J Solid State Electrochem (2012) 16:2877–2881
DOI 10.1007/s10008-012-1718-3

ORIGINAL PAPER

Highly enhanced electrocatalytic oxidation of glucose on $Cu(OH)_2$/CuO nanotube arrays modified copper electrode

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Received: 9 November 2011 / Revised: 2 March 2012 / Accepted: 7 March 2012 / Published online: 20 March 2012

Abstract A highly sensitive and fast-response biosensor based on cupric hydroxide/oxide ($Cu(OH)_2$/CuO) nanotube arrays (CNA) was successfully fabricated in this work. CNAs were prepared on copper electrode surface by simply immersing copper electrode in an aqueous solution of NaOH and $(NH_4)_2S_2O_8$. The morphology and the composition of the CNAs were characterized by scanning electron microscopy (SEM) and X-ray diffraction spectroscopy (XRD), respectively. The electrocatalytic activity of the CNA modified copper electrodes (CNA/Cu) towards glucose oxidation was investigated by cyclic voltammetry and amperometry. The CNA/Cu showed good non-enzymatic electrocatalytic responses to glucose in alkaline media and can be used for the development of enzyme-free glucose sensors.

Keywords Cupric hydroxide · Glucose · Modified electrode · Nanotube array · Electrocatalysis

Introduction

Diabetes is a metabolic disorder and a major world health problem. There are over 170 million diabetics worldwide (WHO 2004), and the number is projected to 300 million in 2025, so glucose detection is becoming incredibly important to the patients suffering from diabetes [1, 2]. Due to its high sensitivity and selectivity to glucose and stable activity over a broad range of pH [3], glucose oxidase (GOx) has been widely used to construct various amperometric biosensors for glucose detection [1, 4–12]. However, due to the intrinsic feature of enzymes, GOx-based biosensors suffer from a stability problem [13]. Direct electrocatalytic oxidation of glucose at an enzyme-free electrode would exhibit conveniences and advantages to avoid the drawbacks of the enzyme electrode. In recent years, much attention has been paid to develop enzyme-free electrodes [14–19]. Precious metals [14, 15, 17, 20], metal alloys [18, 21], and metal nanoparticles [16, 22–24] have been extensively investigated in the development of nonenzymatic glucose sensors. However, these electrodes have drawbacks such as low sensitivity and costliness and also suffer from the poisoning of chloride ions [15, 19, 25]; thus, their application is greatly limited. Therefore, the development of a cost-effective, sensitive, and reliable enzyme-free glucose sensor is still greatly demanded [13].

Cupric oxide (CuO) has been studied intensely because of its numerous applications in catalysis, semiconductors, batteries, gas sensors, biosensors, and field transistors [26–31]. CuO–carbon black modified composite and CuO-coated glass beads have been reported for the detection of glucose, but their application is limited by the tedious fabrication processes [32, 33]. With the development of nanotechnology, nanostructured CuO is promising in the development of nonenzymatic glucose sensors because of its highly specific surface area, good electrochemical activity, and the possibility of promoting electron transfer reactions at a lower overpotential. Various attempts have been made during recent years, and modified electrodes made from Cu_2O/MWCNTs nanocomposites [34], CuO nanowire [35], and CuO nanospheres [36] were widely used. These developed sensors showed improved sensitivity. However, the synthesis of CuO nanostructure is still tedious and involves multiple steps. Therefore, there still remains a need

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for simpler processes to synthesize novel CuO nanostructures with superior catalytic property for fast, sensitive, and stable detection of glucose.

In this article, a new type of catalyst, cupric hydroxide/oxide ($Cu(OH)_2$/CuO) nanotube arrays, with enhanced sensing properties of glucose, was prepared on copper electrode surface via a facile alkali assistant surface oxidation technique. It is well known that the faradaic current for glucose oxidation depends significantly on the active area of electrode. Taking advantage of the high surface area of the three-dimensional nanostructured arrays in electrocatalytic oxidation of glucose, we developed an enzyme-free glucose sensor based on the $Cu(OH)_2$/CuO nanotube array electrodes. The interference coming from ascorbic acid (AA), uric acid (UA), and dopamine (DA) was also investigated, and a suitable glucose detection condition was chosen.

