



Gold nanoparticles embedded electropolymerized thin film of pyrimidine derivative on glassy carbon electrode for highly sensitive detection of L-cysteine

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ABSTRACT

This paper demonstrates the fabrication of novel gold nanoparticles incorporated poly (4-amino-6-hydroxy-2-mercaptopyrimidine) (Nano-Au/Poly-AHMP) film modified glassy carbon electrode and it is employed for highly sensitive detection of L-cysteine (CYS). The modified electrode was characterized by scanning electron microscope (SEM), cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). SEM images of modified electrode revealed the homogeneous distribution of gold nanoparticles on poly (4-amino-6-hydroxy-2-mercaptopyrimidine) thin film modified glassy carbon electrode. The modified electrode was successfully utilized for highly selective and sensitive determination of L-cysteine at physiological pH 7.0. The present electrochemical sensor successfully resolved the voltammetric signals of ascorbic acid (AA) and L-cysteine with peak separation of 0.510 V. To the best of our knowledge, this is the first report of larger peak separation between AA and CYS. Wide linear concentration ranges (2 μM –500 μM), low detection limit (0.020 μM), an excellent reproducibility and stability are achieved for cysteine sensing with this Nano-Au/Poly-AHMP/GCE.

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1. Introduction

Cysteine (2-amino-3-sulphydrylpropanoic acid) is a sulphur containing amino acid plays a vital role in biological systems [1]. Cysteine (CYS) can be easily oxidized to form disulphide bond which is essential in construction of the secondary protein [2,3]. It acts as an active site in the catalytic activity of certain enzymes such as cysteine proteases and in many other peptides and proteins [4]. It is also called paravitamin, due to its derivatives role similar to vitamins particularly antioxidative vitamins by maintaining oxidant/antioxidant balance and by indirectly regulating the metabolic processes [5]. Hence, CYS has essential role in the human body in protein synthesis, detoxification and metabolism [6]. Many studies reveal that CYS deficiency causes series illness such as slow growth, leucosite loss, hair depigmentation, oedema, skin lesions, liver damage, lethargy and loss of muscle [7,8]. Moreover, it is acting as physiological regulator for various diseases such as heart disease, rheumatoid arthritis and AIDS [9].

Monitoring the concentration of CYS in physiological samples such as blood plasma, saliva and urine is one of the protocols in clinical analysis and the typical concentration range of CYS is 5 μM to 30 μM [10–13]. Variations in the concentrations of CYS in human body have been related to many diseases, such as arteriosclerosis, leukemia and cancer [14,

15]. Wealth of literature available for the determination of CYS in past decades which includes chromatography [16,17], spectrophotometry [18], electrophoresis [19], chemiluminescence [20], spectrofluorimetry [21] and electrochemical [22–24] techniques. Among these, electrochemical method provides simplicity, high sensitivity, rapid detection and cost efficiency [25]. Because of electroactive nature of CYS molecule, various modified electrodes have been developed such as nanomaterial based electrode [26], chemically modified electrode [27], enzyme based biosensors [28]. Even though these modified electrodes showed good electrocatalytic oxidation of CYS, there are still some challenges lingering such as low sensitivity, less electrode stability and high overpotential. Hence, it is necessary to design high sensitive, highly selective and easy methods for the determination of CYS. Most of the time, ascorbic acid (AA) is a main interferent in the determination of CYS and therefore it is essential to determine them either selectively in presence of other or simultaneously.

Many different kinds of nanoparticles such as noble metal, metal oxides and semiconductor nanoparticles have been developed for electrochemical sensing and biosensing and they played essential roles in various sensing systems [29–33]. In recent time, active research involving metal nanoparticles incorporated polymer film have drawn attention of researcher tremendously due to their easy and simple method of preparation [34]. Gold nanoparticles (Nano-Au) are having more catalytic tendency than their bulk counterparts which would enable fast electron transfer kinetic and decreases high overpotential. Gold

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nanoparticle modified electrode plays essential role in electroanalysis, catalysis and electrochemical sensing [35]. Electropolymerization is the efficient and promising technique to immobilize the conducting polymer onto GCE in order to prepare the modified electrode. Electrodes modified by electropolymerization are precise control in thickness of the film, wide choice of electrode materials, strong adherence power on surface of the electrode, broad potential window, large surface area which promotes higher turn-over efficiency, ease in preparation, high stability and sensitivity [36,37].

The combination of Nano-Au and electropolymerized thin film produce the synergetic effect which brings the enhanced conductivity, facilitation of electron transfer, amplification of the electrochemical response and improvement of detection limit [35]. By self-assembly process, Nano-Au strongly bound to the polymer functional groups, such as $-\text{CN}$, $-\text{NH}_2$, or $-\text{SH}$ and gets incorporated into the thin film of modified electrode [38]. 4-Amino-6-hydroxy-2-mercaptopyrimidine (AHMP) is a low molecular compound which has five potential coordination sites: two nitrogen atoms in pyrimidine ring, one $-\text{NH}_2$ group, one $-\text{OH}$ group and one $-\text{SH}$ group. The Poly-AHMP film layer contains numerous functional groups such as $-\text{NH}_2$ and $-\text{SH}$, which can facilitate the binding of Au-nanoparticles covalently on Poly-AHMP [39,40]. In this paper, we report the preparation of Nano-Au/Poly-AHMP composite by using electrochemical method on glassy carbon electrode (GCE) and its usage for the ultrasensitive and selective determination of CYS in the presence of AA.

