Ultrasensitive non-enzymatic glucose sensors based on different copper oxide nanostructures by in-situ growth

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Abstract

Different nanostructures of copper oxide (CuO) by in-situ growth on carbon clothes (CC) are prepared to develop ultrasensitive non-enzymatic glucose sensors. The electrochemical performance of the CuO-based electrodes for detecting glucose has been investigated by cyclic voltammetry (CV) and chronoamperometry. The CuO nanosheets (CuO NSs)/CC electrode demonstrates a high sensitivity of 4902 μ A mM⁻¹ cm⁻² at an applied potential of 0.55 V (vs. Ag/AgCl/ 3M KCl) in alkaline solution, and it shows 2973 μ A mM⁻¹ cm⁻² and 1246 μ A mM⁻¹ cm⁻² for the CuO nanowires (CuO NWs)/CC and CuO nanoparticles (CuO NPs)/CC, respectively. Ascribing to high conductivity of CC, high specific surface-area from CuO nanostructures, and facilitated charge transfer through in-situ grown structure, the electrodes demonstrate ultrasensitive, selective, stable and fast amperometric sensing (<3 s) of glucose, which presents a new strategy to develop non-enzymatic glucose sensors.

Keywords: Copper oxide nanostructures; in-situ growth; glucose; non-enzymatic biosensor.

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1. Introduction

The development of rapid and reliable methods of monitoring glucose is important in both medical area and food industry. For the past years, various enzymatic sensors that immobilize enzymes to perform selective recognition and quantitative analyses have been studied due to their good selectivity and high sensitivity[1, 2]. However, the use of enzymes may limit the application of enzymatic sensors due to their high cost, complicated immobilization procedure along with inherently instability. Recently, much attention has been concentrated on the development of non-enzymatic glucose sensors. One main strategy is based on electrochemical detection with utilization of transition metal oxides, such as CuO [3, 4], Co₃O₄[5], NiO[6], Fe₂O₃[7], MnO₂[8]. Comparing with other methods, such as surface plasmon resonance (SPR) sensors based on optic fiber [9, 10], which involve complicated fabrication process, the electrochemical method attracts more attention due to its simple fabrication process, excellent stability and electro-catalytic performance [11-13].

Among various metal oxides, CuO is a promising material due to its high electrochemical activity, low cost, non-toxic, and it can be easily integrated with other materials. Recently, CuO has been widely studied in supercapacitors [14, 15], lithium ion batteries [16, 17], gas sensors [18, 19] and photo detectors [20]. Different CuO nanostructures for non-enzymatic glucose sensing have also been explored, such as CuO nanoparticles [21], CuO nanocubes [22], CuO nanoneedles [23], CuO nanowires [24], CuO nanoflowers [25], etc. Meanwhile, carbon-based materials (carbon nanotubes (CNTs), graphene) have been integrated to improve the sensitivity and conductivity through forming composite structures such as CuO/CNTs [26], CuO/carbon sphere [27] and CuO/graphene [28]. Nevertheless, the high-cost of graphene and CNTs along with the complicated procedures make it difficult for large-scale fabrication, and the introduction of polymer binders may degrade the device performance.

In-situ growth of CuO micro/nanostructures on conductive substrate can avoid the use of binder and improve the performance[29, 30]. For example, free-standing porous CuO nanowires grown on Cu foils are directly employed in detecting glucose, which show a remarkably sensitivity of 1420.3 μ A cm⁻² mM⁻¹ [31]. But Cu foil is easily poisoned by chloride ions, making it a necessity to find an alternative conductive substrate. Carbon clothes, consisting of bundles of carbon fiber with multiple channels, are emerged recently as a kind of three-dimensional flexible conductive substrate[32-34]. Compared to planar substrate, CC can provide more sites for active substance and enhance the electrochemical catalysis towards glucose[29].

In this work, we develop non-enzymatic sensor based on in-situ growth of CuO nanostructures (CuO NPs, CuO NWs and CuO NSs) on conductive carbon clothes. The effects of CuO nanostructure on the sensing performance such as sensitivity are investigated. As a result, the as-prepared CuO/CC electrodes exhibit high sensitivity and long-term stability, which are promising for practical applications.

