Formation of hybrid nanocomposites polymethylolacrylamide/silver

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Abstract. In this study, polymethylolacrylamide/silver composites have been formed by incorporating silver nanoparticles into the pre-electrosynthesized polymer film. The composites were formed in a two-step process involving the sorption of silver nitrate by a polymer matrix followed by chemical reduction of Ag-ions. The presence of crystalline silver phase in the polymer was confirmed by X-ray phase analysis (XRD), plasmon resonance and scanning electron microscopy (SEM). The small-angle X-ray scattering (SAXS) method has obtained the distribution functions of silver particles over radii. It is established that the content of silver in composites without chitosan is 10-15 times higher than with its additive. The dependences of cyclic voltammetry in pure phosphate buffer (pH 6.86) and in the presence of hydrogen peroxide were obtained. It has been shown that polymer/silver composites exhibit selectivity to hydrogen peroxide.

1. Introduction
Hybrid materials containing inclusions of metal nanoparticles in the polymer matrix are of particular interest among the polymer composites formed by the method of electropolymerization. Nanoparticles (NPs) are promising for use in catalysis, biology, computer technology, solar batteries, in medicine and optoelectronic devices [1-4]. For example, silver NPs (Ag) are widely used to increase the sensitivity of a surface in certain spectroscopic measurements, such as fluorescence, Raman scattering and second harmonic generation, various optical materials, configurable plasmon structures, biocidal coatings, and also in photochemistry, electrochemistry, etc. [5-8]. Recently, polymers that react to various changes in the environment (pH, temperature, ionic strength, the presence of certain substances, the electric field, etc.) have been developed. That so called "smart" polymers have found wide application in biotechnology and medicine as chemical and biological sensors [9,10].

At present the method for the electrochemical formation of polymers based on acrylamide and its derivatives has been thoroughly investigated [11]. Studies are under way to create hybrid polymer/metal materials on their basis. In this vein, it is of interest to investigate the possibilities of forming polymethylolacrylamide/silver composites for use as biosensors or electrocatalysts [10,12-14].

The aim of this investigation was to study the method of incorporating silver particles into the polymer matrix formed by the electro(co)polymerization of acrylamide, formaldehyde, N,N'-methylene-bis-acrylamide and chitosan.
2. Experimental

Formation of polymer films was carried out from an aqueous solution of acrylamide (AA), formaldehyde, N, N’-methylenebisacrylamide (MBA), chitosan (Chit) and zinc chloride. The substances were taken at the required concentrations in potentiostatic electrolysis at E = -1.16 V with respect to saturated silver chloride electrode [15].

The electropolymerization time was 3 minutes. Synthesis of polymers and electrochemical studies of composites were carried out using potentiostat/galvanostat IPC-Pro 8.0, "Cronas" (Russia). The working electrode (cathode) was a rod of stainless steel AISI 304, platinum plate S = 7.5 cm$^2$ was an anode. Stainless steel electrodes were previously degreased with a fine magnesium oxide paste, rinsed thoroughly with deionized water. Electrolysis was carried out in glass cells with a volume of 10 cm$^3$ without separating of the anode and cathode spaces and without preliminary solution degassing. The zinc metal sublayer was removed in 0.5 M sodium sulfate solution for 48 hours and washed with deionized water.

The introduction of silver ions into the polymer matrix was carried out by immersing the electrode with a polymethylolacrylamide film for 96 hours in a solution of AgNO$_3$ of various concentrations. Silver chemical reduction was carried out in a freshly prepared 0.01M solution of sodium tetrahydroborate (NaBH$_4$), by placing composite 25-30 seconds and then thoroughly washed with deionized water [5].

X-ray phase analysis (XRD) was performed on an Advance D-8 diffractometer (Bruker-AXS, Germany), PDF-2 data base was used. Scanning field emission electron microscope S5500 (Hitachi, Japan) was used to investigate the structure, morphology, and element analysis of polymer films.

The distribution of silver particles was carried out by small-angle X-ray scattering (SAXS) method using a HECUS S-3 diffractometer (Micro-Pix, Austria).

