Talanta 174 (2017) 514–520

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

3D CuO nanosheet wrapped nanofilm grown on Cu foil for high-performance non-enzymatic glucose biosensor electrode

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ARTICLE INFO

Keywords:
CuO
Binder-free
Non-enzymatic
Glucose biosensor

ABSTRACT

3D binder-free CuO nanosheets wrapped nanofilms has been in situ synthesized on Cu substrate by a simple and facile procedure, with an aim of fabricating high-performance glucose sensor. The complex morphology that the nanosheet grown on Cu subtract evolved into nanofilms and eventually converged to nanowires, is benefit for the mass transport and electro-catalysis. Compared the ECSA of the CuO modified electrode to that of the bare Cu electrode, the effective surface area during the electro-catalysis of the CuO/Cu electrode is much larger. The glucose sensor based on CuO products exhibited high sensitivity (4201 μA cm^{-2} mM^{-1}), low detection limit (0.5 μmol/L) and quick response time (0.7 s). And the stability and selectivity is also fantastic. According to the serum sample analysis, it transpires that the CuO/Cu sensor displayed excellent recovery compared to the concentration values measured by medial method. So this material shows great potential applications in glucose sensors.

1. Introduction

Diabetes is a metabolic disorder disease and has been a public health issue all over the world. The diabetes of an alarming rate has drawn great attention. By 2035, there will be 5920 million people in the world suffering diabetes. And this disease is one of the main causes of death and deformity. The rapid and precise monitoring of glucose level in body liquid is closely related to the diagnosis of diabetes mellitus [1]. Besides, the monitor of glucose determination is urgent in areas, such as biotechnology and food industry [2]. The sensitive materials are used for modified electrode to transform the signal of chemical and physical reaction into electric signal which is more easily recorded and quantified. So far, most studies report that the redox active enzyme has been applied for glucose monitor owing to its accurate and fast response [3]. However, its electrochemical property is greatly affected by pH, temperature, etc., during the synthesis and determination process, leading to unstable results. Thus, attentions have been payed to enzyme-free glucose sensors with stable and sensitive performance. In recent years, the electrochemically active nanomaterials, noble metal (e.g. Au [4], Pt [5], etc.) and their alloys (e.g. PtAu [6], PtRu [7], etc.), are widely researched for glucose determination taking into account their great stability. But most of the above mentioned materials are expensive, and the properties like sensitivity and selectivity need further optimization. Compared to noble metals, non-enzyme glucose sensors based on transition metal oxide (e.g. ZnO [8], NiO [9], MnO_2 [10], CuO [11–13], etc.) are stable, low-cost, sensitive and accurate. CuO, a p-type semiconductor material with a narrow band gap of 1.2 eV [14], have great potential for glucose sensors due to its impressive advantages on mass transportation and electro-catalysis.

Numerous factors may significantly affect the properties of glucose sensors, like the nanostructure and binder. The nanostructure of CuO, such as nanosheets [15], nanocubes [16], nanowires [11] and nanoparticles [17], has an obvious influence on the specific surface area and dominates the efficiency of electron and mass transportation. During the preparation of working electrodes, for example powder-like samples, the binder is necessary to fix sensitive materials on the surface of bare electrode. The binder filling in the interspace among the powder particles dramatically interferes the electron and mass transportation and therefore a self-supporting electrode materials are being expecting.

In this report, a 3D CuO nanosheet wrapped nanofilm sample was synthesized in situ on Cu substrate via a facile process in an alkaline ammonium persulfate solution at 60 °C. The process is simple without using any complicated step and equipment. In addition, the products are employed directly to determine the glucose without any further treatment. For the high surface area and special nanostructure of the product, the CuO nanomaterial shows exhilarating properties on electro-catalysis and glucose oxidation.

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http://dx.doi.org/10.1016/j.talanta.2017.06.030
Received 7 February 2017; Received in revised form 27 May 2017; Accepted 10 June 2017
Available online 21 June 2017
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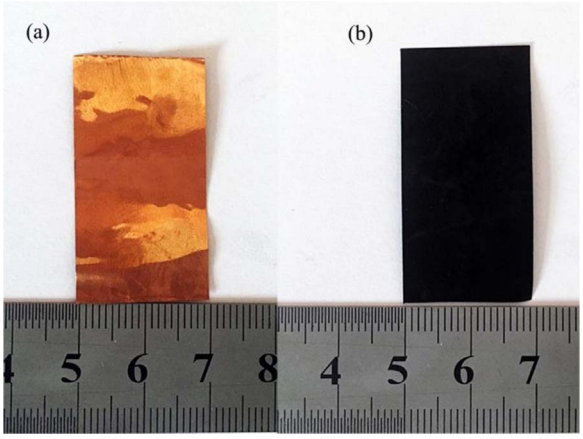

Fig. 1. Digital photos of the samples (a) before and (b) after the chemical reaction. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article).

