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CuO Nanowhiskers Grown from Cu Nanowire Electrode as Highly Efficient Electrocatalysts for Glucose Detection

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Abstract: Nonenzymatic electrochemical glucose sensors are normally based on an electrode that owns a conductive substrate decorated with nanosized electrocatalysts. However, these sensors often suffer from drawbacks originating from the use of polymer binder or substrate of low specific surface area. In this work, a porous Cu nanowire (CuNW) electrode fabricated by thermal annealing of CuNWs is employed as the conductive substrate, and the electrocatalysts, namely CuO nanowhiskers with a length ranging from 1 μm to 2 μm, are in situ grown from the CuNW electrode via anodic deposition and subsequent calcination. Electrochemical measurements by cyclic voltammetry indicate that the as-formed electrode is stable in alkaline medium and responds well to the addition of glucose. An investigation on the performance of this CuO nanowhiskers/CuNWs electrode as a nonenzymatic glucose sensor via amperometry under optimized conditions reveals a wide linear range of 3 μM to 7135 μM, a high sensitivity of 3506 $\mu A \cdot mM^{-1} \cdot cm^{-2}$, and a low detection limit of 0.96 μM at a signal-to-noise ratio of 3. Testing the interfering signals produced by Cl^- ions and some easily oxidizable compounds at a level of physiological concentration suggests a strong anti-interference ability of the as-prepared sensor. In addition, this new glucose sensor also possesses good stability and reproducibility and is successfully tested for detection of glucose in human serum sample.

Keywords: Cu nanowires; CuO nanowhiskers; Electrocatalysts; Glucose; Nonenzymatic sensor

1. Introduction

The measurement of glucose concentration is of great importance in many fields ranging from food industry[1] to clinical medicine[2]. In clinical practice, for example, diabetes mellitus is characterized by high blood sugar, and regular detection of blood glucose level is thus crucial for diabetic patients to avoid diabetic emergency. Glucose concentration can be determined by a number of analytical techniques, such as chromatography[3], optical methods[4] and electrochemical methods[5]. Among them, the electrochemical methods have been extensively studied since Clark and Lyons reported the first enzymatic electrode for glucose sensing in 1962[6]. Although the glucose sensors on market are commonly based on enzyme-modified electrodes, they suffer from several drawbacks originating from the use of enzyme, including poor stability, high cost and complicated immobilization procedures. As a result, non-enzymatic glucose sensors based on direct electrochemical oxidation of glucose have also drawn great attention over the past three decades[5,7,8].

The performance of non-enzymatic electrochemical glucose sensors can be influenced by a number of factors including the type and shape of electrocatalysts, the additives (e.g. promoters and polymer binders used in modified electrode), and the structure of the electrode. Because of its high activity for electro-oxidation of glucose, cupric oxide (CuO) is an attractive electrocatalyst used for glucose sensing and has been extensively studied in the past[9-22]. To fabricate a CuO-based glucose sensor with good performance, nanostructured CuO with a variety of morphologies, such as nanospheres[9], nanofibers[10], nanowires[11], nanoparticles[12], hollow polyhedron[13], nanoellipsoids[14] and nanosheets[15], are often selected due to their higher specific surface area in comparison with the bulk counterpart. Normally these nanosized materials are coated on a conductive substrate, for example, glassy carbon electrode (GCE), with the help of polymer binder. However, the presence of the binder may not only cause an increase in charge transfer resistance and a reduction in the number of electrocatalytic active sites but also hinder the mass transport. To overcome the shortcomings resulting from the use of polymer binder, in situ growth of various micro/nanostructures, e.g. CuO microflowers[16], nanoporous CuO[17], CuO nanowires/microflowers[18], CuO/Cu_2O nanosheets[19] and flower-like nanostructured CuO[20], on a conductive substrate (often Cu foil) has also been investigated. Although in situ growth of CuO can avoid the use of polymer binder, these electrodes still suffer from the use of Cu foil that offers a low surface area and thus cannot provide enough room for the growth of CuO. Therefore, the choice of a substrate that not only has excellent electric conductivity but also possesses a high specific surface area is also important, and recently the use of three-dimensional Cu foam as the conductive substrate for in situ growth of CuO is found to be an effective way for improving the sensitivity of the fabricated sensors[21,22].

