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Electrochemical deposition of Ni nanoparticles decorated ZnO hexagonal prisms as an effective platform for non-enzymatic detection of glucose

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ABSTRACT

Zinc oxide hexagonal prisms (ZnO) decorated with nickel nanoparticles (Ni) onto a glassy carbon by a facile two-step electrochemical strategy. The resulting Ni-ZnO modified electrode was characterized by scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) and electrochemical methods. Incorporating the lager surface area of ZnO 3D scaffold and high electrocatalytic activity of Ni, the prepared Ni-ZnO modified electrode possessed strong electrocatalytic ability toward glucose. At the optimum conditions, the calibration curve for glucose determination was linear in the range of 1 μM to 8.1 mM, a high sensitivity of 824.34 μA mM^{-1} cm^{-2} and a low detection limit (S/N = 3) of 0.28 μM were obtained. In addition, the proposed sensor was successfully applied to analyze glucose level in human blood serum samples.

1. Introduction

Diabetes is a major health problem causing 4 million deaths each year and 171 million people suffering worldwide. Although there is no cure for diabetes, nevertheless, the blood glucose level of diabetic patients should be monitored tightly to avoid further complications [1]. Thus, it is necessary and urgent to develop a fast, remarkable sensitivity, high selectivity, reliable and stable technology to detect glucose levels. In addition to spectroscopy [2], chromatography [3], colorimetry [4], iodometry [5] and photoelectrochemical method [6], electrochemical sensors are attractive due to low-cost, simplicity, and reliability [7–8]. Electrochemical sensors for glucose determination are basically classified into two major types which are enzymatic and non-enzymatic modified sensors. Enzymatic glucose sensors, based on the immobilization of glucose oxidase (GOD) on various substrates, are the focus of most previous studies on this subject due to their high selectivity and sensitivity. However, these GOD based biosensors lacked long-term stability and its activity was easily subjected to the influence of immobilization, pH, humidity, temperature and toxic chemicals, which limit their practical application [9–10]. To address these limitations, an alternative way based on the direct electrooxidation without the use of enzyme, "non-enzymatic" sensors have been tried.

Non-enzymatic electrochemical sensors employing precious metals like platinum [11], gold [12–13] and their alloys [14–15] are reported. However, most of these electrodes suffered from the poisoning of chloride and intermediate products which resulted in low sensitivity and selectivity [16–18]. Therefore, the search for novel material and appropriate architectures is the key step in the fabrication of highly sensitive non-enzymatic glucose sensors. Transitional metal, such as Co [19–20], Ni [21–23], Mn [24], and Cu [25–26], are reported to be viable candidates. Among these, Nickel (Ni) based nanostructures have shown great potential for the determination of glucose in alkaline medium owing to their excellent electrocatalytic activity, environmental benignity, and low cost. On the other hand, ZnO nanostructures with unique advantage including non-toxicity characteristics, highly chemical stability, ease of fabrication, electrochemical activity and high electron transfer properties, has strongly attracted researchers [27–30]. However, rare efforts started to build non-enzymatic glucose sensors based on zinc oxide by electrochemical methods [30].

In this work, we constructed a nonenzymatic glucose sensor based on the Ni-ZnO modified electrode. To prepare Ni-ZnO modified electrode ZnO hexagonal prisms were firstly prepared through the electrochemical deposition of $Zn(NO_3)_2$ and $(CH_2)_6N_4$ solution, and then Ni were electrodeposited onto the composite surface through the electrochemical reduction of nickel cations. Incorporating the lager surface area of ZnO 3D scaffold and high electrocatalytic activity of Ni, the Ni-ZnO modified electrode was adapted to constructing enzyme-free glucose sensor and exhibited strong electrocatalytic ability to glucose in alkaline media. The resulting Ni-ZnO modified electrode was characterized by scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) and electrochemical methods. The electrocatalysis of Ni-ZnO/GCE electrode toward the oxidation of glucose was evaluated by cyclic voltammetry (CV) and chronoamperometry.

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2. Experimental

2.1. Chemicals

β-D-(+)-Glucose, D-fructose(F), uric acid(UA) and ascorbic acid (AA) were obtained from the Sinopharm Group Chemical Reagent Co. Ltd.(China). Other chemicals used were purchased from the local companies. All chemicals were of analytical reagent grade and used as received. All solutions used throughout were prepared with ultra pure water obtained from a Millipore system (resistivity > 18 MΩ cm).

2.2. Apparatus

Scanning electron microscope (SEM) and energy dispersive spectroscopy (EDS) were conducted to characterize the surface morphology and elemental composition of materials (FEI-Quanta-200). All electrochemical measurements were performed on a CHI 660A Electrochemical Workstation (Chenhua, China). A conventional three-electrode cell was used with a glassy carbon (GC, with a diameter of 3 mm) electrode as the working electrode, a platinum wire as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. All the potentials in this paper were referred to SCE. Temperature was controlled by thermostatic water baths (Tianjin, China).

2.3. Preparation of Ni-ZnO/GCE modified electrode

Prior to modification, the bare GCE was polished carefully with 0.5 and 0.05 μm alumina slurries, After 3 min of ultrasonication in ethanol and water successively, the electrode was rinsed with water and then dried.

The Ni-ZnO modified GCE (Ni-ZnO/GCE) was prepared as follows: firstly, ZnO hexagonal prisms was prepared by electrodeposition in 10 mL $Zn(NO_3)_2 + (CH_2)_6N_4$ solution (4:1 *v*/*v*), using a constant potential of −0.9 for 4000 s at 70 °C.·The obtained electrode was washed and dried in the air, and then immersed in 10 mM $NiSO_4$ solution and electrochemically reduced at a constant potential also of −0.9 (vs. SCE) for 60 s at room temperature. For comparison, ZnO/GCE and Ni/GCE electrode were also prepared according to the above procedure.

