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A new method for fabricating a CuO/TiO_2 nanotube arrays electrode and its application as a sensitive nonenzymatic glucose sensor

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ABSTRACT

In this report, we presented a new method to fabricate TiO_2 nanotube (TiO_2 NT) arrays modified with cupric oxide (CuO) nanofibers, getting a novel TiO_2 NT arrays composition electrode for sensitive nonenzymatic glucose detection. For the preparation of CuO nanofibers, Cu nanoparticles were firstly electrodeposited onto the TiO_2 NT arrays, and then oxidized to CuO nanofibers followed by annealing in air. The CuO nanofibers modified TiO_2 NT (CuO/TiO_2 NT) arrays electrode for electrocatalytic detection of glucose was investigated by cyclic voltammetry and chronoamperometry in 0.10 M NaOH solution. The linear range of detection of glucose extended up to 2.0 mM ($R = 0.997$, $n = 10$) at a potential of 0.50 V (vs. SCE). The sensitivity was 79.79 $\mu A\,cm^{-2}\,mM^{-1}$, and the detection limit was 1 μM (S/N = 3). Significantly, the poisoning by chloride ion and the interferences from ascorbic acid, uric acid, lactose, sucrose, fructose and dopamine were negligible. Particularly, the CuO/TiO_2 NT arrays electrode showed excellent stability and repeatability over 1 month. The sensor was also investigated detecting glucose in human blood serum samples.

1. Introduction

The development of electrochemical glucose sensor has attracted much attention due to its importance in many areas such as clinical [1,2] and industrial applications [3,4]. Glucose oxidase (GOx) with the property of high sensitivity and selectivity to glucose has been widely used to biosensors for glucose detection. However, there are some disadvantages of the enzyme-modified electrodes, for instance, the electrode is instability, the immobilization procedure is complicated and the enzymes are expensive and easy to lose activation. In order to solve these problems, many efforts have been done to develop nonenzymatic electrode [5]. However, some of the nonenzymatic electrodes have drawbacks just like high cost, which greatly limit their applications. Thus, it is necessary to develop a cheap, stable, high sensitivity and selectivity glucose sensor. There have been some reports of electrochemical sensor based on nanostructured CuO [6–9] because of its highly specific surface area, good electrochemical activity, and the capability of promoting electron transfer rate at low overpotentials [10–12].

CuO is a p-type semiconductor with narrow band-gap (1.2 eV). It exhibits good electrochemical activity and has numerous applications in many fields such as the fabrication of electrical, optical and photovoltaic devices [13], heterogeneous catalysis [14], gas sensors [15], and field-emission emitters [16]. The shape and dimensions of the nano materials have a great influence on their properties [17]. Many kinds of nanostructured CuO have been produced such as nanowires [18], nanorods [19], nano-flowers [19], and these nanostructures can enhance their intrinsic characteristics and their performances on amperometric determination of glucose. However, the fabrications of these nanostructures are time-consuming and complicated. Additionally, enzymatic glucose biosensor based on flower-shaped CuO with a wide linear dynamic range from 0.01 to 10.0 mM must be stored in a 0.01 M PBS at 4 °C after the experiment [20]. Considering these complicated procedures and limited conditions, it would be important to improve a simple method to synthesize nanostructured CuO with excellent catalytic properties for sensitive and stable detection of glucose. At present, many synthetic procedures have produced high-quality CuO nanostructures. However, there is another challenge to research into a method to attach these nanostructures onto a certain solid support and keep their morphology, so that this kind of nanostructure can be available in the applications. So any efforts for fabricating CuO nanostructures on specific substrates and making their growth easier should be promoted.

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Well-aligned TiO_2 nanotube (TiO_2 NT) arrays with large specific surface area and many active sites has attracted extensive interest because of its low cost, and long-term stability, and it has been widely used for photocatalysis [21], dye-sensitized solar cells [22,23], sensors [24,25]. Varghese et al. [26] reported that the TiO_2 NT arrays with highly orientated and excellent semi-conductivity was a sensitive hydrogen gas-responsive material. The TiO_2 NT arrays modified by PtAu nanoparticles [27] had been used to detect H_2O_2. After coating a layer of GOx, the as-prepared electrode had been used as a glucose sensor. However, the detection limit of the electrode of glucose (0.10 mM) was relatively high comparing to the other reports. In order to improve the conductivity of the TiO_2 NT arrays sensor, an amperometric glucose oxidase biosensor TiO_2/carbon nanotubes(CNT)/Pt/GOx was fabricated, and a sensitive response to glucose was achieved [28]. All the successful research results indicated that the TiO_2 NT arrays was a promising functional material for sensor substrate. In this work, we presented a novel and simple seed-mediated synthesis method for the preparation of CuO nanofibers with network-like architectures directly growing on the well-aligned TiO_2 NT arrays for glucose detection.