In this article, we report the use of a Cu nanowire (CuNW) electrode as the conductive substrate, and the electrocatalyst, namely CuO, is directly grown from the CuNW electrode via anodic deposition and subsequent calcination. Interest in this work is based on the following considerations. Although Cu is commonly used as the conductive substrate due to its superior electrical conductivity and easy conversion into CuO, there is no work on the use of other Cu substrates for in situ growth of CuO except for Cu foil and Cu foam. To fabricate a new sensor with its performance different from those of Cu foil or Cu foam based sensors, it is essential to choose a Cu substrate of a special structure for in situ growth of CuO. Furthermore, while the replacement of Cu foil by Cu foam can greatly improve the sensitivity of the glucose sensor as evidenced by two recent studies[21,22], the upper ends of the linear ranges of the reported sensors (up to 0.5 mM[22] or 2 mM[21]) are equal to or smaller than those of the Cu foil based sensors. Since the CuNW electrode, fabricated by thermal annealing of CuNWs at 600 °C, owns a porous network structure and can offer an electrochemical active surface area 200 times higher than that of a Cu wire electrode with a nearly identical geometrical surface area[23], the use of the CuNW electrode as the substrate favors the growth of CuO via electrochemical deposition and thus increases the surface area of the resulting sensor. An improvement in linear range is therefore expected when Cu foil is replaced by the CuNW electrode. The purpose of this work is to reveal that, by using the CuNW electrode as the substrate for in situ growth of CuO via anodic deposition and subsequent calcination, CuO nanowhiskers with a length typically ranging from 1 μm to 2 μm can grow from the nanowire network and the as-formed CuO nanowhiskers/CuNWs electrode exhibits excellent performance as a non-enzymatic glucose sensor with its linear range up to more than 7 mM.

2. Materials and Methods

All chemicals were of analytical grade and used as received without further purification. Ascorbic acid (AA, >99.0%), acetaminophen (AP, 99.0%), sucrose (99.5%), and fructose (99.0%) were purchased from Aladdin. The CuNWs used in our experiments were synthesized via a cheap and environmentally friendly method developed by our group, and the detailed preparation procedure can be found in our previous work[24].

The fabrication of CuO nanowhiskers/CuNWs electrode includes four steps, namely preparation of a CuNW film, thermal annealing of the CuNW film to obtain a CuNW electrode, growth of $Cu(OH)_2$ on the CuNW electrode via anodic deposition, and conversion of $Cu(OH)_2$ into CuO via calcination. The CuNW film was prepared by a method different from that reported in our previous study[23]. Rather than transferring CuNWs into a filter membrane and then filtering[23], the CuNW film was obtained by filling a mould (used for controlling the shape and size of the electrode) with dense CuNW slurry (obtained by adding small amount of ethanol into CuNW powder) and then removing the mould after the CuNWs in the mould being dried in N_2 atmosphere. The resulting CuNW film was connected with a Cu wire and then annealed under Ar atmosphere at 600 ^{o}C for 30 min to form a CuNW electrode with a size of about 0.5 × 0.4 × 0.05 cm^3. To obtain the CuO nanowhiskers/CuNWs electrode, the CuNW electrode was anodized in a 50 mM KOH solution at room temperature for 30 min at a potential of 0.1V (*vs*. a saturated calomel electrode, SCE) to form blue $Cu(OH)_2$. The as-anodized electrode was washed with deionized water and ethanol, and then dried in a N_2 atmosphere at room temperature for 12 h. Finally, the electrode was calcined in a N_2 atmosphere at 300 ^{o}C for 3 h to convert $Cu(OH)_2$ into CuO.

The surface morphology of the electrodes was examined by scanning electron microscope (SEM, Hitachi S-4700) operating at 15 kV. The phase composition of the samples was analyzed by x-ray diffraction (XRD), which was performed on a Thermo ARL XTRA x-ray diffractometer using Cu Kα X-ray source. Electrochemical measurements were conducted at room temperature with a CHI660E workstation (CHI Instruments). The setup was a conventional three-electrode cell with a platinum wire as counter electrode and SCE as reference electrode. Cyclic voltammetry (CV), carried out in a NaOH electrolyte at 50 mV/s, was employed to characterize the electrocatalytic activity for glucose oxidation, and amperometry was chosen for glucose detection at room temperature with the solution being stirred at 400 rpm.

3. Results and Discussion

3.1 Characterization of the CuO Nanowhiskers/CuNWs Electrode

The surface morphology of the resulting CuO electrode prepared by anodic oxidation of a CuNW electrode in alkaline medium and subsequent calcination is illustrated in **Figure 1**. From the low-magnification SEM image (**Figure 1a**), it is obvious that the as-prepared electrode still contains large numbers of nanowires (see arrows in **Figure 1a**). At high magnification (**Figure 1b**), however, we can observe many nanowhisker-like materials protruding from the surface of these nanowires, and the length of these nanowhiskers is typically in the range of 1 to 2 microns. A close examination of these nanowhiskers reveals that the size of each nanowhisker often decreases from one end to another, thus forming a tip as indicated by arrows in **Figure 1c**. To determine the phase composition of these nanowhiskers, XRD measurement was performed on the as-prepared electrode and the result is illustrated in **Figure 1d** (see the pattern before acid treatment). All the peaks observed can be indexed to CuO with a monoclinic structure (JCPDS 65-2309), and the peaks at 32.6^{o}, 35.5^{o}, 38.9^{o}, 48.9^{o}, 53.6^{o}, 58.5^{o}, 61.7^{o}, 66.0^{o}, 66.6^{o}, 68.4^{o}, 72.8^{o}, and 75.2^{o} correspond to the diffractions of (110) (-111), (111), (-202), (020), (202), (-113), (022), (-311), (220), (311) and (004) planes, respectively. The result clearly demonstrates that the as-formed nanowhiskers are CuO. However, the absence of diffraction peaks of Cu surprises us because this disagrees with the SEM observation that a large number of nanowires are still present. To confirm that CuNWs were not completely converted into CuO, we removed part of CuO nanowhiskers by immersing the electrode into a diluted hydrochloric acid for a while and then took a XRD measurement again after the electrode was dried (see the pattern after acid treatment in **Figure 1d**). Clearly, the treated electrode mainly consists of Cu, with the peaks at 43.3^{o}, 50.4^{o}, and 74.1^{o} being indexed to a face-centered cubic Cu phase (JCPDS 04-0836) and corresponding to the diffractions of (111), (200) and (220) planes, respectively. In addition, the Cu_2O phase, resulting from the oxidation of Cu, is also observed. These observations imply that CuNWs, serving as the skeleton of the electrode, are still present.

