

Supplementary materials

Electrolyte-Controllable Synthesis of Cu_xO with Novel Morphology and their Application in Glucose Sensor

Xia Li^a, Changting Wei^a, Jinying Fu^a, Li Wang^a, Shouhui Chen^a, Ping Li^a, Hongbo Li^a, Lanlan

Sun^b and Yonghai Song^{a,*}

^aCollege of Chemistry and Chemical Engineering, Jiangxi Normal University, 99 Ziyang Road, Nanchang 330022, People's Republic of China

^bState Key Laboratory of Luminescence and Applications, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, 3888 East Nan-Hu Road, Changchun 130033, People's Republic of China

* Corresponding author: Tel/Fax: +86-791-88120861. E- mail: yhsonggroup@hotmail.com (Y. Song).

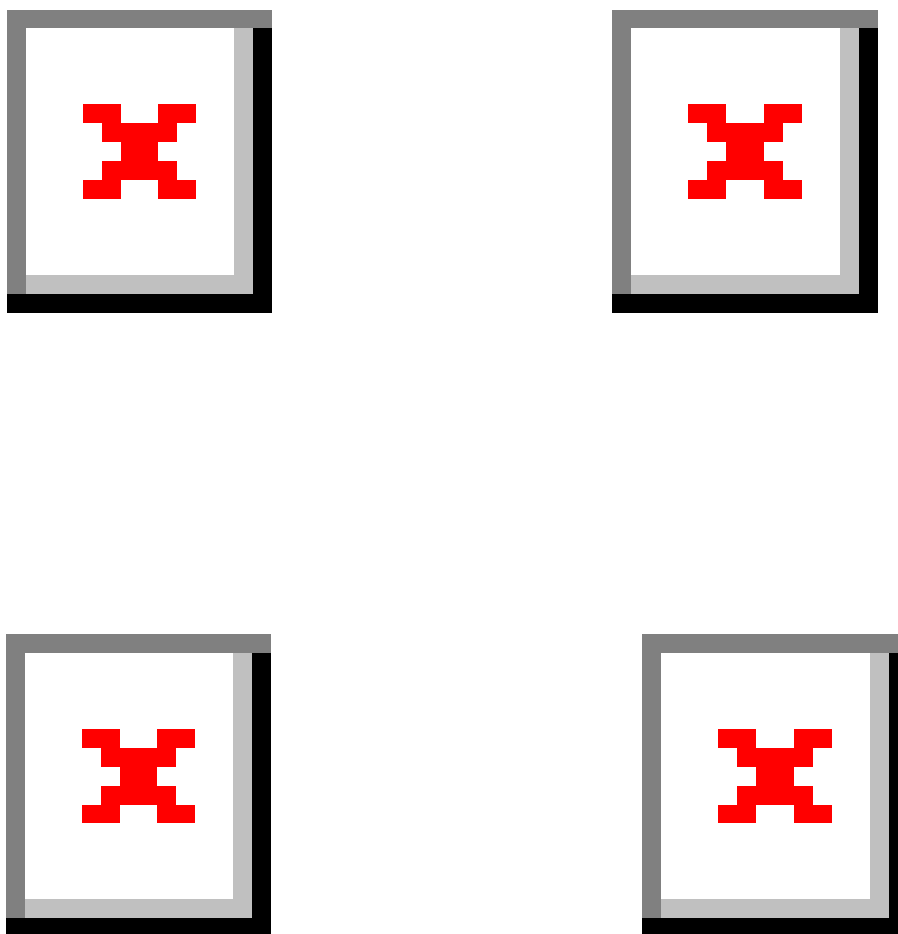


Fig. S1 SEM images of Cu_xO synthesized in the electrolyte of 0.05 M NaClO₄ obtained at different time: (A) 1 min, (B) 5 min, (C) 10 min and (D) 30 min.

Fig. S1A-D showed the morphology of Cu_xO micro/nano materials prepared by electrolyzing Cu foils in 0.05 M NaClO₄ for 1 min, 5 min, 10 min and 30 min, respectively. It was found that when the reaction time was 1 min, monolayer of fine and complete thin film was formed on the surface of the Cu foils electrode (Fig. S1A). As observed from the enlarged image of Fig. S1A

(inset), the film was consists of a number of small NPs and cracks. With the increase of reaction time,, the cracks and NPs were increased significantly (Fig. S1B). When the reaction time was extended to 10 min, the profile of the particles is clearer. The distribution of the crystal was in cluster and in irregular star shapes (Fig. S1C). When the reaction time increased to 30 min, the crystal was gathered into block crystals with small particles distributed on its surfaceas shown in Fig. S1D.