2. Experimental

2.1. Reagents

Titanium foil (99.8%, 0.25 mm thick), NaF, NaOH, $NaHSO_4$, sodium dodecylsulfate (SDS), $K_2S_2O_8$, $CuSO_4{\cdot}5H_2O$, citric acid, D-glucose, dopamine, ascorbic acid (AA), uric acid (UA), D-fructose, lactose and sucrose of analytical reagent grade were purchased from commercial sources and used as supplied. Double distilled water was used throughout the experiments. All the electrochemical measurements were carried out in 0.10 M NaOH solution unless otherwise specified.

2.2. Synthesis of CuO nanofibers/TiO_2 NT arrays nanostructures

Titanium foils (250 μm thick, 1 cm × 4 cm, 99.8%) were cleaned with ethanol and deionized water to remove impurities prior to anodization. These foils (1 cm × 4 cm) were anodized at 15 V for 1.5 h in a two-electrode electrochemical cell with a platinum foil as a counter electrode in an inorganic electrolyte containing 0.50 M $NaHSO_4$ and 0.10 M NaF, and then washed several times with deionized water followed by heating in atmosphere at 500 °C for 3 h.

A typical three-electrode electrochemical cell was equipped with a Pt foil as the counter electrode, saturated calomel electrode (SCE) as the reference electrode, and the TiO_2 NT arrays (on Ti foil) as the working electrode. The electrolyte solution was $CuSO_4$ aqueous solution with the concentration of 0.005 M. Firstly, the electrodeposition of Cu was carried out with a rectangular potential pulsed mode at an "on" potential of −2.0 V for 0.2 s, and the "off" potential of −0.0001 V for 1 s, with proper pulses. Subsequently, the Cu modified TiO_2 NT arrays (Cu/TiO_2) were washed several times with distilled water. Then, the Cu/TiO_2 NT arrays were immersed into 20 mL of 0.25 M NaOH aqueous solution containing 10 mM $K_2S_2O_8$ and 20 mM SDS at room temperature for different duration time to obtain TiO_2 NT arrays modified by CuO nanofibers. After reaction, the modified TiO_2 NT arrays were rinsed with deionized water and dried in air. Then the products were heated at 120 °C for 1 h and at 180 °C for another 2 h under atmosphere. After being cooled to ambient temperature, the CuO/TiO_2 NT arrays electrode was obtained.

2.3. Characterization

The microstructures of the samples were characterized by scanning electron microscopy (SEM) (JSM 6700 F, JEOL, Japan). The crystal structures of the samples were examined by an X-ray diffractometer (XRD, M21X, MAC Science Ltd., Japan) with Cu Kα radiation (λ) 1.54178 Å.

2.4. Electrochemical experiments

All of the electrochemical experiments were performed by using an electrochemical workstation (CHI600D) with a standard three-electrode system equipped with a Pt foil as the counter electrode and a saturated calomel electrode as the reference electrode. The CuO/TiO_2 NT arrays electrode was evaluated as a glucose sensor in 0.10 M NaOH solution unless otherwise specified. Cyclic voltammetry (CV) measurements were carried out in the potential range of 0–0.8 V (vs. SCE). Linear sweep voltammetry was performed to select the proper concentration of NaOH solution. The amperometric curves were obtained after successive adding the proper amount of glucose into 0.10 M NaOH solution under constant stirring. All the measurements were carried out at room temperature.

3. Results and discussion

3.1. Characterization of the as-prepared CuO nanostructures

The morphologies and crystal phase structures of the prepared vertically aligned TiO_2 NT arrays, Cu/TiO_2 NT arrays and CuO/TiO_2 NT arrays were depicted in Fig. 1. The as-prepared TiO_2 nanotubes (Fig. 1A) show a uniform open-top morphology and highly orientated growth with 90 nm pore size and 20 nm wall thickness. Fig. 1B shows that different sizes of Cu nanoparticals are grown on the surface of the TiO_2 NT arrays. After the sample was oxidized for 3 min in 20 mL of 0.25 M NaOH aqueous solution containing 10 mM $K_2S_2O_8$ and 20 mM sodium dodecylsulfate (SDS), the Cu nanoparticals were partially oxidized to nanofibers that formed to network structure on the surface of the TiO_2 NT arrays without blocking the nanotubes (Fig. 1C). With the oxidation time extension to 6 min, the Cu nanoparticals were oxidized to nanofibers completely (Fig. 1D). Fig. 1E is the 5-fold amplified image of Fig. 1D. As shown in Fig. 1E, the surface of the nanofibers is not smooth but with large numbers of wrinkles, which is very advantageous to increase the specific surface area of the electrode and improve the adsorption capability for glucose.