The absorption spectra of the composites were taken in the far ultraviolet and visible regions in the range 300-900 nm, at room temperature on a Shimadzu UV-2550 (Japan) spectrophotometer with a film holder.

3. Results and discussion

One way to modify polymer films is to immobilize various particles in them to create composite materials with different properties. In this paper we have applied the chemical reduction method for silver particles implantation into the polymer matrix.

The composites were labeled according to the concentration of AgNO$_3$ (mol·L$^{-1}$) solution in which immobilization of silver ions was carried out: 10-3–(I-1); 5·10$^{-3}$–(I-2); 10$^{-2}$–(I-3); 5·10$^{-2}$–(I-4)–for composites without Chit and 10$^{-3}$–(II-1); 5·10$^{-3}$–(II-2); 10$^{-2}$–(II-3); 5·10$^{-2}$ (II-4)–for composites with Chit.

![Figure 1. X-ray diffraction patterns of polymers with silver particles I-1 – (1) and II-3 – (2).](image-url)
To confirm the inclusion of silver particles in the composite, the structure of the film surface was studied and X-ray phase analysis (XRD) was performed. The study of thin films with silver was carried out with grazing incidence X-ray diffraction, when the signal is formed mainly in the film material, thereby significantly increasing the intensity of the diffraction lines. X-ray diffractograms (figure 1) of nanocomposites differentiate the amorphous halo of the polymer matrix and the intense Bragg reflections in the relevant fields, which corresponds to the presence of zero-valence metallic silver (face-centered cubic crystals) [16]. Silver is fixed in all composites.

Scanning electron microscopy (SEM) was used to investigate the morphology of the surface of composites and to confirm the shape, size, and distribution of silver particles both on the external surface of the polymer and in the near-electrode layer. Figure 2 shows SEM images (with different magnifications) of the outer surface of polymer/silver composites without chitosan (I-2)–(a, c) and with chitosan (II-2)–(b, d).

**Figure 2.** SEM images of the outer surface of composites without chitosan I-2 (a, b) and with chitosan II-2 (c, d).

SEM images (figure 2) shows the silver particles are found in spherical forms on the surface of the polymethylolacrylamide/Ag composite which does not contain Chit (a, b). That aggregates are 80-90 μm in size, and consisting of smaller particles with a diameter less than 50 nm. The surface of the composite polymethylolacrylamide/Ag with the addition of Chit is denser, silver is detected as individual fine particles (c, d).

An elemental analysis can be carried out simultaneously with scanning electron microscopy, as addition to the surface morphology study [16].

On the outside of the composite without Chit, the amount of silver is 15 times larger (Ag = 51.42 ± 1.42 at.%) than on the surface of the chitosan containing composite (Ag = 3.36 ± 0.57 at.%), which may be due to the formation of a complex of silver with Chit.

According to the SEM data, no silver was found on the near-electrode side of the polymer, both in the composite without chitosan and with the addition of Chit. Perhaps this is due to the fact that the solution of silver nitrate, in which the samples were kept, did not penetrate to the surface of stainless steel due to the increased density of the electrode near the electrode layer, in agreement with literature
As a result, after the reduction of silver ions by NaBH4, the silver particles were localized in the volume and near the outer surface of the polymer.

As revealed by the SEM, the aggregation of particles in the polymer/silver composite is observed, leading to a change in their size and shape, and therefore we obtained the distribution functions of the silver particles along the radii for all polymer films by the SAXS (figure 3). It is established that the silver particles have a radius from 120 Å to 145 Å. The polymer substrate does not significantly affect the SAXS results since the magnitude intensity is 3 orders lower and the average polymer particles radius is less than 10 Å.

Figure 3. The distribution functions of Ag particles along radii for composites (I) without Chit – (a, c) and (II) with the addition of Chit – (b, d) obtained in Ag (NO₃)₃ (mol·L⁻¹): 10⁻³ – (a, b), 5 10⁻² – (c, d), the blank polymer substrate (e).

