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Electropolymerization of thiophene on gold nanoparticle modified electrode in aqueous media

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ABSTRACT

New surfaces were created by modifying gold electrode for electropolymerization of thiophene in aqueous media. The first step in modified electrode production was self assembled monolayer (SAM) coating. Thereby, surfaces with controllable chemical functionalities were obtained. The second step was gold nanoparticle (AuNP) deposition above this coating. Characterization of surfaces was made with electrochemical and spectroscopic methods.

In this study, initially, the surface was insulated with inserting Au electrode into 11-mercaptoundecanoic acid (MUA) solution. Conductivity of surface was increased by gold nanoparticle deposition and gold nanoparticle pores were used as a platform for thiophene polymerization. Electropolymerization of thiophene in the aqueous media was achieved with the obtained modified electrode. At the end of study, voltammograms were taken in the 5 mM $Fe(CN)_6^{4-/3-}$ redox probe containing 0.1 M KCl and 0.1 M $HClO_4$ solutions. The characterization of modified surfaces was carried out by Scanning Electron Microscopy (SEM) and Attenuated Total Reflectance (ATR) methods.

1. Introduction

Self assembled monolayers (SAMs) of thiols on metal surfaces are used to generate chemically functionalized surfaces. SAMs are organized molecular groups which occur themselves with chemisorption of functionalized long-chained alkanes on the surfaces of appropriate solid matters [1–3]. SAMs can be used as a platform for electropolymerization of conducting polymers [4]. The attachment of gold nanoparticles on electrode surfaces can be also carried out by using SAMs with terminal groups that are able to bind to the metal nanoparticle surface [5].

Nanostructured particles of noble metals, especially gold nanoparticles (AuNPs) are in great demand depending on their catalytic properties, effective electronic, optic and thermal properties and also potential applications in the field of physics, chemistry, biology, medicine and materials science and in their different interdisciplinary fields [6]. Preparation of AuNPs generally occurs from the chemical reduction of gold salt in water, organic phase or binary phase [7]. In terms of electroanalysis, using nanoparticle modified electrode has a lot of advantages like catalysis, mass transport, high effective surface area and control over electrode micro environment [8,9]. In general, compared to the gold electrode, nano-Au layer provides fast electron transfer kinetics and causes a decline in residual voltage. Nanoparticle coated Au surfaces can attach strongly to the functional groups such as —CN, —NH_2 or —SH [10–12]. Therefore, conducting polymer films that are prepared with electropolymerization of an electroactive monomer can interact strongly with Au-nano particles and generate good links over chemical bond in nano-level. A lot of applications such as direct electron transfer (DET) from redox protein, immunosensors, genosensors, electrocatalysis and electrochemical sensors of AuNPs are possible.

Conducting polymers are polyconjugated polymers with both keeping the properties of conventional organic polymers and also electronic properties similar to metals [13]. Nanocomposite materials exhibit exceptional electrical properties and optical properties compared to conducting polymer or metal nanoparticles used individually [14,15]. The electrocatalytic properties of nanoparticles are enhanced by the favourable environment supplied by the polymeric matrix [16]. The composite of conducting polymer–metal nanoparticle can be obtained from different metals and π-conjugated polymers as well as oligomer linkers which have received considerable attention due to the possibilities of creating suitable materials for electrocatalysis, chemical sensor and microelectronics [15,16].

Polythiophenes (PThs) are obtained from polymerization of thiophenes and can become conductive with doping by adding or removing of electrons from π orbitals. Polythiophenes can be synthesized electrochemically or chemically by using cross-linked catalysts or in the presence of $AlCl_3$ initiator and carbon disulphide (CS_2) solvent system [17]. Potential applications of PThs include

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field-effect transistors [18], electroluminescent devices, solar cells, photochemical resistors, non-linear optical devices [19], batteries, diodes and sensors [20]. Electrochemical polymerization is a very good strategy to immobilize redox active groups on the surface of electrode and to prepare conducting polymer thin films. However, there are some problems about the polymerization of thiophene in aqueous media. These are the electrooxidation potential of thiophene which is higher than the decomposition potential of water and the strong nucleophilic effect of water which occurs in the electropolymerization of thiophene in aqueous medium [21,22]. To overcome these problems, gold nanoparticle modified surfaces can be used which provide better contact between the monomer and the electroactive surface [23].

In this work, thiophene was polymerized in aqueous medium on gold nanoparticle modified electrode. In the first part of the study, SAM formation was provided by immersing of Au surfaces to the solution of 11-mercaptoundecanoic acid (MUA). Then, gold nanoparticles (AuNPs) were coated and electropolymerization of thiophene was performed with cyclic voltammetry and constant potential electrolysis methods. Electrochemical behaviours of the obtained surfaces were investigated in the solutions of 5 mM $Fe(CN)_6^{4-/3-}$ redox probe containing 0.1 M KCl and 0.1 M $HClO_4$. The characterization of the modified surfaces was performed with Scanning Electron Microscopy (SEM) and Attenuated Total Reflectance (ATR).