Fig. 1F shows the XRD patterns of the bare TiO_2 NT arrays and CuO modified TiO_2 NT arrays. Although the major peaks of the CuO crystallites at $2\theta = 35.5^\circ$ and 38.4° are overlapped with the characteristic peaks of Ti, the peak intensity at $2\theta = 35.5^\circ$ of CuO/TiO_2 NT is much stronger than that of bare TiO_2 NT arrays. The peaks of CuO on TiO_2 NT arrays can be indexed to the monoclinic phase of CuO without the peaks of Cu and Cu_2O, indicating that the CuO nanostructure is pure and well crystallized after being annealed in the air. The results confirmed that the CuO was well crystallized on the surface of the TiO_2 NT arrays.

3.2. Electrochemical measurements

The cyclic voltammetry (CV) measurements of the TiO_2 NT arrays electrode and the CuO/TiO_2 NT arrays electrode were conducted in 20 mL 0.10 M NaOH solution in the presence or absence of glucose to investigate the electro catalytic activities. A broad reduction peak at +0.60 V (vs. SCE) that might due to the conversion of Cu(III) to Cu(II) [29,30] is observed at the CuO/TiO_2 NT arrays electrode in 0.10 M NaOH solution (Fig. 2b). However, the oxidation peak corresponding to Cu(II)/Cu(III) range from +0.20 to +0.70 V [31,32] is not obviously observed at the CuO/TiO_2 NT arrays electrode, which could be overlaid by the oxidative peak of water breakdown [33–35]. A single broad oxidative peak, corresponding to the irreversible glucose oxidation, is observed at the CuO/TiO_2

