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Facile synthesis of nanospindle-like Cu_2O/straight multi-walled carbon nanotube hybrid nanostructures and their application in enzyme-free glucose sensing

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ABSTRACT

A type of nanospindle-like Cu_2O/straight multi-walled carbon nanotubes (SMWNTs) nanohybrids modified electrode for sensitive enzyme-free glucose detection has been fabricated, where the morphology of the nanohybrids were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and X-ray powder diffraction (XRD). The electrochemical characteristics of this electrode material were investigated by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). The as-prepared nanospindle-like Cu_2O/SMWNTs nanohybrids exhibit much higher electrocatalytic activity on the oxidation of glucose than the SMWNTs or Cu_2O alone as the electrode modifying material, which attributes to high catalytic active sites provided by the nanospindle-like Cu_2O and high electron transfer rate provided by an efficient electrical network formed by Cu_2O and SMWNTs. The proposed sensors exhibit linear behavior in the concentration range from 500 nM to 2.5 mM for glucose with a high sensitivity of 2143 $\mu A\,mM^{-1}\,cm^{-2}$ and a limit of detection of 200 nM (3σ). More importantly, the nanohybrids modified electrode also show good stability, reproducibility and high resistance against poisoning by chloride ion and the commonly interfering species such as ascorbic acid, dopamine, uric acid and acetamidophenol. These good analytical performances make the nanospindle-like Cu_2O/SMWNTs nanohybrids promising for the future development of enzyme-free glucose sensors.

1. Introduction

The development of sensing devices for the reliable and fast monitoring of glucose is of considerable importance in many areas such as clinical diagnostics, biotechnology, and the food industry [1,2]. Due to the inevitable drawbacks of the intrinsic nature of enzymes such as the chemical and thermal instability, direct electrocatalytic oxidation of glucose through enzyme-free sensors has aroused great interest in recent years [3–6]. In the fabrication of enzyme-free glucose sensing devices, it is crucial to develop the highly electrocatalytic activity of the electrode materials. Currently, different metals (Au, Pt, Pd, Cu, Ni,) metal oxides (CuO, NiO) and alloys (Pt–Pb, Pt–Ir, Pt–Au) have been explored as electrode materials to construct enzyme-free sensor devices for the glucose detection [7–13,6,14,15]. Among these, as an important class of p-type semiconductor metal oxides, copper oxides (CuO, Cu_2O) have attracted considerable attention in enzyme-free glucose sensors due to their high electrocatalytic activity, resulting from the multi-electron oxidation mediated by surface metal oxide layers [16–24]. Because of the fact that the catalytic activities of the nanoscaled materials are closely related to their shapes, many efforts have been made on amperometric determination of glucose using nanostructured copper oxides with various morphologies including particles [16], fibers [17], platelets [18], spindles [18], wires [18,21], rods [19], flowers [19,20], urchins [22], cubes [23] and spheres [24]. For example, Wang et al. synthesized CuO nanostructures of flowers and rods and successfully applied them for glucose sensing [19], and Zhuang et al. developed an improved sensitivity glucose sensor based on CuO nanowires modified Cu electrodes [21]. Nanospindles, which are made up of nanoparticles, exhibit larger surface and more electron transfer passage compared to other morphologies [18]. These unique structures and electrical properties endow them with new and important catalytic activities. However, the synthesized CuO nanospindles are easily agglomerated, which greatly limits their application in enzyme-free glucose sensors.

Carbon nanotubes (CNTs) have been widely used as metal or metal oxides scaffolds in enzyme-free sensors due to large surface area, high electrical conductivity, and excellent mechanical properties [25,26]. The physical and chemical properties of the nanotubes deposited metals or metal oxides may be changed to obtain desired properties [27–31]. For example, the combination of CNTs and copper oxides has been successfully applied for glucose determination [32–34]. However, these methods involve harshly acid-oxidized pretreatment of CNTs, which losses their high electrical conductivity and results in the poor sensitivity for glucose detection.

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Herein, we prepared a type of nanospindle-like Cu_2O/straight multi-walled carbon nanotubes (SMWNTs) hybrid nanostructures by precipitation method and developed an enzyme-free glucose sensor with high electrocatalytic activity. Comparing with the tangled CNTs widely applied in nonenzymatic sensors, SMWNTs can be more easily dispersed in solution after mild sonication pretreatment due to the weaker van der waals attraction force in SMWNTs bundles, and keep their high electrical conductivity and mechanism properties. These properties facilitate Cu_2O nanospindles homogeneously distributed in the SMWNTs conductive networks. The well-distributed Cu_2O nanospindle can be easily and fully accessing to glucose, and amplifying the electrochemical signal for glucose determination. An efficient conductive network formed by Cu_2O nanospindle and SMWNTs can promote the electron transfer rate and improve the sensitivity. In these nanohybrids, SMWNTs act as the conductives for dispersing and connecting nanospindle-like Cu_2O catalysts. Moreover, the Cu_2O/SMWNTs nanohybrids can be prepared on a large scale by homogeneous reaction, thus making them exhibit excellent reproducibility in the real sample analysis. This new nanocomposite material combined the advantageous features of SMWNTs and nanospindles-like Cu_2O, and greatly improved the electrocatalytic properties of glucose oxidation and detection.

