the local domain structures [8] that contain Ag particles. The method was first introduced for protein crystallography by Phillips et al., in 1977, and very recently by Goerigk et al. [9, 10].

Figure 3 depicts the total scattering curves of the  $Ag^0$  nanoparticles stabilized in PVP with different molecular weights. For both systems the intensity of the total scattering curve decreases as the energy of the incident X-ray approaches the absorption K-edge of silver at 25514 eV. This behaviour clearly demonstrates that the  $Ag^0$  nanoparticles contributes to the X-ray scattering, and that these nanoparticles are denser than the PVP matrix. Although the samples contain a little amount of  $Ag^0$ , a strong fluorescence can be also observed, mostly for the total scattering curves obtained at higher energies (25512 eV). Dispersion of  $Ag^0$  nanoparticles in low molecular weight PVP produced a sigmoidal-like dependence of total scattering on the scattering vector, with a little dependence on the energy (at q < 0.1 Å-1). Therefore, it is possible to affirm that there is no spatial correlation between the  $Ag^0$  clusters,

which scatter as independent particles.



Fig. 3. Total SAXS curves of PVP/Ag<sup>0</sup> samples having  $4 - \text{wt \% Ag}^0$  nanoparticles for PVP with  $M_w = 8000 \text{ g/mol}$  (left); PVP with  $M_w = 12600 \text{ g/mol}$  (right)

The molecular weight of the PVP matrix has also an influence on the total scattering pattern. The total scattering curves of the  $Ag^0$  nanoparticles stabilized by high molecular weight PVP has a shoulder at q = 0.1 Å-1, which could suggest some micro-structural organization. This indicates an poor-correlated system, having higher polydispersion of particle diameter and/or inter-particle distance. Since the total scattering curves are not parallel to each other, it is possible to affirm that the PVP/Ag<sup>0</sup> can be regarded as systems containing at least three phases: the PVP matrix; the PVP chains at the surface of the Ag<sup>0</sup> nanoparticles themselves. The Figure 4 illustrates the effect of the molecular weight of the PVP matrix on the scattering pattern.



Fig. 4. Total SAXS curves of PVP/Ag<sup>0</sup> samples having  $4 - wt \% Ag^0$  nanoparticles. Molecular weight PVP matrices are 8000 and 12600 g/mol. Energy of incident X-rays 24589 eV (left) and 25477 eV (right)

Similar observations can be done through the analysis of the total scattering pattern of  $Ag^0$  nanoparticles stabilized by PVFA. Both PVFA/Ag<sup>0</sup> samples have SAXS pattern typical of un-correlated scatterers

ASAXS data showed that  $Ag^{0}/PVP$  samples are composed of at least three phases: the polymer matrix, PVP chains at the surface of silver nanoparticles, and the nanoparticles themselves. Contrary,  $Ag^{0}/PVFA$  samples exhibit a typical two-phase system.

# Conclusions

Silver nanoparticles with shapes which varied from spheres to polygons were prepared with a chemical approach in water/ethanol mixtures in the presence of PVP using as the stabilizing and reducing agent. Very good dispersions of Ag<sup>0</sup> nanoparticles stable to aggregation were obtained and stored for 6 months without agglomeration using PVP and PVFA.

It was found that the nanoscale morphology of nanoparticles depends critically on the initial polymer/metal ratio, as well as by the ratio of monomers. Dominantly hexagonal shaped and twinned nanoparticles with sizes of 5–100 nm and a large amount of small clusters (1–4 nm) were observed for nanosystems after high-temperature spray drying.

A model for the shape conversion is also proposed which provides the clue for the synthesis of anisotropic Ag nanoparticles with other shapes (rods, wires, cubes, etc.).

Hybrid materials developed are of potential interest as drugs with antibacterial and reparative activity.

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