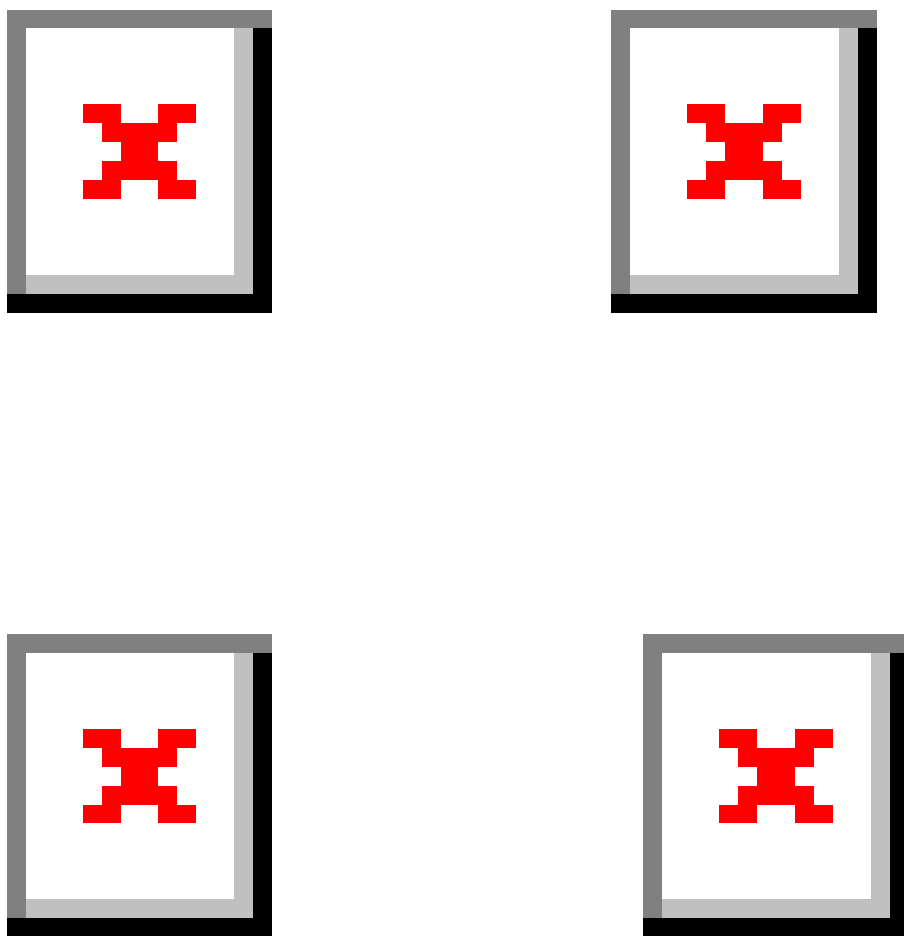


Fig. S2 SEM images of Cu_xO synthesized in the electrolyte of 0.01 M CoCl_2 obtained at different time: (A) 30 s, (B) 5 min, (C) 10 min and (D) 30 min.

Fig. S2A-D showed the morphology of Cu_xO micro/nano materials prepared by electrolyzing Cu foils in 0.01 M CoCl_2 for 30 s, 5 min, 10 min and 30 min, respectively. It can be observed that in the initial stage there were only several single Cu_xO nanosheets growing vertically on the substrate surface (Fig. S2A). The length, width and thickness of the nanosheets were about 1-3 μm , 300-700 nm and 10-30 nm, respectively. With the increase of the reaction time, the Cu_xO

nanosheet self-assembled into planar triangle structure and the large Cu_xO nanosheet further vertically grew on the planar triangle edge to set up a triangular fence structure (Fig. S2B). The enlarged triangular fence (inset in Fig. 3B) revealed some substrate on its undersurface. Fig. S2C showed that those Cu_xO nanosheets were assembled into large triangular fence with smooth undersurface, indicating the Cu_xO nanosheets could be integrated together and recrystallized. Some edges of the fences disappeared and only the triangular undersurface was maintained as shown by inset in Fig. S2C. A large number of Cu_xO micro/nano materials formed and stacked compactly into three-dimensional structure. As shown in Fig. S2D, with the reaction time further increasing, the stacking density increased and some new Cu_xO nanosheets formed and grew on the original structure.