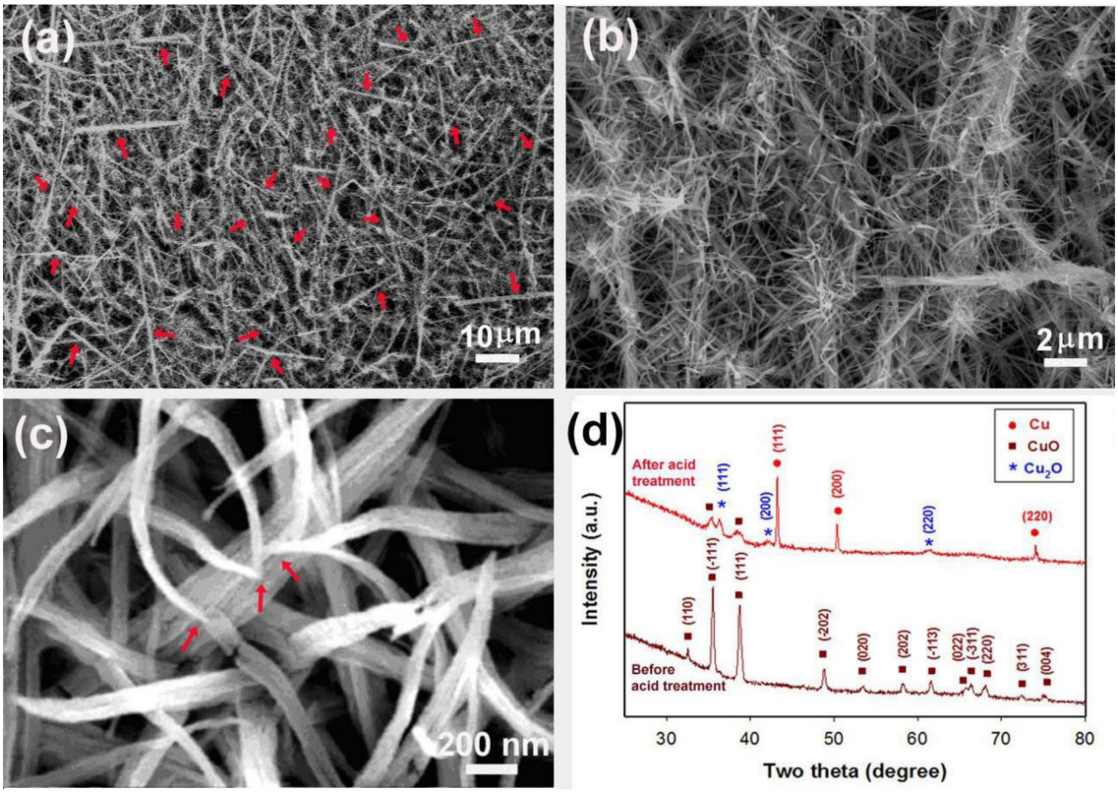

Figure 1. (a-c) SEM images of the CuO nanowhiskers/CuNWs electrode at different magnifications, and (d) XRD patterns of the CuO nanowhiskers/CuNWs electrode before and after acid treatment

3.2 Electrochemical Properties of the CuO Nanowhiskers/CuNWs Electrode

Since the detection of glucose by CuO based sensors was normally conducted in alkaline media, we first investigated the electrochemical stability of the CuO nanowhiskers/CuNWs electrode under alkaline condition. **Figure 2a** presents the repetitive CV curves of CuO nanowhiskers/CuNWs electrode in 200 mM NaOH solution. Although there is a slight decay in cathodic current density when the scan number increases from 1 to 2, no change in anodic current density can be observed. Moreover, when the scan number is further raised (namely from 2 to 10), the cathodic current density is almost kept unchanged. These observations imply that the CuO nanowhiskers/CuNWs electrode can rapidly reach a stable state under alkaline conditions, which is essential for its use as an effective sensor to detect glucose.