2. Experimental

2.1. Reagents and materials

Straight multi-walled carbon nanotubes (SMWNTs) were prepared according to the previous report [35]. Prior to use, SMWNTs were pretreated by sonicating in a mixture of concentrated HNO_3 and H_2SO_4 (1:3) for 30 min, and then washed with ultrapure water until the pH of the resulting solution become neutral. D-(+)-Glucose, dopamine (DA), 4-acetamidophenol (AP), ascorbic acid (AA), uric acid (UA), $Cu(NO_3)_2$ were obtained from Alfa Aesar. All of other reagents were of analytical grade and used without further purification. Double distilled ultrapure water with an electric resistance >18.3 MΩ was used for all solution preparation.

2.2. Apparatus

Electrochemical measurements were executed on a CH Instruments model 760D electrochemical analyzer (Shanghai, China) controlled by a PC. Scanning electron microscopy (SEM) images were conducted using FEI Nova NanoSEM 200. Transmission electron microscopy (TEM) was taken with a Tecnai G2 F30. X-ray diffraction analysis (XRD) was recorded on a Smart APEX CCD, Bruker, Germany.

2.3. Synthesis of the Cu_2O/SMWNTs hybrid nanostructures

The nanospindle-like Cu_2O/SMWNTs nanohybrids were synthesized using a simple precipitation procedure. In brief, 15 mg of $Cu(NO_3)_2$ and 30 mg of pretreated SMWNTs were first dissolved in 20 mL distilled water and ultrasonicated for 30 min at room temperature. Then, 60 mL of 2 mM NaOH solution was dropwise added to the above mixture solution under constant stirring at 80 °C. The reaction was carried out for 2 h and a brown precipitate of $Cu(OH)_2$/SMWNTs nanohybrid was produced. Finally, the $Cu(OH)_2$/SMWNTs nanohybrids were filtered and rinsed several times with deionized water, followed by heat treatment at 180 °C for 2 h to get the Cu_2O/SMWNTs nanohybrids.

2.4. Electrochemical measurement

Glass carbon (GC) electrode with a diameter of ~3 mm was polished on a microcloth with 0.3 and 0.05 μm alumina slurry for 5 min, followed by sonicating in ultrapure water and ethanol for 5 min, respectively. And then these electrodes were dried under mild nitrogen stream. 4 mg of the Cu_2O/SMWNTs nanohybrids was dispersed in 1 mL of distilled water and sonicated for 1 h to obtain uniformly dispersed 4 mg mL^{-1} Cu_2O/SMWNTs nanohybrids solution. 10 μL of the suspension was cast onto the surface of the pretreated GC electrode with a microsyringe and the electrode was dried at ambient temperature. In order to immobilize the Cu_2O/SMWNTs nanohybrids, 10 μL 0.2% nafion was dropped onto the surface of the nanohybrids modified electrode and dried at ambient temperature. A Cu_2O-modified GCE and SMWNTs-modified GCE were prepared by employing aforementioned procedure.

Electrochemical measurements were performed using a three-electrode system consisting of a KCl saturated calomel reference electrode (SCE), a platinum counter electrode and a Cu_2O/SMWNTs nanohybrid modified GC working electrode. Prior to electrochemical detection of glucose, the electrodes were cycled 20 times in 0.1 M NaOH between 0 and 1.2 V through cyclic voltammogram (CV) until a reproducible background voltammogram was obtained. Amperometric measurements of glucose were carried out in 0.1 M NaOH solution at a desired potential (+0.4 V vs SCE).