For composites formed from a low-concentration AgNO₃ solution, two peaks are observed, which corresponds to the shape of two spherical particles connected to each other. As the AgNO₃ concentration increases, the amount of silver particles in the composite increases and the shape of the particles changes markedly. At the maximum concentration of AgNO₃, the particle distribution function corresponds to the shape of one large spherical particle consisting of smaller particles.

Figure 4 shows the absorption spectra of wet films in the far ultraviolet and visible regions, taken for all samples. It can be seen from the figure that most of the spectra have a pronounced absorption band in the range of 380-420 nm, in which plasmon resonance of silver nanoparticles is detected. The shape of the bands indicates a wide range of nanoparticle size distribution. According to the literature [18-20], the position of the maximum of the plasmon resonance band at 410 nm and higher in the long-wavelength region of the spectrum indicates that the diameter of the obtained nanoparticles is more than 20 nm. Indirectly, the brown color of the films indicates the sufficiently large size of the obtained particles. Analysis of the intensity of radiation absorption in the spectra shows that very few nanoparticles are formed at low concentrations of AgNO₃ (samples 1, 2), while an increase in the AgNO₃ concentration by a factor of 10 in composites 3 and 4 significantly increases the amount of silver nanoparticles. This is evidenced by the high intensity of the absorption bands in the spectra. A similar conclusion about the effect of the experimental conditions can be made in composites with chitosan (II) in which, in comparison with composites without it (I), a more complete reduction of
silver is observed together with the formation of a larger number of nanoparticles in the bulk of the polymer.

![Figure 4](image-url)  
**Figure 4.** Plasmon resonance absorption spectra in the far ultraviolet and visible regions for composites without Chit – (I), with Chit – (II), obtained in a solution with different content of Ag(NO)₃, mol/l: 10⁻³ – (1), 5 10⁻³ – (2); 10⁻² – (3); 5 10⁻² – (4).

The electrochemical properties of composites were studied by using cyclic voltammetry (CVs) of the hydrogen peroxide reduction [21]. A comparison of the reduction rate of H₂O₂ on polymer/silver composites without Chit (I-2) and with Chit (II-2) in 0.1 M phosphate buffer saline (PBS) at pH 6.86 are shown in figures 5 and 6.

![Figure 5](image-url)  
**Figure 5.** CVs for the composite I-2 in 0.1 M PBS-(1) and in PBS with addition of H₂O₂ (mol·L⁻¹): 0.12–(2), 0.24–(3), 0.36–(4), 0.48–(5), (scan rate: 100 mV/s).
Figure 6. CVs for composite II-2 in 0.1 M PBS-(1) and in PBS with addition of H$_2$O$_2$ (mol·L$^{-1}$): 0.12–(2), 0.24–(3), 0.36–(4), 0.48–(5), (scan rate: 100 mV/s).

The addition of hydrogen peroxide leads to an increase in the values of the anodic and cathodic peaks of the current density for all the studied composite electrodes. An increase of the hydrogen peroxide concentration leads to an increase of the hydrogen release rate for polymer/silver I-2 composites (without Chit), which have the hydrogen peroxide current density at -0.6 V almost 5 times higher than polymer/silver II-2 composites (with Chit) (figure 7).

Figure 7. Cathodic current density dependence (at E = -0.6 V) on hydrogen peroxide concentration in 0.1 M PBS for polymer/silver composites.

Most likely, such a result is associated with the morphology of the surface of composites with chitosan, coarsening of the particles, which are included in the volume of the polymer.
4. Conclusions

Thus, it has been shown that the introduction of silver particles into a matrix performed by the electro(co)polymerization method is possible in a two-step process involving the sorption of silver nitrate by a polymer matrix followed by its chemical reduction. The presence of a crystalline silver phase in the composite was confirmed by X-ray diffraction analysis. By the methods of SAXS and SEM it was established that the content of silver particles with average sizes from 10 to 20 nm in composites without chitosan is 10-15 times higher than with chitosan. Using cyclic voltammetry, it has been found that polymer/silver composites exhibit selectivity to the presence of hydrogen peroxide in solutions.

Acknowledgments

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