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Highly sensitive nonenzymatic glucose sensor based on electrospun copper oxide-doped nickel oxide composite microfibers

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ABSTRACT

An improved nonenzymatic glucose sensor based on copper oxide-doped nickel oxide composite microfibers (CuO-NiO-MFs) modified fluorine tin oxide (FTO) electrode was prepared by electrospinning and calcination technologies without using any immobilization. The results of cyclic voltammetry (CV) and chronoamperometry demonstrated that the CuO-NiO-MFs modified electrode displayed much higher electrocatalytic activity than the nickel oxide microfibers (NiO-MFs) modified electrode toward glucose. The nonenzymatic glucose sensor based on CuO-NiO-MFs showed the highest sensitivity of 3165.53 $\mu A\,mM^{-1}\,cm^{-2}$ with the lowest detection limit of 1×10^{-9} M (signal/noise ratio (S/N) = 3) in the nonenzymatic glucose sensors that have been reported in the literature. Additionally, its application for detecting glucose concentration of human serum sample showed good agreement with the results obtained from automatic biochemical analyzer.

1. Introduction

Diabetes mellitus is known as a worldwide public health problem [1]. Since the disease is one of the leading causes of death and disability in the world, the efforts to develop various sensors for fast and reliable monitoring glucose for the diagnosis of diabetes have received continuous interest [2]. Electrochemical glucose sensor has been widely investigated for its simplicity, high reliability, sensitivity and low cost [3,4]. The electrochemical glucose sensors usually have two major types, the enzymatic and nonenzymatic sensors. Although the enzymatic glucose sensor based on glucose oxidase shows high selectivity and sensitivity, their inevitable drawbacks such as the chemical and thermal instabilities originated from the intrinsic nature of enzymes have turned recent efforts to direct determination of glucose at nonenzymatic glucose sensors [1,5]. Nonenzymatic glucose sensors can exhibit conveniences and advantages to avoid the drawbacks of enzymatic glucose sensors. Previous studies have focused on the use of noble metal such as gold (Au), platinum (Pt), lead (Pb), palladium (Pd) and their metal alloy electrodes for developing nonenzymatic glucose sensors [6–9]. However, the high cost of the electrode materials may limit their commercial applications since the ability to produce glucose sensors in large numbers at low cost is a major market requirement [10]. Now considerable research has been concentrated on the use of low-cost metal oxide materials such as nickel oxide (NiO) [11–13], copper oxide (CuO) [14,15], manganese oxide [16] and cobalt oxide [17] for nonenzymatic glucose sensors. Among these relatively low-cost metal oxides, NiO materials by virtue of good electrochemical stability and electrocatalytic activity are of particulars interest.

NiO is a p-type semiconductor compound especially if thermally treated at moderate temperatures ranged between 300 and 700 °C [18]. Its conductivity can be increased by the increase of interstitial oxygen atom in NiO [19]. The oxygen atom can lose gradually from NiO with rising the calcination temperature [20]. Therefore, the conductivity of NiO will increase with decreasing the treating temperatures, which leads to the increase of electrocatalytic activity of NiO toward the oxidation of glucose. Beside oxygen atom in NiO, trivalent nickel ions (Ni^{3+}) in NiO are also considered as lattice defects contributing to its electric conductivity. The increase of Ni^{3+} can be realized by doping a lower-valence cation in NiO [21]. In our studies here, the increase of Ni^{3+} was finished by doping CuO in NiO-MFs.

Currently, great efforts have been made to fabricate metal oxide nanofibers by electrospinning and calcination technologies for nonenzymatic glucose sensors, which is because the one dimensional metal oxide nano- or micromaterials exhibit peculiar and fascinating electrochemical performance due to very large surface-to-volume ratio, dimensions comparable to the extension of surface charge region [13,17,22–24]. However, in those reports, immobilization matrix (Nafion solution) has been required to entrap metal oxide nanofibers for electrode attachment. This process is