2. Experimental

2.1. Reagents

11-mercaptoundecanoic acid was purchased from Sigma–Aldrich, Thiophene 99% was from solution from Merck and Thiophene solutions were prepared by dissolving in $HClO_4$ solution. $K_4Fe(CN)_6$ was from JT Baker, $K_3Fe(CN)_6$ and KCl were from Fischer Scientific Company. All the other reagents were in analytical grade. Before starting the analysis, pure N_2 gas was passed from all of the prepared solutions for sufficient period of time to extract oxygen.

2.2. Apparatus

Electrochemical experiments were performed on CH Instruments CHI660C model potentiostat with a conventional three electrode system comprising platinium wire as the counter electrode, saturated calomel electrode (SCE) as the reference electrode and gold electrode with 0.0314 cm^2 area. In characterization studies, gold (Au) plate with 0.5 cm^2 area was used. ATR analyses were taken by using of Nicolet IS 10 model device. SEM images were obtained with Zeiss Evo 60 EP-SEM Scanning Electron Microscope.

2.3. Synthesis of gold nanoparticles

Colloidal gold nanoparticles were prepared by the reduction of $H[AuCl_4]·3H_2O$ solution in the presence of sodium citrate which was described by Turkevich and Frens and stored at 4 °C [24]. It was observed that synthesized gold nanoparticles were in spherical and colloidal form and the SEM results showed that diameter of the resulting gold nanoparticles were about 20 nm. The maximum UV–vis absorption of the colloidal gold was 520 nm.

2.4. Preparation of MUA/Au, AuNP/MUA/Au and PTh/AuNP/MUA/Au electrodes

Before starting the analysis, gold electrode was polished with 0.05 and 1.0 μm alfa alumina powder and then cleaned electrochemically with successive cycling in 1 M H_2SO_4 solution between −0.2 V and +1.5 V vs. Ag/AgCl until a steady state current was obtained. Then, Au electrodes were immersed into ethanol solutions containing 0.1 M of 11-mercaptoundecanoic acid (MUA) for 15 min and then washed with ethanol and distilled water. This modified surface was denoted as MUA/Au electrode.

Au nanoparticles were electrochemically deposited on the MUA/Au electrode by immersing into gold nanoparticle solution and scanning the potential between −0.2 V and +1.4 V vs. SCE for 90 cycles. The modified electrode was named as AuNP/MUA/Au electrode.

Electropolymerization of thiophene on AuNP/MUA/Au electrode was performed in 59 mM thiophene and 0.1 M $HClO_4$ solution [23,25]. The applied potential during electropolymerization was between −0.4 V and +1.6 V vs. SCE for 90 cycles. Finally, the electrode was washed with distilled water and denoted as PTh/AuNP/MUA/Au electrode.

3. Results and discussion

3.1. Electropolymerization of thiophene on bare Au and AuNP/MUA/Au

Voltammetric responses of AuNP/MUA/Au and Au electrodes were shown in Fig. 1a and b. As can be seen from Fig. 1a and b, gold oxide reduction peak was observed at around +0.8 V vs. SCE for both bare Au electrode and AuNP/MUA/Au surface. No thiophene oxidation appeared on bare Au electrode however, a peak appeared at +1.3 V vs. SCE which could be attributed to thiophene oxidation was obtained for AuNP/MUA/Au surface. Thus, it was thought that,

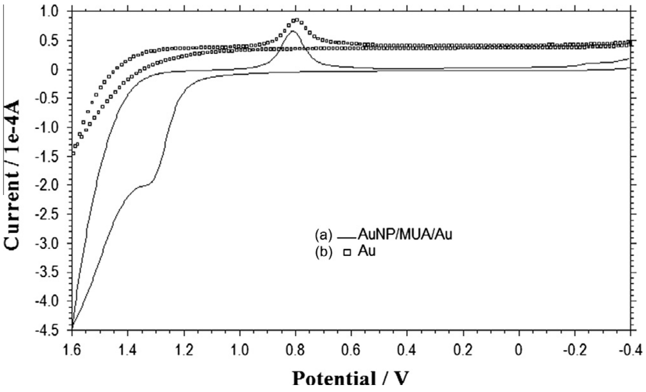

Fig. 1. Cyclic voltammograms of AuNP/MUA/Au and bare Au in 59 mM thiophene and 0.1 M $HClO_4$ solution between −0.4 V and + 1.6 V vs. SCE (scan rate:100 mV/s).

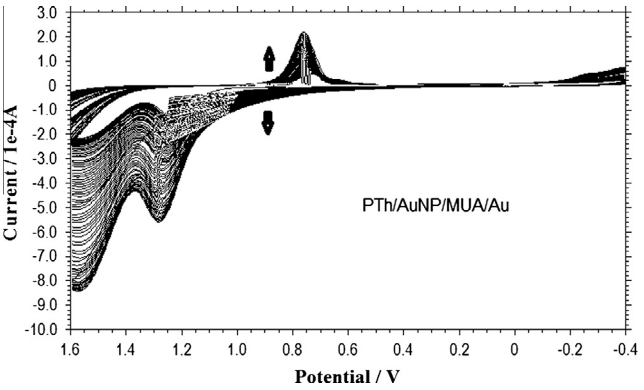

Fig. 2. Potential cycling of thiophene in 59 mM thiophene and 0.1 M $HClO_4$ solution between −0.4 V and + 1.6 V vs. SCE for 90 cycles (scan rate:100 mV/s).