PEDOT-Au nanocomposite film for electrochemical sensing

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Abstract

In this work, conducting polymer incorporated gold nanoparticles are synthesized through a sequence of chemical and electrochemical routes. These materials are characterized using TEM and FE-SEM techniques. The advantages of these films are demonstrated for sensing biologically important compounds such as dopamine and uric acid in presence of excess ascorbic acid. The PEDOT matrix is recognized to be responsible for the peak separation (selectivity) while also favouring catalytic oxidation of the above compounds and the nanometer-sized gold particles allow nanomolar sensing of DA and UA (sensitivity). Thus, it is possible to detect nanomolar levels of DA and UA in presence of excess of AA.
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1. Introduction

Conducting polymer incorporated metallic or semiconducting nanoparticles provides an exciting system and these materials hold potential application in electronics, sensors and catalysis [1–6]. They have synergistic chemical and physical properties based on the constituent polymer and introduced metal. By tuning the polymer backbone with nanoscale materials, realization of nano-electronic sensor devices with superior performance is possible.

Sensors fabrication based on nanoparticle-incorporated polymeric matrices are of recent technological interest [7,8]. Metal nanoparticles can be grown inside the polymer matrix by simultaneous electrodeposition of polymer along with metal nanoparticles. Arrays of gold (Au) nanoparticles have been utilized for electrochemical sensors as they exhibit excellent catalytic activity towards various reactions [9,10].

In this work, Au nanoparticles incorporated poly(3,4-ethylenedioxythiophene) (PEDOT) film was utilized as the sensing matrix by demonstrating sensitivity at nanomolar levels. This is a one-component system where the polymer matrix offers the selectivity from the complex environment and the nanoparticles offer the required sensitivity, which is lacking in the polymer matrix alone. The sensitivity of the nanocomposite film was demonstrated in detecting the biomolecules such as dopamine (DA) and uric acid (UA) at nanomolar levels.

2. Experimental methods

For voltammetric studies, a glassy carbon (φ 3 mm, BAS, Inc.) working electrode (GCE), a platinum wire auxiliary electrode and an Ag|AgCl (3 M NaCl) reference electrode were used. Phosphate (0.1 M) buffer solution (PBS) of pH: 7.4 were employed as the electrolytic medium in electroanalysis experiment.

Electrochemical experiments were carried out using a Potentiostat/Galvanostat Autolab PGSTAT-30 (Eco-Chemie B.V., The Netherlands) at ambient temperature ($25 + 1$ °C). To record the differential pulse voltammograms (DPV), the following input parameters were used: scan rate: 30 mV s^{-1}, sample-width: 17 ms, pulse-amplitude: 50 mV, pulse-width (modulation time): 50 ms, pulse–period (interval): 200 ms and quiet-time: 2 s.

Transmission electron microscope (TEM) measurements were made using a Philips CM 200 machine using 400-mesh ultra thin carbon type-A copper grid. Field emission scanning electron microscope (FE-SEM) measurements were made using Hitachi Model S 4700 with an acceleration voltage of 10 kV.

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3. Results and discussion

3.1. Synthesis of Au nanoparticles

Au nanoparticles are prepared based on the biphasic procedure of Brust et al [11]. The Au nanoparticles are protected by monomer of 3,4-ethylenedioxythiophene (EDOT) by self-assembly of thiophene rings on gold surfaces [12]. An aqueous solution of hydrogen tetrachloroaurate (0.5 mM) was added to a solution of tetra *n*-octylammonium bromide (TOABr) in toluene (25 mL, 40 mM). The organic layer was separated out after the phase transfer of $AuCl_4^-$. EDOT (10 mM) in toluene was added to this organic phase and the mixture was stirred for about 6 h. A freshly prepared aqueous solution of sodium borohydride (20 mL, 10 mM) was added. A wine red colouration of the organic phase indicated the formation of Au nanoparticles protected by EDOT. Toluene was evaporated using a rotary evaporator and the resulting residue was washed with acetone to remove the stabilizer (TOABr). Then, Au nanoparticles protected EDOT was redissolved in acetonitrile. These particles are characterized by transmission electron microscopy which revealed (Fig. 1) that the particles are near-monodisperse around an average size of ~ 10 (± 0.1) nm, as calculated in unit surface area (1.1 cm^2) containing approximately 30 particles.

3.2. Preparation of Au-PEDOT composite on Glassy Carbon Electrode surface

Au$_{nano}$-PEDOT was electrochemically deposited as a continuous film on GCE from a solution of EDOT-protected AuNPs in acetonitrile containing tetrabutylammonium perchlorate as supporting electrolyte by potential scanning between -0.5 to 1.9 V vs Ag wire pseudo-reference electrode. The composite film was allowed to grow on GCE surface for five successive scans and the cycling was intentionally limited in order to obtain a thin film.