2. Experimental

2.1. Chemicals

4-Amino-6-hydroxy-2-mercaptopyrimidine, gold chloride (HAuCl_4), L-cysteine, ascorbic acid were purchased from Aldrich and were used as received. All other chemicals were used in this experiment were of analytical grade. Phosphate buffer solutions were prepared with 0.1 M Na_2HPO_4 and 0.1 M NaH_2PO_4 and adjusting the pH using 0.1 M H_3PO_3 and 0.1 M NaOH. Doubly distilled deionized water was used for the preparation of all solutions and washing.

2.2. Instruments

All electrochemical experiments were carried out in a CHI 6088D (Austin, TX, USA) electrochemical workstation with a custom-made three-electrode cell setup. A mirror polished BASi glassy carbon electrode (GCE-3 mm diameter) used as the working electrode, platinum wire used as counter electrode. A dry leakless electrode (DRIFEF-2) was purchased from World Precision Instruments, USA and used as reference electrode. Glassy carbon discs with a diameter of 1 cm were purchased from HTW, Germany and were used as substrates for SEM (scanning electron microscopy). SEM measurements were performed using FEI Nova™ NanoSEM Scanning Electron Microscope 450 with an accelerating voltage of 10 kV under high vacuum.

2.3. Preparation of Nano-Au/Poly-AHMP modified electrode

The GC working electrode was mirror polished with alumina slurry of 0.5 μm and 0.3 μm , respectively and subsequently sonicated in double distilled water for 10 min to get rid of the physically adsorbed alumina particles from the GC surface. The quality of the polished electrode was electrochemically tested using $[\text{Fe}(\text{CN})_6]^{3-/4-}$ redox couple in 0.1 M KCl. Electropolymerization of AHMP on GC electrode was carried out by 10 successive potential sweeps between -0.5 V and 2 V at a scan rate 0.05 Vs^{-1} in 0.1 M H_2SO_4 solution containing 1 mM AHMP. After electropolymerization, the AHMP polymerized GC electrode (Poly-AHMP/GCE) was removed from the solution and washed with ample

amount of 0.1 M H_2SO_4 to remove the free monomer molecules from the electrode surface [41].

Gold nanoparticle was electrochemically deposited on Poly-AHMP/GCE by applying -0.2 V for 90 s in 0.5 mM HAuCl_4 solution [38]. The obtained modified electrode is denoted as Nano-Au/Poly-AHMP/GCE.

3. Results and discussion

3.1. Surface morphology studies of the modified electrode

The morphology of modified electrode was studied by scanning electron microscopy (SEM). Fig. 1A & B shows the typical SEM images of electrodeposited nano-Au particles on Poly-AHMP film. These images reveal that the gold nanoparticles are well distributed on the surface of the Poly-AHMP film with size ranging from 100 nm to 500 nm. Crystallite aggregation of flower-like structured gold nanoparticles caused the increase of porosity and roughness of modified electrode with high electrochemical surface area. Also, the gold nanoparticles look very pretty, and the sharp-edged leaves possess a large specific surface area. Interestingly, the Poly-AHMP film induces the formation flower like structured gold nanoparticle. This was confirmed by electrodeposition of gold on bare GCE (Fig. 1C) which shows homogeneous surface coverage of gold nanoparticles. The SEM images indicated that the gold nanoparticles are effectively immobilized on Poly-AHMP/GC electrode. It is corroborated with the increased oxidation peak currents of AA and CYS.

3.2. Characterization of the modified electrode

We firstly investigate the electrochemical behaviour of different modified electrodes using cyclic voltammetry in 1 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ solution containing 0.1 M KCl as redox probe. Fig. 2A describes cyclic voltammetry curves of bare GC (curve a), Poly-AHMP/GC (curve b) and Nano-Au/Poly-AHMP/GC (curve c) electrodes in 1 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}/\text{K}_3[\text{Fe}(\text{CN})_6]$ (1:1) containing 0.1 M KCl. On bare GC and Poly-AHMP/GC electrodes, a definite redox peaks were obtained without appreciable change in peak potential and peak current. However, the background current of Poly-AHMP/GC electrode (curve b) is slightly higher than that of bare GCE (curve a). But in the case of Nano-Au/Poly-AHMP/GCE, (curve c) the peak current was larger than bare GC and Poly-AHMP/GC electrodes, which could be ascribed to the conductivity of gold nanoparticles on Poly-AHMP film and also, increased background current of same electrode implying that the larger electroactive surface area of modified electrode compared to Poly-AHMP/GCE.

Electrochemical Impedance Spectroscopy (EIS) is a versatile tool for studying resistivity changes and interface properties of electrode surface during modification process. In the Nyquist plots of EIS contains both semicircle part at high frequency and linear part at low frequency region which correspond to an electron transfer limited process and diffusion process respectively [42]. The diameter of the semicircle in the impedance spectrum is equal to charge transfer resistance, R_{ct} . Fig. 2B shows the results of impedance spectra of bare GCE (curve a), Poly-AHMP/GCE (curve b) and Nano-Au/Poly-AHMP/GCE (curve c) in 1 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ solution containing 0.1 M KCl. On the bare GCE, the value of R_{ct} was obtained 6954 Ω (curve a). After fabrication of Poly-AHMP on GCE surface, the value of R_{ct} was obtained 2541 Ω (curve b). The R_{ct} for Nano-Au/Poly-AHMP/GCE (curve c) is estimated to be 830 Ω . The decreased R_{ct} value for Nano-Au/Poly-AHMP/GCE has been indicated that the highly conducting of gold nanoparticles behaves as an electron-transfer channel, which further improved the conductivity of modified electrode [35] and also it can be observed that the gold nanoparticles are homogeneously distributed within the film as conduction centers, which can accelerate the electron transfer between the analyte molecules and surface of the modified electrode.

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