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Layer-by-layer assembly of copper nanoparticles and manganese dioxide-multiwalled carbon nanotubes film: A new nonenzymatic electrochemical sensor for glucose

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ABSTRACT

A nonenzymatic glucose sensor based on Cu/MnO_2/MWCNTs nanocomposite modified glass carbon electrode was fabricated by an electrochemical method. Transmission electron microscopic (TEM) measurement showed that MnO_2 in the nanocomposite held a nanostructure of three-dimension (3D) spheres assembled by many densely arranged nanosheets. The electrocatalytic activity of the present sensor toward the oxidation of glucose was investigated by amperometry. The current response was linearly related to glucose concentration in a range from 6.4×10^{-7}–2.0×10^{-3} mol L^{-1} with a sensitivity of 494 μA mM^{-1} cm^{-2} and a correlation coefficient of 0.9990, and another range from 10 to 1000 μM with a sensitivity of 1302 μA mM^{-1} cm^{-2} and a correlation coefficient of 0.9990. The detection limit was estimated to be 0.17 μM at a signal-to-noise ratio of 3, and the response time was found to be 3 s.

1. Introduction

The determination of glucose plays an important role in such different field as clinical analysis, food, pharmaceutical, industrial and environmental analyses, and so on. As a result, glucose biosensors based on glucose oxidase have been developed rapidly due to their high selectivity [1–3]. However, some drawbacks of enzymatic sensors are also founded in glucose oxidase-based biosensors, like it is too sensitive to the thermal and chemical information [3–5]. These drawbacks have affected the application of glucose oxidase-based biosensors greatly. Whereas, they can not be overcome in enzymatic sensors for that they originate from the nature of enzyme.

To address these problems, many attempts have been made to develop glucose sensors without glucose oxidase. Numerous nanostructured materials have been applied to develop innovative nonenzymatic glucose sensors due to their catalysis to the oxidation of glucose. The nonenzymatic glucose sensors based on metal oxides (Cu_xO [6], MnO_2 [7], Co_3O_4 [8], etc.) and metal hydroxide ($Cu(OH)_2$ [9],etc) are of great interest in recent years and display a lot of advantages of fast response, high sensitivity, low detection limit, good stability and low cost, although their selectivity is not satisfied toward other carbohydrates, such as fructose and sucrose.

In order to solve the problem, nanocomposites which constituted by metal and metal oxide have been synthesized to fabricate electrochemical sensors. Combination of metal and metal oxide could improve the properties of electrochemical sensors due to their synergistic effect. Because of their huge specific surface area, excellent chemical stability, low cost, and fabrication flexibility, the metal oxides such as SiO_2, CuO_2, ZnO, ZrO_2, and MnO_2 have earned more attention [10–13]. For example, Tarlani et al. synthesized New ZnO nanostructures as non-enzymatic glucose biosensors [14]. Prasad et al. combined multi-wall carbon nanotube with NiO nanoparticle to detect glucose in human blood serum [15]. Badhulika et al. prepared nonenzymatic glucose sensor based on decorate Platinum Nanoflowers on multi-wall carbon nanotube and graphene [16]. Particularly, in these nonenzymatic glucose sensors, the Cu or MnO_2-based sensors have excellent electrocatalysis toward glucose. In order to take full advantage of the two kinds of nanomaterials, Meng et al. created Cu/MnO_2 nanocomposites and disclosed that the novel Cu/MnO_2 nanocomposites could present good performance towards the determination of glucose. [17], demonstrating the unique properties of each material can be integrated, and the interactions between the two components could bring out novel properties. Thus, Cu/MnO_2 nanohybrids seem to be a promising electrocatalysts in glucose sensors. However, the activity of Cu/MnO_2 for glucose oxidation needs to be further enhanced.

MWCNTs has been considered an interesting material in the world and widely concerned in both experimental and theoretical

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scientific communities in recent years. In the field of electrochemistry, MWCNTs is considered as an ideal material for sensing application since MWCNTs can play an important role in improving the performance of sensors due to their large specific surface area and excellent electrical conductivity [18–24]. To further explore the application of MWCNTs, one choice using nanoparticles to decorate MWCNTs is interesting and has attracted much attention in recent years. In the past few years, increasing numbers of researches in this field have been devoted to the hybrid of MWCNTs with polymer and metal nanoparticles [15,25–30]. The researchers demonstrated that the hybridization of MWCNTs with functional nanomaterials may not only enhance the functional properties of each component but also yield new properties via cooperative interaction [31–34].

In this paper, a nonenzymatic glucose sensor based on a Cu/MnO_2/MWCNTs nanocomposite modified glassy carbon electrode was proposed and its electrochemical behaviors were studied. To our knowledge, this is the first time that Cu/MnO_2/MWCNTs nanocomposite is applied to fabricate a nonenzymatic electrochemical sensor. Therefore, the present work can be expected not only to develop an excellent electrochemical sensing platform but also expand the application of MWCNTs in the field of electrochemical sensor.