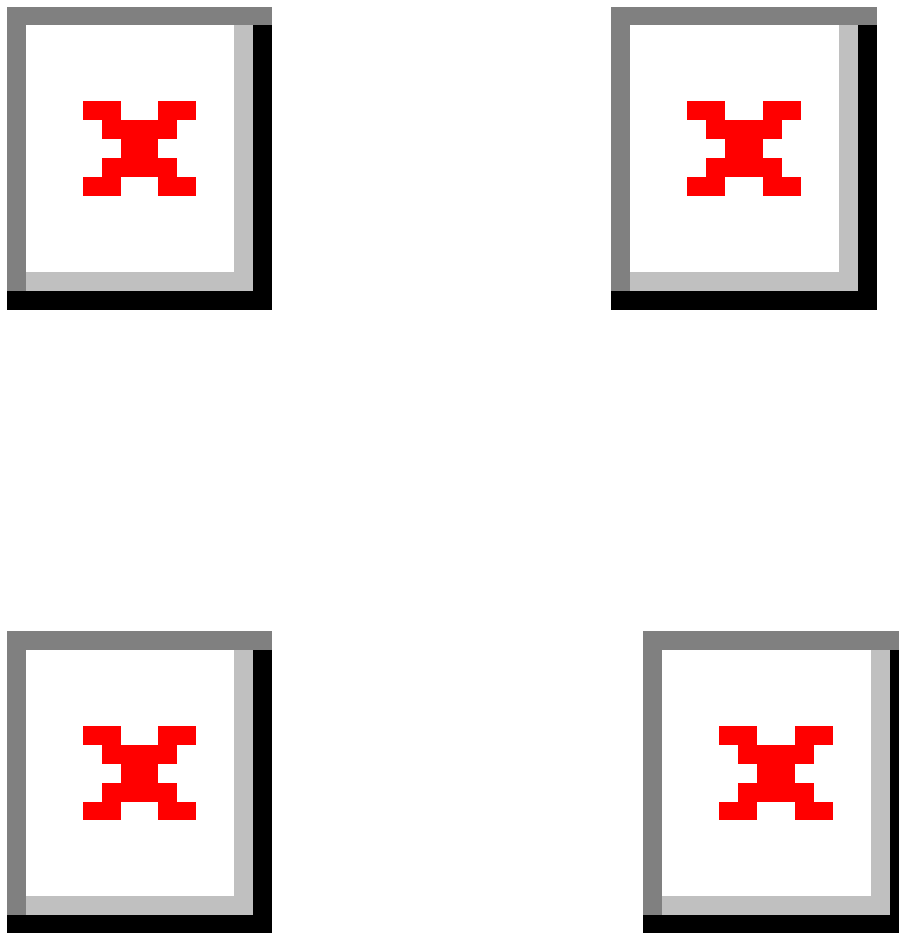


Fig. S3 SEM images of Cu_xO synthesized in the electrolyte of 0.05 M NaClO_4 + 0.01 M CoCl_2 obtained at different time: (A) 1 min, (B) 5 min, (C) 10 min and (D) 30 min.

Fig. S3A-D showed the growing process of Cu_xO micro/nano materials prepared by electrolyzing Cu foils in 0.05 M NaClO_4 + 0.01 M CoCl_2 for 1 min, 5 min, 10 min and 30 min, respectively. At the initial stage, 2D Cu_xO nanosheets were formed and grew vertically on the Cu foil surface, similar to that in 0.01 M CoCl_2 (Fig. S3A). When the reaction time was increased to 5 min, Cu_xO nanosheets grew into irregular

tetrahedron with large porosity in the middle (Fig. S3B). After 10 min, many Cu_xO NPs were formed and spread not only all over the outer surface of the solid but also distributed in the inner surface of the irregular tetrahedron (Fig. S3C). As the reaction time was further increased, the original irregular tetrahedron has been covered by some large particles and the middle pores of the irregular tetrahedron were also filled by larger particles (Fig. S3D). As shown by the inset in Fig. S3D, these large particles were consisted of gathered Cu_xO NPs.

