

Electrochemical one-step synthesis of hybrid nanocomposites Au/polymer

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Abstract. Possibility of one-step formation of composites – polymeric film/Au nanoparticles by electropolymerization of monomers (acrylamide and its derivatives, formaldehyde, chitosan) at presence of a tetrachloroauric acid in the aqua medium is shown. It is confirmed by X-ray diffraction and Transmission electron microscopy that gold particles exist in nonconductive polymeric matrix as Au⁰. The distribution of AuNPs by size was revealed by small-angle X-ray scattering method. It was found that the radius of gold particles is affected by the adding of chitosan into the original monomer composition. The maximum radius of the AuNPs is 35 Å in the absence of chitosan, whereas after its addition, gold particles have been aggregated and their sizes increased to 140 Å. The masses of polymer films and composites based on them rise with electropolymerisation time increasing and reach maximum after 600 seconds of electrolysis. The masses of hybrid films with AuNPs are 26-40% higher than for blank polymethylolacrylamide film.

1. Introduction

Polymers are a very important class of compounds but the increasing request for superior performance needs the improvement of their physical and mechanical properties. It drives researchers towards the synthesis of composite materials, such as hybrid materials obtained by coupling organic polymers with inorganic fillers [1,2]. The incorporation of polymers with other materials can produce new hybrids with distinct properties that are not observed in the individual components. Usually, conductive polymers (polyaniline, polypyrrole, polythiophene and their derivatives [3]) or nonconductive polymers (polymethylolacrylamide [4]) are used as polymer matrix. Noble metal nanoparticles (Au, Ag, Pt and Pd) [3-7], graphene [6] and metal oxides (SnO₂, Fe₃O₄) [8,9] can be used as inorganic fillers.

Among numerous hybrids, polymer/noble metal nanoparticle materials have attracted the most intensive attention in the past few years. Recently, gold nanoparticles (AuNPs) are considered as an effective catalyst for chemical, electrochemical, and photochemical reactions [10-12]. In this case, the AuNPs can be present in the reaction medium either by themselves or in the volume of a solid inert carrier which can be a polymer film or other polymeric material. In this case, the introduction of an AuNPs into an inert matrix is more preferable, since an active reaction medium (for example, electrically conductive polymers) can have a destabilizing effect on nanoparticles, cause the aggregation of AuNPs, and, as a consequence, the loss of initial catalytic properties inherent in exactly non-aggregated AuNPs.



There are two main ways to implement this concept. In the first case, a polymer film is first synthesized, which is then impregnated with an Au^0 precursor (HAuCl_4) and then conditions are created under which the precursor is converted to an AuNPs [12,13]. Such a technology, at least, is a three-stage process. In the second case, the precursors Au^0 and the polymer film (monomers, initiators) are together in one electrolyte and during the course of the corresponding reactions simultaneously AuNPs and a polymer film are formed [14,15]. Such a one-step approach allows to significantly reducing the time of obtaining this type of catalyst.

The electropolymerization reaction allows one to combine the formation of a polymer film and AuNPs in one process. At the moment, an electropolymerization system based on polypyrrole is known, which makes it possible to produce polymer (polymer film)/AuNPs composites [14]. This composition has the feature that the polymer obtained on its basis belongs to the class of electroconductive, which contributes to the electrochemical formation of the AuNPs. However, our studies have shown that nanoparticles of a noble metal can also be introduced into a non-conductive polymer matrix. So, it was shown [4] that the electropolymerization composition developed by us on the basis of acrylamide and formaldehyde makes it possible to obtain a polymethylolacrylamide film/Pt. It was found that carrying out electropolymerization in a monomer composition with the addition of H_2PtCl_6 leads to the simultaneous occurrence of several processes: the formation of a polymer matrix, the electro reduction of PtCl_6^{2-} ions to Pt^0 , and the introduction of platinum nanoparticles into the volume of the polymer film. Moreover, it was found that the introduction of such an additive as chitosan into the electropolymerization composition intensifies the process of formation of the polymethylolacrylamide/Pt composite. Based on these data, we investigated the possibility of expanding the range of metal-polymer compositions by introducing an AuNPs into a non-conductive polymer film (carrier) during the electropolymerization process.

2. Materials and methods

The following substances were used for the formation of metal-polymer composites: Acrylamide (AA) 2 crystallized (Paneco), Formaldehyde (F) GOST 1625-89 (Neva Reactive), N, N'-methylene-bis-acrylamide (MBAA) 98% (Paneco), Zinc chloride 97-100.5% Extra Pure (Scharlau), $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ (Voikov plant), chitosan hydrochloride (Cht) (Russia), hydrochloric acid (Neva Reactive).