2. Experimental

2.1. Reagents and materials

High purity multiwall carbon nanotubes (MWCNTs, >95% purity) were purchased from Chengdu Organic Chemicals Co. Ltd., of the Chinese Academy of Science. 50% (wt/wt) hydrazine solution was purchased from Tianjin Yaohua Chemical Reagent Co. Ltd. (Tianjin, China). $CuSO_4 \cdot 5H_2O$ (98%), $NaBH_4$ were obtained from Yixing Fandao Chemical Factory (Yixing, China). D-glucose (99.5%) was obtained from Sigma. Glucose stock solutions were allowed to mutarotate for at least 24 h prior to use and stored at 4 °C. All the other reagents were analytical grade and used as received. All solutions were prepared with ultrapure water obtained from a Millipore Milli-Q water purification system.

2.2. Apparatus

Scanning electron microscopic measurements were carried out on a scanning electron microscope (SEM, JEOL JSM-6390) at 15 kV. The transmission electron microscope (TEM) image was carried out by Tecnai G2 F20 S-TWIN (FEI, USA); all electrochemical experiments were carried out in a three-electrode cell controlled by EC 550 electrochemical workstation (Gaoss Union Technology Co., Ltd., Wuhan, China) and CHI 660 electrochemical workstation (Shanghai CH Instrument Co. Ltd., China). A saturated calomel electrode and a platinum wire served as the reference and counter electrodes, respectively. All the electrochemical experiments were conducted at room temperature (25 ± 2 °C).

2.3. The preparation of nanocomposites

2.3.1. Functionalization of MWCNTs

According to take a certain amount of MWCNTs scattered in H_2SO_4-HNO_3 in mixed acid solution (volume 3:1), ultrasonic oscillations 4 h and make the MWCNTs centrifugal separation, then dispatch the pH to neutral. After repeated washing with acetone vacuum drying for a quick functional MWCNTs.

2.3.2. Synthesis of MnO_2-MWCNTs

In a typical procedure, MWCNTs (20 mg) were mixed with $KMnO_4$ (43.6 mg). The mixture was then suspended in 24 mL doubly distilled water and sonicated for 30 min, after which, ethylene glycol was added into the suspension slowly, then sustained magnetic stirred at 50 °C for about 30 min until the color of the $KMnO_4$ was faded, suggesting that MnO_2 were completely deposited on MWCNTs. Finally, the composite products were obtained through centrifuging, water washing, ultrafiltration and drying 10 h at 70 °C.

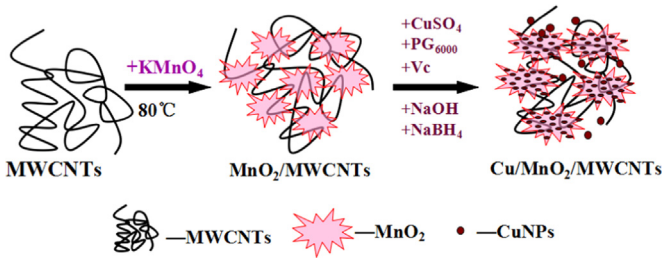

Fig. 1. Schematic illustration of the preparation of Cu/MnO_2/MWCNTs.

2.3.3. Synthesis of Cu-MnO_2-MWCNTs

MnO_2-MWCNTs powder (25 mg) was dispersed in 50 mL water. In turn add $CuSO_4 \cdot 5H_2O$ (0.05 mM), polyethylene glycol (6000, 0.1 mM), ascorbic acid (0.01 mM), with NaOH (0.1 M) to adjust pH value to neutral. At last, add $NaBH_4$ reduction (0.05 M). The whole process needs to be done in the case of a magnetic stirring and last 90 min. Wash, centrifugal drying to Cu-MnO_2-MWCNTs black powder product. As shown in Fig. 1.

2.4. Electrode modification

The glass carbon electrode (GCE) surface with 1.0 μm and 0.05 μm γ- Al_2O_3 powder grinding, and then rinsed with doubly distilled water, anhydrous ethanol ultrasonic washing 10 min. Take 0.1 mg Cu-MnO_2-MWCNTs powder, add 1 mL of 0.5% chitosan (CS) solution and sonicated for 30 min, the suspension (5 μL) was dropped onto the pre-polished mirror like surface of GCE and then dried in air at room temperature.

3. Results and discussion

3.1. Characterizations of Cu/MnO_2/MWCNTs

From the characterization of MnO_2/MWCNTs in Fig. 2A and B, corrugated and thin GE flakes had been synthesized. And from Fig. 2C and D, it was obviously that Cu nanoparticles had been electro-decorated on the surface of MnO_2/MWCNTs, In addition, although the diameter of the nanoparticles was relatively big, the nanoparticles were assembled by many densely arranged nanosheets. Accordingly, the nanoparticles had a large specific surface area and were suitable for electrode fabrication.

Fig. 3. shows the XRD pattern of Cu/MnO/MWCNTs nanocomposite. The diffraction pattern clearly showed three major peaks at 43.50° and 50.50° in the range of 30–60°, which can be assigned to the diffraction from Cu. Some peaks (36.8°, 38.3°, 43.9°) that belonged to MnO_2 were observed (JCPDS 05-0331), which demonstrates the formation of MnO_2 films. The XRD results clearly indicated that the layers of Cu/MnO_2/MWCNTs films were attached onto the electrode surface by electrodeposition.

3.2. Cyclic voltammograms of modified electrodes

From Fig. 4, it was obviously that there was a pair of asymmetric redox peaks appeared on the cyclic voltammograms (curve