3. Results and discussion

The morphologies of SMWNTs and the as-prepared Cu_2O/SMWNTs nanohybrids were characterized using SEM. Fig. 1A gives a typical SEM image of the SMWNTs sample, where a cleaved CNT film with a thickness of ~45 μm can be observed. Moreover, all of the CNTs are almost straight and aligned along a uniform direction. This property makes them more easily dispersed in solution after mild sonication pretreatment due to the weaker van der waals attraction force in SMWNTs bundles compared to the tangled CNTs [36]. Fig. 1B depicts the morphology of the as-synthesized Cu_2O/SMWNTs nanohybrids. It can be observed that the Cu_2O nanospindles are homogeneously dispersed in the SMWNTs networks, and SMWNTs appear to be in good contact with Cu_2O nanospindles. The high-magnification SEM in Fig. 1C and TEM image in Fig. 1D further reveal that SMWNTs can contact with Cu_2O nanospindles by point-contact pattern. The length of the as-prepared Cu_2O nanospindles ranges from 300 to 400 nm, and the width is about 100 nm. The surface of the nanospindles is rough, which endues them with large aspect ratio and be favorable for glucose adsorption. The corresponding high-resolution TEM (HRTEM) image in Fig. 1E shows a clear interplanar spacing of 0.24 nm, corresponding to the (1 1 1) plane of the Cu_2O [32]. A typical XRD pattern of the as-prepared nanospindle-like Cu_2O/SMWNTs nanohybrids is shown in Fig. 1F. The peak observed at 25.9° is attributed to the plane of (0 0 2) of graphite of SMWNTs [23]. Four characteristic diffraction peaks positioned at 36.50°, 42.40°, 61.50° and 73.70° could be corresponding to the (1 1 1), (2 0 0), (2 2 0) and (3 1 1) crystalline planes of the cubic phase Cu_2O [32], respectively.

Prior to applying the Cu_2O/SMWNTs nanohybrids for the electrocatalytic oxidation of glucose, electrochemical impedance spectroscopy (EIS) and cyclic voltammogram (CV) were used to characterize the electrochemical properties of the Cu_2O/SMWNTs nanohybrids. As shown in Fig. S1, the SMWNTs-modified electrode exhibits an almost straight line in the frequency range of 0.01 Hz to 100 kHz, which is characteristic of the diffusion limited electrochemical process [37]. For Cu_2O/SMWNTs nanohybrids-modified