Experimental

All chemical reagents used in this experiment were of analytical grade. All solutions were prepared with doubly distilled water. CNAs were synthesized on copper electrode under ambient conditions. The copper electrode (3-mm diameter) was ultrasonically cleaned in ethanol and deionized water for about 5 min, respectively, followed by immersing the copper electrode in 50 mL aqueous solution of 2.5 M sodium hydroxide and 0.1 M ammonium persulphate at room temperature for 2.0 min. The colour of the copper electrode surface turned gradually to blue during the immersing process. Then, the copper electrode was taken out from the solution, fully rinsed with deionized water, and dried in nitrogen stream.

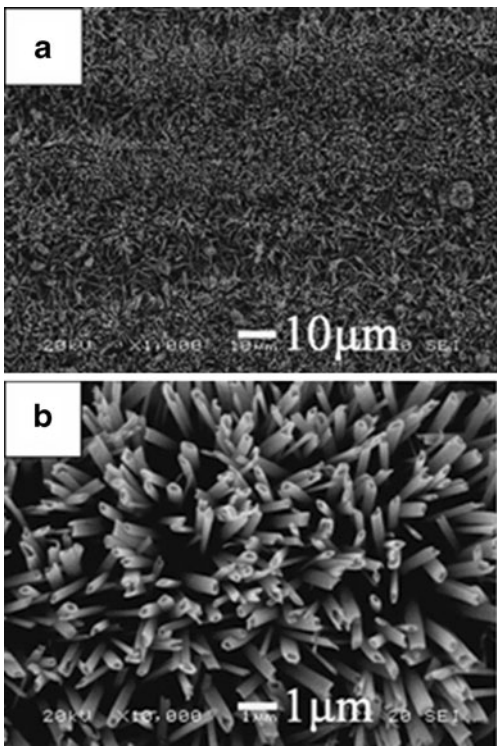

Fig. 1 SEM images of $Cu(OH)_2$ nanotube arrays: **a** low magnification (1000×) and **b** high magnification (10,000×)

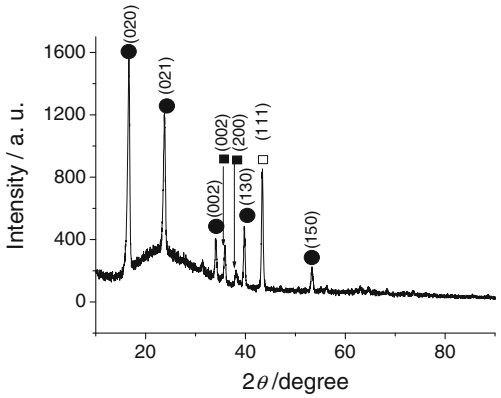

Fig. 2 XRD pattern of as-prepared $Cu(OH)_2$ nanotube arrays on copper electrode surface

A three-electrode electrolytic cell was employed for electrochemical tests. A CNA modified copper electrode was used as the working electrode, while a platinum wire was used as the auxiliary electrode. The Ag/AgCl (saturated KCl) electrode was used as the reference electrode. Morphology study of the CNA on the copper electrode surface was carried out with a SEM (JSM-5600LV, JEOL Ltd., Japan). The XRD patterns were obtained by Shimadzu XRD-6000 diffractometer with a Ni filter and Cu Kα radiation (λ=1.54056 Å). The electrochemical tests were carried out with a CHI 660b potentiostat (Chen Hua Company, China).

Results and discussion

The surface morphologies of the CNAs on copper electrode were investigated by SEM (Fig. 1a, b). As seen in Fig. 1a,

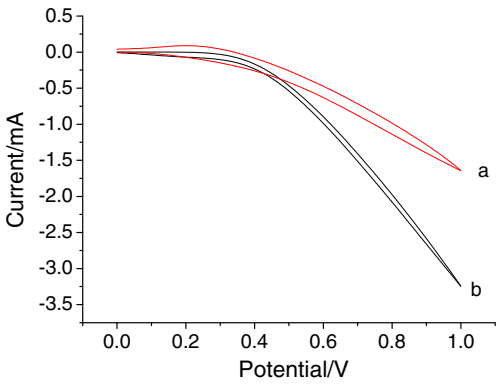

Fig. 3 The cyclic voltammetric behaviors of the CNA in the absence (**a**) and presence (**b**) of 10 mmol L^{-1} glucose in 0.1 M NaOH solution at 100 mV s^{-1}