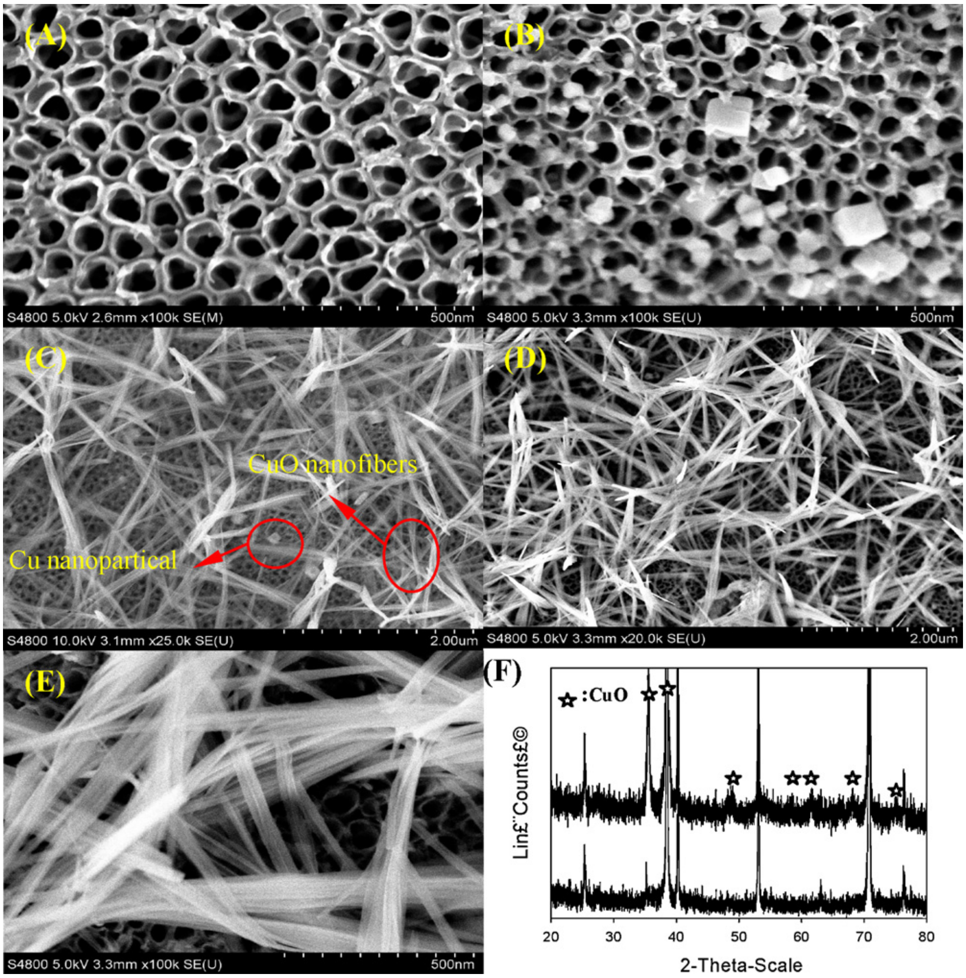

Fig. 1. SEM images of (A) the top view of the TiO_2 NT arrays, (B) Cu nanoparticals modified TiO_2 NT arrays, (C) and (D) CuO/TiO_2 which were obtained by the oxidization of Cu/TiO_2 for 3 min and 6 min, separately. (E) CuO/TiO_2 was obtained by the oxidization of Cu/TiO_2 for 6 min at higher magnification. (F) XRD pattern of bare TiO_2 NT arrays and CuO/TiO_2. (☆) Reflections of CuO.

NT arrays electrode in the solution of 0.10 M NaOH with 1.0 mM glucose (Fig. 2c). The CuO/TiO_2 NT arrays electrode exhibits significant effect on the oxidation of glucose. The oxidation current of the CuO/TiO_2 NT arrays electrode starts to increase quickly at approximately +0.30 V (vs. SCE) with a peak potential at +0.55 V (vs. SCE) and increases continuously to the potential of about +0.65 V (vs. SCE). This may result from the proposed view that copper (II) and copper (III) surface species acted as an electron transfer mediator in the oxidation of glucose [30,34]. In contrast, as shown in Fig. 2a, no peak is observed at the TiO_2 NT arrays electrode in 0.10 M NaOH solution in the presence of 1.0 mM glucose. This indicates that there is a strong electrocatalytic function of CuO nanofibers towards glucose oxidation, which may be attributed to the large specific surface area, and strong electron transfer rate from electrode to glucose.

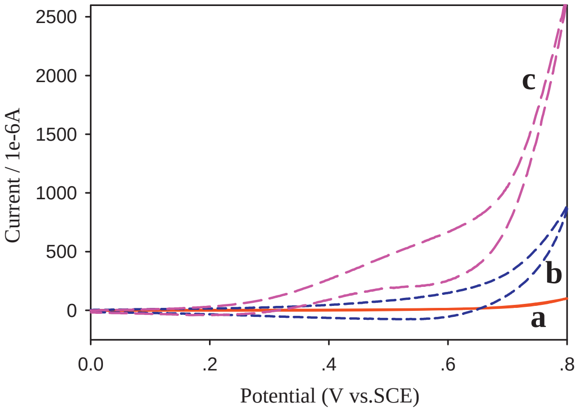

Fig. 2. Cyclic voltammograms of bare TiO_2 electrode (a) and CuO/TiO_2 electrode (c) in the presence of 1.0 mM glucose in 0.10 M NaOH. Cyclic voltammograms of CuO/TiO_2 electrode (b) in 0.10 M NaOH. Scan rate: 100 mV s^{-1}.

Furthermore, we have also investigated the influence of scan rate on the oxidation current of glucose. The oxidative peak current (the corresponding voltage is +0.55 V) of oxidation of glucose exhibited a linear response to the scan rate. As shown in the inset of Fig. 3, a good linearity between scan rate and peak current was obtained within the range of 20–200 mV s^{-1}, $I(\mu A) = 332.62 + 1333V(V\,s^{-1})$, with the correlation coefficient (R) of 0.998. The result indicates that the adsorption ability controlled the electrochemical oxidation of glucose [36].

