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Electrodeposition of polypyrrole–Au nanoparticles composite from one solution containing gold salt and monomer

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ABSTRACT

An easy method of preparation of polymer/metal–nanoparticle composites is reported. $KAu(CN)_2$ and pyrrole do not react (redox reaction) in solutions of moderate pH. The gold complex, due to its inertness, is stable in the presence of 10 μM CN^- for weeks. Therefore the electrodeposition of controlled amounts of polypyrrole and Au nanoparticles on the graphite surface can be done in one solution by applying a sequence of 0.75 and −1.6 V potentials. Pulse deposition of both components leads to substantial improvement of the layer smoothness and homogenous distribution of Au nanocrystallites.

1. Introduction

The interest in conducting polymer composites containing metal or oxide nanoparticles has grown during the past several years. These materials combine properties of each component and often acquire new properties.

Polypyrrole (PPy) is one of the most extensively studied conducting polymers because of its environmental stability, flexibility and high electrical conductivity. Due to these properties, polypyrrole has found applications in the fields of batteries [1], capacitors [2], anti-corrosive coatings [3] and sensors [4].

Various nanoparticles, among them such metals as Au, Ag, Pd, Cu and Pt, can be incorporated into the polymer matrix to obtain a composite material with new properties [5].

Chemical and electrochemical polymerizations are used to prepare conducting polymer composites. One possible way of preparation of nanocomposite material is to use a spontaneous redox reaction of monomer and metal ion, e.g. Ag or Au ions, sometimes in the presence of supporting reagent [6–8]. Another one is the chemical polymerization of monomer dissolved in a solution of colloidal metal particles in the presence of an oxidant [9,10]. Metal nanoparticles/conducting polymer composites can be also obtained by using the electrochemical methods; mainly through the deposition by electrooxidation of monomer from a solution containing colloidal metal particles [11] or electrodeposition of polymer and metal from two separate solutions [12,13]. However, recently, Jung et al. showed that polymerization of pyrrole can be done by cathodic generation of the compounds capable of oxidation of the monomer. Additionally, at that generation potential metallic tin could be deposited together with the polymer [14].

Electrochemical methods of preparation of nanocomposites give a possibility of better control of the synthesis process compared to the chemical methods, because the structure, quantity and properties of both electrodeposited components: nanoparticles and polymer, depend not only on the composition of the solution, but also on electrolysis potential and time [12,15].

In this work, we demonstrate a new approach to synthesis of metal–polymer nanocomposites based on electrodeposition of both components from one solution containing a monomer and a metal salt. For this purpose the inertness of the metal complex and the appropriate difference in the redox potentials were used. We prepared the polypyrrole/gold nanocomposites using pulse deposition. Such approach, in comparison with DC deposition, permits to obtain a more homogeneous and less porous polymer surface [16] and more homogenously distributed gold grains [17].

2. Experimental

Solutions containing pyrrole, $KAu(CN)_2$ as source of metal ions, $NaClO_4$ as supporting electrolyte and a small amount of KCN (added to achieve stability of the gold cyanide complex) were prepared using chemicals of analytical grade purity. A 50-ml glass cell and the three-electrode system were used in all electrochemical experiments. The working electrode was a glassy carbon (GC) disc with geometric area of 0.071 cm^2. The GC electrode surface was polished with 1 and 0.3 μm alumina powder and finally rinsed with deionized water. The counter and reference electrodes were a Pt wire or a Pt foil and a saturated calomel electrode (SCE), respectively. Care is advised in the work with a Pt counter

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electrode, since this may lead to unwanted deposition of platinum at the working electrode. For crystalline and structural analysis the PPy/Au films were deposited on a two-side graphite disc of area 3.53 cm^2.

The electrochemical experiments were done using a EG&G PAR 273A potentiostat. A scanning electron microscope (SEM, model LEO 435 VP, Zeiss) equipped with an energy dispersive spectroscopy unit (EDS, Roentec) was used to examine the composition, and the morphology of the deposited composites. The structural analysis of the obtained materials was also done by using the powder XRD technique. The D8 Discover diffractometer with a Cu Kis lamp ($\lambda = 1.54056$ Å) was made by Bruker. For the estimation of gold crystal size the commercial software TOPAS 3 was used.

Oxygen from the electrolyte solutions was removed by bubbling with argon gas before each experiment. All solutions were prepared from Milli-Q deionized water (resistance 18 MΩ cm). The value of pH was kept constant (pH = 8) by adding NaOH. Measurements were carried out at room temperature.