The compositions of electrolytes for electropolymerization are given in table 1.

Table 1. Electropolymerization compositions.

Component	Concentration	Polymer (Film)			
		1	2	3	4
$\text{CH}_2=\text{CHC}(\text{O})\text{NH}_2$	3 mol/l	+	+	+	+
HCHO	3 mol/l	+	+	+	+
$\text{CH}_2(\text{NHCOCH}=\text{CH}_2)_2$	0.05 mol/l	+	+	+	+
ZnCl_2^a	0.2 mol/l	+	+	+	+
Chitosan	0.1 %	-	+	-	+
HAuCl_4	1 mmol/l	-	-	+	+

^a Zinc chloride is an indirect initiator of the polymerization of acrylamide [16,17].

Synthesis and electrochemical analysis of composites was carried out using the potentiostat/galvanostat IPC-Pro 8.0 ("Cronas". Russia). Electropolymerization was carried out in glass cells with a volume of 10 cm^3 at a cathode potential of -1.2 V for 3 minutes (unless otherwise specified). Separation of the anode and cathode space was not used. The working electrode (cathode) was a stainless steel AISI 304 rod ($S = 1.0\text{-}1.5 \text{ cm}^2$). We used a platinum plate as an auxiliary electrode (anode) ($S = 7.5 \text{ cm}^2$). The reference electrode is a saturated silver chloride electrode EVL-1M3 with a Luggin capillary.

Titanium electrodes were preliminarily subjected to electrochemical polishing for 2-3 seconds in a

hot mixture (3:1) of HNO_3 and HF acids. Stainless steel rods were ground and degreased with a paste of finely dispersed magnesium oxide. All electrodes were thoroughly rinsed with deionized water. To separate the composite polymethylacrylamide film/AuNPs from the electrode surface, the latter was immersed in 0.1 mol/l HCl for ~ 90 -100s, after which the film lost its adhesion to the electrode due to dissolution of a thin metallic zinc sub-layer [17].

X-ray diffraction was performed on Advance D-8 diffractometer (Bruker-AXS, Germany).

Transmission electron microscopy (TEM) was performed on Libra-200FE (Carl Zeiss, Germany).

The particle size distribution of gold nanoparticles was assessed by small angle X-ray scattering (SAXS) using a HECUSS3-MICRO-PIX diffractometer (Austria).

3. Results and discussion

In the process of electropolymerization for all electrolytes, as the polymer layer forms on the electrode surface, the current density is reduced by overlapping the cathode with a layer of a new weakly conducting phase. Under identical conditions (420 s), the smallest residual current (i_r) is observed on a polymer coating that does not contain metallic particles (figure 1, curves 1, 2). While the inclusion of gold nanoparticles in the polymer leads to an increasing i_r (figure 1, curve 3).

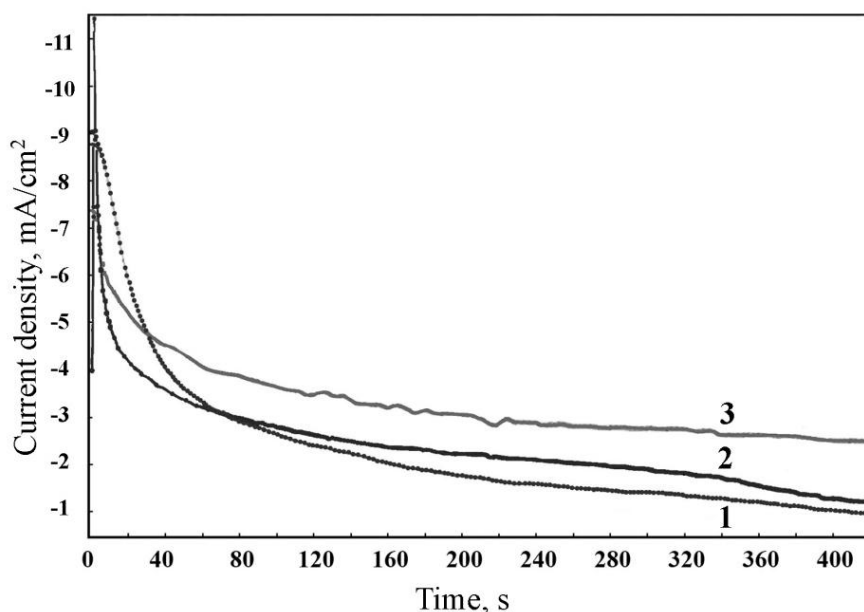


Figure 1. Dependence of current density on the electropolymerization time: polymer 1 (1), polymer 2 (2), polymer 4 (3).