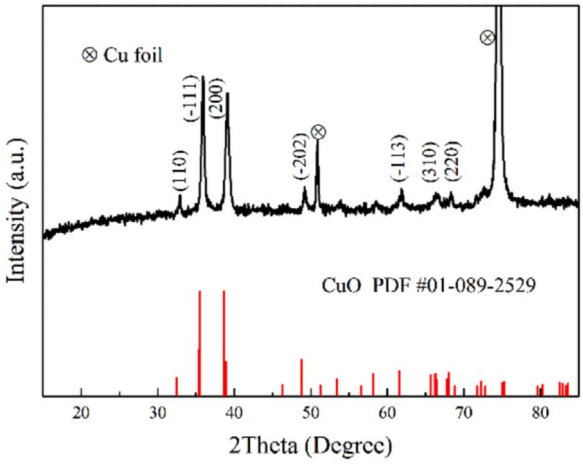

Fig. 2. XRD pattern of the product.

2. Experimental

2.1. Materials and methods

The CuO nanostructure on Cu substrate was fabricated in situ by a wet chemical method in an alkaline ammonium persulfate solution. All the reagents were of analytical grade and used without further purification. A Cu foil (4 × 2 cm^2), ultrasonic rinsing in turn by water and ethanol for minutes to remove the impurity on the surface. Then the samples were immerged into a 60 mL aqueous solution composed of 1.25 mol/L NaOH and 0.05 mol/L $(NH_4)_2S_2O_8$. After strongly stirred for minutes, the solution and the Cu foil was transferred into Teflon-lined stainless steel autoclaves and kept at 60 °C for 24 h. Because of chemical reactions, the copper turned from bright yellow into absolute black (Fig. 1). The product was taken out, washed and dried at 60 °C for 12 h.

2.2. Materials characterization and electrochemical measurements

The phase structure of the product was identified by X-ray Diffraction (XRD, X'Pert ProMPD) with Cu-Kα radiation (λ = 1.5418 Å), and X-ray photoelectron spectroscopy (XPS, PHI-5400, USA) with monochromatic Cu-Kα radiation (h_v = 1486.6 eV). The morphologies and microstructure were recorded on a field mission Scanning Electron Microscopy (SEM, Zeiss Super 55). The electrochemical measurements were carried out on a CS310 electrochemical workstation (Corrtest, China) in a three-electrode electrochemical cell containing 0.1 mol/L NaOH aqueous solution at room temperature with a modified Cu subtract (cut into 1 × 1 cm^2) as working electrode, an Ag/AgCl (saturated with KCl) electrode as reference electrode and a platinum plate (1 × 1 cm^2) as counter electrode. The cyclic voltammograms (CVs) were measured at different scan rate from 10 mV/s to 100 mV/s in the potential range of −0.2 to 0.8 V. The amperometric response tests were measured at +0.55 V under stirred condition, and analytes were added into the electrolyte after the background currents were steady.

3. Results and discussion

3.1. Structural characterization of the product

Because of the good electrical conductivity and light weight, Cu foil is an ideal self-supporting electrode material. In the synthesis process, Cu foil (as Cu source) was oxidized by $S_2O_4^{2-}$ under alkali condition (NaOH aqueous solution) with superfluous NH_4^+. After the chemical reactions, the copper turned from yellow into absolute black (Fig. 1), indicating the formation of CuO. The typical XRD patterns in Fig. 2, conducting the component identification of the product, shows that the Cu foil was covered with monoclinic structured CuO. The diffraction peaks at 32.489°, 35.551°, 38.945°, 48.841°, 61.580°, 66.484°, 68.038° are distinctly recognized, indexed well with (110), (−111), (200), (−202), (−113), (310), (220) planes, respectively (PDF: No. 01-089-2529). The peaks at 5.0375° and 73.997° in accordance with cubic structure of copper originate from the Cu subtract. There is no diffraction peaks of Cu_2O or $Cu(OH)_2$ being detected, indicating the high purity of the CuO product.

The morphology and microstructure of the CuO product were characterized by SEM (Fig. 3). The SEM image of the original Cu foil is exhibited in Fig. 3(a) and the surface of that is rather smooth. Fig. 3(b) shows the top-view image of the CuO. The surface of the copper is fully covered with nanosheet arrays with a thickness about 25 nm (Fig. 3(c)). Afterwards, CuO nanosheets were gradually thinning and expanding to be nanofilms. The nanofilms are extremely thin, which provides great amount active sites for glucose adsorption and determination. At the end, the films were gathered to nanowires (Fig. 3(d)). Every sheet of the nanostructure varied from relatively thick nanosheets into thinner nanofilms, and eventually became nanowires (Fig. 3(b)–(d)). The nanofilm, the main structure among the three kinds of morphologies, is well conducive to the mass transport and catalysis. Coupled with the high specific surface area, the product, CuO nanosheets wrapped nanofilms grown on Cu foil subtract, may show good performance on electrochemical catalysis.