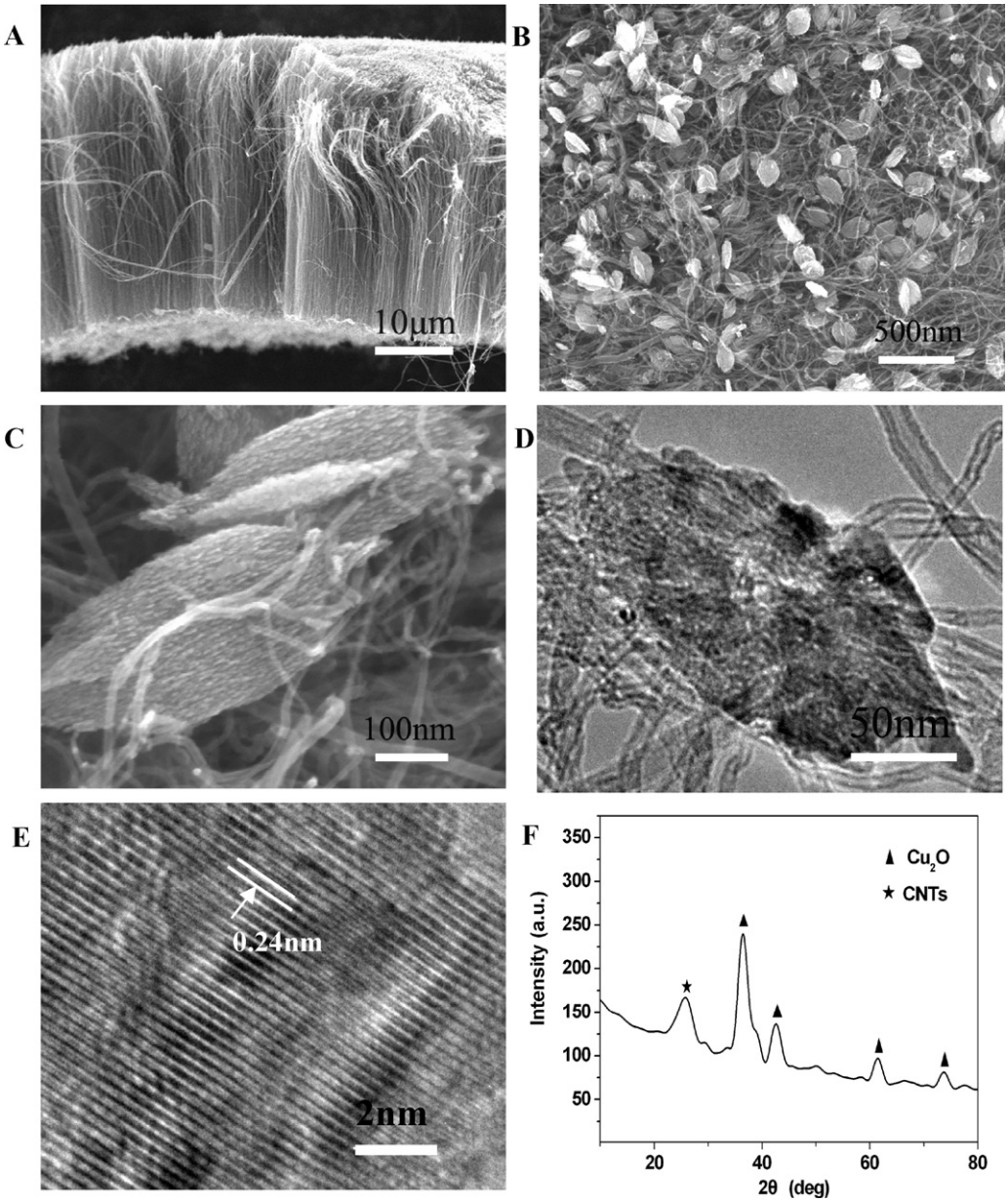

Fig. 1. Typical SEM images of SMWNTs (A), and the Cu_2O/SMWNTs nanohybrids (B and C), and TEM (D) and HRTEM (E) images of the hybrids, and XRD pattern of the hybrids (F).

electrode, another similar straight line is found, suggesting Cu_2O nanospindle does not hinder the electron transfer ability of SMWNTs. Comparing with the high frequency region, it can be easily inferred that smaller internal resistance is obtained for Cu_2O/SMWNTs nanohybrids than that of SMWNTs, which is consistent with the reported literature [25]. These results suggest that Cu_2O nanospindle in the nanohybrids acts as an electron mediator in the electron transfer process and promote the electron transfer rate. The CV responses of Cu_2O/SMWNTs and SMWNTs were further investigated in $K_3[Fe(CN)_6]$ solution, as shown in Fig. S2. A pair of quasi-reversible ferricyanide ion redox peaks was observed on the SMWNTs-modified electrode with a peak separation (ΔE_p) of 80 mV at 50 mV s^{-1}. For Cu_2O/SMWNTs nanohybrids-modified electrode, the peak current was increased and ΔE_p was comparable to that of the SMWNTs-modified electrode. These results suggest that the Cu_2O/SMWNTs nanohybrids-modified electrode can promote the electron transfer rate and exhibit a large electrochemical accessible surface area, which was 0.13 cm^2 according to the Randles-Sevcik equation.

The electrocatalytic activity of the as-prepared nanospindle-like Cu_2O/SMWNTs nanocomposites modified electrodes towards oxidation of glucose was investigated by CVs. Fig. 2A presents the CV responses obtained at the Cu_2O/SMWNTs modified electrode in 0.1 M NaOH solution containing different concentrations of glucose. In the absence of glucose (curve c), a single somewhat broad reduction peak with a peak potential of about +0.58 V can be observed, which might correspond to a Cu(II)/Cu(III) redox couple similar to the previous reports [25]. Upon the addition of 2 mM glucose (curve b), notable enhancement of oxidative peak current corresponding to the irreversible oxidation of glucose is observed, and the voltammetric response increased with a rising concentration of glucose (curve a) at about +0.4 V, where the oxidation peak is due to the conversion of Cu(II) to Cu(III) [28]. These results indicate that the nanospindle-like Cu_2O/SMWNTs nanocomposites