The influence of pH on the oxidation current and potential of glucose was studied at CuO/TiO_2 electrode in a series of NaOH solutions with different concentrations by linear sweep voltammetry (Fig. 4A). The peak current decreased with increasing the NaOH concentration from 0.01 to 0.05 M, and meanwhile the corresponding peak potential dropped from +0.67 to +0.55 V. However, the peak current increased immediately when the NaOH concentration increased to 0.10 M, and then it was almost stable for the NaOH concentration between 0.10 M and 0.30 M, while the peak potential remained steady when the NaOH concentration was between

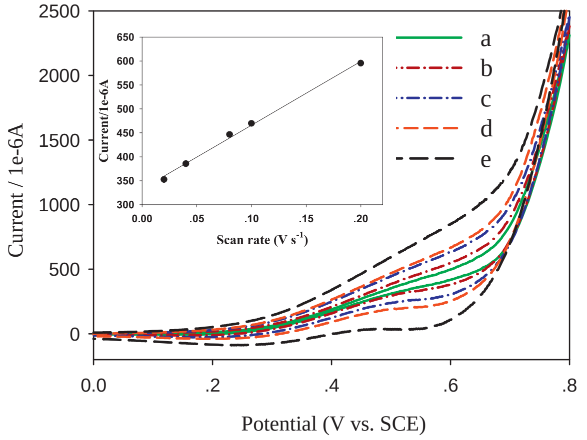

Fig. 3. Cyclic voltammograms of CuO/TiO$_2$ electrode at different scan rates: 20 mV s^{-1}, 40 mV s^{-1}, 80 mV s^{-1}, 100 mV s^{-1}, 200 mV s^{-1} (a–e) in 0.10 M NaOH containing 1.0 mM glucose. Inset shows the dependence of the oxidation peak current of glucose on scan rate.

0.05 M and 0.30 M. The effect of KOH on the electrode response was also investigated. The results showed that there was no difference in the peak current and the peak potential of oxidation of glucose in either 0.10 M KOH solution or 0.10 M NaOH solution. Since higher pH values and higher applied potentials might result in some reactions to disturb the glucose detection [8], 0.10 M NaOH was selected as the assay solution due to its satisfactory response current and peak potential (Fig. 4B).

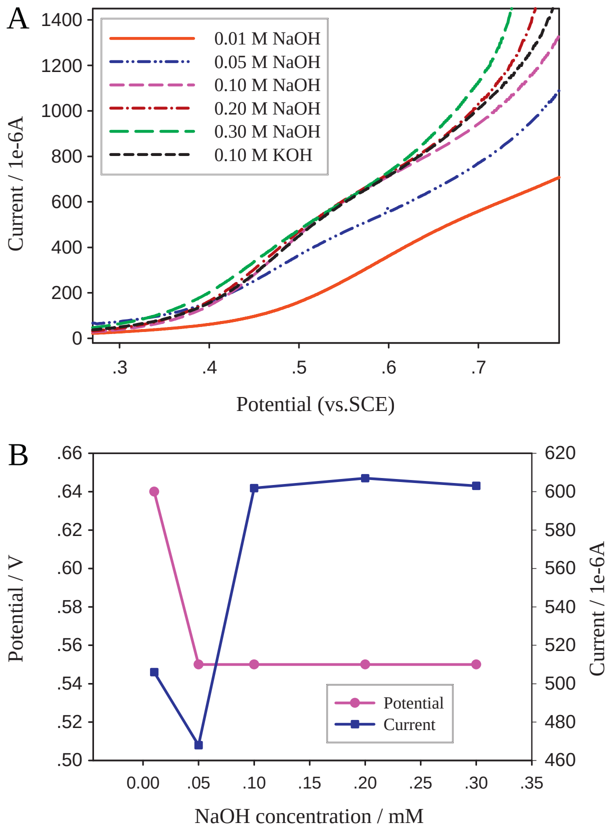

Fig. 4. (A) Linear sweep voltammograms of 1.0 mM glucose at CuO/TiO$_2$ electrode in different concentration of NaOH solution and 0.10 M KOH solution at 100 mV s^{-1}. (B) Effect of NaOH concentrations on peak current and peak potential of oxidation 1.0 mM glucose at CuO/TiO$_2$ electrode.