The electrocatalytic activity for oxidation of glucose at the CuO nanowhiskers/CuNWs electrode was examined by recording its response to glucose of different concentrations during CV scan. As illustrated in **Figure 2b**, the anodic current density rises obviously with increasing the concentration of glucose, indicating a good electrocatalytic activity for oxidation of glucose in alkaline media. However, the cathodic current density decreases as the concentration of glucose increases. Similar result has been reported in a number of CuO-based glucose sensors[11,13,16,17,19,21]. Although the oxidation mechanism of glucose at CuO-based electrodes has not been completely uncovered, the observed negative response of cathodic current density to glucose concentration seems to support the Cu(III) mechanism[25,26]. In this mechanism, surface CuO can be oxidized to CuOOH, an active substance that can oxidize glucose, under alkaline conditions (see Eq. 1) and the cathodic current observed at high potential is related to the reduction of CuOOH to CuO, namely the reverse process of Eq. 1.

$$CuO + OH^- - e^- \rightarrow CuOOH \qquad (1)$$

When glucose is present, the formed CuOOH can immediately oxidize glucose to gluconic acid or other compounds. The consumption of CuOOH favours the forward reaction of Eq. 1 but is unfavorable for its reverse reaction, thus resulting in a rise in anodic current density but a decline in cathodic current density.

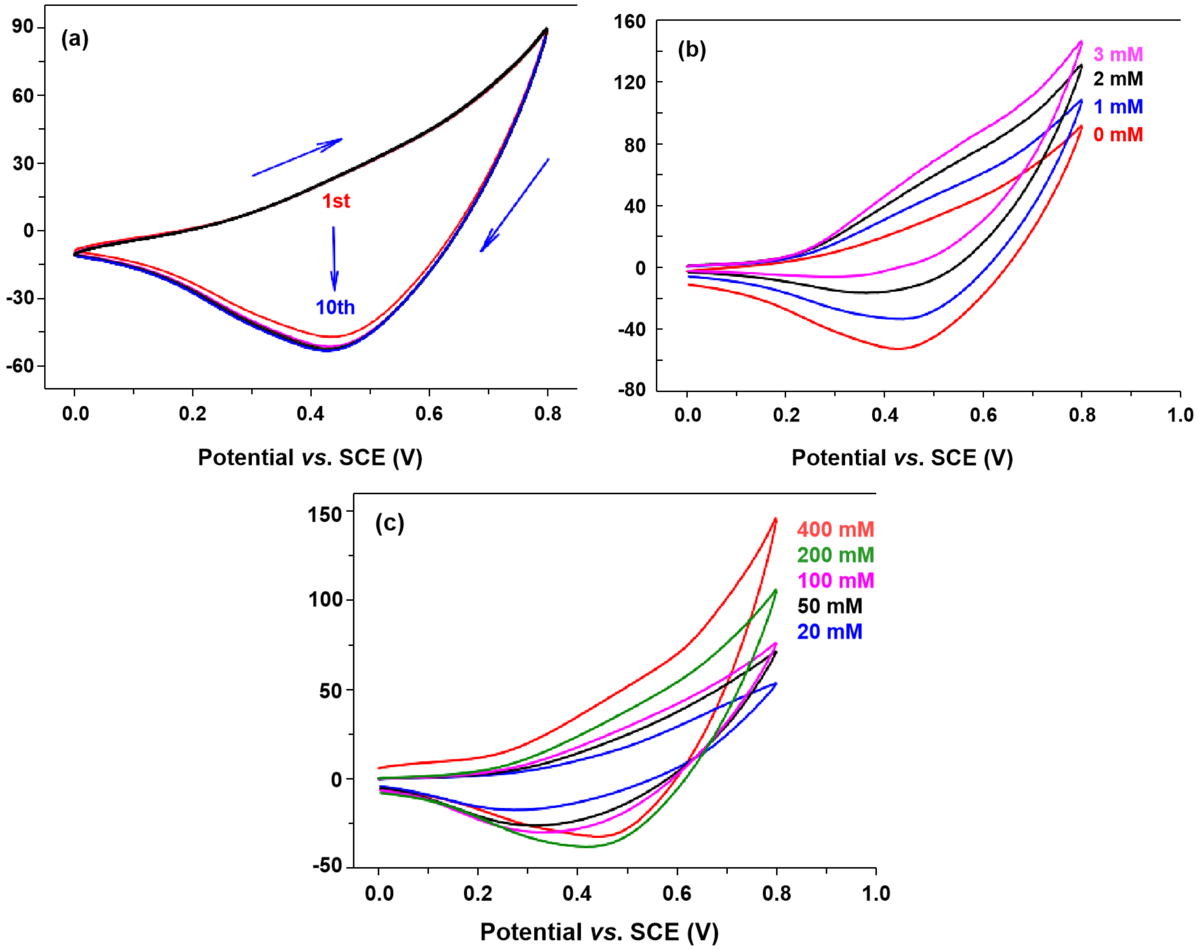

Figure 2. CV curves recorded at the CuO nanowhiskers/CuNWs electrode: (a) in a 200 mM NaOH solution (repeated ten times), (b) in solutions containing 200 mM NaOH and glucose of different concentrations, and (c) in solutions containing 1 mM glucose and NaOH of different concentrations