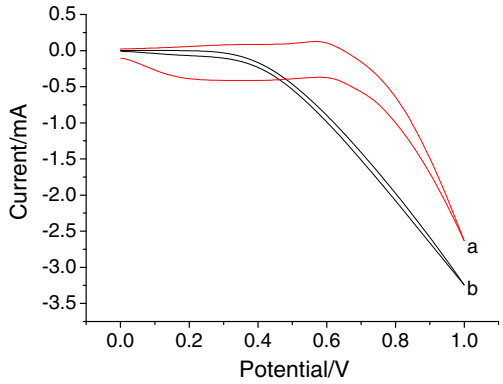

Fig. 4 Cyclic voltammograms of different electrodes in 10 mmol L^{-1} glucose in 0.1 M NaOH solution at 100 mV s^{-1}. **a** Bare copper electrode. **b** CNA modified copper electrode

wire-like cupric hydroxide/oxide ($Cu(OH)_2$/CuO) nanotubes uniformly and completely cover the whole surface of the copper substrate. The higher magnification SEM image (Fig. 1b) reveals that $Cu(OH)_2$ nanotubes with diameters ranging from 100 to 600 nm are standing upright.

XRD analysis was performed to study the crystal structure of $Cu(OH)_2$/CuO nanotube arrays on a copper substrate (Fig. 2). It is seen from Fig. 2 that the peaks marked with a black dot can be readily indexed to the orthorhombic phase $Cu(OH)_2$ (JCPDS card No. 72-0140). The peak marked with a hollow box is indexed to the copper substrate. The weak peaks marked with a black box indexed to the monoclinic phase CuO (JCPDS card No. 80-0076) indicate the presence of CuO.

To address the analytical applicability of the CNAs, electrocatalytic activity of the $Cu(OH)_2$/CuO nanotube arrays modified copper electrode (CNA/Cu) towards the glucose was investigated. As Fig. 3 shows, a significant oxidative current increase was observed with the addition of glucose at the CNA/Cu over the potential range 0.5–1.0 V. For comparison, a bare copper electrode was prepared and tested in a similar manner as the CNA/Cu sensor. In the

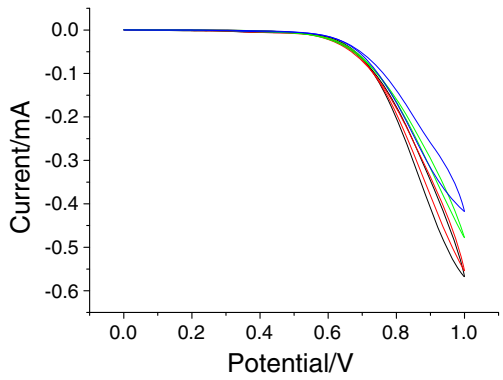

Fig. 5 Cyclic voltammograms of CNA/Cu in 10 mmol L^{-1} glucose in 0.1 M NaOH solution at different scan rates (0.005, 0.010, 0.015, 0.02 V/s)

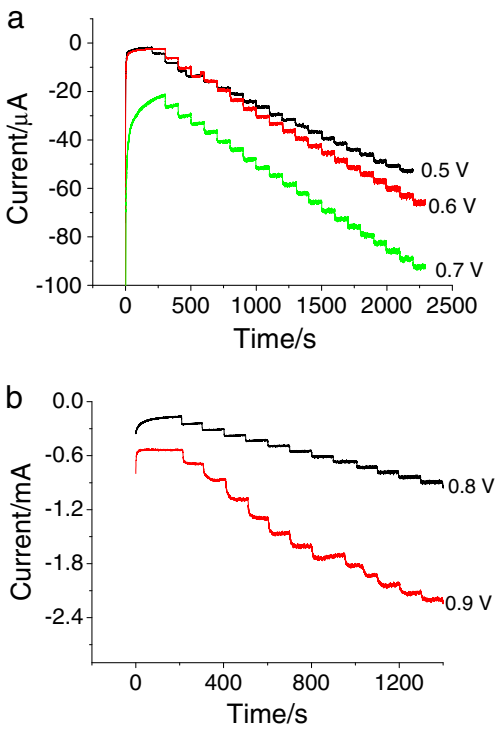

Fig. 6 Amperometric responses of the CNA/Cu toward the successive additions of 10 μL of 10 mM glucose into 10 mL of 0.1 M NaOH at various potentials

