Nonenzymatic glucose and hydrogen peroxide sensors based on catalytic properties of palladium nanoparticles/ poly(3,4-ethylenedioxythiophene) nanofibers

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ABSTRACT

A simple and facile synthetic method to Pd nanoparticles incorporated inside the poly(3,4-ethylenedioxythiophene) nanofibers (Pd-PEDOTn) is reported. The Pd-PEDOTn nanocomposites were characterized by transmission electron microscopy (TEM), scanning electron microscopy (SEM), X-ray diffraction (XRD), and cyclic voltammetry (CV). The Pd-PEDOTn catalyst displays excellent performance for glucose and hydrogen peroxide (H_2O_2) sensing at −0.1 and −0.3 V (vs. Ag/AgCl), respectively. The chronoamperometric measurements showed that the anodic peak currents of the glucose and H_2O_2 were linear to their concentrations in the range of 0.04–9 mM (detection limit was 1.6 μM) and 0.2–25 μM (detection limit was 0.05 μM), respectively. The Pd-PEDOTn modified electrode shows good electrochemical ability to glucose detection in the presence of interfering species such as ascorbic acid (AA), and uric acid (UA) which are commonly found in blood samples. Good stability, high sensitivity and selectivity as well as good reproducibility of Pd-PEDOTn modified electrode can make it as an ideal candidate for preparing inexpensive amperometric glucose biosensor applicable for complex matrices. Finally, the performance of the Pd-PEDOTn modified electrode was evaluated with a human blood sample.

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1. Introduction

Recent activities in electroanalytical chemistry have focused on the design and development of nanoparticles (NPs) based biosensors. Particularly, noble metal NPs have potential applications in the construction of electrochemical sensors and biosensors due to their own fascinating surface structure, good electrical and mechanical properties, good electrocatalytic activity, strong stability and limited aggregation, and high performance [1,2]. Among these noble metal NPs, palladium (Pd) is a very important and rare transition metal that has good catalytic activity and its catalytic activity have been widely recognized in heterogeneous catalysis and electroanalysis [3–5]. Pd NPs have been dispersed on a variety of substrates such as indium tin oxide [6], carbon nanotubes [7,8], epoxy-silver [9], graphene nanohybrids [10], boron-doped diamond [11], and polymers [12–14]. Poly(3,4-ethylenedioxythiophene) (PEDOT), one of the conducting polymers, has been extensively studied due to its easy synthesis, high electrochemical stability, high charge mobility, low

energy band gap, high electrical conductivity, and wide range of applications including solid-state capacitors, printed circuit board, electroluminescent lamps and electrochemical devices [15–18]. PEDOT also is an excellent electrode modified material which it can promote electron transfer reactions and is useful for fabrication of electrochemical sensors [18]. Recently, much attention has been paid on the synthesis of micro- and nanostructured PEDOT due to their unique properties and promising potential applications in nanodevices [19]. Up to now, a several methods were developed for preparing nanostructures of PEDOT, such as interfacial polymerization in presence of the surfactant, template synthesis, dispersion polymerization in alcoholic media, reverse microemulsion polymerization, and so on [20–24]. However, it is difficult to synthesis a PEDOT nanostructure by a simple chemical method without a template. With the known oxidative and solid-state polymerizations, PEDOT exhibits an irregular amorphous shape [25]. It would be highly desirable for PEDOT nanofibers fabrication in the absence of additional structure controlling reagent when considering the economic and green factors of fabrication. Due to the specific properties of nanofibers, the PEDOT nanofibers can make as a supporting materials for construction of Pd NPs with highly disperse.

The glucose sensing is a vital application of electrochemistry because it is of significantly importance in diagnosis and

treatment of diabetes mellitus as well as monitoring and control of food preparation processes [26,27]. The traditional electrochemical sensors for detection of glucose are based on glucose oxidase (GLOx) enzyme. Due to the specificity of enzyme, these sensors have high selectivity and sensitivity. However, the activity of GLOx can be easily affected by temperature, pH and other chemicals, which these factors can cause intrinsic low stability of GLOx and affect the performance of the biosensor. Recently, the design and development of nonenzymatic glucose sensors based on direct oxidation of glucose at modified electrode surface have been found to be interesting research in the fabrication of new biosensors [28,29]. The nonenzymatic glucose sensors would exhibit conveniences and advantages to avoid the enzyme electrode drawbacks. Recently, the interest in a practical nonenzymatic glucose sensor has been centered on the efforts to find an appropriate electrochemical catalyst with highly electrocatalytic activity, which is the important factor that affects both the sensitivity and selectivity of glucose detection. In this regard, different metal NPs (Pd, Au, Pt, Cu, Ni) [30–33], alloys (Pd–Ni, Au–Pd, Pt–Au, Pt–Pb, Cu–Co) [34–38] and metal oxides (CuO, Co_3O_4, NiO) [39–41] have been used as the electrode materials for directly electro-catalyzing glucose. Among these, Pd NPs exhibit excellent electrocatalytic activity for glucose electrooxidation. Pd nanoparticles (Pd NPs) can be incorporated inside the PEDOT matrix by chemical method [42,43] or by electrochemical method such as deposition of Pd nanoparticles on the electropolymerized PEDOT [14]. P. Santhosh et al. [14] were used enzymatic glucose sensor based on GLOx enzyme, which Pd NPs electrochemically incorporated inside the electropolymerized PEDOT matrix. However, the PEDOT nanofibers which is chemically synthesized has not been used so far for the fabrication of a nonenzymatic glucose sensor. To the best of our knowledge, there is no report on the chemically synthesis of nanofibered PEDOT with dispersion of Pd NPs for glucose detection.