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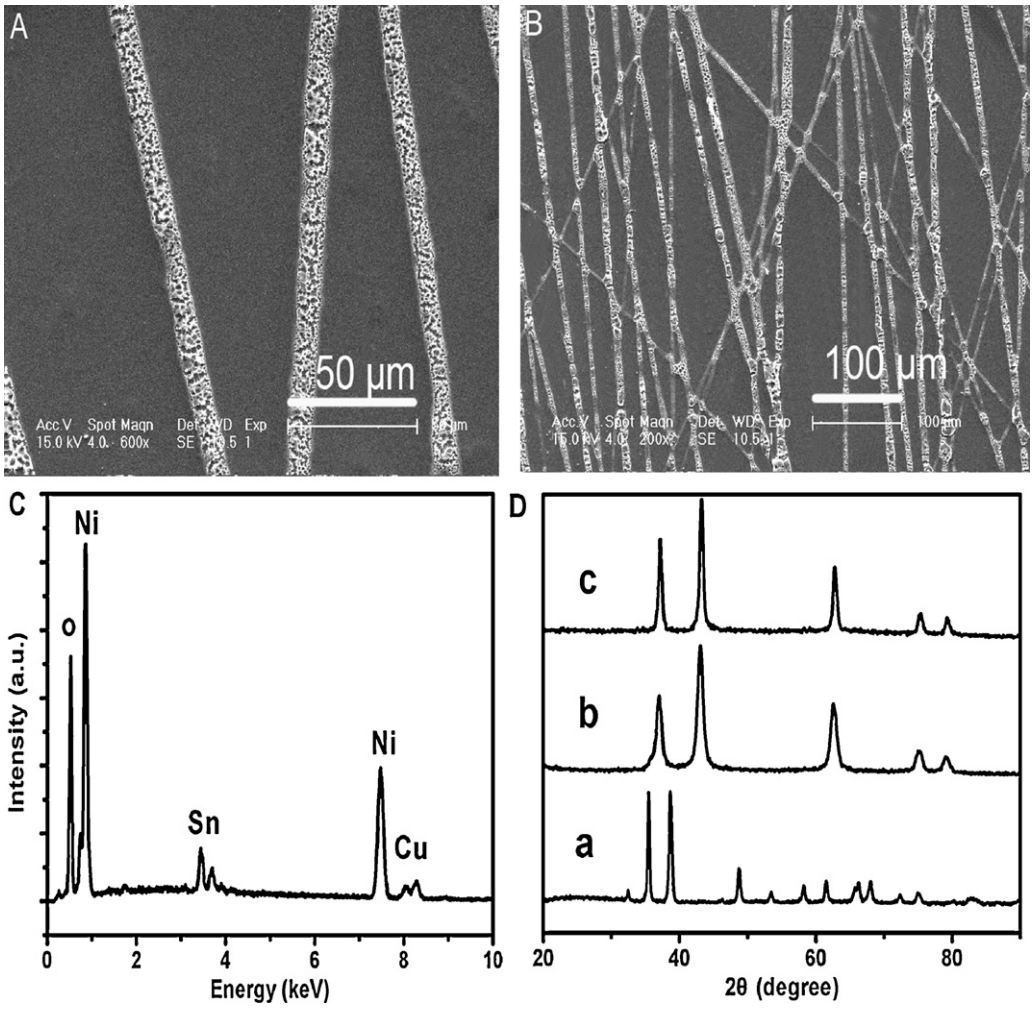

Fig. 1. (A and B) SEM images of the CuO-NiO-MFs immobilized onto FTO electrode; (C) EDX pattern of the CuO-NiO-MFs immobilized onto FTO electrode; (D) XRD patterns of the (a) CuO-MFs, (b) NiO-MFs and (c) CuO-NiO-MFs.

timing-consuming, tedious, and usually leads to poor detecting results. Our interest in this paper is developing a CuO-NiO-MFs modified FTO electrode prepared just by electrospinning and calcination technologies but without using any additional immobilization for nonenzymatic glucose sensor. The nonenzymatic glucose sensor shows the highest sensitivity and the lowest detection limit in the reported nonenzymatic glucose sensors. Meanwhile, an application for determining glucose concentration of human serum sample confirms its high sensitivity and accuracy also.

2. Experimental

2.1. Chemicals and reagents

Polyvinyl alcohol (PVA, Mw = 77,000), nickel nitrate, cupric nitrate and NaOH were purchased from Beijing Chemical Co. (China). Human blood serum sample were provided by Hospital of Northeast Normal University (China). L-Ascorbic acid (AA) and dopamine (DA) were obtained from Sigma–Aldrich. All other chemicals were of analytical grade and used as received without any further purification. Distilled water was used in all experiments.

2.2. Preparation of CuO-NiO-MFs modified electrodes

First of all, FTO substrate (4 cm × 1 cm) was pretreated before it was used for collecting the PVA/copper nitrate/nickel nitrate composite fibers. It was sonicated in acetone, distilled water, concentrated NaOH in 1:1 (v/v) of water/ethanol and distilled water for 10 min, respectively, and dried with nitrogen gas. In order to control the electrode area (1 cm × 1 cm), the FTO substrate was covered partly by a piece of aluminum foil. Secondly, in a typical procedure for electrospinning, 6 g of nickel nitrate and 0.3 g of copper nitrate were added into 5 g of PVA solution (PVA 8.0 wt%) under stirring for 12 h. The viscous sol of PVA with cupric nitrate and nickel nitrate composite was contained in a plastic syringe and connected to a high-voltage power supply for electrospinning. An electric potential of 18 kV was applied between the orifice and the ground at a distance of 10 cm. After electrospinning of 10 min, the piece of aluminum foil was removed from FTO surface. Finally, the precursor FTO substrates were calcined at the setting temperature (300 °C) at a rate of 10 °C/min and remained 3 h to obtain pure CuO-NiO-MFs modified electrodes. The preparation processes of NiO-MFs or CuO microfibers (CuO-MFs) modified electrodes are the same as that of CuO-NiO-MFs modified electrodes, except that 6 g of nickel nitrate or 6 g of cupric nitrate were added into 5 g of PVA solution (PVA 8.0 wt%) under stirring for 12 h for electrospinning.