3.3. *The determination of glucose*

Fig. 5A illustrates the constant potential amperometry responses to successive addition of 0.20 mM glucose into 0.10 M NaOH solution at CuO/TiO$_2$ electrode and bare TiO$_2$ electrode. The upper left inset presents the current–time curve of CuO/TiO$_2$ NT arrays electrode under successive addition of 1.0 μM of glucose with a detection limit of 1.0 μM (S/N = 3). The experiments were conducted under stirring and the applied potential was +0.50 V (vs. SCE). The CuO/TiO$_2$ electrode showed a rapid and sensitive response to the change of glucose concentration, confirming that the CuO nanofibers can increase the electrocatalytic property of the electrode and promote electron transfer in the direct oxidation of glucose. When the glucose was injected into 0.10 M NaOH, the current of the CuO/TiO$_2$ NT arrays electrode immediately achieved stability within 4 s. In contrast, the bare TiO$_2$ NT arrays electrode was hardly active for glucose oxidation. Fig. 5B shows that a linear amperometric response with a wide range of glucose concentrations extends up to 2.0 mM with correlation coefficient 0.997. The sensitivity of CuO/TiO$_2$ NT arrays electrode is 79.79 μA cm^{-2} mM^{-1}. The detection limit of the CuO/TiO$_2$ NT arrays electrode is lower and the sensitivity is higher than other previous reported glucose sensors based on TiO$_2$ NT arrays, CuO nanostructures and noble metals (Table 1). All the data from this sensor show the properties of high sensitivity, low detection limit, wide linear range and fast response time. These results might be attributed to the perfect combination of CuO nanofibers and TiO$_2$ NT arrays, which produced more electrocatalytic active sites and more effective electron transfer for the oxidation of glucose. So the simple fabrication of the CuO/TiO$_2$ NT arrays electrode and its good electrocatalytic ability make it an excellent electrochemical sensor for glucose detection.

3.4. *Reproducibility and stability*

The reproducibility and stability of response current of the CuO/TiO$_2$ NT arrays electrode were tested. Amperometric current responses to succession addition of 0.20 mM glucose were evaluated under the same condition by using five different CuO/TiO$_2$ NT arrays electrodes prepared under the same conditions. The mean value of sensitivity was 79.54 μA cm^{-2} mM^{-1} (Fig. 6A). The relative standard deviation (RSD) was 4.27%, revealing that the preparation method was acceptably reproducible. The current density responses to the addition of 1.0 mM of glucose at the same CuO/TiO$_2$ NT arrays electrode for ten times only changed a little (Fig. 6B), indicating that the CuO/TiO$_2$ NT arrays electrode was stable and can be used repeatedly. In order to investigate the long-term stability of the sensor, the current response to 0.50 mM glucose was also measured during 1 month. The sensor was exposed to air at room temperature and its amperometric current was tested every 2 days. The current density response to the addition of 0.50 mM glucose at the CuO/TiO$_2$ NT arrays electrode after 10 times retained 90% of its original density (Fig. 6C). The results demonstrated that the response changed a little over the investigation period, implying that the electrode can be used in applications for a long time. The good reproducibility and long-term stability of CuO/TiO$_2$ NT arrays electrode can be attributed to both the good stability of CuO modified TiO$_2$ NT arrays in the base solution and good chemical stability of the materials themselves.

3.5. *Selectivity of the CuO/TiO$_2$ NT arrays electrode*

It was reported that most of the electrochemical nonenzymatic glucose sensors based on noble metal [37,38] can easily lose their activities because of the poisoning by the chloride ion, which was abundant in physiological fluids. Thus, the amperometric response

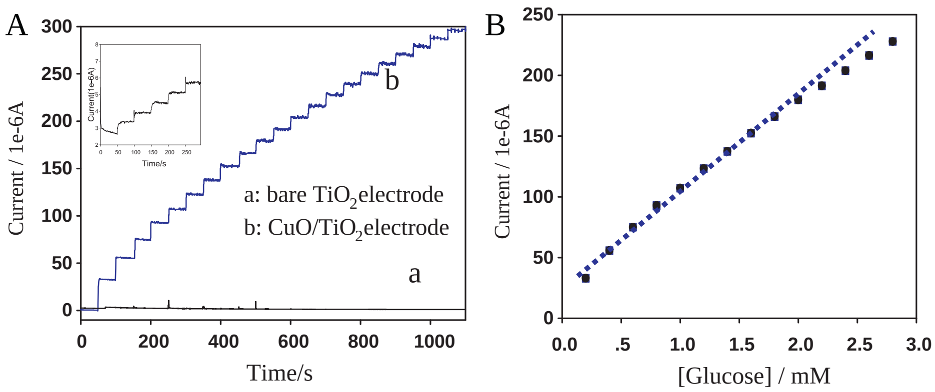

Fig. 5. (A) Amperometric response of sensors: bare TiO_2 electrode (a), and CuO/TiO_2 electrode (b) at +0.50 V to the succession addition of 0.20 mM glucose to the 0.10 M NaOH. The upper left inset shows the response of the CuO/TiO_2 electrode to successive addition of 1.0 μM glucose to the 0.10 M NaOH. (B) The linear relationships between the oxidation current and the concentration of the glucose.

Table 1
Comparison of the performance of the CuO/TiO_2 electrode with other glucose sensors based on different materials.