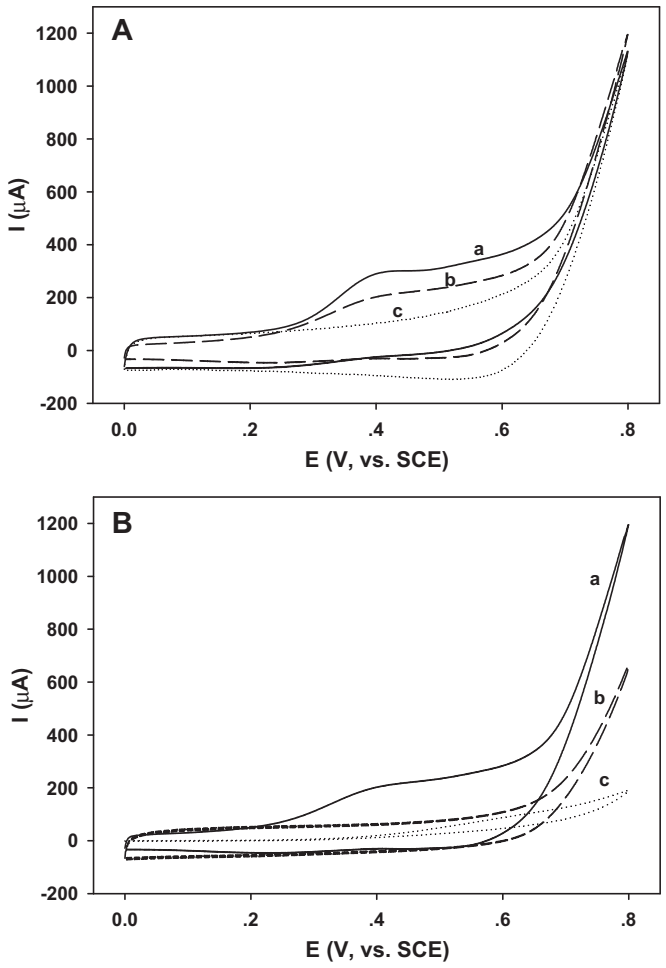

Fig. 2. Cyclic voltammograms of (A) the Cu_2O/SMWNTs electrode in 0.1 M NaOH solution containing different concentration of glucose (a: 0, b: 2 mM, c: 4 mM) at a scan rate of 50 mV s^{-1}, and (B) the Cu_2O (a), SMWNTs (b), and Cu_2O/SMWNTs (c) modified GC electrodes in 0.1 M NaOH solution containing 2 mM glucose at a scan rate of 50 mV s^{-1}.

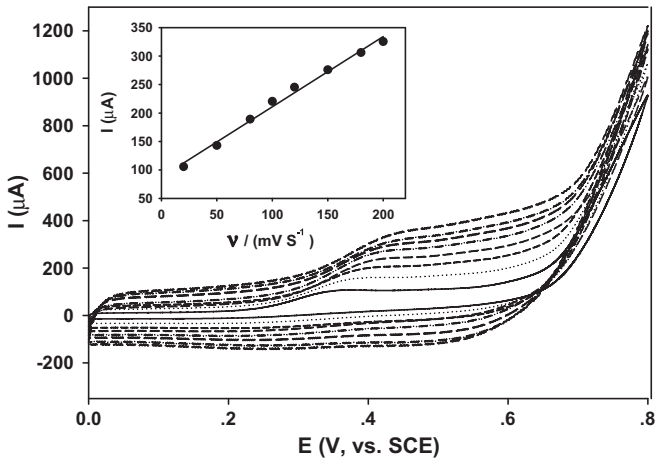

Fig. 3. Cyclic voltammograms curves of the Cu_2O/SMWNTs electrode obtained in 0.1 M NaOH solution containing 1 mM glucose at different scan rates (inner to outer): 20, 50, 80, 100, 120, 150, 180 and 200 mV s^{-1}; and peak current as a function of different scan rate (left inset).

exhibit excellent electrocatalytic activity toward the oxidation of glucose as expected. The oxidation of mechanism involves the surface bound copper species and the major electrocatalytic oxidation product of glucose investigated in alkaline media is formate, originating from C—C bond cleavage of glucose caused by Cu(III) species in alkaline media [38,39].

The electrocatalytic activity of the Cu_2O/SMWNTs nanohybrids was further compared with the SMWNTs or Cu_2O nanospindles alone as the electrode modifying material for oxidation of glucose, as shown in Fig. 2B. As can be seen from the voltammetric response, no obvious oxidation current for glucose can be found at the SMWNTs (curve b) and Cu_2O nanospindles (curve c) modified electrodes. However, the Cu_2O/SMWNTs nanohybrids exhibit typical voltammetric response for the oxidation of glucose (curve a). Such excellent electrocatalytic activity of the Cu_2O/SMWNTs nanohybrids may be attributed to high catalytic active sites for the glucose oxidation provided by the nanospindle-like Cu_2O and high electron transfer rate provided by an efficient electrical network formed by Cu_2O and SMWNTs. The effect of potential scan rate on oxidation peak current at the Cu_2O/SMWNTs electrode has been investigated in the range of 20–200 mV s^{-1} in 0.1 M NaOH containing 1 mM glucose (Fig. 3). As shown, the anodic peak current increased with increased scan rates, and the peak current was proportional to the scan rate (inset). Moreover, the anodic peak potential shifted to positive values with increased scan rates, which may be attributing to the diffusion limitation of glucose at the electrode surface. These results indicate that the electrochemical kinetics is controlled by surface adsorption of glucose.

In nonenzymatic sensors, mediums play a vital role in enhancing the electrocatalytic activity of the catalysts towards glucose. Hence, we systematically investigated the effect of mediums on the responses current of the glucose oxidation using amperometric technique (not shown). These mediums include NaOH solution and physiological mediums such as phosphate buffer, carbonate buffer, and borate buffer. Under the optimal experiment conditions (concentration, pH, applied potential), smaller amperometric responses in the above-mentioned physiological mediums can be obtained than that in NaOH solution, possibly due to less glucose anion (per glucose molecule lost one proton at about −0.12 V) obtained or less catalytic activity of Cu_2O in these physiological mediums. Consequently, 0.1 M NaOH solution was chosen as the optimized medium for the subsequent experiment.