To further identify the surface characterization of these films, the supplementary data were obtained by XPS measurement. In the XPS survey spectra of the product (Fig. 4(a)), the high resolution region of Cu 2p indicated the oxidation of the Cu surface. The Cu peaks of the sample at 933.04 eV and 952.55 eV in Cu 2p main line (Fig. 4(a)) corresponding to Cu $2p_{3/2}$ and Cu $2p_{1/2}$, respectively, which indicates the oxidation state +2 of copper. The shake-up peak in Cu 2p main line investigates the presence of Copper (II) oxide. Besides, there are two peaks exhibited in the O 1s line (Fig. 4(c)), 528.98 eV and 530.38 eV, which means two different chemical environments of oxygen atoms in the sample. Hence, the XPS result evidences the oxidation state +2 of the nanosheet wrapped nanofilm products, and that is coincident with the result of XRD. The XPS measurement prove that the nanofilm of the surface of the copper foil is pure CuO, and the copper (II) oxide is good at electro-catalysis of glucose. So the extremely thin feature of the CuO film can increase the contact area with the test solution sample, and improve the sensitivity and detection limit of the modified electrode.

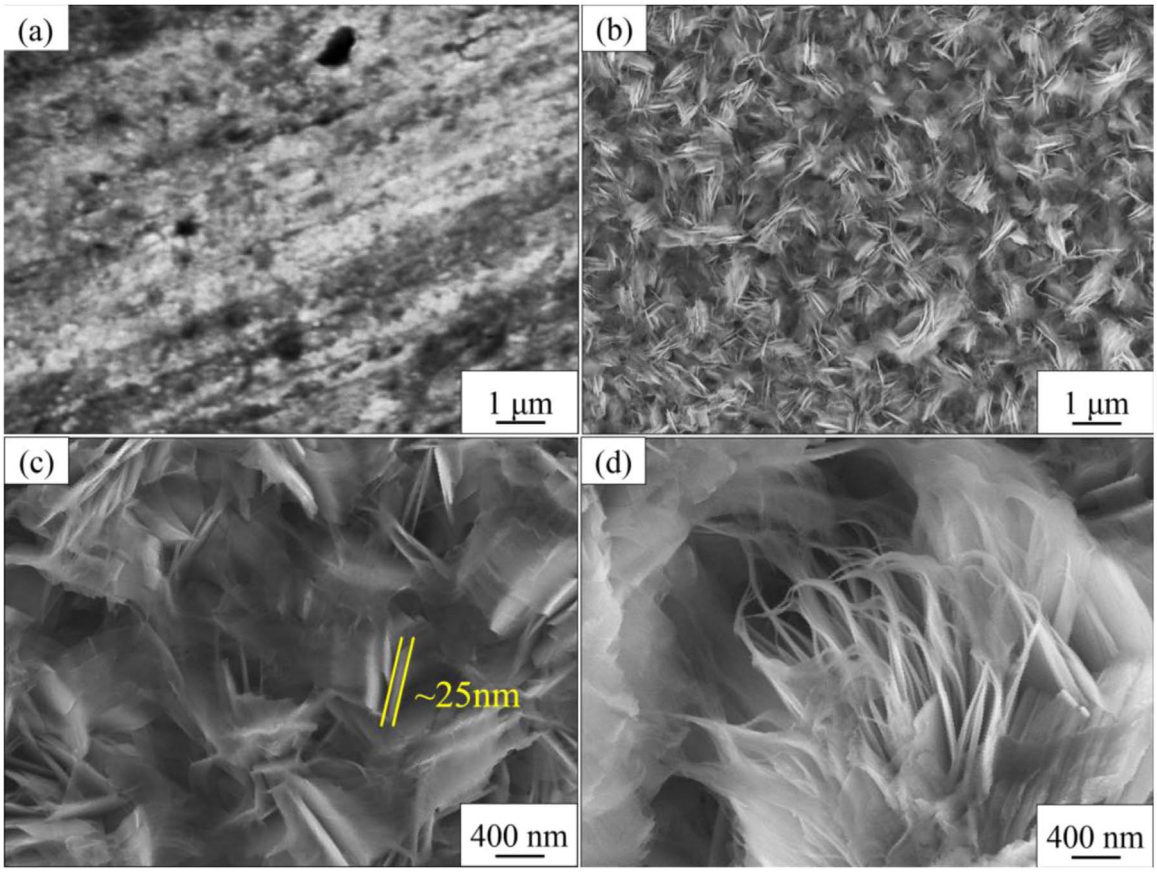

Fig. 3. (a) SEM image of original Cu foil without chemical treatment. (b)–(d) SEM images of the product.

