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Nickel nanoparticles modified conducting polymer composite of reduced graphene oxide doped poly(3,4-ethylenedioxythiophene) for enhanced nonenzymatic glucose sensing

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ABSTRACT

A facile two-step electrochemical strategy was reported to synthesize nanocomposite of reduced graphene oxide (RGO) doped conducting polymer poly (3,4-ethylenedioxythiophene) (PEDOT) decorated with nickel nanoparticles (NiNPs) onto a glassy carbon electrode (GCE). Pure graphene oxide (GO) doped PEDOT composite was firstly electropolymerized onto the GCE through cyclic voltammetry, followed by electrochemical reduction in a solution containing nickel cations at a constant potential of −0.9 V. During the electrochemical reduction process, GO doped in the PEDOT composite would be reduced to a more conductive form of RGO, and at the same time, nickel cations could be reduced to form NiNPs and loaded on the composite surface. The prepared nanocomposite (NiNPs/PEDOT/RGO) modified electrode showed outstanding electrocatalytic activity toward the oxidation of glucose in alkaline media, and it could be developed into a nonenzymatic glucose sensor. Under optimum conditions, the glucose sensor exhibited a linear range from 1.0 μM to 5.1 mM and a detection limit of 0.8 μM (S/N = 3), associated with excellent stability, high reproducibility and favorable selectivity against common interferents. Furthermore, the nonenzymatic sensor was also successfully applied to the detection of glucose in human serum samples, showing promising potential in the clinical application.

1. Introduction

Quantitative determination of glucose is of great importance not only because of the increasing demands for diagnosing diabetes disease but also the urgent requirements in the field of food industry, environmental protection and biotechnology [1–3]. Considering these aspects, the development of electrochemical glucose sensor has triggered extensive attention because of its high sensitivity, excellent selectivity, rapid response and good reliability [4–6]. Traditional enzyme-based biosensors for glucose detection, however, are constrained with respect to complicated immobilization procedure, critical operation situation, high cost and poor stability, which limit their universal application for routine detection. Recently, with the purpose of overcoming such disadvantages and improving the glucose sensor sensitivity and stability, nonenzymatic glucose sensors based on the electrochemical catalytic oxidation of glucose have been developed [7], with the application of various materials, including carbon materials [8,9], polymers [10–15], inorganic composites and nanomaterials [16]. Among them, graphene has been widely applied to design electrochemical sensors [8,9,17], because of its excellent conductivity, high surface area, unusual structural characteristics and good biocompatibility [18–20]. Taking advantages of these unique properties, there is an increasing interest on the fabrication of graphene-based nanocomposites which have particular characteristics originated from the synergistic contribution of two or more functional materials [21,22].

Nowadays, conducting polymers (CPs) have been considered as one of the most promising functional components to prepare graphene/CPs composites because of their good electrical conductivity, chemical stability and high electrochemical capacity [10]. Poly(3,4-ethylenedioxythiophene) (PEDOT) has recently received much attention owing to its good conductivity, high charge injection limit, and excellent physical and chemical stability [11,12]. Considering these attractive properties of graphene and PEDOT, it is expected that the combination of graphene and PEDOT could generate composites with enhanced properties, making graphene/PEDOT an excellent conductive support for the loading of other materials. For example, Lu et al. [23] have reported a new

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one-step electrochemical redox route for the synthesis of high quality graphene/PEDOT nanocomposite film where ascorbic oxidase was entrapped and applied as an ascorbic acid sensor. Si et al. [24] have prepared a novel PEDOT/GO hybrid film by using a simple electrodeposition method, and the composite modified electrode was utilized to detect hydroquinone and catechol simultaneously. Wang et al. [25] have prepared a PEDOT/sulfonated graphene composite film through a one-step electrochemical process, and the composite was further decorated with gold nanoparticles and employed as an electrode material for the detection of L-cysteine.

For nonenzymatic glucose sensors, electrode active materials are considered as the fatal factors that influence the sensor performance. Among various active materials, nickel based materials including Ni, NiO and $Ni(OH)_2$ have triggered tremendous research interests in nonenzymatic glucose sensors, owing to their excellent electrocatalytic activity, environmental benignity, and low cost [26–29]. Nonetheless, experimental and theoretical studies have revealed that metal-based glucose sensors suffer from slow kinetics and surface fouling due to the adsorption of chloride ion and reaction intermediates during glucose oxidation [30,31]. Therefore, these drawbacks will have negative influences on the sensor selectivity and sensitivity during long-term operation. To overcome these disadvantages, metal nanoparticles have been loaded onto different matrixes such as graphene [9,17] and conducting polymers [32] in order to improve metal nanoparticles' stability and dispersity. As graphene itself is not well dispersible, and conducting polymers are normally low in conductance, the combination of graphene and PEDOT as composite matrixes for metal nanoparticles deposition may provide enhanced properties.