2.3. Apparatus

Scanning electron microscope (SEM) images were obtained using a XL-30 ESEM FEG scanning electron microscope operated at 20 kV with gold sputtered on samples with energy-dispersive

X-ray (EDX) analysis attached to SEM. X-ray diffraction (XRD) patterns were performed on a D/Max IIIC X-ray diffractometer using a Cu Kα radiation source. Serum sample was measured by automatic biochemical analyzer (HITACHI 7060). All electrochemical measurements were performed on a CHI 800B electrochemical workstation (Shanghai, China) with a conventional three-electrode system composed of a platinum auxiliary, an Ag/AgCl (saturated KCl) reference, and a CuO-NiO-MFs modified electrode. Amperometric measurements were carried out in 15 mL of NaOH solution under continuous stirring.

3. Results and discussion

3.1. Characterization of CuO-NiO-MFs

The morphology of the CuO-NiO-MFs modified electrode can be observed directly by SEM image. Investigation showed that the CuO-NiO-MFs could be well attached to the surface of FTO after calcination when the content of metal salt was more than 50 wt% in precursor sol solution. The SEM images (Fig. 1 A and B) show the tight adhesion between the CuO-NiO-MFs and the surface of FTO after calcination. The average diameter of the microfibers is wide with about 10 μm which is because of the higher content of metal salt [25]. EDX characterization reveals the presence of nickel, copper and oxygen in the microfibers (Fig. 1C). XRD patterns of the pure CuO (curve a), pure NiO (curve b), and CuO-NiO (curve c) microfibers are illustrated in Fig. 1D, respectively. The XRD pattern of the CuO-NiO-MFs only presents five characteristic diffraction peaks corresponding to pure NiO-MFs. The absence of any characteristic diffraction peaks of CuO phase might suggest the amount of CuO added (5.0 wt%) is below the detection limit of XRD technique employed, which is consistent with previous report [26].

3.2. Electrochemical performance of CuO-NiO-MFs modified electrode

CVs of the NiO-MFs, CuO-MFs and CuO-NiO-MFs modified electrodes in 0.1 M of NaOH solution in the potential window ranging from 0.1 to 0.7 V with a scan rate 50 mV s^{-1} are shown in Fig. 2A. As seen, the NiO-MFs modified electrode exhibits a pair of redox peaks with the anodic and cathodic peaks (curve a), which are assigned to Ni(II)/Ni(III) redox couple forming in alkaline medium. A pair of well-defined redox peaks with anodic peak at about 0.5 V and cathodic peak at about 0.37 V is observed at CuO-NiO-MFs modified electrode (curve c). Meanwhile, no redox peaks (curve b) can be observed at the CuO-MFs modified electrode at the electrochemical window. Therefore, the anodic and cathodic peaks in CuO-NiO-MFs modified electrode should be ascribed to Ni(II)/Ni(III) redox couple. Nevertheless, the anodic and cathodic peak currents at the CuO-NiO-MFs modified electrode are larger than those at the NiO-MFs modified electrode. And the background current at CuO-NiO-MFs modified electrode is increased significantly, compared with that at the NiO-MFs modified electrode. The reason can be explained as follow. As it is known, the electrochemical reactions of the Ni^{2+}/Ni^{3+} peaks may be simply described as $Ni^{2+} \leftrightarrow Ni^{3+} + e^-$. However, the amount of Ni^{3+} spontaneously formed at the surface by the electrochemical reactions is still extremely limited [27]. In fact, NiO solid contains some Ni^{3+} before electrochemical reactions, which are considered as lattice defects contributing to its electric conductivity. The concentration of Ni^{3+} can be increased by doping a lower-valence cation [21]. It has been reported that the concentration of Ni^{3+} in NiO increases with doping CuO [26]. The process of increasing Ni^{3+} by adding a small portion of Cu^+ into NiO can be simplified as follows [26,28]:

$$2Cu^+ + 2Ni^{2+} + 1/2O_2 \rightarrow 2Cu^+(Ni^{2+}) + 2Ni^{3+} + O^{2-}$$

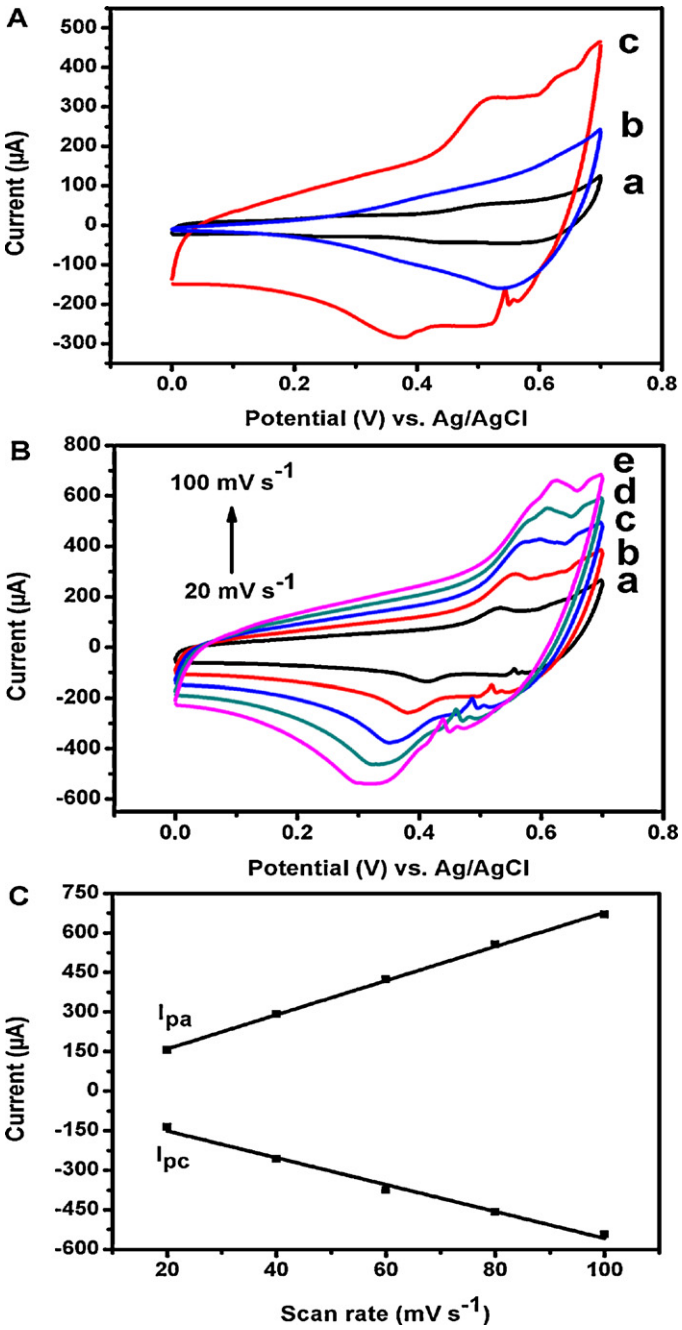

Fig. 2. (A) CVs of (a) the NiO-MFs (b) CuO-MFs and (c) CuO-NiO-MFs modified electrodes in 0.1 M of NaOH solution at a scan rate of 50 mV s^{-1}; (B) CVs of the CuO-NiO-MFs modified electrode in 0.1 M of NaOH solution at scan rates of (a) 20, (b) 40, (c) 60, (d) 80 and (e) 100 mV s^{-1}, respectively; (C) the plot of peak current versus scan rate.

Obviously, the appreciable increase in the Ni^{2+}/Ni^{3+} redox peak currents at CuO-NiO-MFs modified electrode could be thus interpreted in terms of the resulting increase in Ni^{2+}/Ni^{3+} ion pair concentration induced by introducing CuO [29]. Meanwhile, the created Ni^{3+} in NiO due to doping CuO increases the charge carrier concentration and leads to an increase of conductivity. Herein, the drastic increase in background current at CuO-NiO-MFs modified electrode could be ascribed to the resulting increase in conductivity.

Fig. 2B shows the CVs of the CuO-NiO-MFs modified electrode in 0.1 M of NaOH solution at different scan rates. The redox peak currents increase linearly with increasing the scan rate from 20