Electrode	Electrolyte	Detection potential	Detection limit	Sensitivity (μA mM^{-1} cm^{-2})	Linear range	Response time(s)	Ref.
CuO/TiO_2	0.1 M NaOH	0.5 V (vs. SCE)	1 μM	79.79	Up to 2.0 mM	<4	This work
GOx/Pt–Au/TiO_2 NT	pH = 7.3 PBS	−0.2 V (vs. Ag/AgCl)	0.1 mM	0.08366	0–1.8 mM	3	[27]
TiO_2/CNT/Pt/GOx	pH = 7.2 PBS	0.4 V (vs. Ag/AgCl)	5.7 μM	0.24	0.006–1.5 mM	<3	[28]
GE/CuO/GOx/Nafion	pH = 7.4 PBS	0.58 V (vs. Ag/AgCl)	1.37 μM	47.19	0.01–10.0 mM	<5	[20]
Nafion/CuO/GC	0.1 M NaOH	0.6 V (vs. Ag/AgCl)	1 μM	404.53	0–2.55 mM	–	[42]
CuO nanorods/G	0.1 M NaOH	0.6 V (vs. Ag/AgCl)	4 μM	371.43	4 0–8 mM	<10	[19]
CuO flowers/G				709.52	–	∼15	
CuO nanorod	0.1 M NaOH	0.6 V (vs. SCE)	1.2 μM	450 (0–100 μM)	Up to 1 mM	–	[10]
Porous Au	PH = 7.4 PBS	0.35 V (vs. SCE)	5 μM	11.8	2–10 mM	<2	[43]
Pt–Pb/MWCNT	Neutral PBS	0.30 V (vs. Ag/AgCl)	1.8 μM	17.8	Up to 11 mM	12	[44]

GC, glassy carbon; G, graphite; and MWCNT, multi-walled carbon nanotube.

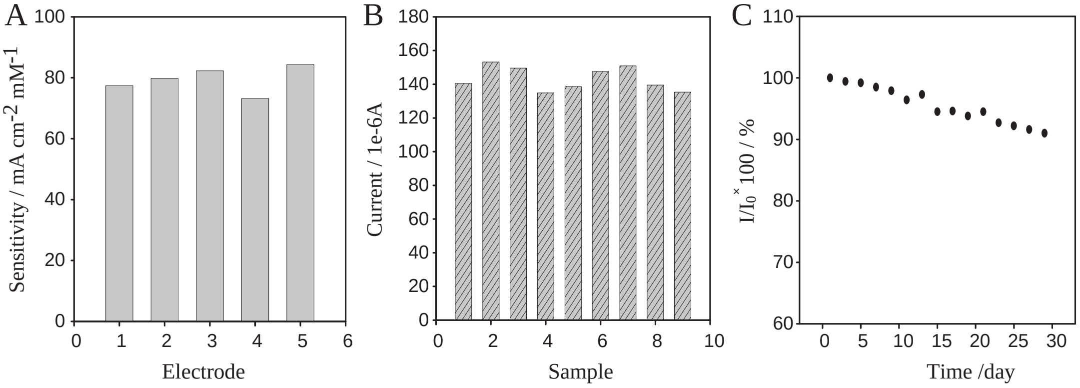

Fig. 6. (A) Sensitivity values of five different CuO/TiO_2 electrodes in glucose concentration range 0.2–2.0 mM. (B) The amperometric responses of one CuO/TiO_2 electrodes to ten different 1.0 mM glucose samples. (C) Long-term stability of a CuO/TiO_2 electrode measured in 1 month.

of the CuO/TiO_2 NT arrays electrode to 0.50 mM glucose in a 0.10 M NaOH solution containing 0.20 M NaCl was examined. The results showed the change of current responses can be negligible in the presence of chloride, indicating the CuO/TiO_2 electrode was hardly poisoned by chloride ion (Fig. 7).

To evaluate the selectivity of the CuO/TiO_2 NT arrays electrode, as shown in Fig. 8, the current responses to several possible interfering biomolecules, such as AA, UA, lactose, sucrose, fructose and dopamine, which normally coexist with glucose in human blood, were examined [39]. Considering that the concentration of glucose in the human blood is more than 30 times of interfering materials, the interference experiment was conducted at CuO/TiO_2 NT arrays electrode by succession addition of 1.0 mM glucose and 0.10 mM interfering materials into 0.10 M NaOH solution. The results showed that a vivid response to glucose, while insignificant responses to interfering materials. The interferences materials current responses ranged from 3.27% (AA) to 1.09% (sucrose) with respect to the current response to 1.0 mM glucose at +0.50 V (vs. SCE) (Table 2). These interference values were much

Table 2
Effect of interfering materials on glucose determination at the CuO/TiO_2 NT arrays electrode.