According to Eq. 1, it is clear that the solution alkalinity has an impact on the formation of CuOOH and thus affects the oxidation of glucose. To select a suitable solution alkalinity for detection of glucose, the effect of NaOH concentration on the oxidation of glucose (1 mM) was investigated (**Figure 2c**). Similar to its dependence on the glucose concentration, the anodic current density increases as the solution alkalinity increases. However, the difference is that the cathodic current density also increases with the concentration of NaOH (except for the NaOH concentration being 400 mM), with the peak position shifting to a high potential. These observations suggest that the presence of high concentrations of NaOH favours the electrocatalytic oxidation of glucose. However, when the concentration of NaOH reaches 400 mM, the anodic current density in the potential range of 0 V to 0.2 V is much higher than that observed in 200 mM NaOH solution. This should have an impact on the background noise when the electrode is used for glucose detection. Therefore, although the highest anodic current density is observed in the solution of high alkalinity, we choose a 200 mM NaOH solution for glucose detection.

It is generally accepted that at CuO-based electrodes the electrocatalytic oxidation of glucose occurs at a high potential. However, there is no obvious peak appearing in the potential range of 0.4-

0.7 V in CV curves (**Figure 2b and 2c**). In order to choose an effective potential to detect glucose by amperometry, the amperometric response of the CuO nanowhiskers/CuNWs electrode to glucose at different applied potentials with the successive addition of 0.1 mM glucose was probed. As shown in **Figure 3**, the current density initially increases with the applied potential and then reaches a maximum when the potential is 0.55 V (*vs*. SCE). Further increasing the potential to 0.6 V will lead to a slight decay in current density. As a result, a potential of 0.55 V (*vs*. SCE) is chosen for glucose detection at the CuO nanowhiskers/CuNWs electrode.

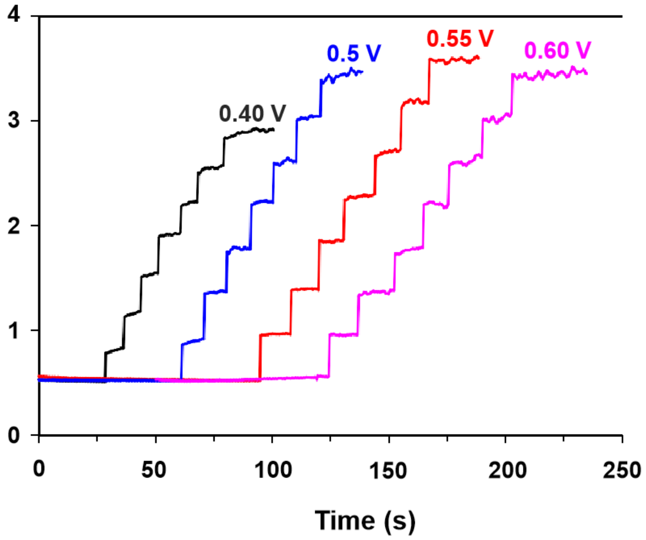

Figure 3. Amperometric response of the CuO nanowhiskers/CuNWs electrode to successive addition of 0.1 mM glucose into a 200 mM NaOH solution at different applied potentials

3.3 Electrochemical Detection of Glucose

To evaluate the performance of the CuO nanowhiskers/CuNWs electrode as a nonenzymatic glucose sensor, the amperometry, an electrochemical technique commonly used for glucose detection, was employed. **Figure 4** presents the response of the CuO nanowhiskers/CuNWs electrode to glucose at different concentration ranges. It is obvious that the new glucose sensor can response well to glucose, either at low concentrations (e.g. several μM) or high concentrations (e.g. several mM). The peak current density is linearly related to glucose concentration in the range of 3-7135 μM with a regression equation of j (mA/cm^2)= 3.506 × 10^{-3} c (μM) + 0.6411 and a correlation coefficient R^2 of 0.998 (**Figure 5**). A sensitivity of 3506 μA•mM^{-1}•cm^{-2} is obtained from the slope of the linear regression line. The limit of detection (LOD) of this sensor is obtained by LOD = 3σ/s, where σ and s are, respectively, the standard deviation of the blank signal and the sensitivity of the sensor. The value of LOD is calculated to be about 0.96 μM. The sensitivity, linear range and LOD of this sensor were compared with CuO-based sensors reported in the literature (**Table 1**), and the conclusions are summarized as follows. (i) Compared with the sensors with CuO being coated on GCE or ITO (Indium-Tin Oxide) glass with the help of binder, our new glucose sensor can offer a much higher sensitivity and a much wider linear range, with its LOD being lower than or comparable to most of these sensors[9-15]. (ii) In comparison with the sensors with CuO in situ grown on Cu foil or carbon electrode[16-20], our new glucose sensor owns a much higher linear range, as well as a higher sensitivity and a lower LOD than most of these sensors. This observation confirms that the replacement of Cu foil by our CuNW electrode for in situ growth of CuO can greatly improve the performance of the fabricated sensor. (iii) Compared to the sensors with CuO in situ grown on Cu foam[21,22], our new glucose sensor also has its own feature, namely possessing a linear range up to 7 mM and a LOD below 1 μM. Thus, our sensor is not only suitable for detecting glucose of low concentration (several μM) but can also be applied to determining glucose of high concentration (several mM).