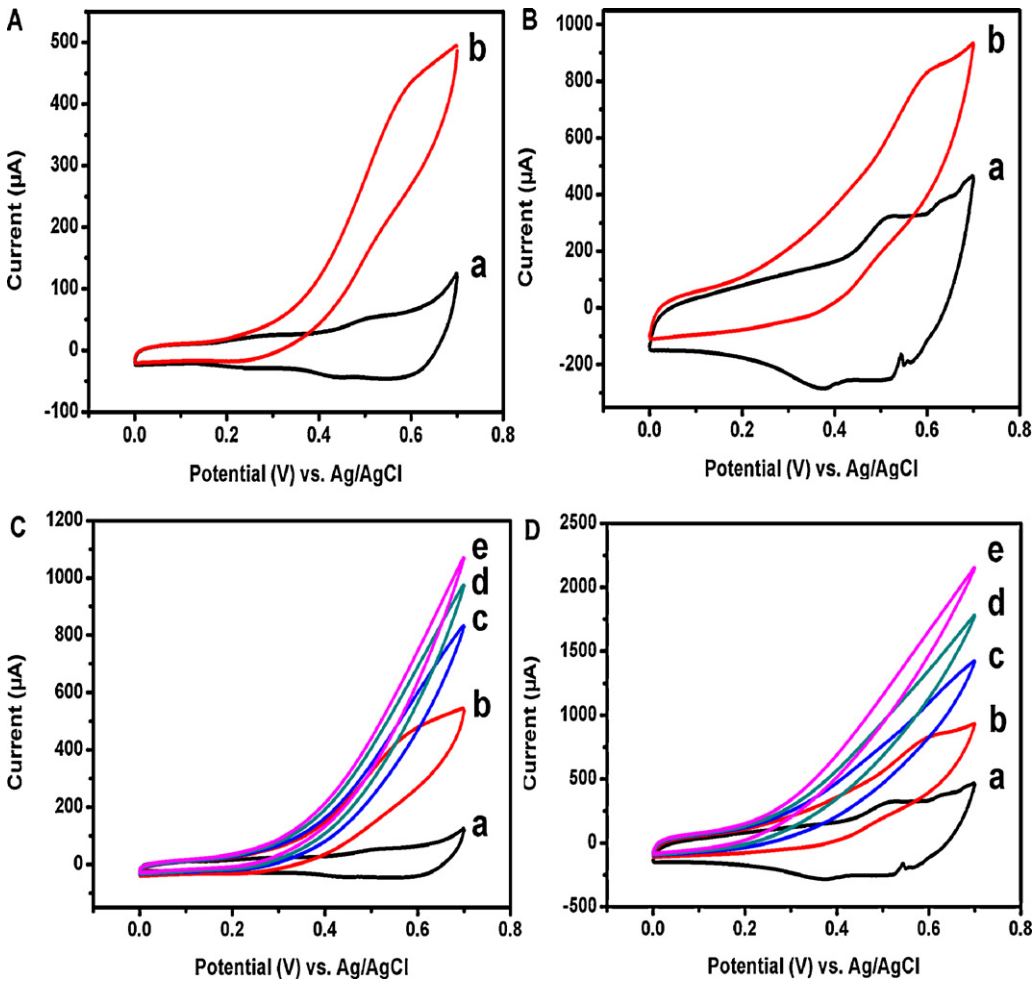

Fig. 3. (A) CVs of the NiO-MFs modified electrode in the (a) absence and (b) presence 1 mM of glucose in 0.1 M of NaOH at a scan rate of 50 mV s^{-1}; (B) CVs of the CuO-NiO-MFs modified electrode in (a) absence and (b) presence 1 mM of glucose in 0.1 M of NaOH at a scan rate of 50 mV s^{-1}; (C) CVs of the NiO-MFs modified electrode in 0.1 M of NaOH at a scan rate of 50 mV s^{-1} with (a) 1, (b) 2, (c) 3, and (d) 4 mM of glucose, respectively; (D) CVs of the CuO-NiO-MFs modified electrode in 0.1 M of NaOH at a scan rate of 50 mV s^{-1} with (a) 1, (b) 2, (c) 3, and (d) 4 mM of glucose, respectively.

to 100 mV s^{-1} (Fig. 2C) with correlation coefficients (R^2) of 0.998 (Ipa) and 0.989 (Ipc), respectively, indicating that the redox process is a typical surface-controlled electrochemical process with a fast electron-transfer behavior [30].

3.3. Electrocatalytic performance of glucose at CuO-NiO-MFs modified electrode

Fig. 3A and B displays CVs behaviors of the NiO-MFs and CuO-NiO-MFs modified electrodes, respectively, in 0.1 M of NaOH solution in the absence (curve a) and presence (curve b) of 1 mM of glucose at 50 mV s^{-1}. Observed from Fig. 3A, oxidation of glucose at the NiO-MFs modified electrode was associated with increasing anodic peak current while diminishing cathodic peak current. As indicated in the literatures [31], the oxidation of glucose to glucolactone was catalyzed by the Ni^{2+}/Ni^{3+} redox couple according to the following reactions:

$$Ni^{2+} \leftrightarrow Ni^{3+} + e^{-}$$

$$Ni^{3+} + \text{glucose} \rightarrow Ni^{2+} + \text{glucolactone}$$

The Ni^{3+} on the electrode surface rapidly oxidizes glucose at anodic, producing Ni^{2+} species and sacrificing Ni^{3+} ones. The produced Ni^{2+} is further oxidized to Ni^{3+} at electrode surface. As

Table 1
Analytical characteristics of the reported nonenzymatic glucose sensors recently.

Electrode	Sensitivity	Detection limit	Linear range	Applied potential	Reference
CuO-NiO microfibers	3165.53 μA mM^{-1} cm^{-2}	0.001 μM	3 μM to 0.51 mM	0.5 V (vs. Ag/AgCl)	This work
NiO nanofibers	32.91 μA mM^{-1} cm^{-2}	1.28 μM	Up to 1.94 mM	0.6 V (vs. Ag/AgCl)	[13]
Co_3O_4 nanofibers	36.25 μA mM^{-1} cm^{-2}	0.97 μM	Up to 2.04 mM	0.59 V (vs. Ag/AgCl)	[17]
CuO nanofibers	431.3 μA mM^{-1} cm^{-2}	0.8 μM	6 μM to 2.5 mM	0.4 V (vs. SCE)	[24]
CuO nanoparticles/MWCTs	2596 μA mM^{-1} cm^{-2}	0.2 μM	Up to 1.2 mM	0.4 V (vs. Ag/AgCl)	[15]
Ni nanowires	1043 μA mM^{-1} cm^{-2}	0.1 μM	0.5 μM to 7.0 mM	0.55 V (vs. SCE)	[31]
Cu nanocubes/MWCTs	1096 μA mM^{-1} cm^{-2}	1.0 μM	Up to 7.5 mM	0.55 V (vs. Ag/AgCl)	[33]
CuO nanoparticles/MWCTs	2190 μA mM^{-1} cm^{-2}	0.8 μM	Up to 3 mM	0.55 V (vs. Ag/AgCl)	[34]
Cu_xO/Cu	1620 μA mM^{-1} cm^{-2}	49 μM	Up to 4 mM	0.5 V (vs. Ag/AgCl)	[35]