2.4. Electrochemical measurements

Electrochemical impedance spectroscopy (EIS) measurements were recorded in a solution containing 0.1 M KCl and 5 mM $[Fe(CN)_6^{4-/3-}]$ at the frequency range from 0.1 to 100,000 Hz. The amplitude of the applied sine was 5 mV with the current potential set as 0.2 V. Cyclic voltammograms (CVs) measurements for glucose was performed in 0.1 K KOH in the potential between 0 V and 1.0 V at scan rate of 50 mV/s. The amperometric current-time (i-t) curves were measured at a potential of 0.5 V in stirring 0.1 M KOH. For the detection of real sample, 50.0 μL of serum sample was added to 5.0 mL 0.1 M KOH 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 ZnO and Ni-ZnO modified electrodes were characterized by SEM. As show in Fig. 1, the ZnO deposited on the GCE displays highly uniform and distributed all over the surface with an average diameter of ~1 μm, showing a three-dimensional (3D) morphological microstructure. This 3D structure of ZnO can provide a large surface area, leading to a large electroactive area on the modified electrode. After the electrochemical reduction in the nickel ion precursor solution (1 mM $NiSO_4$), metal nanoparticles was formed and deposited on the composite film. As show in Fig. 1(C), we can found that the ZnO are successfully decorated with Ni which is about 100 nm in diameter. In addition, energy dispersive spectroscopy (EDS) was used to investigate the components of the Ni-ZnO composite (Fig. 1(D)). It was found that the Ni-ZnO sample mainly contained Zn, O and Ni elements, which further proves that Ni-ZnO were successfully electrodeposited.

$Fe(CN)_6^{3-/4-}$, as an electrochemical probe, is usually used to evaluate the electrochemical properties of the modified electrode. Fig. 2(A) shows cyclic voltammograms obtained at the bare GCE, Ni/GCE and Ni-ZnO/GCE electrodes in 5 mM $Fe(CN)_6{}^{3-/4-}$(1:1) + 0.1 M KCl solution. It is noted that the difference in potential between the anodic and cathodic peaks (Δ*E*p) is 98 mV for the Ni-ZnO/GC electrode, 110 mV for the Ni/GCE electrode and 160 mV for the bare GCE electrode. As ΔEp is a function of the electron transfer rate, the lower ΔE_p, the higher electron transfer rate. According to the reference [31–32], the electron transfer rate constant k_0 for the ferricyanide system decreases with the increase of the value of ΔE_p. Therefore, the order of the k_0 value at different electrodes is as follows: Ni-ZnO/GCE > Ni/GCE > bare GCE. Furthermore, the redox peak currents at the Ni-ZnO/GCE electrode are larger than that at the Ni/GCE and bare GCE electrodes. The smaller value of ΔE_p and the higher redox peak currents indicate that the Ni-ZnO/GCE electrode has better electrochemical properties than the Ni/GCE and bare GCE electrodes. This may result from the 3D structure of ZnO can provide a large surface area, leading to a large electroactive area on the modified electrode.

The electroactive area of the modified electrode on which a reversible redox reaction of $Fe(CN)_6^{3-/4-}$ probe occurs can be calculated by Randles–Sevcik equation [33–34]:

$$I_p = 2.69 \times 10^5 n^{3/2} D_0{}^{1/2} v^{1/2} c_0 A$$

where I_p is the peak current (*A*), *n* is the number of electrons transferred, *A* is the electroactive area (cm^2), D_0 is the diffusion coefficient of the electroactive species (cm^2 s^{-1}), c_0 is the bulk concentration of the same species (mol cm^{-3}), and *v* is the scan rate (V s^{-1}). For potassium ferricyanide dissolved in 0.1 mol L^{-1} KCl aqueous solution at 25 °C, its diffusion coefficient is 1.0×10^{-5} cm s^{-1} [33]. Through the calculation, the electroactive area of the bare GCE electrode is 0.08073 cm^2, this value is larger than its physical area (0.07065 cm^2) owing to the rough GCE surface. Similarly, the electroactive area of the ZnO/GCE electrode is 0.1283 cm^2 and Ni-ZnO/GCE electrode is 0.1335 cm^2. These results indicated that modification of the 3D structure ZnO causes to increase the active surface area of the fabricated electrode.

The capability of electron transfer of different electrodes was further investigated by electrochemical impedance analysis (EIS) and the corresponding results are shown in Fig. 2(B). In general, the EIS spectra have semicircular sections at higher frequencies corresponding to the electron transfer limiting process, and the linear sections at lower frequencies correspond to the diffusion limiting process. Typically, the increase of the diameter of the semicircle reflects the increase of the interfacial charge-transfer resistance (Ret). The order of the value of charge-transfer resistance (*R*ct) for different electrodes is as follows: bare GCE > Ni/GCE > Ni-ZnO/GCE. This result is in accordance with that observed in Fig. 2(A) and reconfirms that Ni-ZnO possesses good conductivity and electrochemical properties. These imply that Ni-ZnO may be a promising electrochemical active material to construct electrochemical biosensors.

3.2. Electrochemical behaviors of the modified electrode

The electrochemical oxidation of glucose on various electrodes was investigated and compared, as shown in Fig. 3. Clearly, there was no significant response of glucose on the bare GCE and ZnO/GCE electrode indicating that electrochemical oxidation of glucose at the bare GCE and ZnO/GCE electrode surface was difficult. Meanwhile, Ni/GCE electrode