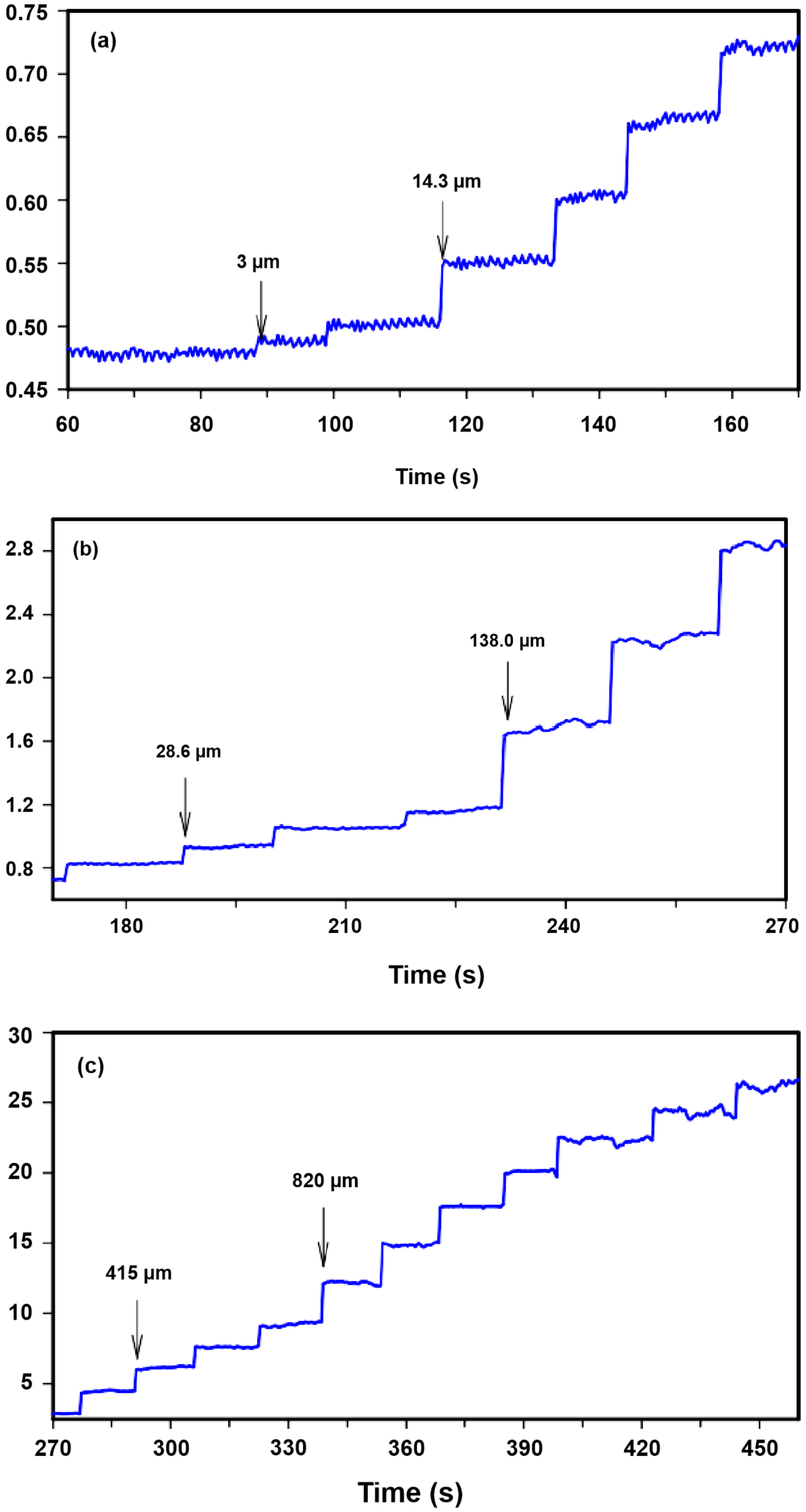

Figure 4. Amperometric response of the CuO nanowhiskers/CuNWs electrode to glucose at different concentration ranges: (a) 0-70 µM, (b) 70-600 µM, and (c) 600-8000 µM

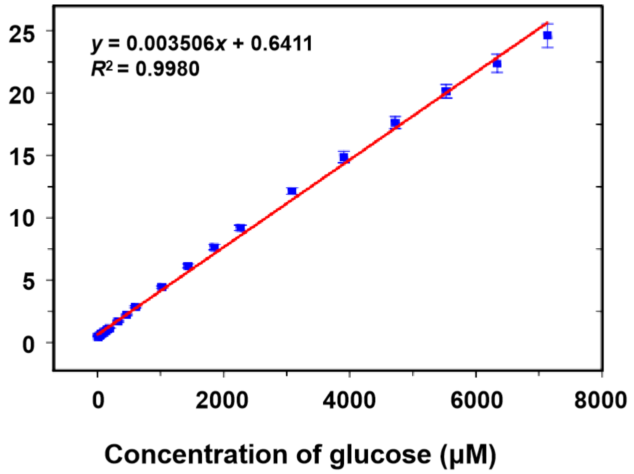

Figure 5. Linear relationship between current density and glucose concentration observed at the CuO nanowhiskers/CuNWs electrode