3.2. Cyclic voltammetry behaviors during the determination of glucose at CuO/Cu modified electrode

The electro-catalytic behavior towards the oxidation of glucose of the CuO nanostructure modified electrode is to be demonstrated. The self-supporting feature of Cu subtract avoids the use of binder that would influence the electrochemical behavior of the sensitive material to decrease the stability and sensitivity. The curves of cyclic voltammetry (CVs), tested in 0.1 mol/L NaOH aqueous solution with different scan rates, ranging from 10 mV/s to 100 mV/s are revealed in Fig. 5. The current peaks of glucose oxidation is in proportion to the square root of the scan rate with a correlation coefficient of 0.9983, so that the electrochemical reactions are controlled by surface diffusion of glucose molecules [2].

To estimate the effective surface area during the electro-catalysis, we measured the electrochemically active surface area (ECSA) of the CuO nanostructure modified electrode through electrical double-layer capacitance (EDLC) measurements in 0.1 mol/L NaOH solution [18], as the double-layer capacitance (C_{dl}) is proportional to the ECSA [19]. The CVs were tracked in the range of 0.00–0.10 V, where the current response should only refer to the charging of the double layer [20]. The CV curves of CuO/Cu and Cu electrodes at various scan rates (10, 30, 50 and 70 mV/s) are displayed in Fig. 6(a) and (b), respectively. At each scan rate, the CuO nanostructure modified electrode provided much higher anodic (i_a) and cathodic (i_c) current densities than the initial Cu foil. And the capacitance of the CuO/Cu electrode (3.67 mF/cm^2) is much higher than that of Cu electrode (0.346 mF/cm^2), implying the higher electrochemical surface area of the nanostructure CuO modified electrode, which indicates that the high electro-catalytic properties of the CuO/Cu electrode.

The CVs of the modified electrode was recorded in 0.1 mol/L NaOH aqueous solution with different concentration of glucose at a scan rate of 50 mV/s, as shown in Fig. 7(a). As a reference, the bare Cu electrode is much inferior to the electrode modified with CuO nanofilms, and the

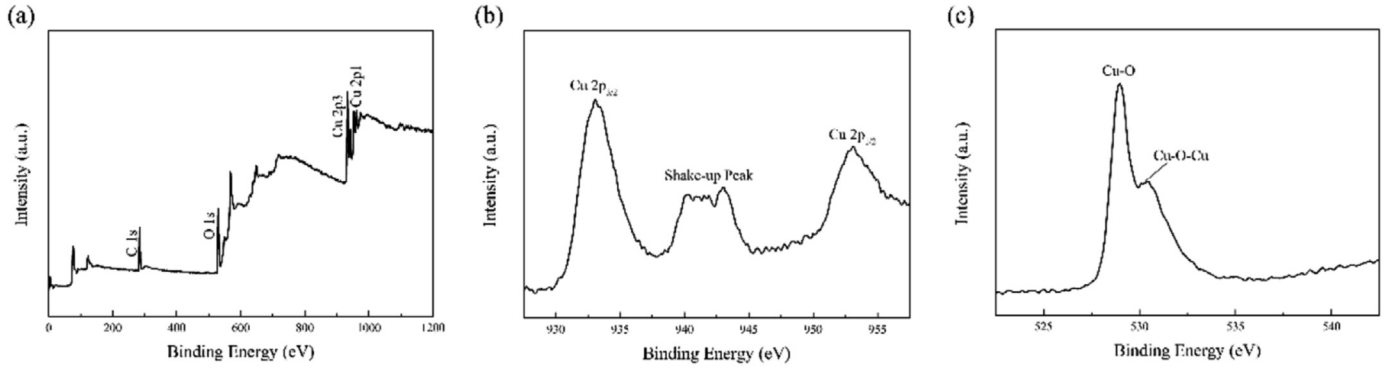

Fig. 4. (a) Survey (b) Cu 2p and (c) O 1s XPS spectra of the product.

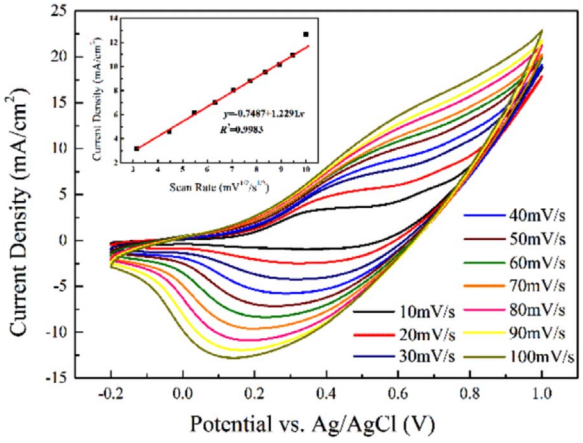

Fig. 5. CV plots of the CuO modified electrode at scan rate of 10–100 mV/s in 0.1 mol/L NaOH solution (Scanning range: −0.2 to 0.8 V). Inset: The calibration line of oxidation peaks at every scan rate.