2. Experiment

2.1. Chemical Reagent

Sodium hydroxide (NaOH), ammonium persulfate (NH₄S₂O₈), glucose, uric acid (UA), L-Ascorbic acid (AA), and Acetaminophen (AP) were obtained from Sigma-Aldrich Chemical Company. The CC (12.5 mg cm⁻², 0.32 cm in thickness) was purchased from W0S 1002 CeTech CO., Ltd., China. All other chemicals used in this investigation were of analytical grade. All the solutions were prepared with deionized water (DI) obtained from a Millipore system

2.2. Synthesis

CC were pre-treated in 1M HNO3 solution for 12 h, and then cleaned under ultra-sonication in acetone, ethanol and DI water, respectively. Next, a layer of copper was sputtered on the CC substrate as a seed layer with a DC current of 5A for 10 minutes. CuO NPs were obtained through calcinations in air at 500°C for 4h. CuO NWs and CuO NSs were prepared in an alkaline oxidative etchant solution (AOES) containing 30 mM (NH₄)₂S₂O₈ and 75 mM NaOH in different temperature[31]. In detail, the CC coated with copper seed layer were first immersed in AOES to grow $Cu(OH)_2$ NWs at room temperature for about 15 min. The sample was then thermally treated at 200 °C for 2 h to dehydrate Cu(OH)₂ into CuO NWs. While the black CuO NSs on CC was directly obtained by keeping CC with copper seed layer in the AOES at the 50°C water bath for 15 min without annealing.

2.3. Instrumentation

The morphology of the CC and CuO nanostructures was characterized by the field emission scanning electron microscopy (FESEM, JSM-7600F, JEOL). XRD analysis (PANalytical PW3040/60) with Cu K α radiation (λ =1.5406 Å) from 10° to 80° was carried out to illustrate the structural and crystalline phase of the as-obtained samples. The electrochemical experiments were performed with a CHI660C electrochemical workstation (Autolab PGSTAT302N, Metrohm Autolab, Utrecht, Netherlands). All electrochemical measurements were carried out by a three-electrode system with CC electrode as the working electrode, a Pt wire as the counter electrode, and a Ag/AgCl/ 3M KCl as the reference electrode. Electrical Impedance Spectroscopy (EIS) measurements were also carried out with the electrochemical station in an electrolyte solution of 100 mM KCl containing 5 mM [Fe(CN)₆]^{4-/3-}, in a frequency range from 0.1 Hz to 10⁵ Hz with an ac probe amplitude of 10 mV.

3. Results and discussion

3.1. Structural characterization



Scheme. 1. Schematic illustration of synthesis of CuO nanostructures on CC

The preparation route of the samples was illustrated in Scheme.1. Briefly, CuO NPs were obtained through calcinations in the air at 500°C for 4h. For CuO NWs, CC with copper seed layer was first etched in AOES at room temperature to form Cu(OH)₂ NWs, and then annealed to give the final product of CuO NWs. CuO NSs were directly obtained in AOES at 50°C water bath for 15 minutes.



Fig. 1. SEM images of CC (A), CuO NPs/CC (B), CuO NWs/CC (C), CuO NS/CC (D), each inset was the high-magnification image; (E) XRD pattern of CC, Cu(OH)₂ NWs/ CC, CuO NWs/ CC, CuO NPs/ CC and CuO NSs/ CC

The SEM image and the enlarged view of CC, CuO NPs/CC, CuO NWs/CC and CuO NSs/CC were presented in Fig. 1A to D, respectively. Among the three

nanostructures, CuO NSs displayed the largest surface area, indicating the most active sites for the adsorption of glucose molecules. As displayed in Fig. 1E, X-ray diffraction (XRD) was used to identify the component. For the CuO NPs and CuO NSs samples, strong diffraction peaks at 35.5°, 38.7°, 48.7°, 58.3°, 61.5°, 66.2°, 67.9° and 75.0° could be assigned to the (11-1), (111), (20-2), (202), (11-3), (31-1), (113), and (311) planes of monoclinic CuO, respectively. Note that the three strong diffraction peaks at 26.4° , 44.4° and 54.5° which were corresponding to the structure of carbon were from the CC substrate. And no diffraction peaks could be attributed to Cu₂O or Cu(OH)₂ for both the samples. For the Cu(OH)₂ NWs sample, diffraction peaks at 16.7°, 23.8°, 33.8°, 35.9°, 38.2°, 39.8° and 53.2° corresponded to the (020), (021), (040), (111), (041), (130) and (150) planes of orthorhombic structured Cu(OH)₂, respectively. The CuO NWs sample gave two faintly recognizable peaks at 35.5° and 38.7°, corresponding to the (11-1) and (111) planes of the monoclinic CuO. And no diffraction peaks of Cu₂O or Cu(OH)₂ for the CuO NWs samples were observed. In conclusion, the XRD results showed that the final samples were all with the purity of the CuO phase, and the samples could be used as non-enzymatic electrodes for glucose sensing.