Table 1. Comparison among the performances of CuO-based non-enzymatic electrochemical glucose sensors

Electrode materials	Binder used or not	Sensitivity (μA•mM^{-1}•cm^{-2})	Linear range (μM)	LOD (μM)	Correlation coefficient R^2	Ref.
CuO nanospheres/GCE	used	404.53	up to 2550	1	0.999	[9]
CuO nanofibers/GCE	used	431.3	6-2500	0.8	0.998	[10]
CuO nanowires/GCE	used	46.28	0.5-488	0.045	0.9959	[11]
CuO nanoparticles/GCE	used	1430	40-6000	5	–	[12]
CuO hollow polyhedron/GCE	used	1112	1.0-4000	0.33	0.998	[13]
CuO nanoellipsoids/GCE	used	2555	100-1000	–[a]	0.9994	[14]
CuO nanosheets/indium-doped tin oxide (ITO) glass	used	2272	2.0-600	1.0	0.9985	[15]
CuO flowers/Cu foil	not used	4077.7	5-2000	1.2	0.9996	[16]
Nanoporous CuO/Cu foil	not used	1066	100-2040	2	0.9962	[17]
CuO nanowire-microflower/Cu foil	not used	1943	up to 4000	4	0.998	[18]
CuO/Cu_2O nanosheets/Cu foil	not used	1541	up to 4000	0.57	–	[19]
Flower-like nanostructured CuO/ carbon electrode	not used	1460	40-2000	2.5	0.997	[20]
CuO nanothorn/Cu foam	not used	5984.3	0.5-2000	0.276	0.9974	[21]
CuO nanowire arrays/Cu foam	not used	32330	0.1-500	0.02	0.9926	[22]
CuO nanowhiskers/CuNW electrode	not used	3506	3-7135	0.96	0.9980	This work

[a] Despite a value of 0.072 μM reported in Ref. 14, this value was obtained by using the standard deviation of amperometric response to 100 μM glucose, rather than the standard deviation of the blank signal.

One of major challenges in non-enzymatic glucose sensor based on direct electrochemical oxidation of glucose is the interfering signals produced by easily oxidizable compounds co-existing with glucose in human blood serum. These compounds include ascorbic acid (AA), acetaminophen (AP), sucrose, fructose, uric acid (UA) and dopamine (DA). To test the anti-interference ability of our new CuO-based sensor, AA, AP, sucrose, and fructose at a level of physiological concentration (namely 0.10 mM AA, 0.10 mM AP, 74 μM sucrose and 8.1 μM fructose) was successively injected before measuring the response to 5 mM glucose (also at a level of physiological concentration). As illustrated in **Figure 6a and 6b**, the amperometric response of our CuO nanowhiskers/CuNWs sensor to 5 mM glucose was not affected by addition of AA, AP, sucrose, and fructose at a physiological concentration, indicating negligible interferences from AA, AP, sucrose, and fructose. Besides the interferences from easily oxidizable compounds, the interference from Cl^- ions, which co-exist with glucose in human blood serum and can poison the noble metals (e.g. Pt and Au) based glucose sensor, was also investigated. It is clear from **Figure 6c** that the presence of Cl^- ions has no impact on the performance of our sensor.