CV curve of the former one shows no redox peaks for its low specific surface area and poor reproducible carbohydrate currents [21]. For the CuO modified electrode, the current peaks of potentials around +0.55 V vs. Ag/AgCl has been attributed to the formation of Cu (III) species, and the reverse scan reveals a broad cathodic peak about +0.3 V vs. Ag/AgCl, which is corresponding to the reduction of Cu (III) [22,23]. The most accepted oxidation mechanism of glucose on the copper-based materials was first suggested by Marioli and Kuwana [24]. The glucose molecule was absorbed onto the surface of the modified electrode and oxidized during the process that the Cu (III) transformed into Cu (II). The possible determination mechanism is indicated as follows [25]:

$$CuO + OH^- \rightarrow CuOOH + e^-$$

$$CuOOH + glucose + e^- \rightarrow CuO + OH^- + gluconic\ acid$$

Under the condition of adding 3 mmol/L glucose, the peak of oxidation wave is much more notable, which testifies that CuO is efficacious to catalyze the process of glucose decomposition.

The Fig. 7(b) shows the CV curves for CuO/Cu electrode with different concentration of glucose. The current response was obvious and that increased with the increasing concentrations of glucose in the electrolyte.

3.3. Effect of pH

As discussed above, the electrolyte has to be alkaline solution. In order to study the effect of pH for the CuO/Cu modified electrode, 0.01 mol/L NaOH solution (pH = 12), 0.05 mol/L NaOH solution (pH = 12.7), 0.1 mol/L NaOH solution (pH = 13) and 1 mol/L NaOH solution (pH = 14) were taken separately in different beakers and the cyclic voltammograms were recorded for each solution. And in order to test the value of response current with the glucose, we also recorded the CVs after adding 3 mmol/L glucose in every solution. The cathodic current densities (i_{pc}) of all CVs were recorded and illustrated in a histogram (Fig. 8). When the electrolyte was pure NaOH solution, i_{pc} increased with the increasing pH of the electrolyte, which is owing to the larger number of ions in these solutions. After the addition of the 3 mmol/L glucose, the current response in 0.1 mol/L NaOH solution is most significant, and that in 1 mol/L NaOH solution is similar to the former one. So the 0.1 mol/L NaOH solution is the most suitable electrolyte in this work.

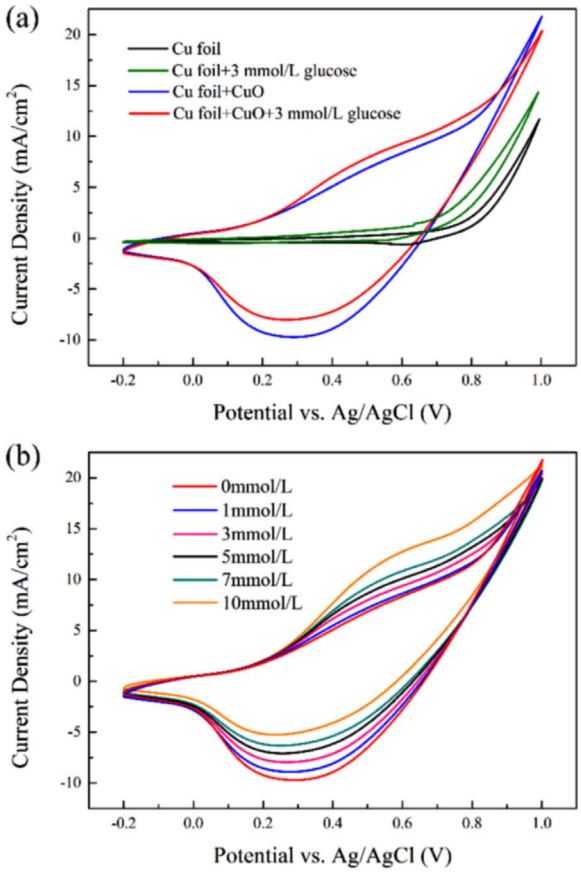

Fig. 7. (a) Cyclic voltammetry (CV) curves of Cu subtract (in black line), CuO/Cu in the absence (in blue line) and in the presence (in green and red line, separately) of 3 mmol/L glucose. (b) The CV traces for CuO/Cu electrode with different concentration of glucose (Concentration: 0–10 mmol/L). Electrolyte: 0.1 mol/L NaOH aqueous solution. Scan rate = 50 mV/s. Scanning range: −0.2 to 1.0 V. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