presence of glucose, the CV displays a much higher oxidative current on CNA/Cu than that on bare copper electrode at potentials between 0.5 and 1.0 V (Fig. 4). This dramatic increase of current indicates the significant catalytic activity of CNAs to glucose. The effect of scan rate on the electrochemical response of glucose at CNA/Cu was studied (Fig. 5). As the scan rate was increased from 5 to

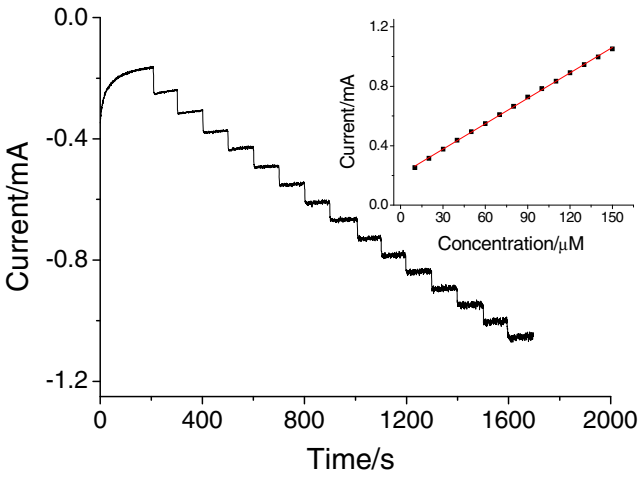

Fig. 7 Amperometric responses of the CNA/Cu toward the successive additions of 10 μL of 10 mM glucose into 10 mL of 0.1 M NaOH at 0.8 V. The *inset* summarizes the relation between response current and the glucose concentration (R=0.99943)

Table 1 The comparison of the analytical characteristics of CNA/Cu with other electroanalytical techniques for glucose detection

Sensor type	Method	Linear range (mol L^{-1})	Detection limit (mol L^{-1})	Ref.
CuO nanospheres modified GCE	Amperometry	5.0×10^{-6} to 2.55×10^{-3}	1.0×10^{-6}	36
CuO nanowire modified Cu rod	Amperometry	0.4×10^{-6} to 2.0×10^{-6}	4.9×10^{-8}	35
CuO coated glass beads	Flow-through detection	5×10^{-5} to 1×10^{-2}	1.0×10^{-9}	33
Cu_2O/MWCNT (multi-walled carbon nanotubes) nanocomposites modified GCE	Amperometry	5.0×10^{-8} to 5.0×10^{-6}	5.0×10^{-8}	32

20 mV s^{-1}, the oxidation current of glucose also increased gradually.

For amperometric sensing application, electrodes are generally evaluated by measuring current response at a fixed potential with the analyte added. In order to improve the electrocatalytic performance of CNA/Cu modified electrode, the effect of the applied potential on the response current of the sensor was investigated. As shown in Fig. 6, although at 0.90 V the signal is highest, we choose 0.80 V as the operating potential because above 0.80 V, there is increased noise, which is a disadvantage for measuring low glucose concentrations. Figure 7 displays the amperometric current–time curve of the CNA/Cu electrode under the optimized experimental conditions with successive additions of glucose. As expected, the modified electrode showed good linear response to the changes of glucose concentration. It took less than 3 s to achieve the steady-state current, indicating the fast amperometric response of the modified electrode. The calibration curve for the glucose sensor is shown in the inset of Fig. 7. The modified electrode gives a linear dependence in the glucose concentration range of 1×10^{-6} to 1×10^{-3} mol L^{-1} with a correlation coefficient of 0.99943, a sensitivity of 5.696 μA μmol L^{-1}, and a detection limit of 5×10^{-7} mol L^{-1}. The above elctrocatalytic studies of CNA/Cu modified electrode reveal the properties of high sensitivity, low detection limit, and fast response time. This is attributed to the $Cu(OH)_2$/CuO nanotube array, which greatly increases the electrocatalytic active areas and promotes electron transfer in the oxidation of glucose. The comparison of the analytical characteristics of CNA/Cu with other electroanalytical techniques for glucose detection is presented in Table 1.