In this work, we constructed a nonenzymatic glucose sensor based on the NiNPs/PEDOT/RGO nanocomposite, which could overcome the shortcomings of those metal-based sensors. To prepare the NiNPs/PEDOT/RGO nanocomposite, PEDOT/GO composite was firstly prepared through the electrochemical polymerization of 3,4-ethylenedioxythiophene (EDOT) and water-dispersible GO, and then NiNPs were electrodeposited onto the composite surface through the electrochemical reduction of nickel cations. Along with the electrochemical reduction of nickel cations, GO in the PEDOT/GO composite could be reduced to RGO, which is more conductive and therefore can increase the conductivity of the resulting composite. In short, the NiNPs/PEDOT/RGO composite can be easily prepared through an all-electrochemical process, and it can be used for the nonenzymatic glucose sensing owing to its excellent catalytic activity toward the electrochemical oxidation of glucose.

2. Experimental

2.1. Reagents

Graphene oxide was purchased from Nanjing Xian Feng Nanomaterials Technology Co., Ltd. (Nanjing, China). 3, 4-Ethylenedioxythiophene (EDOT), D(+)-glucose, ascorbic acid (AA), uric acid (UA), dopamine (DA), nickel sulfate ($NiSO_4$), sodium hydroxide (NaOH) were obtained from Aladdin regent (Shanghai, China). All used reagents were of analytical grade and used without purification. Millipore water which was produced by a Milli-Q water purifying system was used throughout all experiments. Human blood was provided by Qingdao Chengyang People's Hospital and stored at 4 °C and the glucose detection was carried out within a week. Human serum samples were prepared by centrifugation of fresh blood for 5 min at 10,000 rpm, the supernatants were collected without dilution afterwards. Fresh serum samples were analyzed with an Automatic Analyzer (Hitachi 7600 automatic biochemical analyzer).

2.2. Apparatus

Electrochemical measurements were performed on a CHI660D electrochemical workstation (Shanghai CH Instruments Co., China). A conversational three-electrode system was applied with a saturated calomel electrode (SCE) as the reference electrode, modified glassy carbon electrode (GCE) as the working electrode and a platinum wire as the counter electrode. Scanning electron microscope (SEM) and energy dispersive spectroscopy (EDS) were conducted to characterize the surface morphology and elemental composition of materials (JEOL JSM-7500F SEM instrument Hitachi High-Technology Co., Ltd., Japan). The X-ray diffraction (XRD) was carried out on a XB-3A diffractometer using Cu Ka radiation.

2.3. Fabrication of the NiNPs/PEDOT/RGO modified electrodes

GCE was polished, washed and eletrochemically pretreated in phosphate buffered saline (PBS) according to a previous report [33]. The procedure can be briefly described as followed. Firstly, GCEs (3 mm in diameter) were polished by sequentially using 1.0, 0.3 and 0.05 mm alumina slurries and were then ultrasonically washed in water and in ethanol for about 2 min each, respectively. Secondly, the GCEs were scanned between −0.2 and +0.6 V with a scan rate 50 mV/s for 10 circles in PBS (pH 7.0). Thirdly, the GCEs were held at a potential of +1.80 V in a stirred solution of pH 5.0 PBS for 300 s. And finally, the electrodes were scanned between +0.3 and +1.25 V with a scan rate of 50 mV/s until steady-state cyclic voltammograms were obtained. The NiNPs/PEDOT/RGO nanocomposite was prepared as follows: firstly, PEDOT/GO nanocomposite was prepared by electrochemical polymerization in a solution containing 2 mg/mL GO and 0.02 M EDOT, using cyclic voltammetry (CV) scanning from −0.2 to 1.2 V at a scan rate of 100 mV/s for 15 cycles (Fig. S1, Supporting Information). The obtained modified electrode was washed and dried in the air, and then immersed in 0.01 M $NiSO_4$ solution and electrochemically reduced at a constant potential of −0.9 (vs. SCE) for 300 s. During this reduction process, GO was simultaneously reduced into RGO [34]. Therefore, the NiNPs/PEDOT/RGO modified electrode (NiNPs/PEDOT/RGO/GCE) was prepared. For comparison, PEDOT/GO/GCE and NiNPs/GCE were prepared similarly but with only the first or the second procedures respectively.

2.4. Electrochemical measurements

Electrochemical impedance spectroscopy (EIS) measurements were recorded in a solution containing 0.1 M KCl and equimolar 50 mM $[Fe(CN)_6^{4-/3-}]$ at the frequency range from 1 to 100,000 Hz. The amplitude of the applied sine was 5 mV with the current potential set as 0.25 V. CV measurements for glucose was performed in 0.1 M NaOH in the potential between −0.3 V and 0.9 V at scan rate of 100 mV/s. The amperometric current–time (i–t) curves were measured at a potential of 0.5 V in stirring 0.1 M NaOH. For the detection of real sample, 50.0 μL of serum sample was added to 10.0 mL 0.1 M NaOH solution, and the current response was recorded using i–t curve at 0.5 V. All measurements were performed at room temperature.

3. Results and discussion

3.1. Characterization of the modified electrode

The surface morphology of the NiNPs/PEDOT/RGO and PEDOT/GO modified electrodes were characterized by SEM. As shown in Fig. 1A, the PEDOT/GO film deposited on the GCE displays a rough surface with many wrinkles, showing a three-dimensional (3D) morphological microstructure due to the presence of GO