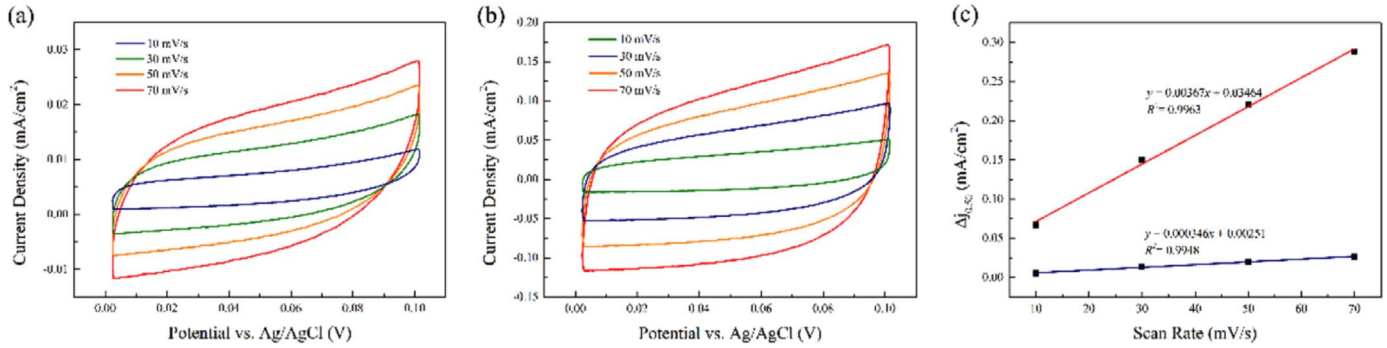

Fig. 6. CVs for (a) bare Cu and (b) CuO/Cu electrode with different scan rates. (c) The capacitive currents at +0.50 V as a function of scan rate for CuO/Cu and bare Cu electrode ($\Delta j_0 = j_a - j_c$).

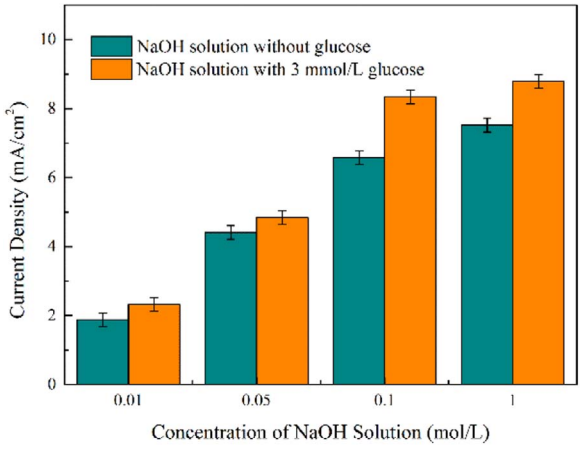

Fig. 8. The current density of the product in NaOH solution with different concentrations. 0.01 mol/L NaOH solution: pH = 12; 0.05 mol/L NaOH solution: pH = 12.7; 0.1 mol/L NaOH solution: pH = 13; 1 mol/L NaOH solution: pH = 14.

3.4. Amperometric determination of glucose at CuO/Cu modified electrode

Fig. 9(a) indicates the current response with the stepwise addition of 1 mmol/L glucose solution at different potentials between +0.50 V and +0.65 V. The current response increased with the increasing potential. At +0.65 V, the background current is too high, and some interfering species may be oxidized, obstructing the oxidation on glucose. With the similar background current, higher response current is favorable for the current measurement to minimize the measurement error. Hence, +0.60 V is a proper potential for glucose determination. Fig. 9(b) indicates a well-defined, stable and fast amperometric response of the CuO nanosheet wrapped by nanofilm grown on Cu foil subtract in a stirred 0.1 mol/L NaOH solution with successive stepwise addition of aqueous glucose solution at the voltage of +0.60 V vs. Ag/AgCl. At the lowest concentration (0.5 μmol/L), the current response is pretty illustrious to be discovered. The sensor demonstrated a linear range from 0.5 μmol/L to 4 mmol/L glucose with a sensitivity of 4201 μA cm^{-2} mM^{-1} and a correlation coefficient of 0.9800. The results suggest that the modified electrode is rather sensitive. The response time to glucose of CuO nanofilms (Fig. 9(c)) is around 0.7 s. The electrochemical behavior of the CuO/Cu nanomaterial exhibit low detection limit, high sensitivity and quick response time on glucose oxidation and determination.

Table 1 shows the comparison between the performances of CuO modified electrode in this work and those reported before. The comparison exhibits great performance of the electrode material in this work on glucose determination, especially the sensitivity and response speed, which means the CuO/Cu electrode material has great applications in glucose determination.

3.5. Anti-interference and stability

As a sensor, the properties of anti-interference and stability are significant to be indexed. The electron transfer rate of some small molecules, like uric acid (UA) and ascorbic acid (AA), may be higher than glucose. Moreover, some other carbohydrates will also affect the determination of glucose. The anti-interference test was started from adding 1 mmol/L glucose aqueous solution into 0.1 mol/L NaOH aqueous solution, and continuingly adding 0.1 mmol/L NaCl, 0.1 mmol/L glycine, 0.1 mmol/L UA, 0.1 mmol/L AA, 0.1 mmol/L L-Cysteine and 0.1 mmol/L sucrose into the NaOH solution in turn. As seen in Fig. 10(a), the disturbance of the interference terms is all weak. The feeble interference in quantity of each terms are shown in Fig. 10(b), the biggest influence just around 3%, which is so weak that could be ignored.