Studies have shown that the mass of different types of polymer films depends on the time of synthesis (figure 2).

It should be noted, that the films of the initial polymer with chitosan (figure 2, curve 2) have a lower mass than without chitosan (figure 2, curve 1). This effect is due to the less moisture-absorbing capacity of films containing a water-insoluble fraction of chitosan, their greater density and smaller thickness. On the other hand, films with inclusion of gold particles (figure 2, curves 3, 4) have a large mass in comparison with films without AuNPs (figure 2, curves 1, 2). And this difference reaches 10-15 mg at a synthesis time of more than 60 s, which is 26-40% of the total mass of the composite.

Polymer films obtained by electropolymerization from an aqueous solution based on acrylamide are an elastic, colorless and transparent material in the swollen state in water. With electropolymerization in the presence of HAuCl_4 , the color of the films becomes a pink-lilac, which visually confirms the inclusion of gold particles in the polymer. The intensity of coloration depends on

the amount of AuNPs in the film. The color of the composite becomes intensive lilac in the presence of chitosan in the electrolyte solution.

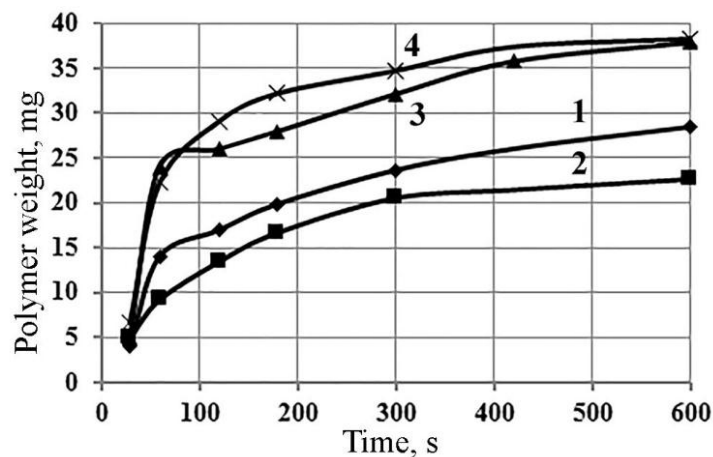


Figure 2. Dependence of the polymer mass on the polymerization time: polymer 1 (1), polymer 2 (2), polymer 3 (3), polymer 4 (4).

It should be noted, that the initial electropolymerization solution acquires a yellow color after the addition of HAuCl_4 . This color does not change for at least 20 minutes, despite the fact that the solution contains such a strong reducing agent as formaldehyde (table 1). X-ray small-angle scattering (SAXS) study of the solutions 3 and 4, which contain HAuCl_4 , showed the absence of any nanoparticles in electrolytes (the solutions were held for 15 minutes). This is evidenced by the fact that the intensity curves for both solutions are identical (merged) and represent a practically straight line (figure 3), which does not allow us to construct a particle size distribution spectrum. The result obtained allows us to conclude that formaldehyde does not reduce gold in this water-monomer composition.

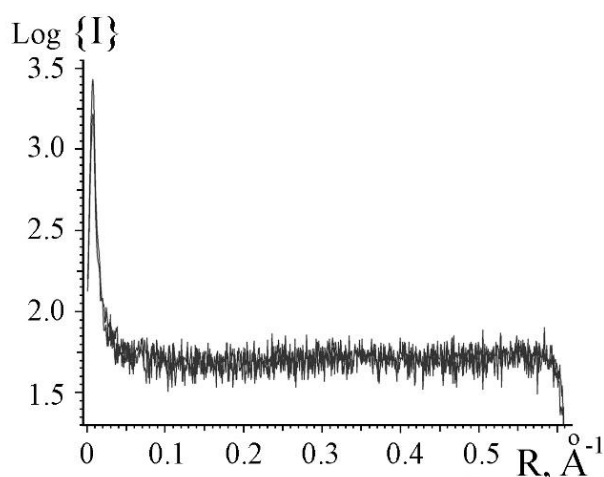


Figure 3. Spectrum of small-angle X-ray scattering of solutions 3 and 4.

Further studies have shown that gold nanoparticles are formed and embedded in the film during the electropolymerization process, i.e. simultaneously with the formation of the polymer film itself. The

presence of metallic gold in polymer films is confirmed by the results of X-ray diffraction analysis (figure 4) and Transmission electron microscopy (TEM) (figure 5).