a result, the change in concentrations of Ni^{2+} and Ni^{3+} species causes the increase of the anodic peak current and the decrease of the cathodic peak current [31]. Although NiO-MFs and CuO-NiO-MFs modified electrodes all can catalyze the electro-oxidation of glucose, the oxidation peak current at CuO-NiO-MFs modified electrode is significantly larger than that at NiO-MFs modified electrode (Fig. 3B). The observed remarkable electrocatalytic activity at CuO-NiO-MFs modified electrode can be attributed to an enhanced conductivity of CuO-NiO-MFs. Fig. 3C and D presents the CVs in absence and presence of different glucose concentrations at NiO-MFs and CuO-NiO-MFs modified electrodes, respectively. Compared to NiO-MFs modified electrode, with increasing glucose concentration from 1 to 4 mM, the oxidation peak current obtained at CuO-NiO-MFs modified electrode increases steadily. This is because of the saturation of the reaction sites in NiO-MFs [32]. Owing to the resulting increase in Ni^{3+} concentration induced by introducing CuO, the CuO-NiO-MFs can provide more reaction sites on the surface of electrode than NiO-MFs. Therefore, it is reasonable to believe that CuO-NiO-MFs have higher saturation of the reaction sites than NiO-MFs.

3.4. Amperometric performance of glucose at CuO-NiO-MFs modified electrode

3.4.1. Amperometric analysis

Fig. 4A presents a typical amperometric response of glucose in 0.1 M of NaOH recorded at the NiO-MFs (curve a) and CuO-NiO-MFs (curve b) modified electrodes, respectively. Amperometric response curves further demonstrate that the CuO-NiO-MFs modified electrode presents remarkable amperometric determination of glucose compared with NiO-MFs. A well-defined, stable and fast amperometric response with 95% of the steady-state current achieved within 3 s can be observed at CuO-NiO-MFs modified electrode at potential 0.5 V, indicating a rapid oxidation process. Meanwhile, the calibration curve for CuO-NiO-MFs based glucose sensor is worked out, as indicated in Fig. 4B. The proposed glucose sensor displays a linear range from 3×10^{-6} to 0.51×10^{-3} M of glucose with a correlation coefficient of 0.9989, a high sensitivity of 3165.53 $\mu A\,mM^{-1}\,cm^{-2}$ and a low detection limit of 1×10^{-9} M (S/N = 3). The excellent sensing properties of CuO-NiO-MFs modified electrode can be mainly attributed to the resulting increase in Ni^{3+} concentration induced by doping CuO. The created Ni^{3+} in NiO increases the charge carrier concentration which leads to an increase of conductivity. The sensitivity and detection limit of sensor mainly depends on its conductivity. And the increase in Ni^{3+} also provides more reaction sites in CuO-NiO-MFs, resulting in the wide linear range and fast response. Additional, CuO-NiO-MFs immobilized onto electrode surface by direct electrospinning and calcination without using any immobilization matrix ensures that direct electron transfer can be achieved between CuO-NiO-MFs and electrode [32]. That is also an important reason of fast and sensitive catalytic performances. Table 1 shows the comparison of analytical performance of our sensor with other published nonenzymatic glucose sensors. These results show that the glucose sensor based on CuO-NiO-MFs exhibits the characteristics of the highest sensitivity and the lowest detection limit.

NiO is harmful to human health. It can cause intense itching in case of skin contact. Meanwhile, it is toxic to lungs, and causes very hazardous in case of inhalation. Repeated or prolonged exposure to it can produce target organs damage. And it can also cause cancer. To our knowledge, NiO is not an implantable material for detection of glucose in vivo. However, the superior sensing makes CuO-NiO-MFs a good material for amperometric detection of glucose in vitro.

The proposed sensor was applied to the detection of glucose concentration of human serum sample. Fig. 4C demonstrates the amperometric response to successive three repeated additions of analytes in the sequence of 4 μL of blood serum sample, 4 μL 4 mM of glucose, 8 μL of blood serum sample and 8 μL 4 mM of glucose in 0.1 M of NaOH solution. The glucose concentration of human serum sample was calibrated by standard glucose solution and the result was presented in the inset table in Fig. 4C. The same serum sample was also measured by automatic biochemical analyzer in hospital. The good agreement between the results obtained by our proposed sensor and those read from the automatic biochemical analyzer indicates the practical application of the proposed glucose sensor.