The FE-SEM images of the electropolymerised PEDOT film and Au$_{nano}$-PEDOT nano composite film coated on ITO glass substrates are shown in Fig. 2. PEDOT alone shows fibrillar network structure with a fiber dimension of ~ 20 nm. The polymer network with a highly porous structure can be seen, which might easily entrap Au nano-aggregates. The image of the PEDOT after incorporation of AuNPs shows that the structure and morphology of the polymer film change significantly. As
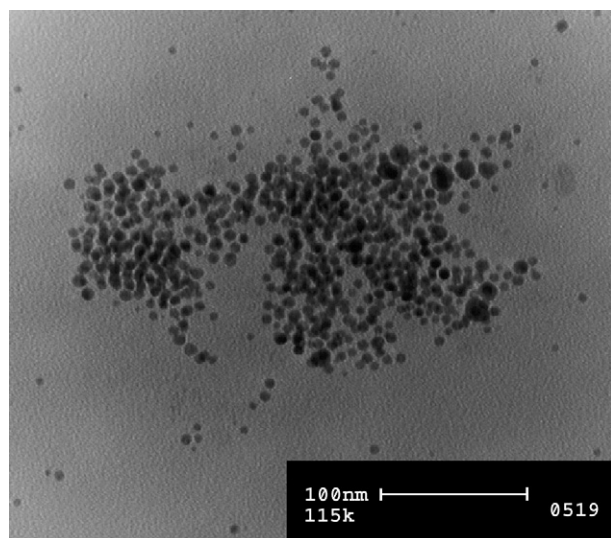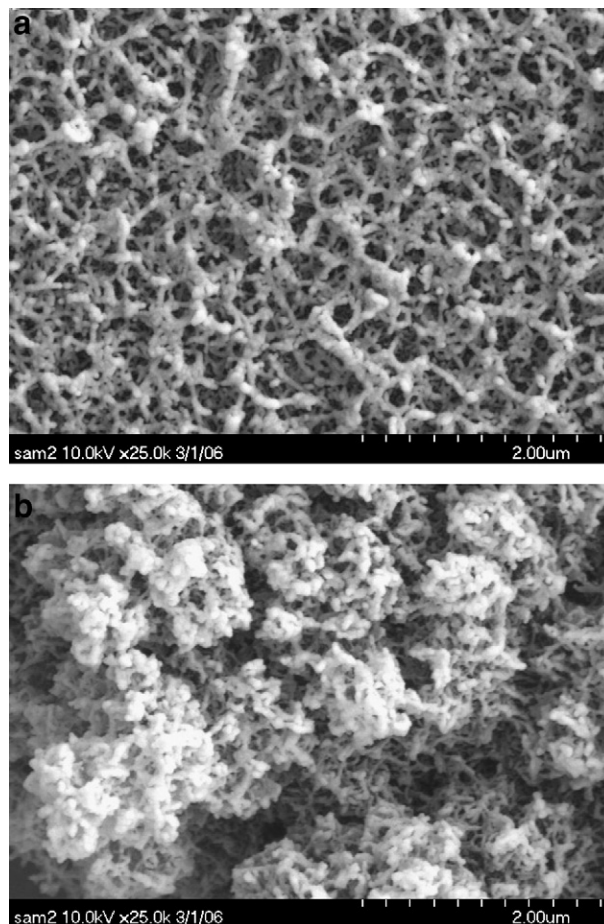

Fig. 2. SEM micrographs of (a) PEDOT and (b) Au$_{nano}$-PEDOT.
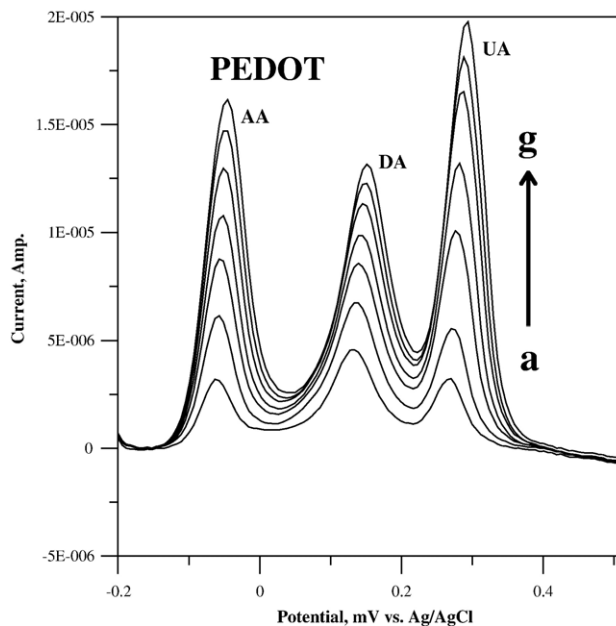

Fig. 3. DPV of AA, DA, UA at PEDOT modified GCE electrode in PBS (pH 7.4). AA concentrations (from a to g): 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5 mM; DA concentrations (from a to g): 20, 30, 40, 50, 60, 70, 80 μM; UA concentrations (from a to g): 20, 30, 50, 70, 90, 110, 130 μM.