Hydrogen peroxide (H_2O_2) has wide applications in pharmaceutical, clinical, environmental, and industrial research. It is also an intermediate or a product in biochemical reactions catalyzed by oxidase. Thus, the detection of H_2O_2 is important in biomedical and environmental applications. The electrocatalytic activity of Pd NPs towards the oxidation of H_2O_2 was also studied [8,44].

In this work, we report a facile and environmentally friendly approach for the synthesis of highly disperse palladium nanoparticles incorporated on PEDOT nanofibers (Pd-PEDOTn). The (Pd-PEDOTn) nanocomposites were characterized by transmission electron microscopy (TEM), scanning electron microscopy, X-ray diffraction (XRD), and cyclic voltammetry (CV). The nonenzymatic glucose and H_2O_2 sensors were constructed using the Pd-PEDOTn nanocomposites as sensing materials. The Pd-PEDOTn displays excellent performance for glucose and H_2O_2 sensing at −0.1 and −0.3 V (vs. Ag/AgCl), respectively.

2. Experimental

2.1. Apparatus and reagents

Scanning electron microscopy (SEM) is performed by field emission scanning electron microscopy of Philips XL-30 instrument with the operation of 17 kV. Transmission electron microscopy (TEM) analyzes were performed by LEO 912AB electron microscope. The content of Pd in the Pd-PEDOTn was determined by AA-680 Shimadzu (Kyoto, Japan) flame atomic absorption spectrometer (AAS). Voltammetric experiments were performed using a μAutolab Type III electrochemical system. A conventional three-electrode cell consisting of a glassy carbon working electrode (modified and unmodified), a platinum wire counter electrode and a saturated Ag/AgCl reference electrode were used for voltammetric

experiments. A digital pH-meter (Ion Analyzer 827, Metrohm) with precision of ±0.001 was used for pH measurements. All experiments were done at room temperature (25.0 ± 1 °C). Glucose and H_2O_2 were obtained from Merck. Palladium chloride ($PdCl_2$) and 3,4-ethylenedioxythiophene (EDOT) were purchased from Merck. A 0.1 M NaOH solution was used as supporting electrolyte. All Other reagents used were of analytical grade, and all solutions were prepared with double distilled water.

2.2. Preparation of PEDOTn

The PEDOT with fiber morphology was synthesized by a template-free method using $FeCl_3$ as oxidant and HCl as the dopant as described previously [45]. Briefly, 1.5 mmol EDOT was dispersed in 90 ml HCl (1.0 M) under ultrasonic stirring for 10 min. Then, 10 mL acid solution (HCl, 1.0 M) of $FeCl_3$ (0.75 mmol) was added into the above mixture quickly and immediately shaking to ensure sufficient mixing before polymerization begins. The polymerization reaction was carried out at 20 °C for 22 h without any disturbance. The synthesized PEDOTn precipitate was obtained through centrifugation and then washed with de-ionized water several times to remove the redundant dopant and oxidant. Finally, the dark-blue product was obtained after being dried in vacuum at 60 °C for 24 h.

2.3. Preparation of the Pd-PEDOTn

Aqueous solution of $PdCl_2$ (0.26 g in 3 mL) and PEDOTn (0.2 g in 10 mL) were mixed and placed in an ultrasonic bath (50 KHz) for 10 min to well disperse metal ions on the surface of PEDOTn. Mixture was stirred at room temperature for 8 h and the reduction was carry out by the addition 0.08 mL of aqueous solution of $NaBH_4$ (0.01 M) to the mixture and stirring at room temperature for 1 h. It was filtered under vacuum, washed well with ethanol and water (2×20 mL) and dried under vacuum at 50 °C for 4 h. According to AAS experiments, the amount of Pd contained in the nanocomposite was found to be 5.53 wt.%.

2.4. Preparation of the Pd-PEDOT modified glassy carbon electrodes

Prior to the electrode modification process, a glassy carbon electrode (GCE) (2 mm diameter) was washed with deionized water and ethanol after polishing was performed with 0.05 μm alumina slurry on a polishing cloth. Typically, a stable suspension of Pd-PEDOTn/GCE containing 2.0 mg ml^{-1} in DMF using 20 min ultrasonic agitation was prepared. After the electrode surface was air dried, 5.0 μL of this suspension was cast onto the surface of the pretreated GC electrode with a microsyringe and then it was dried in air. Furthermore, the suspension of PEDOTn/GCE was prepared and used with the same procedure.

2.5. Analytical procedure

After fabricating each electrode to get reproducible current-potential curves, cyclic voltammetry (CV) were performed at scan rate of 50.0 mV s^{-1} between −0.8 and 1.0 V for 10.0 times in 0.1 M NaOH solution. In addition, the NaOH solution was purged with high-purity nitrogen for at least 5.0 min prior to each electrochemical measurement.

3. Results and discussion

3.1. Characterization of the prepared electrocatalysts

In this part, the synthesized PEDOTn were characterized by using SEM, TEM, and XRD. Fig. 1A show typical SEM image of the