EIS measurement was also performed to investigate the interfacial charge transfer performance of the electrodes, as shown in Fig. S1. Compared with the bare CC electrode, all the electrodes modified with CuO nanostructures showed smaller semicircle at high frequency, indicating improved charge transfer.

3.2. Electrocatalytic activity of CuO/CC toward glucose oxidation

3.2.1 Cyclic voltammetry measurements



Fig. 2. (A) and (B) CV curves of CC (curve a, e), CuO NPs/CC (curve b, f), CuO NWs/CC (curve c, g) and CuO NSs/CC (curve d, h) electrode in the absence and presence of 2.0 mM glucose in 100mM NaOH respectively. Scan rate: 10 mV s⁻¹. (C) CVs of CuO NS/CC electrode at different scan rates from 5 mV s⁻¹ to 100 mV s⁻¹ in 100mM NaOH with 0.5 mM glucose. (D) Calibration plots of anodic peak current vs. scan rate.

The CV of the pure CC electrode and electrodes modified with different CuO nanostructures was examined via cyclic voltammetry (CV) in 100 mM NaOH solution in the absence and presence of 2.0 mM glucose recorded at a scan rate of 10 mV s⁻¹. As shown in Fig. 2A, in the absence of glucose, there was no oxidation peaks for the pure CC electrode (curve a), CuO NPs/CC electrode (curve b) and the CuO NWs/CC electrode (curve c). The CuO NSs/CC electrode (curve d) showed a small and broad reduction which might correspond to a Cu(II)/Cu(III) redox couple, which was similar to the previous report [35]. The large oxide tail observed over +0.65 V was attributed to the onset of water breakdown. As shown in Fig. 2B, in the presence of 2.0 mM glucose, oxidation peaks was not observed either for the bare CC (curve e). On the other hand, for the CuO-based electrodes (curve f, g, h), a rapid increase in current starting at about +0.35 V was observed, corresponding to the oxidation of glucose, indicating the major role of CuO in the process of oxidation. The explicit mechanism for CuO-catalyzed electro-oxidation of glucose in alkaline had not been completely

clarified, and the generally accepted point suggested the formation of a high valence Cu^{III} intermediate that readily oxidized glucose into gluconic acid[36, 37], which could be described with the following reactions:

 $CuO + 2OH^- + H_2O \longrightarrow Cu(OH)_4^- + e^-$

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

CuIII+ glucose \rightarrow CuII + gluconic acid

The reaction was completely irreversible as confirmed by the absence of a cathodic peak in the CV, which was quite similar to the reports of Yang et al [38, 39]. As shown in Fig. 2B, for the CuO NWs/CC electrode (curve g), an obvious shoulder oxidation peak at around +0.65V was observed, while the CuO NSs/CC electrode (curve h) showed substantially higher current. Furthermore, an obvious 150 mV negative shift in peak potential was observed, indicating a stronger electro-catalytic oxidation towards glucose. Based on the descriptions above, it was implied that CuO NSs/CC electrode had an enhanced electro-catalytic performance comparing with other CuO modified electrodes. It was suggested that surface area was responsible for the phenomena (CuO NSs> CuO NWs> CuO NPs).

The effects of different scan rates on the oxidation of glucose at the CuO NSs/CC electrode in 100 mM NaOH in the presence of 0.5 mM glucose were also investigated. As shown in Fig. 2C, the anodic peak current (Ip) increased with the rising of scan rates owing to the oxidation of glucose, and the anodic peak potential shifted to a more positive region (from 0.40 V to 0.70 V) at the same time. As shown in Fig. 2D, Ip vs. scan rate v (from 5 mV s⁻¹ to 100 mV s⁻¹) plot was highly linear (R = 0.995): Ip = 0.000618 + 0.10641 v, indicating a typical surface-controlled process with a fast electron-transfer behavior [8, 40-42], which was ideal for quantitative analysis in practical applications.

3.2.2 Optimization of sensor



Fig. 3. Sensitivity of CuO NSs/CC electrode at different potentials in 100 mM NaOH with a drop addition of 0.1 mM glucose (detection potential: +0.30–0.60 V).

To improve the performance of the sensor, the applied potential influencing the response of the sensor was investigated. The optimal detection potential was determined by a drop addition of 0.1 mM glucose to 100 mM NaOH solution under different potentials for CuO NS/CC electrode. As shown in Fig. 3, the sensitivity was very small at potentials lower than 0.3 V. When the detection potential was increased from 0.4 to 0.6 V, the maximum response was observed at 0.55 V. Therefore, +0.55 V was selected as the optimal detection potential. The effect of NaOH concentration on the response of the sensor was also investigated and shown in Fig. S2. From the plot, 0.10 M NaOH was chosen as the optimal supporting electrolyte in the following measurements.