At last, in order to testify the stability of the 3D CuO/Cu sensor, it was immersed in 0.1 mol/L NaOH solution with 1 mmol/L glucose for

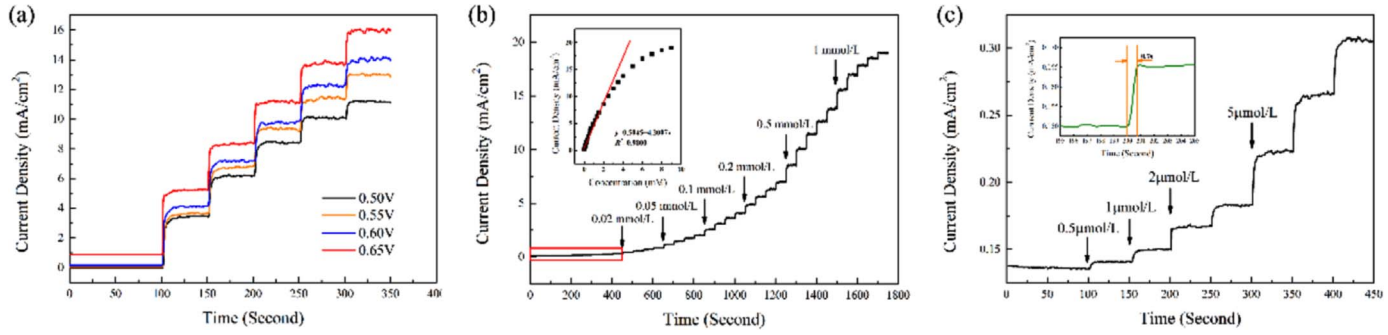

Fig. 9. (a) The time-current curves of CuO modified electtrode with +0.50 V, +0.55 V, +0.60 V, +0.65 V. (b) Amperometric response of the CuO modified electtrode with successive addition of glucose to the 0.1 mol/L NaOH solution at regular intervals. The applied potential is +0.60 V (vs. Ag/AgCl (saturated KCl) reference). Inset: The calibration curve of the plot. (c) The enlarge pattern of the curve in the red rectangle in part (b). Inset: the response time to the glucose of the CuO modified electrode. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

Table 1
Comparison of the performance of CuO modified electrode.

Electrode material	Response speed (s)	Sensitivity (μA cm^{-2} mM^{-1})	Linear range (up to mmol/L)	Detection limit (μmol/L)	Reference
CuO microspheres	–	622.2	1.95	1	[26]
CuO nanourchins	–	1634	5	1.97	[27]
CuO/Carbon spheres	< 5	2981	1.2	0.2	[28]
Ni/Cu/MWCNTs	1	2633	0.8	0.025	[29]
3D CuO nanowire arrays	2	1420.3	2.55	5.1	[30]
Chrysanthemum-like CuO film	< 5	3251.9	2.3	0.6	[31]
CuO Nws	< 5	684.2	3	2	[32]
CuO TiO_2	< 10	1321	2	0.39	[33]
CuO/Cu nanomaterials	0.7	4201	4	0.5	This work

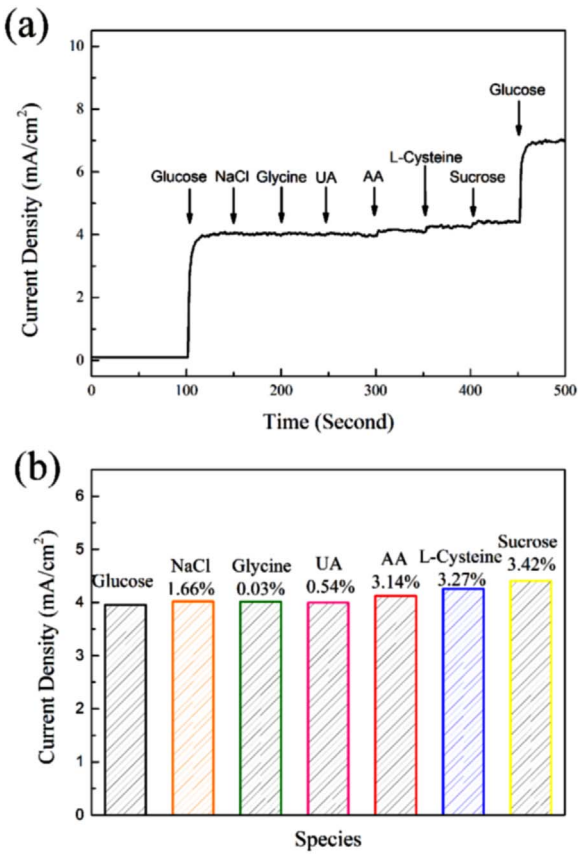

Fig. 10. (a) Anti-interference property of CuO/Cu to the stepwise addition of 1.0 mmol/L glucose, 0.1 mmol/L NaCl, 0.1 mmol/L glycine, 0.1 mmol/L UA and 0.1 mmol/L AA, 0.1 mmol/L L-Cysteine, 0.1 mmol/L sucrose, followed by the successive addition of 1.0 mmol/L glucose. (b) The influence in quantity of each interference terms.