Interfering materials	Molar ratio (glucose:interferent)	Current ratio (%)
Ascorbic acid	10:1	3.27
Lactose	10:1	1.62
Sucrose	10:1	1.09
Fructose	10:1	2.87
Dopamine	10:1	1.32
Uric acid	10:1	2.88

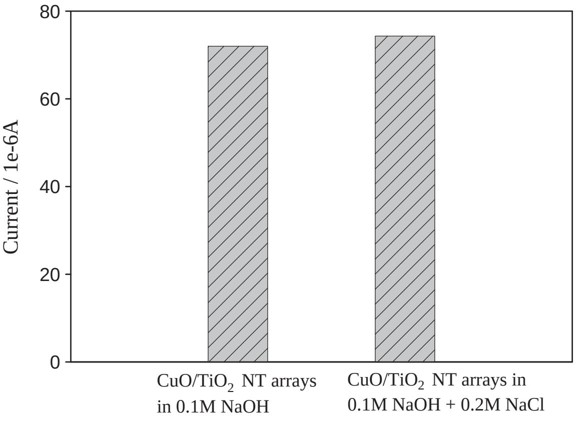

Fig. 7. The current responses of the CuO/TiO_2 electrode to the addition of 0.50 mM glucose in 0.10 M NaOH and 0.10 M NaOH solution containing 0.20 M NaCl, respectively. Data are given the average of three measurements of 0.50 mM glucose.

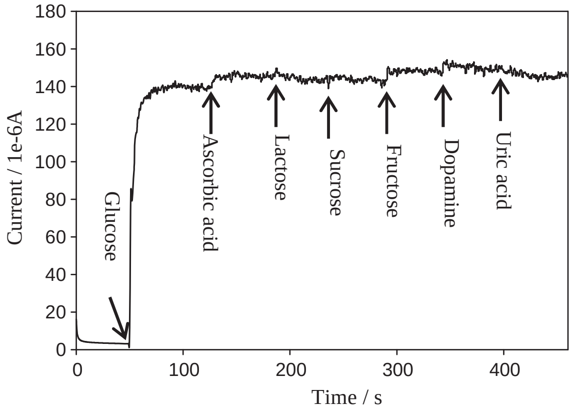

Fig. 8. Amperometric curve of CuO/TiO_2 electrode with successive addition of 1.0 mM glucose, 0.10 mM AA, lactose, sucrose, fructose, dopamine and UA in 0.10 M NaOH solution at 0.50 V.

lower than those of many other glucose sensors [40,41] and even lower than that of the CuO nanospheres electrode, which was modified by Nafion to improve the selectivity [42]. It can be concluded that the CuO/TiO_2 NT arrays electrode showed high selectivity for glucose detection.

3.6. *The detection of real samples*

The applicability of the sensor based on the CuO/TiO_2 NT arrays was explored by detecting glucose in human blood serum sample. 80 μL serum sample was added to 20.0 mL 0.10 M NaOH testing solution under the potential of +0.50 V. The recovery of the glucose was measured by addition of 0.10 mM pure glucose to the solutions containing the serum samples and the results exhibited a good recovery range from 96% to 99% better than that of other sensors [7,45,46]. The determination results were given in Table 3, which demonstrated that the sensor might have a potential application in practice.

Table 3
Determination of glucose in blood serum samples.

Samples	Concentration (mM)	RSD (%)	Added glucose (mM)	Recovery (%)
1	4.2	3.05	0.1	97
2	4.6	1.98	0.1	99
3	5.1	2.54	0.1	96

Each sample was tested in triplicate.

4. Conclusions

In this study, we have successfully prepared TiO_2 NT arrays modified with CuO nanofibers by a novel and simple method. The CuO/TiO_2 NT arrays nanocomposite electrode is used to construct a novel nonenzymatic glucose sensor, which exhibits many attractive features including highly electrocatalytic activity, low detection limit, excellent selectivity, and good stability and reproducibility. This is ascribed to the large electroactive surface area of the CuO/TiO_2 NT arrays electrode and good synergistic effect resulting from the combination of CuO nanofibers and TiO_2 NT arrays. The results show that CuO/TiO_2 NT arrays hybrid nanostructure is an attractive material for the fabrication of excellent amperometric sensor.

Acknowledgments

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