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Research Article

Direct Growth of Copper Oxide Films on Ti Substrate for Nonenzymatic Glucose Sensors

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Copper oxide (CuO) films directly grown on Ti substrate have been successfully prepared via a hydrothermal method and used to construct an amperometric nonenzymatic glucose sensor. XRD and SEM were used to characterize the samples. The electrochemical performances of the electrode for detection of glucose were investigated by cyclic voltammetry and chronoamperometry. The CuO films based glucose sensors exhibit enhanced electrocatalytic properties which show very high sensitivity (726.9 μA mM^{-1} cm^{-2}), low detection limit (2 μM), and fast response (2 s). In addition, reproducibility and long-term stability have been observed. Low cost, convenience, and biocompatibility make the CuO films directly grown on Ti substrate electrodes a promising platform for amperometric nonenzymatic glucose sensor.

1. Introduction

Reliable and fast determination of glucose is important in areas such as clinical diagnostics [1], biotechnology [2], and environmental and food chemistry [3], so the development of electrochemical glucose sensors has received continuous interest. Glucose oxidase (GO_x) has been widely used to construct various amperometric biosensors for glucose detection due to its high sensitivity and selectivity to glucose [4]. However, GO_x-based biosensors suffer from problems because of the disadvantages of the enzyme-modified electrodes, such as instability, high cost, complicated immobilization process, the requirement of low temperature storage, and their PH and toxic environment [5–8]. To resolve this problem, many attempts have been made to develop nonenzymatic glucose sensors in recent years. For example, the direct electrocatalytic oxidation of glucose on electrodes modified with metal nanoparticles has been explored in the development of nonenzymatic glucose sensors because it shows good performances through increasing the surface area and enhancing the mass transport and catalysis [9–14]. However, metallic nanoparticles based electrodes usually suffer from the stable problems [15] or high cost [16], which hinders their practical applications. Hence, it is important to develop a fast, sensitive, highly selective, stable, and inexpensive nonenzymatic glucose sensor. In contrast, metal oxides based glucose sensors have been widely investigated for nonenzymatic detecting due to their good stability and low cost.

CuO, as a *p*-type semiconductor with a narrow band gap of 1.2 eV, has been widely studied because of its numerous applications in catalysis, gas sensors, lithium-ion battery, and field transistors [17–20]. Meanwhile, nanostructured CuO is a very economic functional material which is promising in the development of nonenzymatic glucose sensors because of its highly specific surface area, good electrochemical activity, and the possibility of promoting electron transfer reactions at a lower overpotential [21]. It is well known that the microstructures (crystal size, aspect ratio, density, etc.) and morphologies of metal oxide nanoparticles play a determining role for the activity, selectivity, and stability in a catalytic process. Thus, a variety of CuO nanomaterials with different morphologies including nanowires [22], nanospheres [23], nanosheets [24], and flower-like nanostructures [25] have been synthesized in order to achieve enhanced performance for the monitoring and detection of glucose. In comparison to nanostructures, structured CuO films could avoid the drawbacks of complex fabrication processed, harsh modification

conditions for electrodes, expensive glassy carbon electrode, and possible decline of electron transfer rate between isolated nanostructures and electrodes. Recently, CuO nanostructures (nanosheets [26], nanobelts [27], and nanowalls [28]) on Cu foils directly applied for glucose sensing have been explored. To the best of our knowledge, CuO grown directly on electric and biocompatible substrate, which acts as electrode for detection of glucose have been rarely reported. Here, we design a new CuO film on Ti substrate (CuO/Ti) electrode by effectively taking advantage of the conductivity and biocompatibility of the substrate. The CuO/Ti electrode, fabricated simply by a template-free hydrothermal method, can be an inexpensive and high-performance alternative to conventional CuO electrodes for use in biosensors. There is no need to use extra binders or other classical electrodes such as glassy carbon and Au electrode. We investigated the application of this new electrode for glucose determination. In addition, we demonstrated that the fabricated glucose biosensor exhibited high sensitivity, fast response, an appropriate linear range, and good stability. The good analytical performance, low cost, and one-step preparation method make this electrode material promising for the development of a nonenzymatic glucose sensor.

2. Experimental Details

2.1. Reagents and Materials. $Cu(NO_3)_2{\cdot}3H_2O$, NaOH, urea, and glucose are purchased from Shanghai Chemical Co. (China). All chemicals used are analytical grade and are used as received without further purification. The titanium foil is of 99% purity. Glucose solution containing various concentrations is freshly prepared daily. All aqueous solutions are prepared in distilled water.