Fig. 1. TEM micrograph of EDOT protected Au nanoparticles.

To demonstrate the utility of nanoparticles incorporation in the polymer film, electroanalysis of DA and UA in presence of excess of AA was performed using Au_{nano}-PEDOT nanocomposite film. Fig. 4 exhibits the DPV's obtained for varying DA and UA concentrations in the presence of a fixed concentration of AA on Au_{nano}-PEDOT modified electrode. The voltammetric peak current of AA oxidation remains unchanged, whereas the oxidation current of DA and UA increases linearly as the bulk concentration of DA and UA is increased. The Au_{nano}-PEDOT electrode shows better performance and the detection limit of DA/UA in the presence of 0.5 mM of AA was found to be 2 ($\pm$0.05) nM. The calibration for DA and is found to be linear with a correlation coefficient (R^2) of 0.99 and 0.98 and with a slope value of 0.20 and 0.12 μA nM^{-1} for dopamine and uric acid respectively.

4. Conclusions

Au_{nano}-PEDOT nanocomposites were prepared successfully using chemical and electrochemical routes. FE-SEM morphology reveals that the AuNPs were found to attach stably to the polymer nanofibrillar matrix. The advantages of these films are demonstrated for sensing biologically important compounds such as dopamine and uric acid in presence of excess ascorbic acid, one of the major interferants in the detection of DA and UA (mimicking the physiological conditions), with superior selectivity and sensitivity when compared to the polymer film alone.

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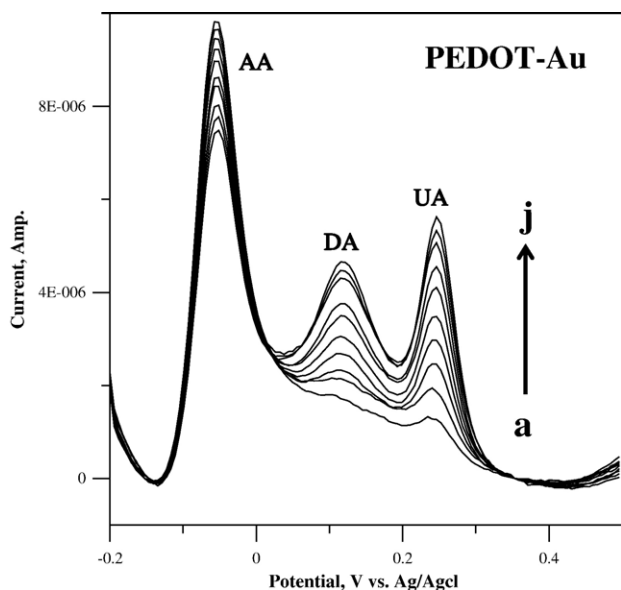[14] S. Senthil Kumar, J. Mathiyarasu, K.L.N. Phani, J. Electroanal. Chem. 578 (2005) 95.

Fig. 4. Differential pulse voltammograms of Au-PEDOT coated electrode in phosphate buffer solution (pH 7.4) containing 0.5 mM AA with different concentrations of DA and UA (a–j correspond to mixed solutions of 2, 4, 6, 8, 10, 12, 14, 16, 18 and 20 nM).

can be seen from Fig. 2b, the fibrils are coated with AuNP aggregates with high porosity indicating its possible application in producing high surface area materials. On independent examination using the voltammetric response of Au (figure not shown), the AuNPs were found to be very stably attached to the polymer nanofibrillar matrix.

3.3. Sensing behavior of PEDOT & Au-PEDOT compsite

PEDOT is known to contain a distribution of hydrophobic (reduced) and hydrophilic (oxidized) regions [13]. We have earlier established this feature using current-sensing AFM [14]. On polymerization of EDOT, the Au_{nano} tend to reside within these "hydrophobic regions" of PEDOT. Hydrophobic analytes such as dopamine interacts with these regions and the more hydrophilic ones prefer the oxidized regions of PEDOT. This behavior is favourable for selectivity and sensitivity in electroanalysis of molecules.

The differential pulse voltammogram (Fig. 3) gives the oxidation of AA, DA and UA at various concentrations at PEDOT modified GCE. It can be seen that the peak current individual analyte increases with concentration but the detection limits on PEDOT modified GCE were found to be in the range of micro-molar concentrations. The linear rang of detection limits are AA — 500–3500 μmol^{-1}, DA — 20–80 μmol^{-1} and UA — 20–130 μmol^{-1}.