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Conducting polymer-coated, palladium-functionalized multi-walled carbon nanotubes for the electrochemical sensing of hydroxylamine

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ABSTRACT

Electrochemical sensors of hydroxylamine were fabricated on glassy carbon electrodes (GCEs) by the electropolymerization of 3,4-ethylenedioxypyrrole (EDOP) and 3,4-ethylenedioxythiophene (EDOT) on palladium (Pd) nanoparticles attached to thiolated multi-walled carbon nanotubes (MWCNTs), denoted as PEDOP/MWCNT-Pd/GCE and PEDOT/MWCNT-Pd/GCE. The sensors were characterized by field emission scanning electron microscopy and electrochemical impedance spectroscopy. They showed strong catalytic activity toward the oxidation of hydroxylamine. Cyclic voltammetry and amperometry were used to characterize the sensors' performances. The detection limits of hydroxylamine by PEDOP/MWCNT-Pd/GCE and PEDOT/MWCNT-Pd/GCE were 0.22 and 0.24 μM (S/N = 3), respectively. The sensors' sensitivity, selectivity, and stability were also investigated.

1. Introduction

Hydroxylamine (NH_2OH) is an intermediate in two important microbial processes of the nitrogen cycle, being formed during nitrification and anaerobic ammonium oxidation [1,2]. It is a mutagen, moderately toxic, and harmful to human, animals, and even plants [3], and has been reported to cause both reversible and irreversible physiological changes [4]. It is industrially used as pharmaceutical intermediates and in final drug syntheses, in nuclear fuel reprocessing, and in manufacturing semiconductors [5]. Therefore, the reliable, reproducible, and highly sensitive detection of low level of hydroxylamine is important in industry, environmental monitoring, clinical diagnostics, and biological processing [6,7]. Hydroxylamine determination methods include spectrophotometry [8], high-performance liquid chromatography [9], gas chromatography [10], potentiometry [11], polarography [12], and biamperometry [13]. These methods are extremely complex, and have limited linear ranges, high detection limits and low precision. Electrochemical sensors can provide portable, inexpensive, rapid, and selective detection with low detection limits. However, the majority of bare electrodes are limited in the electrochemical detection of redox active species, showing low sensitivity and reproducibility, low stability, and high overpotential of electron transfer. Using nanoparticles as redox-active materials offers significant advantages in the development of electrochemical sensors. Various chemically modified electrodes have been prepared and used to determine hydroxylamine [6,14–16], showing significantly lower overpotentials and increased oxidation current responses. The surface modification of electrodes with carbon nanotubes (CNTs) has facilitated the electrocatalytic detection of bio-organic and inorganic compounds on CNT matrices [17–20]. CNTs exhibit π-conjugative structures with highly hydrophobic surfaces [21], allowing them to interact with various compounds through π–π electronic and hydrophobic interactions [22,23]. They have also been used in the preparation of sandwiched film-modified electrodes for electrocatalytic tests [24,25]. Nobel metal nanoparticles are useful because of their strong redox catalytic activities. Metal nanoparticles have been used in the fabrication of sensors as nanocomposites or when covalently bonded with CNTs [6,14,26,27]. Pd nanoparticles are preferable to platinum or gold due to their lower price. They have been reported to enhance the reaction mechanism of oxygen reduction reactions. Electropolymerization is a simple and powerful method for the target selective modification of electrodes with specific matrices. Conducting polymers can provide several advantages such as low ohmic drops and enhanced rate constants of electron transfer in some electroactive species [6]. The great advantage of conducting polymer based sensors over other available techniques is that the conducting polymers have the potential to exhibit improved response properties and are sensitive to small perturbations. Earlier inert polymers were being used only to provide mechanical strength to the membranes but conductive polymers improve the sensitivity of the sensors due to their electrical conductivity or charge transport properties. Conducting polymers (3,4-ethylenedioxythiophene (EDOT) and 3,4-ethylenedioxypyrrole (EDOP)) have been electrochemically synthesized for use in chemical and biochemical sensors [28–35].

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This work reports the electrochemical detection of hydroxylamine using easily fabricated sensors consisting of multi-walled carbon nanotubes (MWCNTs) functionalized with PEDOP- and PEDOT-coated Pd nanoparticles on glassy carbon electrodes (GCEs) (PEDOP/MWCNT-Pd/GCE and PEDOT/MWCNT-Pd/GCE). The sensors' electrocatalytic behaviors were evaluated by cyclic voltammetry (CV); they showed well-defined oxidation peaks at +0.2 V and +0.25 V, respectively, vs. Ag/AgCl. The mechanism of the oxidation of hydroxylamine at both sensors was also studied, and was demonstrated to be an irreversible adsorption-controlled electrode process. Wide linear ranges, low detection limits, and excellent storage stabilities were shown by the amperometric responses. These results show that the proposed electrodes displayed better electrocatalytic activity towards hydroxylamine oxidation than previously reported modified electrodes. Therefore it could be used for the sensitive determination of hydroxylamine.