2.2. Preparation of CuO Films on Ti Substrate Electrodes. In a typical process, 1 m mol $Cu(NO_3)_2{\cdot}3H_2O$ and 10 m mol urea were dissolved in 80 mL distilled water to form a blue transparent solution. Then, the solution was transferred into a Teflon-lined autoclave (a piece of Ti substrate washed by hydrofluoric acid/water was placed upright in the autoclave). After that, the autoclave was placed in an electric oven at 120°C for 12 h. Lastly, the substrate was washed with distilled water and dried at room temperature. In this way, CuO films could be fabricated on the Ti substrate by a simple method with low cost. This opened up the possibility of large-scale preparation of the novel probe which can be applied as the electrode for a glucose sensor.

2.3. Sample Characterizations and Electrochemical Test. The film was characterized using powder X-ray diffraction (XRD, Y-2000) with Cu Kα radiation (λ = 1.5418 Å) and scanning electron microscopy (SEM, JSM-6700F). All electrochemical measurements were performed on a CHI 660C electrochemical workstation (Shanghai, China) with a conventional three-electrode system composed of a platinum auxiliary, a saturated calomel electrode (SCE) reference, and CuO films grown on Ti substrate as working electrodes. All electrochemical experiments were performed in 0.1 M NaOH solutions under continuous stirring at room temperature. Glucose concentration was controlled by addition as desired.

3. Results and Discussion

3.1. Morphology and Structure of Obtained Sample. XRD pattern of the as-obtained sample is displayed in Figure 1(a). Except for the peaks originating from the Ti substrate, others are the peaks of monoclinic phase of CuO (JCPDS number 89-5899) with lattice constants of a = 0.469 nm, b = 0.342 nm, and c = 0.513 nm. The major sharp peaks at 35.5° and 38.7° are attributable to the (002) and (200) plane, respectively, indicating pure phase monoclinic crystallites. Figure 1(b) illustrates a typical optical image of CuO film grown on Ti substrate. As it is obvious from the image, the prepared CuO film is uniform on Ti substrate on a large scale. The typical morphology of the as-obtained CuO film, as observed by SEM, is illustrated in Figures 1(c) and 1(d) at different magnifications. Figure 1(c) is the low-magnification SEM image. It can be seen that the substrate is absolutely covered by uniform maize cob-like CuO nanostructures. From Figure 1(d), it is displayed that maize cob-like nanostructure is composed of many small nanoparticles, which has the potential to provide large surface area and high surface energy for catalytic reaction. The mechanism for the direct growth of CuO film on Ti substrate could be ascribed to the uniform roughness of etched Ti substrate surface. Roughness of substrate surface is especially valuable to the reduction of binding energy between seeds and substrate [29]. Therefore, it is more convenient for the nucleation and adhesion of seeds to be done on rough surface than on smooth surface.

3.2. Electrochemical Activities. The electrocatalytic activity of the CuO/Ti electrode towards the oxidation of glucose in alkaline solution was demonstrated by voltammograms (CV_s). The CV_s of the CuO/Ti electrode were conducted in 0.1 M NaOH solution in the presence and absence of glucose, respectively, at a scan rate of 100 mV/s.

As shown in Figure 2, only small background current and no peak are observed for the pure Ti electrode, while a dramatic increase of current signal with a wave potential of about +0.58 V is observed when the CuO/Ti electrode is used, which should correspond to a Cu(II)/Cu(III) redox couple. This result is similar to precious reports [30, 31]. This indicates that CuO nanostructures have greatly improved the performance of the electrode and increased the electrocatalytic ability towards glucose oxidation, which may be attributed to their large surface, high surface energy, and enhanced electron transfer ability [23]. The good electrochemical ability and easy fabrication method make the as-obtained CuO/Ti electrode an excellent electrochemical sensing platform for glucose detection. Figure 3(a) displays a typical amperometric response curve of the CuO/Ti electrode to the successive addition of glucose at an applied potential of +0.58 V in 0.1 M NaOH recorded at an interval of 50 s. A well-defined, stable, and fast amperometric response could be observed with successive addition of glucose to NaOH. As the