To evaluate the selectivity of the proposed biosensor, three possible interfering biomolecules, AA, DA, and UA, which normally coexist with glucose in real samples (human blood), were examined. Considering that the concentration of glucose in the human blood is about 30 times of AA, DA, or UA, the voltammetric response of the CNA/Cu towards the addition of 1 μM glucose and 1 μM AA, DA, and UA was examined in 0.10 M NaOH solution, and the $i_{\text{glucose + interferent}}/i_{\text{glucose}}$ is 97 %, 102 % and 99 %, respectively (Fig. 8). To sum up, the selectivity was improved so much on this enzyme-free biosensor that the three common interfering biomolecules, AA, DA, and UA, caused negligible interference to the response of glucose at the CNA/Cu electrode.

Electrodes based on metals or alloys towards the oxidation of glucose usually lose their activity due to the poisoning of chloride ions [37]. In order to understand whether chloride ions will poison the CNA/Cu electrode, the CV was measured in the solution with high concentration of chloride ions (i.e., replacing 0.10 M NaOH with 0.10 M KCl+ 0.10 M NaOH as the electrolyte). The current response of CNA/Cu towards glucose oxidation remains almost unchanged, implying that the CNA/Cu is also highly resistant to poisoning by chloride ions and can be used as a glucose sensor even in the presence of high concentration of chloride ions.

Conclusion

In summary, an enzyme-free glucose sensor based on the CNA/Cu was fabricated by the direct growth of $Cu(OH)_2$/CuO nanotube arrays on copper electrode surface via a facile alkali assistant surface oxidation technique. SEM

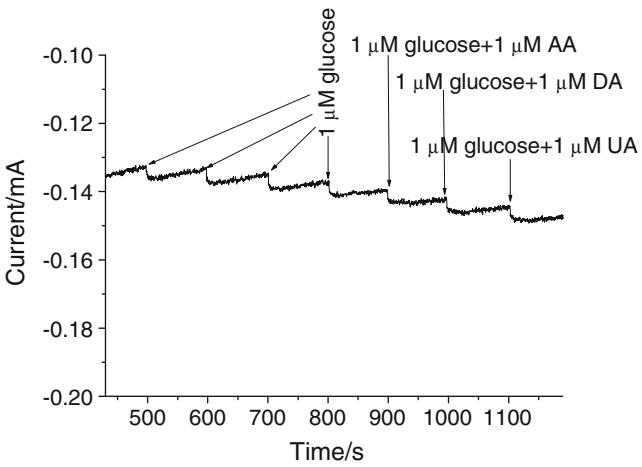

Fig. 8 Amperometric responses of the CNA/Cu toward the successive additions of 10 μL of 1 mM glucose, 10 μL of the mixture of 1 mM glucose and 1 mM AA, 10 μL of the mixture of 1 mM glucose and 1 mM UA, and 10 μL of the mixture of 1 mM glucose and 1 mM DA into 10 mL of 0.1 M NaOH at 0.8 V

images showed that the CNA exhibited a well-aligned three-dimensional structure, and the XRD results indicate the existence of CuO and $Cu(OH)_2$ in the CNA. Direct glucose oxidation on such CNA/Cu was investigated in detail. As a result, we found that the CNA/Cu exhibited high electrocatalytic activity to glucose oxidation in alkaline condition. The linear range and sensitivity of 5.696 μA μmol L^{-1} of the CNA/Cu to glucose oxidation was obviously good enough for the potential application in practical glucose detection.

Acknowledgments The author acknowledges financial support by the High-Level Talent Foundation of Xuchang University (No. 2010GC032).

