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Selective deposition of gold nanoparticles on the top or inside a thin conducting polymer film, by combination of electroless deposition and electrochemical reduction

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ABSTRACT

In this paper we present the procedures allowing for synthesis of the composite systems in which Au nanoparticles are located: (i) only on the surface of the polymer film, (ii) only inside the polymer matrix or (iii) both on the polymer surface and in the polymer film. Thin poly(1,8-diaminocarbazole) (PDACz) films were electrodeposited on gold or highly oriented pyrolytic graphite (HOPG) electrodes from acetonitrile solution. Then, Au nanoparticles (NPs) were formed either by electroless deposition on the polymer layer in the solution of $HAuCl_4$ or by electrochemical reduction of $AuCl_4^-$ incorporated into the polymer matrix, carried out in the solution of $HClO_4$. The amount of deposited Au was determined from electrochemical quartz crystal microbalance measurements and from the reduction charge. The role of protonation of amino groups of the polymer in the process of $AuCl_4^-$ insertion into the polymer matrix has been discussed. A distribution of Au nanoparticles on the top and inside the polymer film was studied by SEM and TEM images of the polymer cross sections prepared by focused ion beam (FIB) method.

1. Introduction

Metal nanoparticles have attracted a wide-spread interest due to their unique size-dependent optical and electronic properties, different from bulk materials, and potential applications in chemistry, physics and biology [1,2]. Among various metal nanoparticles studied to date, gold nanoparticles (AuNPs) have been extensively investigated for the use in sensors and biosensors owing to their excellent biological compatibility [3], in various electroanalytical systems as well as in industry and environmental protection due to good catalytic properties [4]. A great attention has been focused on synthesis of composite materials in which Au nanoparticles are embedded in conducting polymer matrix [5–7] or deposited on the solid metal oxide (TiO_2) [8,9]. Encapsulation of metal particles inside the polymer matrix prevents their aggregation and allows diminishing their size down to the nanometer range. Since the polymer and metal components may be obtained by chemical and electrochemical methods, many different procedures leading to the hybrid systems of different arrangement and morphology have been developed (see [7] and references therein). For example, polyaniline fibers decorated with Au or Ag nanoparticles may be obtained in the solution by one-pot chemical synthesis with the use of metal precursor ($AuCl_4^-$ and Ag^+ respectively) as the monomer oxidant [10]. Two-step procedures are usually applied for fabrication of the hybrid polymer/NPs systems deposited on the surface of conducting electrode. This may be achieved by electrodeposition of the polymer in the presence of presynthesized NPs, stabilized by anionic ligand [11,12] or by incorporation of the metal nanoparticles into the polymer film previously electrodeposited on the electrode. In the latter approach one can use electrochemical methods [13,14] or electroless deposition due to a difference between oxidation potential of the polymer and reduction potential of metal precursor [15]. In electrochemical deposition one can control the size of nanoparticles and their spatial distribution in the polymer matrix by the change of deposition parameters (concentration of reagents, value of applied potential or current density) [6,16,17]. Formation and distribution of the metal particles in/on the polymer film by electroless technique is a complex interplay between the film properties, related to the synthesis conditions, identity of the metal precursor as well as pH of the solution [18,19]. Synthesis and quality of the hybrid system may be also influenced by properties of the polymer component because of specific interactions between precursor metal ions and the polymer [20]. The advantage of electroless deposition is a negligible influence of structural microdefects of the polymer film which during electrodeposition are filled in by metal microstructures. On the other hand, it is more difficult without electric aid to control the spatial distribution of the nanoparticles in the polymer film.

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In this work we demonstrate how one can manipulate the form, size and location of Au nanoparticles in the polymer matrix due to special properties of poly(1,8-diaminocarbazole) (PDACz). The monomer units in PDACz are linked mainly via C—(NH)—C head-to-tail coupling, as in the case of polyaniline, but only one of amino groups of each monomer molecule is involved in the bonding [21]. Our strategy was to employ the remaining "free" amino groups to incorporate the Au precursor ($AuCl_4^-$) into the bulk of the polymer film due to strong protonation of the polymer matrix [22]. On the other hand, relatively low oxidation potential of the polymer allows deposition of Au nanoparticles by electroless reduction of $AuCl_4^-$. We applied these properties of PDACz to elaborate the procedures for deposition of Au NPs on the polymer surface and/or in the polymer film. An electrochemical quartz microbalance (EQCM) was employed for quantitative analysis of these processes, whereas SEM and TEM studies were performed to examine a distribution of metal particles on the top and across the polymer film after electrochemical and chemical reduction of the metal precursor.

2. Experimental

2.1. Electrochemical measurements

1,8-Diaminocarbazole (DACz) was synthesized in three steps, in 30% overall yield, from cheap carbazole starting material [23]. Acetonitrile (AN) (Aldrich, HPLC grade), $LiClO_4$ (Aldrich, ACS reagent), $HClO_4$ (Aldrich, ACS reagent, 70%) and $HAuCl_4$ (Aldrich) were used as received. All aqueous solutions were prepared with deionized water (Millipore).