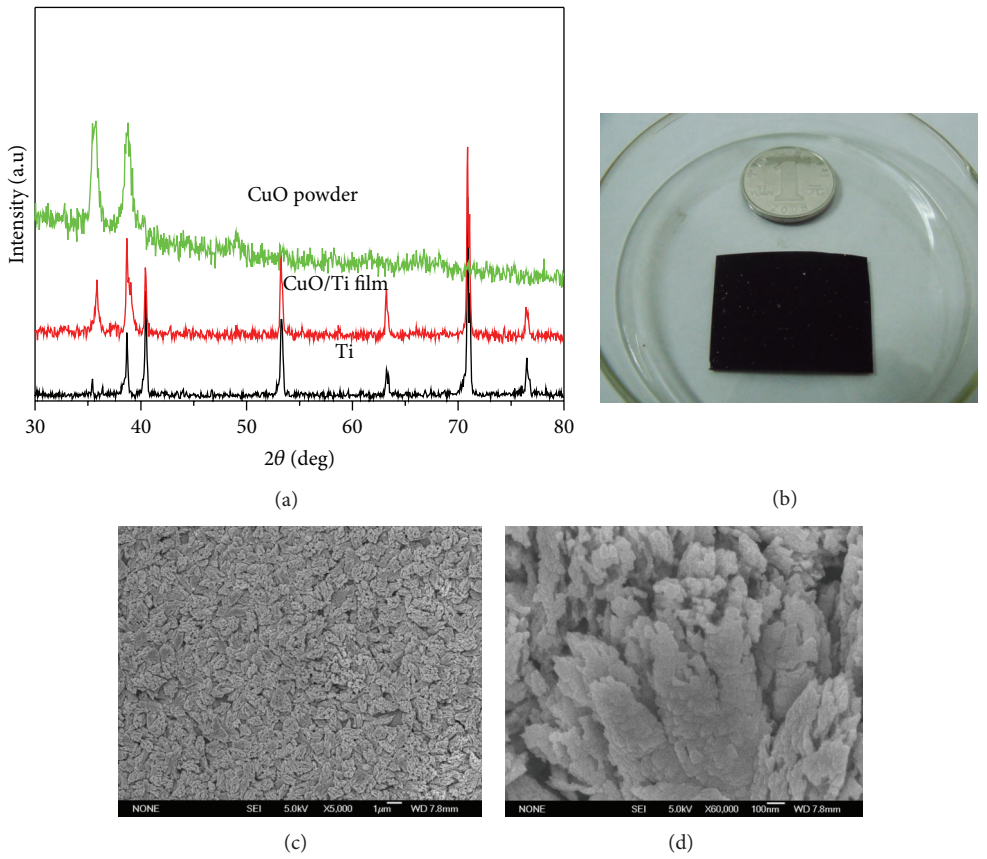

Figure 1: (a) XRD pattern of Ti substrate, CuO film on Ti substrate, and CuO powder, (b) optical image, (c) low-magnification, and (d) high-magnification SEM images of as-prepared CuO film on Ti substrate.

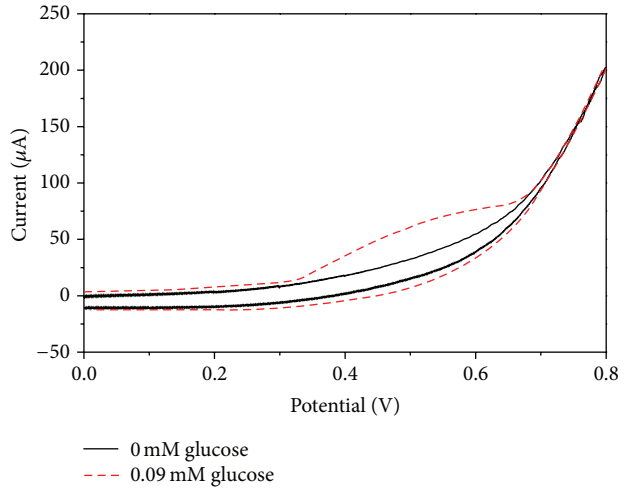

Figure 2: Cyclic voltammograms of CuO film electrode in absence and presence of glucose in 0.1 M NaOH solution at a scan rate of 100 mV/s.

glucose was injected, the biosensor yields a typical steady-state amperometric response. The average time required to reach the stable response is less than 2 s, demonstrating a fast current response to glucose. Meanwhile, as can be seen from Figure 3(b), the CuO/Ti electrode gives a linear dependence range from 5 μM to 1.6 mM of glucose, a remarkably high sensitivity of 726.9 μA mM^{-1} cm^{-2}, and a low detection limit of 2 μM.