2. Experimental details

2.1. Apparatus and chemicals

Three-electrode cell assemblies were used, each consisted of a modified glassy carbon working electrode (3.0 mm diameter), a platinum-wire auxiliary electrode, and an Ag/AgCl (3.0 M NaCl internal filling solution, BAS, Model MF-2052) reference electrode. All potentials were reported with respect to the Ag/AgCl electrode at room temperature under an argon atmosphere. Electrochemical testing by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and chronoamperometry (CA) were performed using a BAS 100B/W voltammetric analyzer (Bioanalytical Systems, West Lafayette, IN, USA) in a grounded Faraday cage. The pH measurements were performed using a pH glass electrode with a JENCO meter. Scanning electron microscopy (SEM) images were carried out on JSM-7500F field emission scanning electron microanalyzer (JEOL, Japan) at an operational voltage of 15 kV. MWCNTs (diameter, 20–30 nm; length, 1–2 μm; Carbon Nano Tech. Co., Ltd. South Korea) were used to prepare the MWCNT-Pd nanoparticles after acid treatment [36]. $NH_2OH \cdot HCl$ was from Junsei Chemical Co. (Japan). EDOP, EDOT, and tetrabutylammonium perchlorate (TBAP) were from Aldrich. All other reagents used were of analytical grade and used without further purification. All electrochemical experiments were carried out at room temperature. The pH of phosphate buffer solution (PBS) was adjusted with 0.1 M H_3PO_4 and 0.1 M NaOH. High-purity argon was used for deaeration. Doubly distilled water with resistivity over 18 MΩ cm in quartz apparatus was used to prepare all the aqueous electrolyte solutions.

2.2. Formation of MWCNTs-Pd nanoparticles

The MWCNTs were first oxidized in a hot acid solution of HNO_3 and H_2SO_4 (1:3 by volume) at 90 °C for 3 h to remove impurities and to generate surface functional groups.

The acidified MWCNTs were dispersed in tetrahydrofuran; aqueous NaSH was then added to produce surface thiol groups. Thiolated MWCNT-supported Pd catalysts then were synthesized at room temperature using colloidal Pd. Sodium tetrachloropalladate (II) (Na_2PdCl_4, 249.83 mg) was dissolved in deionized water (30 mL), to which 10 mL 4-dimethylaminopyridine (119.9 mg) solution and thiolated MWCNTs (223.8 mg) in 100 mL deionized water were added sequentially. $NaBH_4$ solution was slowly dropped into this mixture and vigorously stirred for 30 min until its pale yellow color became black. The resulting slurry was filtered, washed thoroughly with deionized water, and dried in a vacuum oven to give MWCNTs-Pd nanoparticles.

2.3. Electrode modification

The GCEs' surfaces were highly polished with alumina paste, washed with 1.0 M HCl, rinsed several times with distilled water, and finally rinsed with methanol. They were then coated with 5.0 μL black MWCNTs-Pd suspension. The solvent was evaporated in air at room temperature and the MWCNTs-Pd-coated GCEs were further covered by the electropolymerization of 1.0 mM EDOP or 1.0 mM EDOT in 0.05 M TBAP/acetonitrile under sweeping potentials of 1.5 to −1.5 V, at a scan rate of 100 mV/s for 10 cycles of CV. They were then washed with distilled water. Finally, PEDOP/MWCNTs-Pd/GCE and PEDOT/MWCNTs-Pd/GCE were immersed in 0.1 M PBS. The modified electrodes were washed with distilled water before and after each experiment. Hydroxylamine testing was carried out in 15 mL electrolytic cells with 4.0 mL PBS, with oxygen removed by continuous purging with high-purity argon.

3. Results and discussion

3.1. Surface morphology

The surface morphologies of MWCNTs-Pd, PEDOP/MWCNTs-Pd, and PEDOT/MWCNTs-Pd on GC were examined by SEM (Fig. 1). They showed excellent formations of compact 3D structures. Long tube chain structures were observed in the MWCNTs-Pd film (Fig. 1a), the average tube diameter was measured as 20 nm. The surface of the MWCNTs-Pd became coating by electropolymerized EDOP (Fig. 1b). A smooth coating was observed with PEDOT (Fig. 1c). The confirmation of the conduction polymers' coatings of the surfaces of the MWCNTs-Pd tube chains was significant. The smooth and homogeneous PEDOT coating could take part in electron transfer, and was likely responsible for its high current intensity responses towards hydroxylamine (Fig. 3e).

3.2. EIS measurement

EIS can provide information about electrodes' impedances. Nyquist plots have two regions: one semicircular portion and one linear. The semicircular portion at higher frequencies corresponds to

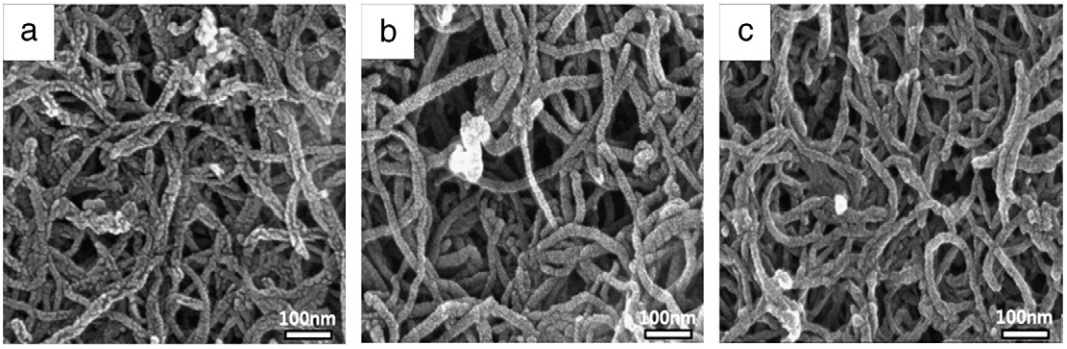

Fig. 1. SEM images of (a) MWCNT-Pd/GCE; (b) PEDOP/MWCNT-Pd/GCE and (c) PEDOT/MWCNT-Pd/GCE after 10 cycles of electropolymerization.