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Development and characterisation of a novel composite electrode material consisting of poly(3,4-ethylenedioxythiophene) including Au nanoparticles

C. Zanardi[a,1], F. Terzi[a,1], L. Pigani[a,1], A. Heras[b,1], A. Colina[b,1], J. Lopez-Palacios[b,1], R. Seeber[a,*,1]

[a] Department of Chemistry, University of Modena and Reggio Emilia, via G. Campi, 183-41100 Modena, Italy
[b] Department of Chemistry, University of Burgos, Plaza Misael Bañuelos s/n, 09001 Burgos, Spain

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Abstract

Composite material consisting of poly(3,4-ethylenedioxythiophene) (PEDOT), including Au nanoparticles encapsulated by *N*-dodecyl-*N*,*N*-dimethyl-3-ammonium-1-propanesulphonate (SB12) is synthesised by constant-current method on ITO glass, in aqueous medium, leading to an electrode coating. The synthesis process is followed by UV–vis spectroelectrochemistry, both in normal-beam and in parallel-beam configurations. Under the same experimental conditions PEDOT is also synthesised by electropolymerisation only in the presence of $LiClO_4$ supporting electrolyte, as well in solutions also containing SB12. The data relative to the electrosynthesis of the three materials are compared. The composite material based on the conductive polymer matrix including Au nanoparticles has been characterised by SEM, TEM, ICP, Raman and UV–vis spectroscopies. The behaviour of the three different electrode coatings with respect to p-doping process has been studied by conventional electrochemical techniques and by potentiostatic and potentiodynamic UV–vis spectroelectrochemical methods. Conclusions are drawn out about the effect of the presence of the surfactant and of Au nanoparticles on the electrochemical properties of the electrode system.

Keywords: Poly(3,4-ethylenedioxythiophene); Gold nanoparticles; Composite material; Spectroelectrochemistry; ITO electrode

1. Introduction

Polythiophene derivatives are widely investigated as electrode modifiers for electroanalytical applications, due to possible improvement of the performances of the resulting sensors, with respect to bare electrodes [1–5]. Among polythiophenes, poly(3,4-ethylenedioxythiophene) (PEDOT) has emerged as one of the most effective modifiers, thanks to the occurrence of the p-doping process at particularly low potentials and to the possibility of easy electrogeneration in aqueous solution. The applications of PEDOT modified electrodes in electroanalysis are well documented in a number of recent publications [6–12]. We report here synthesis and characterisation of a composite material based on such a polymer, including gold nanoparticles (Au-NPs). The aim of the development of the composite material is to improve the electrocatalytic properties of the simple polymeric electrode coating. For gaining such a goal, the metal core of the NPs should be in contact both with the molecules of the hosting polymer matrix, in order to allow efficient charge transfer within the composite, and with the solution, in order to be reached by the electroactive species and to possibly activate electrocatalytic reactions [13].

Our synthetic approach consists in the formation of the composite during the electrogeneration–deposition of the polymer onto the electrode surface, carried out in an aqueous solution also containing pre-synthesised Au-NPs. The synthesis of the Au-NPs is carried out by a *bottom-up* approach: a Au salt dissolved in suitable solvent is chemically reduced in the presence of an encapsulating agent. Such a synthesis strategy allows mean size and size distribution of the Au-NPs, as well nature of the encapsulating agent, to be varied over a wide range. In order to guarantee the contact between the NP metal core both with the polymer and with the solution, the nature of the encapsulating species is of basic importance. As an example, the commonly used long thiol molecules are ineffective,

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[*] Corresponding author. Tel.: +39 059 2055027; fax: +39 059 373543.
E-mail address: seeber@unimore.it (R. Seeber).
[1] ISE member.

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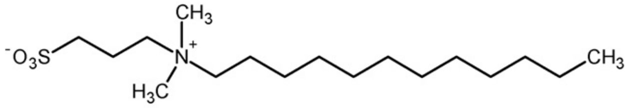

Scheme 1. Formulation of *N*-dodecyl-*N*,*N*-dimethyl-3-ammonium-1-propanesulphonate (SB12).

since they build up an electrically insulating shell around the metal; besides the electrons, the chemical species can also only move with difficulty through this shell [14–16]. In order to overcome these heavy problems, we have started a study of the behaviour of different encapsulating agents; in this paper we focus our attention on a tetraalkylammonium derivative. Tetraalkylammonium species are labile encapsulating agents, reasonably partially substituted by polythiophene chains once inside the polymeric film, thanks to the stronger interaction of the metal core with the sulphur atoms and even with the π clouds [17]. With the goal of enhancing the metal loading inside the polymeric material, we choose using *N*-dodecyl-*N*,*N*-dimethyl-3-ammonium-1-propanesulphonate (SB12, see Scheme 1) as encapsulating agent. In agreement with the adsorption geometry of tetraalkylammonium salts on the noble metal surface of Au-NPs [18], it is quite reasonable to postulate that positively charged N atoms strongly interact with the Au core, implying that, in the case of the zwitterionic SB12 molecule, a very major fraction of deprotonated sulphonic groups is oriented outward from the NP core. The relevant NPs (Au-SB12) result to be surrounded by negative charges, which renders the inclusion into the growing positively charged polymer easier. Thanks to the formulation of the specific species chosen, it is also reasonable that the metal core of the Au-NP may be reached by species in solution. As a further, essential requirement to the developed NP system, we could verify that such as an encapsulating agent also prevents from the occurrence of Au cores aggregation, under the experimental conditions followed in the syntheses of NPs and of the composite.