The amperometric responses at the nanospindle-like Cu_2O/SMWNTs modified electrodes for glucose were further evaluated under the optimal experimental conditions, as shown in Fig. 4A. One can see that after each addition of glucose solution, notable enhancement of current responses was obtained and 95% of the steady-state current was achieved within 3 s in 0.1 M NaOH at +0.4 V. These results indicate that the Cu_2O/SMWNTs nanohybrids exhibit very sensitive and rapid response characteristics, which is ascribed to the highly electroconductivity and good electrocatalytic activity of the Cu_2O/SMWNTs nanohybrids. It is noted that the background current increased with the concentration of glucose, which caused by growing intermediate species adsorbed onto the electrode. Fig. 4B depicts the correlation between the amperometric responses and glucose concentration range from 500 nM to 4 mM. As is obvious, the Cu_2O/SMWNTs nanohybrids modified electrode displays a good linear range from 500 nM to 2.5 mM with a correlation coefficient of 0.997 and a sensitivity of 2143 μA mM^{-1} cm^{-2}. The limit of detection was estimated to be 200 nM at a signal to noise ratio of 3. The key performance characteristics of the as-prepared nanospindle-like Cu_2O/SMWNTs catalyst are compared with some of existing nonenzymatic sensors from a copper source, as given in Table 1. It can be seen that the proposed sensor shows a good superiority in terms of sensitivity, selectivity, response time and linear calibration range. This superiority can be attributed to the synergistic effect of Cu_2O nanospindles and SWMNTs including high electrocatalytic activity of Cu_2O nanospindles and the promoted electron transfer

Table 1
Comparison of the key performance characteristics of some of existing catalysts for enzyme-free electrooxidation of glucose.

Type of electrode	Response time (s)	Potential (V)	Sensitivity ($\mu A\,mM^{-1}\,cm^{-2}$)	Linear range	LOD (μM)	Ref
Cu_2O/SMWNTs	3 s	+0.40	2143	0.5 μM–2.5 mM	0.2	Present work
CuO fibers	1 s	+0.40	431.3	6.0 μM–2.5 mM	0.8	[17]
CuO nanoparticles	–	+0.75	629	5.0 μM–6 mM	2.4	[16]
Cu_xO flowers	–	+0.50	1620	50 μM–4.0 mM	49	[20]
CuO nanoshpere	–	+0.60	404.53	1.0 μM–2.55 mM	1	[24]
CuO NPs/MWCNTs	1 s	+0.40	2596	0.5 μM–1.2 mM	0.2	[33]
CuO nanowires	–	+0.33	490	0.4 μM–2.0 mM	0.49	[21]
CuO nanorods	<10 s	+0.6	371.43	4.0 μM–8.0 mM	4	[19]
Cu nanocluster/CNTs	5 s	+0.65	250	0.7 μM–3.5 mM	0.21	[29]
Cu NPs/MWCNTs	5 s	+0.35	710	10 μM–0.3 mM	0.5	[28]
Cu_2O NPs/CNTs	10 s	−0.2	–	0.05 μM–10 μM	0.05	[32]

originating from the electrical network formed by Cu_2O nanospindles and SMWNTs.

A number of oxidizable species such as AA, DA, AP, and UA usually co-exist with glucose in real samples. Although at low concentrations relative to glucose, they exhibit high electron transfer rates and often interfere with the determination of glucose. Therefore, interference tests were conducted in 0.1 M NaOH solution with continuous additions of 1 mM glucose, 0.1 mM UA, 0.1 mM DA, 0.1 mM AP, and 0.1 mM AA at a potential of +0.4 V. As can be seen from Fig. 5A, the current response for the electroactive interfering species to that of the glucose was below 10%, indicating that the Cu_2O/SMWNTs nanohybrids are very favorable for the specific determination of glucose even in the presence of several interfering species.