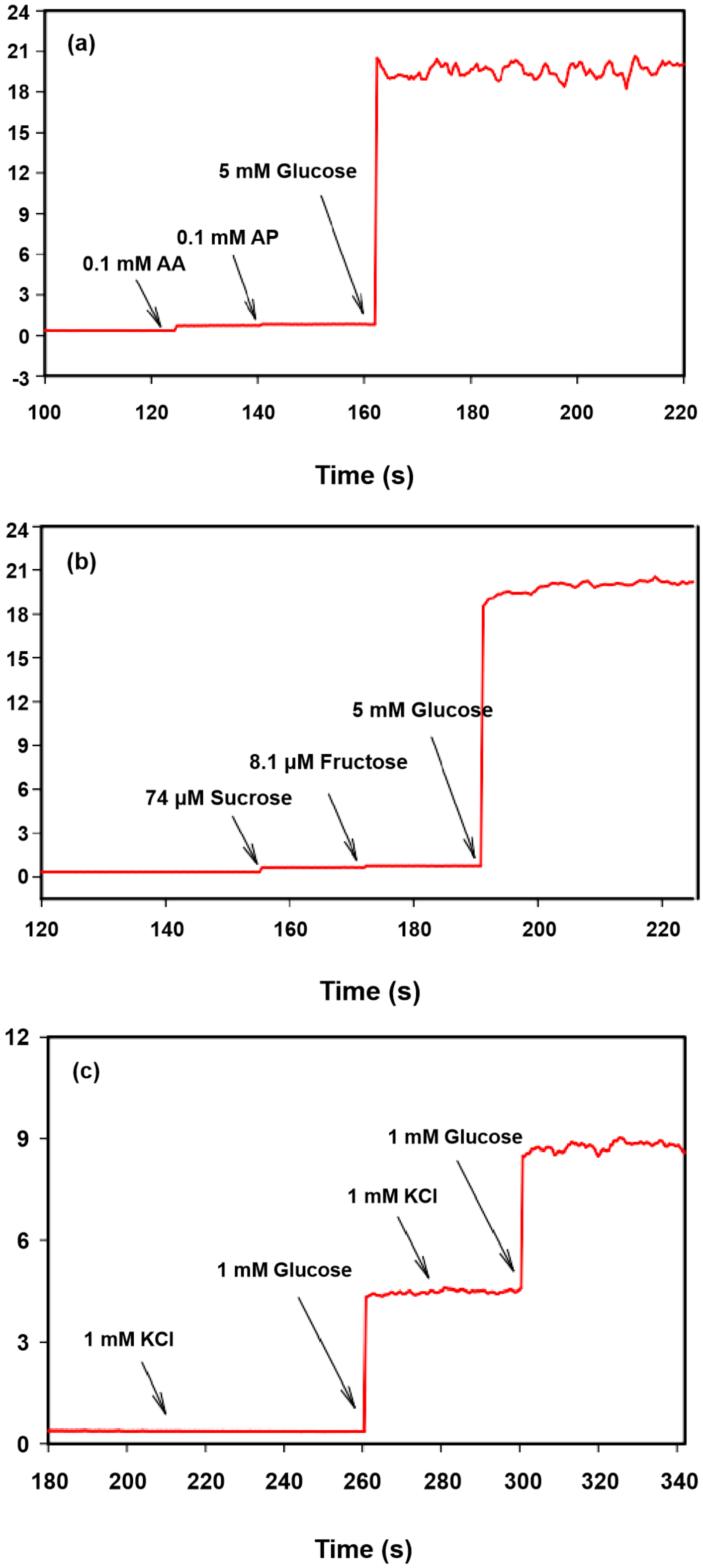

Figure 6. Amperometric response of the CuO nanowhiskers/CuNWs electrode to several interfering compounds: (a) AA and AP, (b) sucrose and fructose, and (c) KCl

The reproducibility, stability and practical application of our sensor were also studied. To test the inter-electrode reproducibility, four CuO nanowhiskers/CuNWs electrodes were prepared, and their response to the oxidation of 1 mM glucose was tested. The current density recorded at these independent electrodes shows a relative standard deviation (RSD) of 4.1%, indicating a good inter-electrode reproducibility. To evaluate the intra-electrode reproducibility, a solution of 1 mM glucose was measured six times by one electrode under the same conditions. A RSD of about 1.8% observed hints a good repeatability. A good stability of the CuO nanowhiskers/CuNWs electrode is also confirmed by the result that after being kept in air at room temperature for 30 days, the electrode shows an amperometric response to 1 mM glucose (at 0.55 V) being about 96.4% of the value observed on the first day. The practical application of our sensor was evaluated by measuring the glucose concentration in human serum sample. The human serum sample with a glucose concentration of 3.96 mM was divided into two parts, one of which was added into a given amount of glucose (2 mM). The glucose concentrations of the two parts found by our sensors are, respectively, 3.82 mM and 5.77 mM, with the corresponding recoveries being about 96.4% and 96.8%. These results indicate that our CuO-based sensor can be applied to the determination of glucose in human serum samples.

4. Conclusions

In summary, we have developed a novel non-enzymatic glucose sensor based on in situ growth of CuO from a porous CuNW electrode via anodic deposition and subsequent calcination. SEM and XRD investigations have revealed that the as-prepared electrode owns a novel structure, in which CuNWs serve as its skeleton and CuO nanowhiskers with a length typically ranging from 1 μm to 2 μm are distributed on the nanowire network. This CuO nanowhiskers/CuNWs electrode, which is stable under alkaline conditions, is catalytically active for electro-oxidation of glucose and exhibits an excellent performance as a non-enzymatic glucose sensor with a linear range up to more than 7 mM, a detection limit below 1 μM, and a high sensitivity of 3506 $\mu A{\bullet}mM^{-1}{\bullet}cm^{-2}$. Combining with its strong anti-interference ability as well as good stability and reproducibility, therefore, this new CuO-based glucose sensor can be applied to detection of glucose of both low concentrations (several μM) and high concentrations (several mM).

Author's Contributions

Conceived and designed the experiments: Liang J and Liu Z

Performed the experiments: Xue Z and Liang J

Wrote the paper: Xue Z and Liu Z

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Availability of Supporting Data

Data is contained within the article.

Conflict of Interest

The authors declare no conflict of interest.

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