Free SB12 molecules are necessarily also present in the polymerisation solution containing Au-SB12; this is required in order to avoid desorption of the encapsulating agent and, hence, to assure the stability of the NPs toward aggregation. In order to deconvolve the effect of the metal core from that of free SB12 molecules, this paper also reports investigations on PEDOT coatings electrogenerated in the presence of merely SB12 (PEDOT/SB12). This last study constitutes an innovative investigation on its own, due to the zwitterionic nature of this molecule. It is worth noticing, in fact, that literature reports the use of anionic surfactants during the electrogeneration of polythiophenes [19]; however, only few articles concern the use of the non-ionic surfactants [20,21], seemingly because most of these are reactive species, leading to poorly defined materials as the result of the polymerisation process. To our best knowledge, only one paper deals with cationic surfactants [22] and the use of a zwitterionic surfactant constitutes a novelty.

In this work different techniques have been employed in order to study the polymerisation process and to define the properties of the resulting materials: UV–vis spectroelectrochemistry, Transmission and Scanning Electron Microscopy (TEM and SEM, respectively), Inductively Coupled Plasma (ICP) and Raman spectroscopy. In order to compare the results collected with the different techniques, Indium–Tin Oxides coated glass (ITO glass) has been chosen as the most suitable electrode support.

As a final consideration, the complexity of such systems should be emphasised. The present study constitutes a step towards the development of new composite materials for effective electrode coatings. A systematic analysis of the influence of the experimental conditions of the composite electrogeneration, e.g. NP concentration and current density, on the properties of the systems is out of the aim of the present article.

2. Experimental

2.1. Preparation of the samples

Au-SB12 were synthesised [23] dissolving $NaAuCl_4 \cdot 2H_2O$ in water (1.30 dm^3, 0.88 mM). Then, an excess of SB12 (1.54 g) encapsulating agent and Li_2CO_3 (1.36 g) were added under stirring. Finally, an aqueous solution of $NaBH_4$ (78 cm^3, 100 mM) was quickly added to the mixture. The reaction was left to proceed for 3 h at room temperature under stirring. The metal cores of the resulting NPs possess a ca. 5 nm mean size, as evidenced by the TEM images. The UV spectrum shows a maximum located at 520 nm, relative to the plasmon band of the same metal core.

The electrochemical synthesis of PEDOT in the presence of NPs (PEDOT/Au-SB12 resulting system) was performed on ITO glass under galvanostatic conditions, 0.4 mA/cm^2 current density. The polymerisation solution consisted of 10 mM EDOT (Aldrich), of 109 mg/dm^3 Au-SB12 and of 0.1 M $LiClO_4$ (Aldrich, puriss) supporting electrolyte, in ultrapure H_2O solvent. A 2.3 mM concentration of free SB12 was also estimated to be present in this solution, by considering that the quantity of SB12 adsorbed on the metal cores, as estimated on the basis of the number and the dimension of the NPs, is a very minor fraction of the overall SB12 present. The charge spent in polymerisation was constantly equal to 6.4×10^{-2} C/cm^2. This value of charge, as well that of the concentration of EDOT in solution, have been chosen on the basis of results reported elsewhere by us for PEDOT/ClO_4^- [11]. In the case of the synthesis of the PEDOT/Au-SB12 system, the concentration of NPs in solution was that leading to the highest loading, compatible with complete coating of the electrode. The results gained with such an electrode coating have been compared with those obtained, under comparable experimental conditions, with electrode coatings consisting of PEDOT electrogenerated under two different conditions: (i) only in the presence of 0.1 M $LiClO_4$ (PEDOT/ClO_4^- electrode system); (ii) in the presence of 0.1 M $LiClO_4$ and of 2.3 mM SB12 (PEDOT/SB12 electrode system). SB12 concentration is slightly higher than the critical micellar concentration (ca. 2 mM in these conditions [24]).

After each polymerisation procedure, the coated electrodes were carefully washed with H_2O, before transferring them into 0.1 M $LiClO_4$, H_2O solvent. The electrode coatings were undoped at −0.75 V for 30 s; then, 10 subsequent voltammetric