3.2.3. Amperometric measurements



Fig. 4. (A) I-t curves at +0.55 V with an increasing glucose concentration per 15 s for the CuO NPs/CC (curve a), CuO NWs/CC (curve b) and CuO NSs/CC (curve c) electrode. (B and C) the partly enlarged picture of (A). (D) The current response vs. glucose concentration at the CuO NPs/CC (curve d), CuO NWs/CC (curve e) and CuO NSs/CC (curve f) electrode. The lines indicated the calibration curve.

In order determine the lower detection limit of the sensors, amperometric measurement was conducted. Fig. 4A displayed the steady-state I-t curves of the CuO NPs/CC (curve a), CuO NWs/CC (curve b) and CuO NSs/CC (curve c) electrode in 100 mM NaOH solution with the successive addition of glucose in the range of 0.005–2.515 mM at a bias of 0.55 V. From the curves, CuO NSs/CC electrode exhibited the highest amperometric response to glucose at different concentrations while CuO NPs/CC electrode displayed the weakest response current, consistent with the electrochemical testing results shown in Fig. 2A. It was suggested the enhanced performance was due to the larger surface area of CuO NSs/CC, which could provide more sites for glucose, ensuring the adsorption of more glucose molecular and producing a higher catalyzing current. For the CuO NSs/CC electrode, the response was linear up to 1 mM with the slope of 9803.92 μ A mM⁻¹ (4901.96 μ A mM⁻¹ cm⁻² in term of geometry area) and the correlation coefficient of 0.986 as shown in Fig. 4D (curve f). As shown in Fig. 4B, the electro-catalytic current increased sharply after the

addition of glucose and reached the steady-state within 3 s, illustrating a fast response. Besides, lower concentration of glucose was injected to explore the detection limit, and a limitation of 1 μ M was determined (Fig. S3). As for CuO NWs/CC electrode, the amperometric response was linear up to 1.12 mM (curve b) with the slope of 5946.4 μ AmM⁻¹ (2973.2 μ AmM⁻¹cm⁻² in term of geometry area) (curve e) while it was 1.22 mM (curve a) and 2491.8 μ AmM⁻¹(1245.9 μ AmM⁻¹cm⁻² in term of geometry area) (curve d) for CuO NPs/CC, respectively. Noting that, the curves would reach saturation at a higher glucose concentration. The small drift of baseline was observed after continuous injections of glucose, which may due to the faster consumption of glucose in comparison with its diffusion, the slight variation of local pH, or the adsorption of intermediates on the active sites[41, 43].

The performance of as-fabricated sensors was compared to that of some glucose sensors reported in the literature, as listed in Table1.

ensitivity	LOD	Linear range	Applied	Reference
$AmM^{-1}cm^{-2})$			potential	
01.96	1µM	Up to 1 mM	+0.55V	This work
073.2	1µM	Up to 1.12	+0.55V	This work
		mM		
245.9	1µM	Up to 1.22	+0.55V	This work
		mM		
3	40nM	Up to 1.3 mM	+0.48V	[42]
20.3	5.1µM	Up to 2.05 mM	+0.35V	[30]
96	0.2µM	Up to 1.2 mM	+0.40V	[40]
2.7	0.1µM	1–5.3 mM	+0.60V	[23]
	AmM ⁻¹ cm ⁻²) 01.96 73.2 45.9 3 20.3 96 2.7	AmM ⁻¹ cm ⁻²) LOD 01.96 1μM 73.2 1μM 45.9 1μM 3 40nM 20.3 5.1μM 96 0.2μM 2.7 0.1μM	Instituty LOD Linear range AmM ⁻¹ cm ⁻²) 1μ M Up to 1 mM 73.2 1μ M Up to 1.12 mM 45.9 1μ M Up to 1.22 mM 3 40nM Up to 1.3 mM 20.3 5.1μ M Up to 2.05 mM 96 0.2μ M Up to 1.2 mM 27 0.1μ M $1-5.3$ mM	Institutty LOD Linear range Applied AmM ⁻¹ cm ⁻²) potential potential 01.96 1 μ M Up to 1 mM +0.55V 73.2 1 μ M Up to 1.12 +0.55V 73.2 1 μ M Up to 1.12 +0.55V 73.2 1 μ M Up to 1.12 +0.55V MM 45.9 1 μ M Up to 1.22 +0.55V MM 3 40nM Up to 1.3 mM +0.48V 20.3 5.1 μ M Up to 2.05 mM +0.35V 96 0.2 μ M Up to 1.2 mM +0.40V 2.7 0.1 μ M 1–5.3 mM +0.60V

Table.1. Composite based non-enzymatic glucose sensors and their detection performances.