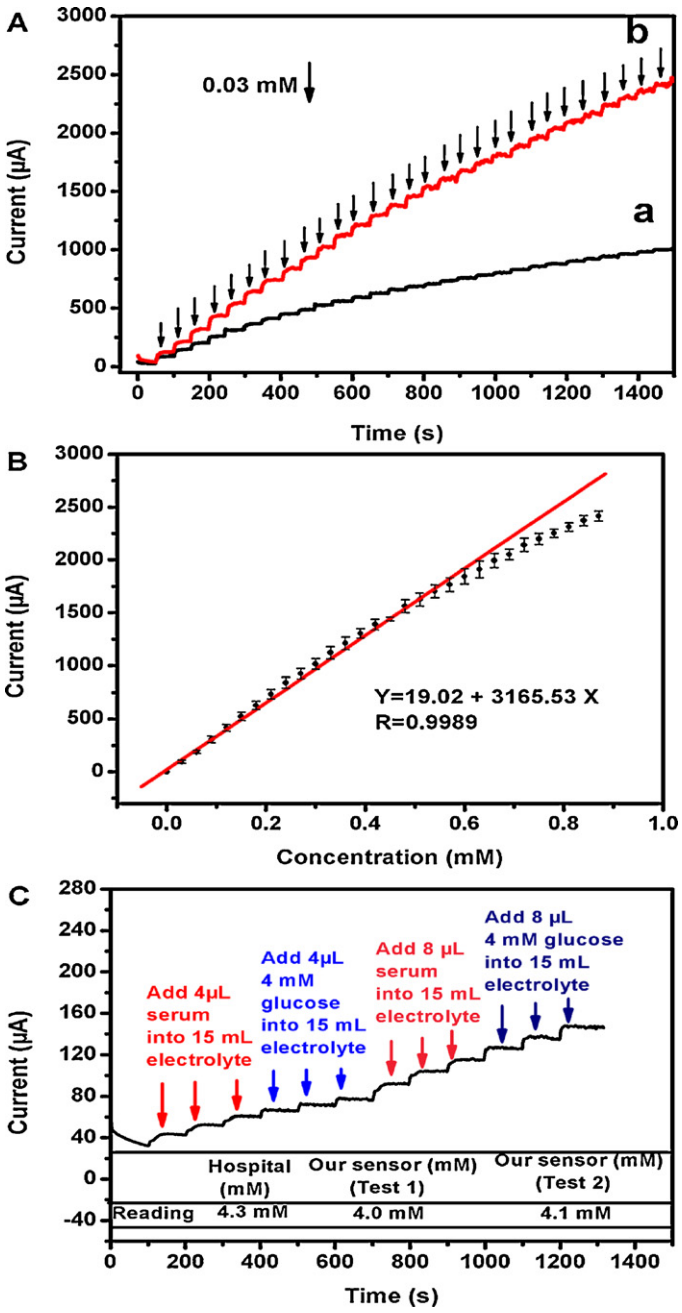

Fig. 4. (A) Amperometric response of (a) the NiO-MFs and (b) the CuO-NiO-MFs modified electrode upon successive addition of glucose at 0.03 mM to 0.1 M of NaOH at an applied potential of 0.5 V; (B) the calibration curve for the amperometric response of the CuO-NiO-MFs modified electrode. Error bars indicate standard deviations for triplicate measurements at each glucose concentration; (C) amperometric response of the CuO-NiO-MFs modified electrode with successive 3-time addition of analytes in the sequence of 4 μL of blood serum sample, 4 μL 4 mM of glucose, 8 μL of blood serum sample and 8 μL 4 mM of glucose in 0.1 M of NaOH solution.

Table 2
Effect of interferents on glucose determination for the CuO-NiO-MFs modified electrode.

Interferents	Glucose:interferent molar ratio	Current ratio (%)
Dopamine	10:1	3.41
Ascorbic acid	10:1	5.90
Urea	10:1	5.23
Lactose	10:1	3.42
Sucrose	10:1	4.02
Maltose	10:1	3.82
Mannose	10:1	2.82

3.4.2. Interferential analysis

As reported, many glucose sensors based on metal and alloy electrodes usually lost their activity because of being poisoned by chloride ions [9]. The poisoning possibility of chloride ions to the activity of CuO-NiO-MFs modified electrode in glucose determination was also examined by adding sodium chloride in the supporting electrolyte in measurement. Our result shows that the linear response of the CuO-NiO-MFs modified electrode remains unchanged toward glucose oxidation, exhibiting good resistance to surface fouling.

AA and DA are the most important interferences normally co-exist with glucose in real samples (human blood). Comparing the amperometric responses for each of the interferences at the same concentration is a more straightforward way to demonstrate selectivity of sensor. Fig. 5A displays the amperometric response to successive four repeated additions of interferences in the sequence of 0.3 μM of DA, 0.3 μM of AA, 0.3 μM of glucose and 3 μM of glucose in 0.1 M of NaOH solution. Investigation demonstrates that the current responses produced by glucose are far higher than that of DA or AA at the same concentration (0.3 μM), implying a good selectivity to glucose. Considering that the concentration of glucose in the human blood is about 30 times of DA or AA [16], the amperometric responses of the CuO-NiO-MFs modified electrode toward the addition of 3 μM of glucose were examined at the same condition. The responses obtained at the CuO-NiO-MFs modified electrode to 0.3 μM of DA and 0.3 μM of AA alone are only 3.41% and 5.90% of that of 3 μM of glucose, respectively. In addition, influences of other carbohydrate compounds on the glucose detection were also examined. The specificity of the senor using various interferents that normally co-exist with glucose in human blood serum is shown in Table 2. The results demonstrate that the CuO-NiO-MFs modified electrode has good selectivity for glucose detection.

3.5. Stability and reproducibility of CuO-NiO-MFs modified electrode

The stability of the CuO-NiO-MFs modified electrode was evaluated by measuring its current response to 2 mM of glucose within a 15-day periods (Fig. 5B). The CuO-NiO-MFs modified electrode was exposed to air and its current response was tested every day. The sensor based on CuO-NiO-MFs shows a good stability with a loss of only approximately 18% in current response after 15 days.