7200 s to record the amperometric response at a permanent potential. As shown in Fig. 11, at the end of 7200 s, the loss of current intensity is merely 1.33%, indicating excellent stability and reliability as a sensor.

3.6. Real sample analysis

To certify the reliability, the CuO modified material was applied to determinate the glucose concentration of mouse serum samples. After the stability of the current density, 20 μL of 0.03 mol/L glucose and 100 μL of three serum samples were successively added into 300 mL 0.1 mol/L NaOH electrolyte at constant potential of +0.60 V. After the

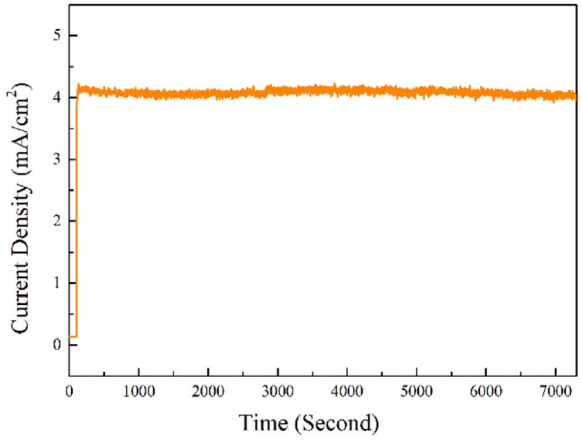

Fig. 11. Amperometric response of the CuO/Cu to 1 mmol/L glucose in 0.1 mol/L NaOH at + 0.55 V for 7200 s, the current loss is 1.33%.

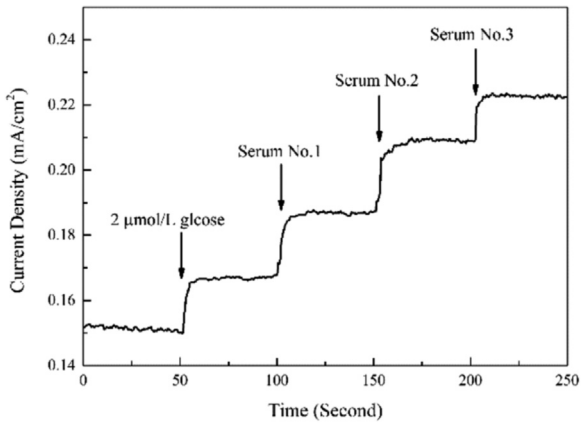

Fig. 12. The amperometric response with the successive addition of glucose and mouse serum samples to the 0.1 mol/L NaOH solution at regular intervals. The applied potential was +0.60 V (vs. Ag/AgCl (saturated KCl) reference).

Table 2
Amperometric determination of glucose in mouse serum samples.

Sample	Medical method (mmol/L)	Proposed method (mmol/L)	Recovery (%)
1	6.5	6.3	97.4
2	7.3	7.4	98.5
3	4.7	4.5	96.0

glucose solution was added into the electrolyte, the glucose concentration in the electrolyte is 2 μmol/L. The current response behavior is shown in Fig. 12, and the results are summarized in Table 2. It transpires that the CuO/Cu sensor displayed excellent recovery compared to the concentration values measured by medial method. These results demonstrate the potential application of the CuO/Cu nanomaterial in glucose determination.

4. Conclusions

A 3D binder-free CuO nanosheet wrapped nanofilm grown on Cu foil for high-performance non-enzymatic glucose biosensor electrode was fabricated by a rapid alkaline solution oxidation process. The complex structure of CuO with pretty thin nanofilm is benefit for mass and electron transport, contributing to electro-catalysis and oxidation of glucose. The electrochemical behavior is noteworthy with high sensitivity (4201 μA cm^{-2} mM^{-1}), low detection limit (0.5 μmol/L) and quick response time (0.7 s). Besides, the anti-interference and stability is remarkable. In testing the glucose concentration in serum samples, the results detected by the CuO/Cu sensor is almost the same to that determined by medical method. Considering the simple, low-cost synthesis process and superb properties on glucose detection, the modified electrode material would be possible for application prospects as non-enzymatic glucose sensor electrode in clinical field, biotechnology and food industry [2].

Acknowledgements

This work was supported by the National Natural Science Funds [Grant number 51521061], the fund of the State Key Laboratory of Solidification Processing in NWPU [Grant number 134-QP-2015], the "111" Project [Grant number 08040] and the Seed Foundation of Innovation and Creation for Graduate Students in Northwestern Polytechnical University [Grant number Z2017009].

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