 Measurements were performed using amperometric technique

CuOnanoleaf	664.3	5.7µM	Up to 0.9 mM	+0.35V	[44]
/MWCNTs					
Ni-Cu/TiO2NTs	1590	5μΜ	Up to 3.2 mM	+0.60V	[45]
CuO/TiO2/Ti	79.79	1µM	Up to 2.0 mM	+0.5V	[46]
MnO2/MWNTs	33.19		up to 28 mM	-0.20 V	[8]
Co3O4	1440	0.15	0.005–12 mM	0.55 V	[47]
microspheres		μΜ			

CNTs: carbon nanotubes, MWCNTs: multi-walled carbon nanotubes, ITO: Indium tin oxide coated glass, GCE: glassy carbon electrode, LOD: Limit of detection

From the table, the performance of the sensor developed in this work was impressive, especially in terms of the sensitivity. The improved performance could be attributed to that: (1) The 3D CC with porous channels had good electrical conductivity and provided more sites for active substance than planar substrate, which was beneficial to adsorb glucose molecules as much as possible. (2) CuO nanostructures could contribute higher specific surface area to providing more active sites and shortening ion diffusion distance. (3) The in-situ growth method avoided the use of polymer binders, facilitating charge transfer and ion transport from the electrolyte to the electrode surface.

3.3. Reproducibility, stability and anti-interference property



Fig. 5. (A) Stability of the sensors over 20 days using 100 mM NaOH with 0.2 mM glucose at +0.55 V for CuO NPs/CC electrode (curve a), CuO NWs/CC electrode (curve c) and CuO NSs/CC electrode (curve b). (B), (C) and (D) Interference tests of the sensors in 100 mM NaOH at +0.55 V with 0.2 mM glucose and 0.02 mM other interferents for CuO NPs/CC, CuO NWs/CC and CuO NSs/CC electrode, respectively.

Long-term stability and reproducibility of sensors were of critical importance for practical applications. The stability of glucose sensors based CuO nanostructures was evaluated by measuring its amperometric current response to glucose during a period of 20 days at a time interval of 24 hours, as shown in Fig. 5 A. After 20 days, the sensitivity of the CuO NPs/CC electrode maintained approximately 93.5% of its original current response. Meanwhile, it was just 86.5% and 76.2% for the CuO NSs/CC and CuO NWs/CC electrode, respectively. The reproducibility of the sensors was estimated by injecting 0.2mM of glucose with five different electrodes respectively. For the CuO NS/CC electrode, the relative standard deviation was obtained to be 2.76% while it was 4.78 % and 1.81% for CuO NWs/CC and CuO NPs/CC electrode, respectively. The outstanding stability of CuO NPs/CC electrode was ascribed to a much stronger binding of active substance on the substrate after high-temperature calcinations. The blood glucose level of a normal human body was usually between 4 mM and 7 mM [48], while the concentration of endogenous AA and UA was about 0.125 mM and 0.33 mM in blood samples, respectively [49]. For practical applications, the interference experiments were carried out to discriminate the interfering species such as UA, AA and AP by successive addition of 0.2 mM glucose and 0.02 mM interfering species in 100mM NaOH at a bias of +0.55 V. As shown in Fig. 5 B, C and D, all the CuO-modified electrodes showed negligible rise in the sensor response to the interfering species and the caused current responses just ranged from 0.2 to 8% comparing with glucose, indicating an excellent selectivity toward common interfering species. To investigate the application of CuO electrodes in real blood samples, calf serum (CS) was chosen as blood samples (Fig. S4). CuO NSs/CC exhibited the similar response for both CS and pure glucose, indicating the electrodes fabricated here had the practical sensing capability for glucose.

4. Conclusion

In this paper, different CuO nanostructures on the conductive CC by in-situ growth have been applied as electrodes to develop ultrasensitive amperometric nonenzymatic glucose sensor. All the electrodes displayed high sensitivity and fast responses (< 3 s), and the sensitivity of the CuO NSs/CC reaches up to 4902 μ A mM⁻¹ cm⁻². Due to high conductivity of carbon clothes, high specific surface-area from CuO nanostructures, fast charge transfer and ion transport from the electrolyte to the electrode surface, the developed electrodes demonstrate ultrasensitive, selective, stable and fast amperometric sensing of glucose, which are promising for developing non-enzymatic glucose sensors with high performance. Besides, the method presented here shows other advantages, such as ease of fabrication, low cost, and good reproducibility.

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20