Although the direct electrocatalytic oxidation of glucose at copper-based electrode remains ambiguous till now, the Cu^{2+}/Cu^{3+} redox couple is considered to be playing an important role for carbohydrate oxidation because it has been reported to be strongly dependent upon the hydroxide concentration. Hydroxyl radicals are probably formed in the OH oxidation at Cu(III) catalytic centre during the potential window, which react with the organic molecules through the abstraction of a hydrogen atom from the carbon in a position with respect to –OH group [32]. Large surface area and strong electron transfer rate from electrode to glucose are two commonly important issues responsible for the excellent sensing properties of nonenzymatic glucose sensors. As for as-obtained CuO/Ti electrode, more accessible reaction sites provided by the high-density nanoscale "maize cob-like" CuO building units may generate more Cu(III) species for the adsorption and reaction of glucose molecules, while abundant spacing among the maize-like building units may facilitate the fast diffusion of glucose molecules. In addition, more electron transfer passages and lower charge transfer

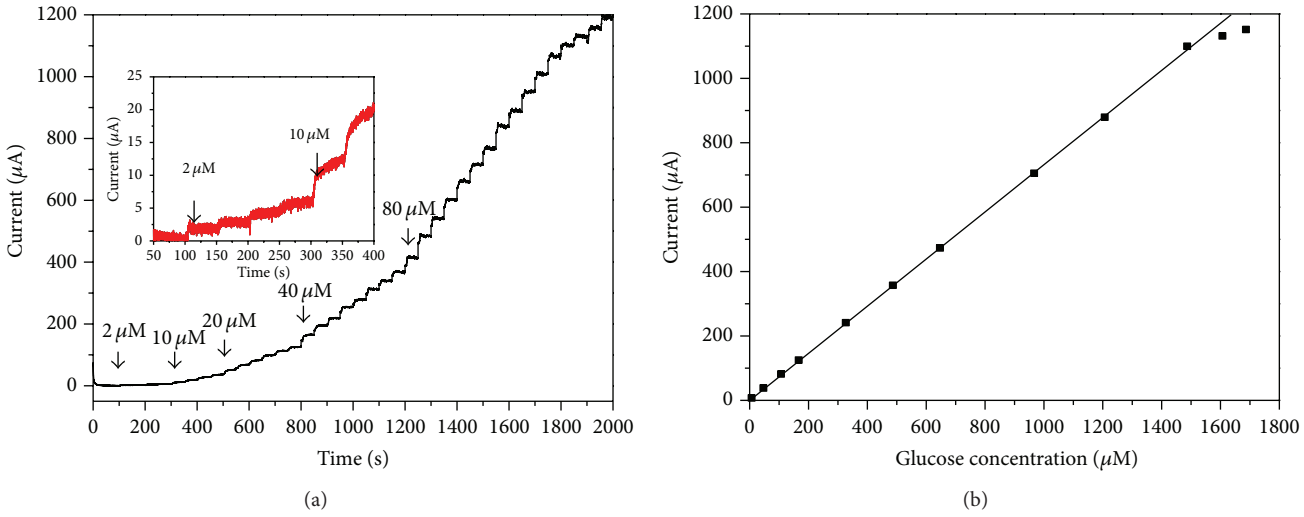

Figure 3: (a) Amperometric responses of the CuO film electrode to successive addition of glucose at applied potential of +0.58 V in 0.1 M NaOH; (b) the calibration curve for the amperometric responses of CuO film electrode. Inset of (a) displays the response to 2 μM and 10 μm glucose of the CuO film electrode.

resistance for hierarchical CuO micro/nanostructures can promote the shuttle of electron between glucose and the working electrode. In a way, in situ fabrication of maize cob-like CuO on Ti substrate may further ensure the direct and fast electron transfer between electrode and electrolyte.

The long-term stability of glucose sensor is a critical factor in practical detection application. The reproducibility and stability of the as-obtained sensor were evaluated by the comparison of the sensitivity of different electrodes. Six different electrodes were made under the same fabrication condition and their current responses to glucose at +0.58 V were investigated. The relative standard deviation (RSD) is 3.5%, which shows highly reproducible. Thirty successive measurements of glucose on one electrode yield an RSD of 4.1%, demonstrating that the sensor is stable. It indicates that the glucose sensor based on CuO/Ti electrode has good reproductivity and long-term stability. The excellent long-term storage stability of the electrode can be attributed to the strong adhesion of CuO/Ti substrate, as well as the chemical stability of CuO in basic solution.

4. Conclusion

We have successfully synthesized CuO films on the Ti substrate by a simple, rapid, and reproducible method. For the first time, we used CuO/Ti as working electrode to detect glucose which is inexpensive and convenient. The novel amperometric glucose sensor based on the CuO/Ti electrode shows high sensitivity, low detection limit, good stability, reproducibility, and fast response time. The CuO/Ti electrode is easily fabricated and afforded an excellent platform for glucose sensor.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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