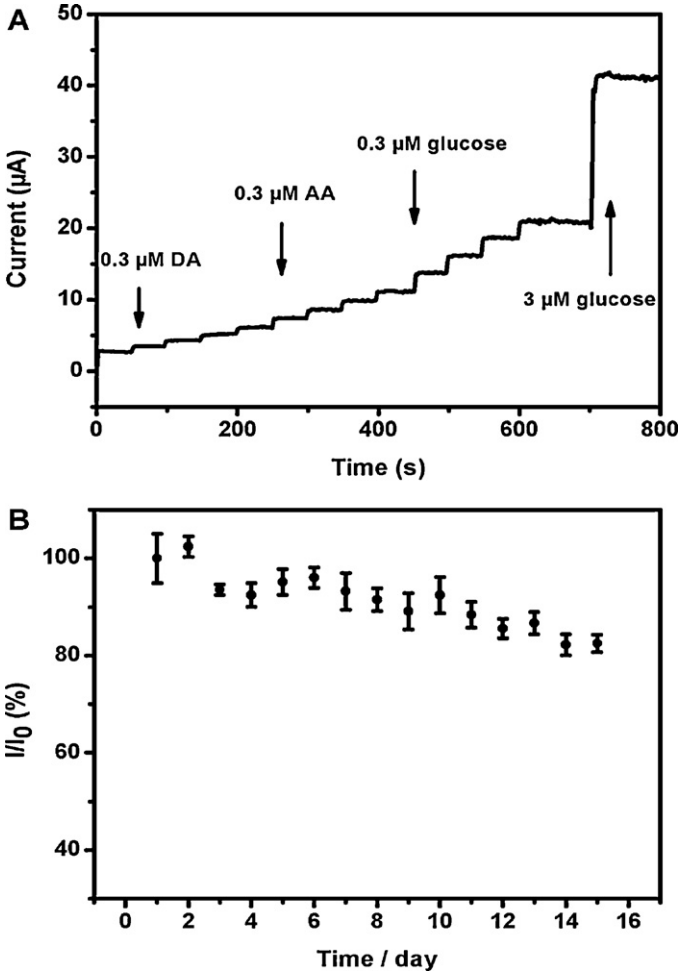

Fig. 5. (A) Amperometric response of the CuO-NiO-MFs modified electrode with successive 4-time additions of interferences in the sequence of 0.3 μM of DA, 0.3 μM of AA, 0.3 μM of glucose and 3 μM of glucose in 0.1 M of NaOH solution; (B) stability of the CuO-NiO-MFs modified electrode stored at ambient conditions over 15-day periods in the presence 2 mM of glucose in 0.1 M of NaOH solution. Error bars indicate standard deviations for triplicate measurements.

Concerning the reproducibility, five CuO-NiO-MFs modified electrodes were prepared with relative standard deviation (RSD) of 5.34% for the current response to 2 mM of glucose, indicating a satisfied electrode-to-electrode reproducibility. Additionally, the RSD of 4.06% ($n = 5$) for 2 mM of glucose demonstrated good intra-electrode reproducibility. Therefore, the CuO-NiO-MFs are good electrode material for preparation of sensitive, stable and reproducible amperometric sensors for glucose determination.

3.6. Determination of glucose in biological samples

In order to further verify the sensor reliability, the recoveries of glucose in urine and serum samples were testified, respectively.

Table 3
Determination of glucose in urine and serum samples.

Sample type	Sample no.	Spiked (mM)	Found (mM)	RSD[a] (%)	Recovery (%)
Urine	1	0.03	0.0306	1.68	102.00
	2	0.06	0.0570	2.65	95.00
	3	0.6	0.565	3.09	94.17
Serum	1	0.03	0.0302	1.02	100.67
	2	0.06	0.0598	1.78	99.67
	3	0.6	0.558	2.90	93.00

[a] There are five measurements.

Urine and serum samples were obtained from a normal healthy man. The urine and serum samples were diluted 50 and 100 times, respectively, with 0.1 M of NaOH before measurements. Amperometric studies were performed before and after addition of glucose into these diluted samples using the CuO-NiO-MFs modified electrode. The results obtained are listed in Table 3. Analytical recoveries indicate that the sensor could be used for the determination of glucose in biological samples.

4. Conclusions

In summary, a nonenzymatic glucose sensor based on CuO-NiO-MFs modified FTO electrode has been successfully prepared by electrospinning and calcination without using any immobilization. The sensor based on the CuO-NiO-MFs exhibits a series of good sensing properties: high sensitivity, low detection limit, wide linear range as well as fast response time. The distinct improvement can be attributed to the tight adhesion between the composite microfiber and the surface of FTO electrode and the increase of Ni^{3+} in NiO microfibers by doping CuO which not only improves the conductivity of the NiO microfibers but also provides more reaction site on the surface of electrode. When these superior sensing performances are combined with long-term stability, good reproducibility and excellent selectivity to glucose in the presence of common interfering species, the CuO-NiO-MFs modified electrode is a promising candidate for effective nonenzymatic determination of glucose. The application for detecting glucose concentrations in real samples was demonstrated.

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