3. Results and discussion

Proposed method of electrodeposition of polymer/metal composites is based on both: kinetic properties of inert Au–cyanide complex and the nobility of the deposited metal. The standard potential of $Au/Au(CN)_2^-$ couple is −0.593 V [18]. This potential is not sufficiently positive to enable the oxidation of pyrrole. Also, the complex is extremely strong (log $\beta = 38.2$ [18]), inert and therefore in the absence of excess cyanide ion it does not dissociate. Further, the absence of considerable amount of cyanide ion prevents the electrodissolution of gold in the positive potential region. Owing to these facts the processes of oxidation of pyrrole and reduction of gold (I) complex may occur independently in the same solution. Nevertheless, the solution of gold–cyanide complexes used for the electrodeposition of gold should not be acidic. In neutral and basic solutions the $Au(CN)_2^-$ complex is stable up to one day; a very small addition of the CN^- ions (resulting in ca. 1×10^{-5} M concentration) inhibits the process of precipitation of AuCN and ensures the stability of the solutions for weeks.

Cyclic voltammetry was used to determine the potential ranges of gold deposition and PPy formation and to optimize the conditions of the composite electrosynthesis. Fig. 1 presents a set of voltammograms obtained in solutions containing either $Au(CN)_2^-$ (a) or pyrrole (b) or both components (c–d). In Fig. 1a and b, the peaks related to the reduction of $Au(CN)_2^-$ and the oxidation of pyrrole can be seen at circa −1.5 and +0.7 V, respectively. In the second cycle the reduction of the

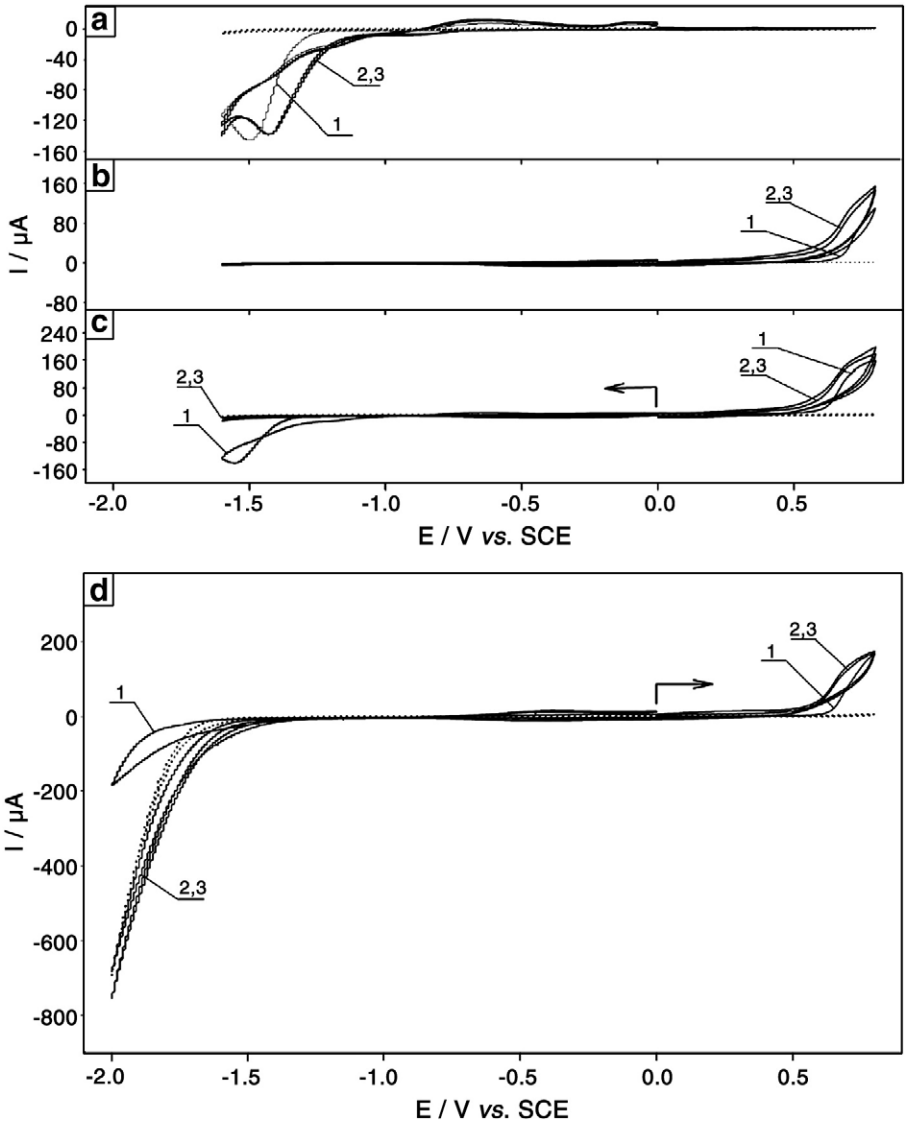

Fig. 1. Cyclic voltammograms obtained in 0.02 M solution of $KAu(CN)_2$ (a), 0.01 M pyrrole (b) and 0.02 M $KAu(CN)_2$ and 0.01 M pyrrole (c–d). Dotted lines: background. Arrows indicate initial potential and direction of potential scan. Numbers at curves indicate scan number. $v = 20$ mV/s. Supporting electrolyte: 0.1 M $NaClO_4$.