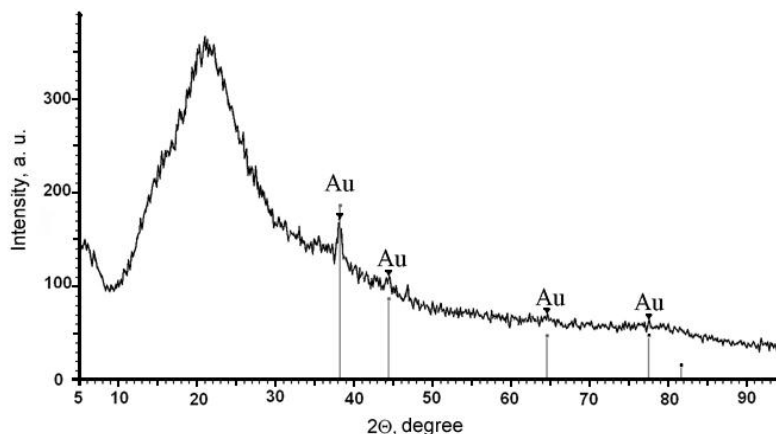


Figure 4. X-ray diffraction patterns of polymethylolacrylamide/AuNPs film.

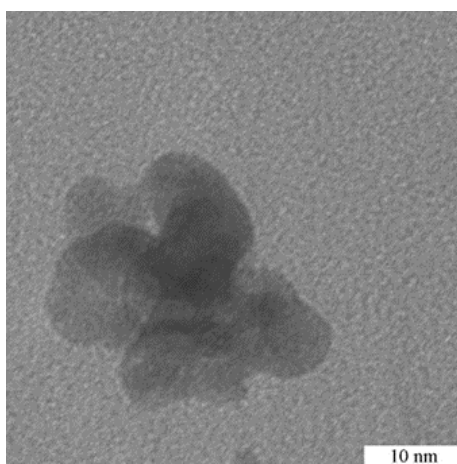


Figure 5. TEM image of polymethylolacrylamide/AuNPs film (polymer 3).

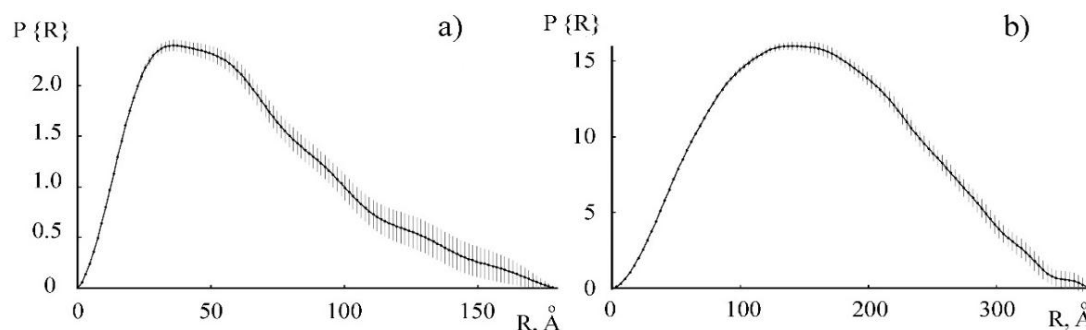


Figure 6. SAXS spectra of the distribution of AuNPs particles in size for polymer 3 (a) and polymer 4 (b).

As follow from figure 5, there are small Au^0 crystalline particles (~ 10 nm) aggregated to ~ 40 nm

in the film. These TEM data and SAXS results are in good agreement. SAXS method revealed the presence of AuNPs in electrosynthesized polymer films (figure 6). The AuNPs distribution by size was established. It was found that the particle size of gold is affected by the adding of chitosan into the original monomer composition. As it follows from figure 6, the maximum size (radius), of the AuNPs is 35-40 Å in the absence of chitosan, whereas after its addition, gold particles have been aggregated to 150 Å.

The chitosan addition effect is in good agreement with the data [18-20]. It follows from [18,19] chitosan and AuCl_4^- are formed a complex. Authors [20] found that the UV initiated synthesis of gold nanoparticles in the chitosan presence, which simultaneously performs stabilizing and restoring functions, results in the formation of larger gold nanoparticles.

4. Conclusions

The possibility of electrochemical formation of metal/polymer composites was studied. It is shown that the method of electropolymerization of aqueous solutions based on acrylamide and formaldehyde in the presence of HAuCl_4 makes it possible to obtain particles of nano-sized gold stabilized in a polymer matrix (polymer film). The peculiarity of this approach is that this process is carried out in one-stage, when simultaneously non-conductive (dielectric) polymer matrix and gold particles are formed and Au^0 is captured by the polymer film. The inclusion of AuNPs in polymethylolacrylamide was confirmed visually, as well as by X-ray diffraction analysis, small-angle X-ray scattering and TEM data.

Acknowledgments

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