References

1. Lin YH, Lu F, Tu Y, Ren ZF (2004) Nano Lett 4:191–195
2. Reach G, Wilson GS (1992) Anal Chem 64:381A–386A
3. White BJ, Harmon HJ (2002) Biochem Biophys Res Commun 296:1069–1071
4. Frew JE, Hill HAO (1987) Anal Chem 59:933A–944A
5. Lee D, Lee J, Kim J, Kim J, Na HB, Kim B, Shin CH, Kwak JH, Dohnalkova A, Grate JW, Hyeon T, Kim HS (2005) Adv Mater 17:2828–2833
6. Wang J, Liu J, Chen L, Lu F (1994) Anal Chem 66:3600–3603
7. Choi HN, Han JH, Park JA, Lee JM, Lee WY (2007) Electroanal 19:1757–1763
8. Chu X, Duan DX, Shen GL, Yu RQ (2007) Talanta 71:2040–2047
9. Kotzian P, Brazdilova P, Rezkova S, Kalcher K, Vytras K (2006) Electroanal 18:1499–1504
10. Nien PC, Tung TS, Ho KC (2006) Electroanal 18:1408–1415
11. Wang JX, Sun XW, Wei A, Lei Y, Cai XP, Li CM, Dong ZL (2006) Appl Phys Lett 88:233106
12. Wei A, Sun XW, Wang JX, Lei Y, Cai XP, Li CM, Dong ZL, Huang W (2006) Appl Phys Lett 89:123902
13. Wang JX, Sun XW, Cai XP, Lei Y, Song L, Xie SS (2007) Electrochem Solid-State Lett 10:J58–J60
14. Cho S, Kang C (2007) Electroanal 19:2315–2320
15. Park S, Chung TD, Kim HC (2003) Anal Chem 75:3046–3049
16. Rong LQ, Yang C, Qian QY, Xia XH (2007) Talanta 72:819–824
17. Song YY, Zhang D, Gao W, Xia XH (2005) Chem Eur J 11:2177–2182
18. Wang J, Thomas DF, Chen A (2008) Anal Chem 80:997–1004
19. Ye JS, Wen Y, Zhang WD, Gan LM, Xu GQ, Sheu FS (2004) Electrochem Commun 6:66–70
20. Li Y, Song YY, Yang C, Xia XH (2007) Electrochem Commun 9:981–988
21. Tominaga M, Taema Y, Taniguchi I (2008) J Electroanal Chem 624:1–8
22. Kang XH, Mai ZB, Zou XY, Cai PX, Mo JY (2007) Anal Biochem 363:143–150
23. Cui HF, Ye JS, Liu X, Zhang WD (2006) Nanotech 17:2334–2339
24. Jena BK, Raj CR (2006) Chem Eur J 12:2702–2708
25. Chen J, Deng SZ, Xu NS, Zhang WX, Wen XG, Yang SH (2003) Appl Phys Lett 83:746
26. Chowdhuri A, Gupta V, Sreenivas K, Kumar R, Mozumdar S, Patanjali PK (2004) Appl Phys Lett 84:1180
27. Lucas E, Decker S, Khaleel A, Seitz A, Fultz S, Ponce A, Li WF, Carnes C, Klabunde KJ (2001) Chem Eur J 7:2505–2510
28. Luque GL, Rodriguez MC, Rivas GA (2005) Talanta 66:467–471
29. Tamaki J, Shimanoe K, Yamada Y, Yamamoto Y, Miura N, Yamazoe N (1998) Sens Actuators B 49:121–125
30. Wang HB, Pan QM, Zhao HW, Yin GP, Zuo PJ (2007) J Power Sources 167:206–211
31. Zheng XG, Xu CN, Tomokiyo Y, Tanaka E, Yamada H, Soejima Y (2000) Phys Rev Lett 85:5170–5173
32. Chung H, Park J (1997) Bull Korean Chem Soc 18:952–957
33. Matsubara H, Kondo T, Kanno W, Hodouchi K, Yamada A (2000) Anal Chim Acta 405:87–92
34. Zhang X, Wang G, Zhang W, Wei Y, Fang B (2009) Biosens Bioelectron 24:3395–3398
35. Zhuang ZJ, Su XD, Yuan HY, Sun Q, Xiao D, Choi MMF (2008) Analyst 133:126–132
36. Reitz E, Jia WZ, Gentile M, Wang Y, Lei Y (2008) Electroanal 20:2482–2486
37. Sun YP, Buck H, Mallouk TE (2001) Anal Chem 73:1599