As reported, many enzyme-free glucose sensors based on metal oxides usually prevent them from being poisoned by chloride ions [30]. Herein, in order to investigate the antifouling ability of the Cu_2O/SMWNTs electrode, CVs measurement was carried out in 0.1 M NaOH containing 0.15 M NaCl. As can be seen from Fig. 5B, the voltammetric responses of the Cu_2O/SMWNTs electrode obtained in 0.1 M NaOH containing 1 mM glucose with and without 0.15 M NaCl are almost identical, indicating that the proposed electrode

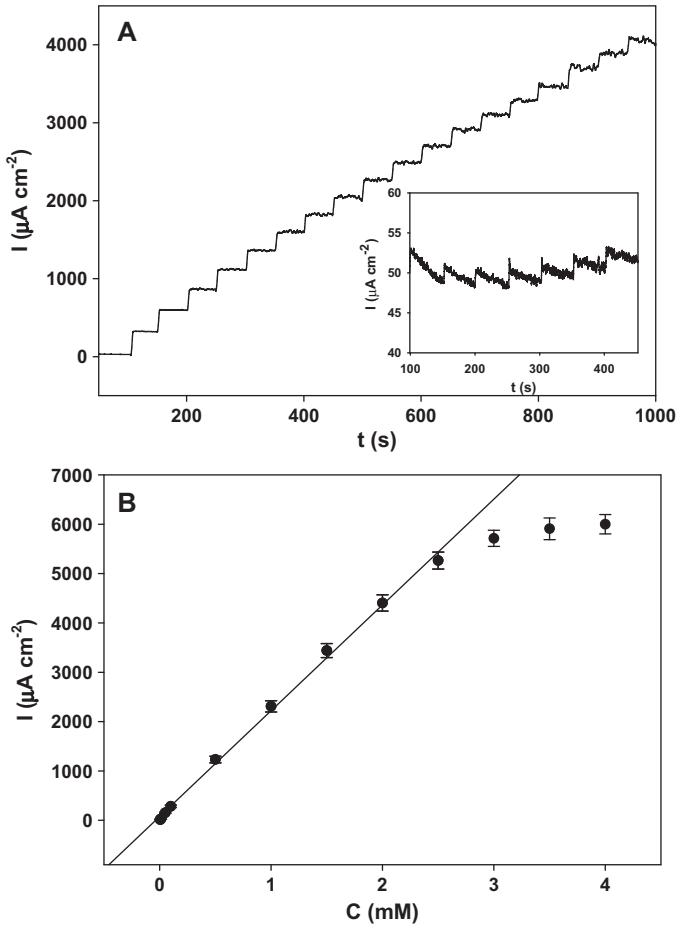

Fig. 4. Amperometric responses of the Cu_2O/SMWNTs electrodes to successive addition of 100 μM glucose in 0.1 M NaOH at +0.4 V (amperometric response of the Cu_2O/SMWNTs electrodes with the addition of 500 nM) (inset) (A) and its corresponding calibration plot (B).

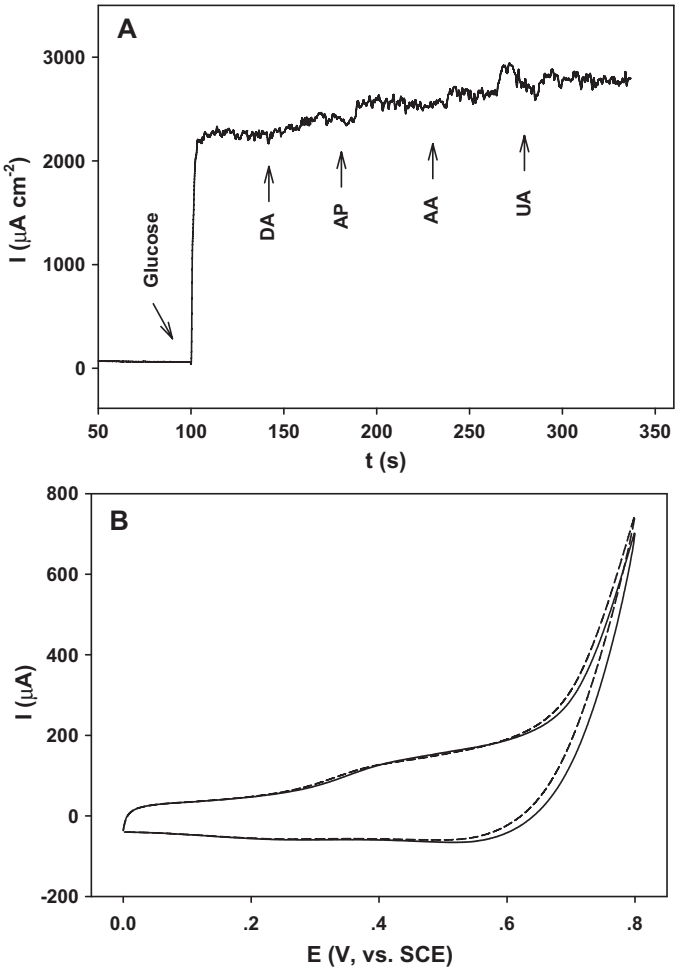

Fig. 5. Amperometric responses of the Cu_2O/SMWNTs electrodes to successive additions of 1 mM glucose, 0.1 mM DA, 0.1 mM AP, 0.1 mM AA, and 0.1 mM UA in 0.1 M NaOH at +0.4 V (A), and cyclic voltammograms of the Cu_2O/SMWNTs electrode in 0.1 M NaOH containing 1 mM glucose with (dash line) and without (solid line) 0.15 M NaCl at a scan rate of 50 mV s^{-1} (B).

