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Pd–Au nanoparticle decorated carbon nanotube as a sensing layer on the surface of glassy carbon electrode for electrochemical determination of ceftazidime

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ABSTRACT

A simple electrodeposition method is employed to construct a thin film modifier of palladium–gold nanoparticles (Pd–AuNPs) decorated multi-walled carbon nanotube (MWCNT) on the surface of glassy carbon electrode (GCE). Morphology and property of Pd–AuNPs–MWCNT have been examined by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). Electrochemical performance of Pd–AuNPs–MWCNT/GCE for detection of ceftazidime (CFZ) has been investigated by cyclic voltammetry (CV). This nanostructured film modified electrode effectively exhibited enhanced properties for detection of ceftazidime (CFZ). The effects of various experimental variables such as, the amount of casted MWCNT, time and potential of deposition of metal nanoparticles and the pH of the buffered solution on the electrode response are optimized. The proposed electrode showed a linear dynamic range of 0.05–50 μM and the detection limit of 1 nM for the CFZ. The modified electrode successfully supports the sensitive detection of trace amounts of the CFZ in pharmaceutical and clinical preparations.

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1. Introduction

Metal nanoparticles (NPs) have drawn tremendous attention along with their electronic, optical, magnetic, and catalytic properties. In the field of the electrochemical sensors and biosensors, due to their potential applicability, metal nanoparticles are more helpful in promoting the redox processes [1–3]. It is well established that palladium is the most active noble metal for heterogeneous catalysis and electrocatalysis, especially in the fuel cells. Its application in the field of analytical electrochemistry is considerable [4–7].

Bimetallic nanoparticle catalysts usually include a primary metal that has a high performance in catalytic activity and a secondary metal that can influence the catalytic activity or prevent poisoning problems [8,9]. Bimetallic nanoparticles often create synergetic catalytic improvement effects in the electrochemical reactions due to their activity, selectivity, and stability compared to the separate components [10,11]. Among various bimetallic materials, palladium–gold (Pd–Au) system is an interesting one as it shows a high activity toward useful chemical reactions, as well as electrochemical reactions [12–15]. Recently, a drug sensing procedure using the Pd–Au modified electrode has been reported [16].

Improving the catalytic activity of metal nanoparticles can be remarkably influenced by the applied substrate [17,18]. Carbon nanotubes (CNTs), become the focus of nanotechnology and current research, due to their special properties such as high surface area, high electrical conductivity, good mechanical strength and fascinating thermal and chemical stability [19,20]. Their ability for accelerating the electron transfer during the electrochemical reactions makes them suitable substrates in reliable devices, such as electrochemical biosensor [21–23]. Their unique nanostructures can play a good role as a substrate in controlling the size and density of distribution of NPs with the optimized properties [24]. Deposition of NPs on CNT has been developed by various deposition procedures [25–28]. The electrochemical deposition methods with some important advantages as rapidness, simplicity, repeatability and low cost have been considered for the fabrication of NPs. Facility to change the deposition parameters in electrochemical techniques provides the possibility to control the morphology of NPs [29]. Therefore, the construction of such hybrid materials, nanoparticle/nanotube is of interest with useful electrical conductive enhancement properties [30].

Ceftazidime (CFZ) is one of the third-generation cephalosporins with a broad spectrum activity against gram-negative and gram-positive bacteria. CFZ is an active agent against *Pseudomonas aeruginosa*, widely used in the treatment of susceptible infections including respiratory-tract infections such as pneumonia and lung infections in patients with cystic fibrosis–urinary tract infections, skin and soft tissue infections, bone and joint infections, peritonitis and other abdominal infections [31,32].

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Although CFZ has shown an excellent record of clinical successes, rigorous control of its dosage is required since its high dosage can cause renal tubular necrosis in humans [33].

Many techniques have been reported for analyzing the CFZ in biological samples including colorimetric, microbiological [34], HPLC [35–42] and voltammetric methods [43–50].

In the present work, a simple electrochemical method is reported for the decoration of Pd–AuNPs on the structure of carbon nanotubes, pre-casted on the surface of glassy carbon electrode. Characterization of the morphology and the NP's distribution on the surface of the surface-casted nanotube is performed by scanning electron microscopy (SEM). The successful application of the prepared modified electrode for the voltammetric determination of CFZ in pharmaceutical and clinical samples is investigated.