The EQCM measurements were performed on Au thin film working electrode (0.21 cm^2) deposited on 10 MHz AT-cut quartz crystals (International Crystal Manufacturing Co. Ltd., Oklahoma City, OK) with piezoelectrically active area of 0.23 cm^2. A QCM unit (Type M3, UELKO, Poland) was combined with AUTOLAB PGSTAT 30 (Ecochemie, The Netherlands). The experiments were carried out in a single compartment cell with a platinum wire counter electrode (CE). A type of reference electrode was dependent on the solvent used in the experiments, i.e. a double frit Ag/Ag^+ (0.1 M $AgNO_3$ in CH_3CN) electrode was used in acetonitrile solutions and Ag/AgCl,3 M KCl (aq.) electrode in aqueous solutions. All measurements were made at room temperature (23 ± 2 °C).

Electropolymerization of DACz was carried out by cyclic voltammetry in the potential range from −0.6 V to 0.8 V vs. (Ag/Ag^+) in the solution of 1 mM 1,8-diaminocarbazole in acetonitrile containing 0.1 M $LiClO_4$ supporting electrolyte, at the scan rate of 40 mV s^{-1}. The detailed EQCM studies on electropolymerization of DACz, presented by us elsewhere [22] have shown that thin polymer films obtained within 1–8 deposition cycles are rigid and therefore, the change of the resonant frequency (Δf) may be recalculated into the change of the mass (Δm) by means of Sauerbrey equation [24], which for 10 MHz AT-cut quartz crystals used in this work may be expressed in the form:

$$\Delta m(g) = -1.1 \times 10^{-9} \Delta f(\text{Hz}) \qquad (1)$$

The coefficient 1.1 in this relation (within ± 2%) was found by calibration for silver deposition from aqueous solution. Dispersion of the slope of Δm–Q plots, obtained from three independent experiments, was within ±(3–5)%. Accuracy of resonant frequency measurements was 0.1 Hz.

2.2. Microscopic studies

Topography of the samples was studied by field-emission scanning electron microscopy (FE-SEM) equipped with EDS detector for elemental mapping (Merlin, Carl Zeiss, Germany). The samples for SEM and transmission electron microscopy (TEM) were deposited on highly oriented pyrolytic graphite (HOPG) according to the same procedure as that on Au electrode. It was found that morphology and electroactivity of the polymer films deposited on both substrates were the same.

The cross-sections for TEM (XTEM) were prepared with the in situ lift-out technique [25] in a focused ion beam system (FIB, Helios NanoLab). In order to protect a top surface from ion beam damage, the samples have been covered by a platinum cap before cutting them out with high-energy gallium ion beam. Two stages of deposition have been used. First, a thin (80 nm) platinum or dielectric (SiO_2) layer has been deposited with the use of electron beam. Then, the 2 μm thick platinum layer has been deposited with ion beam. Such prepared sample is observed in direction parallel to the top surface. It allows for determination of real thickness of the layers, observations of their interfaces and other phenomena occurring beneath sample surface. This technique has been also successfully applied for TEM observation of nanoparticles produced in layered structures e.g. [26–29].

The samples have been characterized by a JEOL JEM-2100 high resolution transmission electron microscope.

3. Results and discussion

3.1. Spontaneous reaction between PDACz and $AuCl_4^-$ complex

The PDACz film was deposited on the Au-coated quartz crystal resonator in seven repetitive voltammetric cycles carried out in acetonitrile solution of the monomer, according to the procedure described above. The polymer-modified electrode was rinsed with acetonitrile to remove traces of the monomer, placed in aqueous solution of 0.1 M $HClO_4$ and cycled in the potential range from −0.2 V to 0.6 V vs. (Ag/AgCl) at the scan rate of 40 mV s^{-1}. The obtained voltammogram is compared in Fig. 1a with the voltammogram recorded on the bare Au electrode in aqueous solution of 0.1 M $HClO_4$ + 0.005 M $HAuCl_4$ (curves 1 and 2, respectively). A difference between redox potentials of the polymer and $Au/AuCl_4^-$ couple (estimated from the mean values between the oxidation and reduction peaks) is high enough (0.57 V) to provide a fast spontaneous reaction between the polymer and $AuCl_4^-$ ions, as in the case of poly(3,4-ethylenedioxythiophene) (PEDOT) [15,30] and polyaniline [19,31].

The process, taking place on the polymer-modified electrode under open circuit conditions after addition of $HAuCl_4$ into the bathing solution of 0.1 M $HClO_4$, was studied quantitatively by electrochemical quartz crystal microbalance combined with measurement of open circuit potential.

As visible in Fig. 1b, addition of $HAuCl_4$ (0.5 ml of 0.2 M $HAuCl_4$, to the final concentration of 0.02 M $AuCl_4^-$) resulted in abrupt increase of the open circuit potential to the value above 0.8 V (curve 1). At the longer time scale the E_{ocp} stabilized at the value of 0.88 V which corresponds to the equilibrium potential of Au electrode immersed in the same solution. In contrast, the mass (recalculated from the change of the resonant frequency (Δf) using the Eq. (1)) after initial jump did not attain a stable value even after 25 min of conditioning but it continuously increased (curve 2), suggesting a complex nature of the process occurring at the polymer/solution interface. In order to exclude possibility that the change of the resonant frequency may be also a result of the variation of the solution density at the electrode upon addition of $HAuCl_4$, a separate "blank experiment" was performed on the bare electrode, without polymer film. Since in such the case the change of the resonant frequency was negligible, the total change of Δf in the experiment with the polymer-modified electrode may be ascribed only to the reaction between the polymer and $AuCl^-{}_4$ ions.