Table 2
Amperometric determination of glucose in human blood serum samples.

Sample	Concentration (mM)	Added (mM)	Found (mM)	RSD[a] (%)	Recovery (%)
1	5.8	0.5	0.65	3.2	106.8
2	4.6	0.5	0.56	4.8	93.6
3	7.5	0.5	0.63	2.1	96.0
4	6.3	0.5	0.64	1.8	102.8
5	5.1	0.5	0.62	3.5	103.6
6	6.5	0.5	0.59	2.9	92.0

[a] RSD (%) calculated from three repetitive trials.

exhibits good resistance to surface fouling and is promising for development of enzyme-free glucose sensor at low cost.

The reproducibility of the as-prepared Cu_2O/SMWNTs electrode has been determined. A set of eight different amperometric measurements of 100 μM glucose at the electrode yielded a reproducible current with a relative standard deviation (RSD) of 3.5%. In addition, five electrodes were separately prepared under the same conditions and the RSD for the current response of the individual determination towards 100 μM glucose were 4.5%, confirming that the fabrication method was highly reproducible. The stability of the Cu_2O/SMWNTs electrode was also checked after stored in air at ambient conditions every week. The proposed sensor retained about 90% of its initial response after 63 days (Fig. 6), suggesting that the Cu_2O/SMWNTs electrode is relatively stable.

The applicability of the Cu_2O/SMWNTs electrode was further evaluated by measuring glucose content in human plasma blood samples by the standard addition method. 50-fold diluted blood samples with glucose standard addition were added into 0.1 M NaOH, and the current responses at +0.4 V were recorded. From Table 2, it can be observed that the sensor gives recoveries in the range of 92.0–106.8%, indicating that species in diluted blood samples did not interfer the determination of glucose in alkaline solution based on the Cu_2O/SMWNTs nanohybrids. Moreover, the Cu_2O/SMWNTs catalyst was further validated using clinical serum specimens with reference to a routine spectrophotometric method in a local hospital (Table S1). These results demonstrate that the proposed sensor provide assay performance comparable to spectrophotometric method in a local hospital and hold potential in real sample analysis.

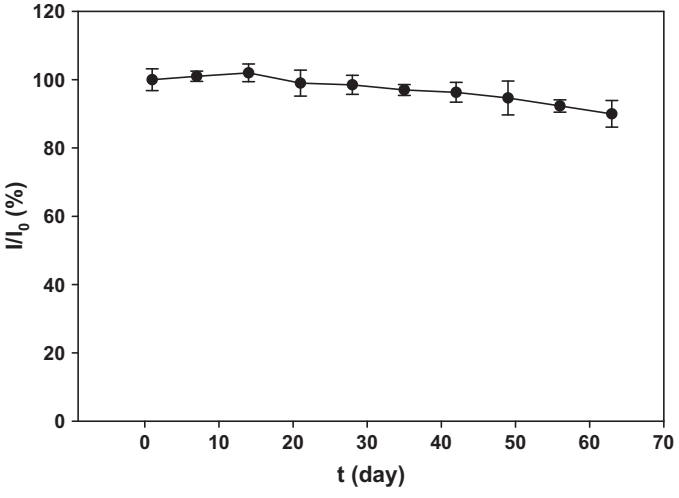

Fig. 6. Long-term stability of the Cu_2O/SMWNTs sensor stored at ambient conditions over 63 days in 0.1 M NaOH with addition of 100 μM glucose at +0.4 V. The error bars indicate standard deviations of five measurements.

4. Conclusions

A type of catalyst nanospindle-like Cu_2O/SMWNTs nanocomposite has been synthesized and successfully applied for directly electrooxidizing glucose. The electrochemical responses reveal that the as-prepared catalysts exhibit much higher electrocatalytic activity to glucose oxidation than the SMWNTs or Cu_2O alone as the electrode modifying material, attributing to high catalytic active sites provided by the nanospindle-like Cu_2O and high promoted electron transfer rate provided by an efficient electrical network formed by Cu_2O and SMWNTs. The proposed sensor has outstanding features of sensitivity, selectivity, response time, and resistance against poisoning by chloride ion, which make the nanospindle-like Cu_2O/SMWNTs nanocomposites a great potential for the future development of enzyme-free glucose sensors.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.snb.2011.12.012.

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