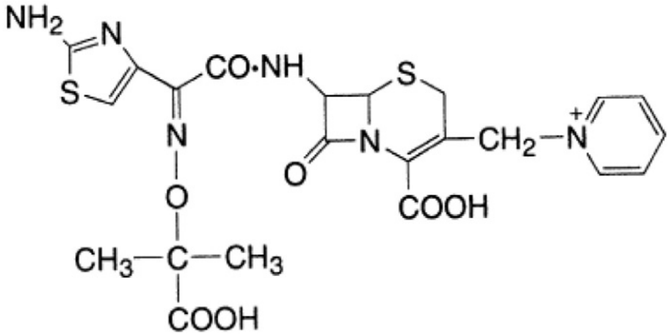
2. Experimental

2.1. Chemicals and reagents

Multi-walled carbon nanotube synthesized by catalytic chemical vapor deposition (CVD, purity > 95%) with outer diameter (o.d.) of 10–20 nm, inner diameter (i.d.) of 5–10 nm and tube length of 0.5–200 nm was obtained from Nanostructured & Amorphous Materials (Houston, TX, USA). Palladium (II) chloride ($PdCl_2$) was purchased from Across Chemical Company, France. Ceftazidime (CFZ, Scheme 1) was purchased from Aldrich. Stock solutions of CFZ were freshly prepared (10^{-5} – 10^{-4} M) in distilled de-ionized water. All other chemicals were of analytical reagent grade and obtained from Merck. The pH of all solutions was fixed by using Britton–Robinson buffer solutions. Vial of CFZ (1000 mg) was purchased from local pharmacies. Fresh frozen human blood serum was obtained from the Iranian Blood Transfusion Organization. Two percent (v/v) pure methanol was added to the serum sample. After vortexing each sample for 2 min, the precipitated proteins were separated by centrifugation for 10 min at 10,000 rpm. Then, the sample was diluted, spiked with different amounts of standard CFZ without extraction or further treatment and used for the recovery tests in the voltammetric measurements.

2.2. Instruments

Cyclic voltammetric experiments and the electrodeposition of Pd–AuNPs on MWCNTs were performed using a Metrohm potentiostat/galvanostat model 797VA. A conventional three-electrode system was used with a glassy carbon working electrode (GC, unmodified or modified, diameter = 2 mm), a saturated Ag/AgCl reference electrode and a Pt wire counter electrode. The morphologies of MWCNTs and Pd–AuNPs electrodeposited on MWCNTs were obtained using a scanning electron microscope (SEM). Voltammetric experiments were carried out in the buffered solutions of CFZ, which were deoxygenated by purging with pure nitrogen (99.999% from Roham Gas Company). Nitrogen gas was flowing over the surface of the test solutions during the experiments. A digital pH/mV/ion meter (Metrohm, pH Lab 827) was used for preparation of the buffer solutions.



Scheme 1. CFZ's structure.

2.3. Preparation of the modified electrode

The MWCNTs were purified in concentrated HNO_3 (65%) at ca. 300 °C for 30 h to obtain more edge sites and a better dispersion of nanotubes by the creation of carboxylate groups, followed by rinsing with deionized water and drying at 70 °C overnight. Before modification, each GC was polished with alumina slurry (0.1 μm) on a polishing cloth and rinsed thoroughly with water. 2.0 mg of the functionalized MWCNTs was dispersed in 2.0 mL of DMF until a homogenous suspension of MWCNTs was obtained (1 mg/mL). For preparation of the MWCNT/GC electrode, 4 μL of the prepared black suspension was applied directly onto a well-polished GC using a micropipette and left to dry at 50 °C in an oven.

The electrochemical deposition of the Pd–AuNPs was conducted for 5 s at a constant potential of −0.2 V (vs. Ag/AgCl) in 0.5 M H_2SO_4 aqueous solution containing 0.5 mM gold (III) chloride and 1 mM palladium (II) chloride ($PdCl_2$). The resulting electrode, renamed as Pd–AuNPs/MWCNT/GC, was rinsed with water. The modification of the electrode surface was refreshed daily.

3. Results and discussion

3.1. Morphological characterization of surface

The surface morphology of the Pd–AuNPs/MWCNT/GC was specified by SEM. A homogeneous layer of MWCNTs with an average diameter of 50 nm was coated on the electrode surface (Fig. 1A & B). The average diameter of well dispersed Pd–AuNPs on MWCNT is approximately 60 nm. The presence of Pd, Au and C on the electrode surface has been shown in EDS results in Supplementary material 1 (S1).

3.2. Electrochemical behavior of the Pd–AuNPs/MWCNT/GC

Studying the electrochemical response of CFZ on the surface of various electrodes including bare GC, MWCNT/GC and Pd–AuNPs/MWCNT/GC was accomplished by using linear sweep voltammetry (LSV). Voltammetric responses of 10 μmol L^{-1} CFZ in 0.04 mol L^{-1} BR buffer solution (pH 5.0), recorded at a scan rate of 100 mV s^{-1} after an accumulation time of 300 s at open circuit, are shown in Fig. 2A (current (I/μA) vs. potential). As shown, the oxidation of CFZ on the surface of bare electrode appeared as a weak voltammetric response with an anodic peak current of about 0.1 μA. On the other hand, at the surface of MWCNT/GC (4 μL casted suspension) a remarkable enhancement in the peak current was observed (10.1 μA). The anodic peak current for CFZ is more increased on the surface of Pd–AuNPs/MWCNT/GC by a factor of 2 (21.5 μA). It can be stated that, immobilization of Pd–AuNPs on the surface of MWCNT/GC with their large surface area increases the adsorptive sites, resulting in a significant increase in the oxidation peak current. In comparison to the bare electrode, only a slight shift in the peak potential is observed in the voltammetric response of CFZ at the Pd–Au/MWCNT/GC. Therefore, it can be concluded that enhancement of the CFZ response is related to the increment of the electrode surface area and the strong adsorption of analyte on the surface of the Pd–Au/MWCNT modified electrode.

3.3. Optimization of the amount of carbon nanotube on the electrode surface

The drop size of the casted MWCNT suspension, prior to the electrochemical deposition of Pd–Au alloy was optimized according to the LSV responses. The results show an increase in the oxidation peak current of 10 μM CFZ, when the amount of casting MWCNTs varies from 0 to 5 μL. As expected, by increasing the volume of MWCNT, the surface area will

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