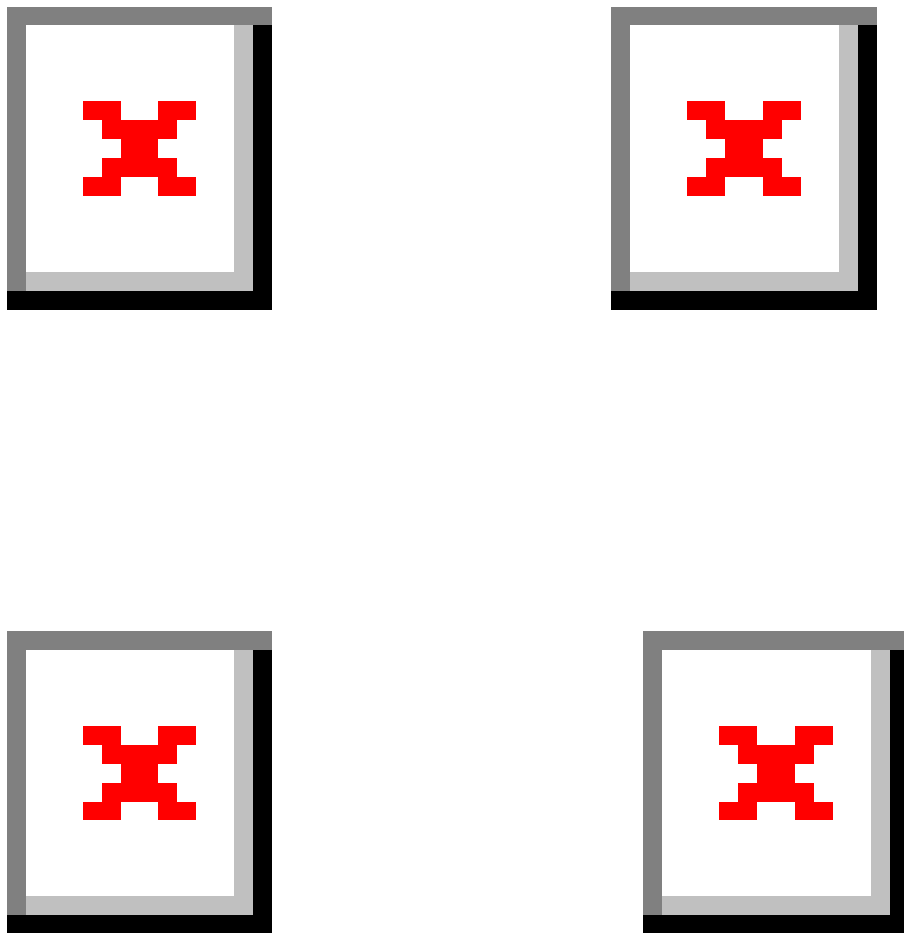


Fig.S4 SEM images of Cu_xO synthesized in the electrolyte of 0.05 M NaClO_4 + 0.025 M SDS + 0.01 M CoCl_2 obtained at different time: (A) 30 s, (B) 1 min, (C) 5 min and (D) 10 min.

Fig. S4A-D showed the morphology of Cu_xO micro/nano materials prepared by electrolyzing Cu foils in 0.05 M NaClO_4 + 0.01 M CoCl_2 + 0.025 M SDS for 30 s, 1 min, 5 min and 10 min, respectively. At 30 s, there are cobbles-like NPs embedded in the surface of Cu foils (Fig. S4A). When the reaction time was increased to 1 min, there was some small irregular tetrahedron with large porosity in the middle (Fig. S4B). After 5

min, there are some cubic crystals distribute uniformly on the surface of those irregular tetrahedron. As shown by the inset in Fig. S4C, some of the crystals have been grow into complete cubic crystals, while others were still in growing process. The size of these cubic crystals was about 100 nm. Finally, there are many cubic crystals densely stacked on the surface of the irregular tetrahedron after 10 min as shown in Fig. S4D. Compare with those cubes in the initial stage, the size of these cubic crystals was increased to 300 nm.

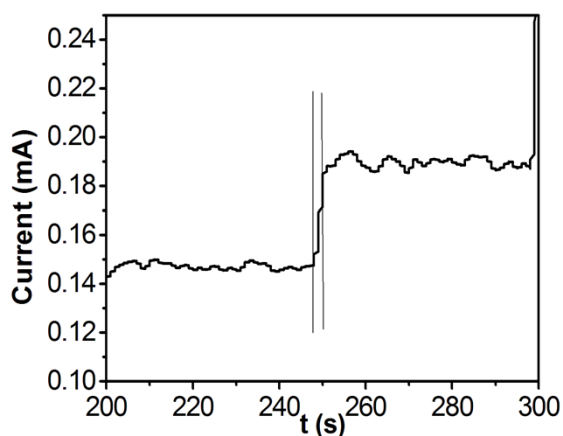


Fig.S5 A segment of amperometric response of the optimized $\text{Cu}_x\text{O}/\text{CuNaClO}_4+\text{CoCl}_2+\text{SDS}$ electrodes to successive injection of glucose into the stirred NaOH.

Table S1 Comparison of the performance of the Cu_xO micro/nano materials modified electrode with other glucose sensors based on different Cu materials.

<i>Electrode type</i>	<i>Detection potential</i>	<i>Detection limit</i>	<i>Linear range</i>	<i>Slope</i>	<i>Ref.</i>
	<i>V</i>	<i>μmol L⁻¹</i>	<i>mM</i>	<i>μA mmol L⁻¹</i>	
Cu ₂ O/Cu	0.6 V (vs.Ag/AgCl)	37	0.05 -6.75	62.29	[1]
Cu/Cu ₂ O hollow microspheres	0.45 V (vs.SCE)	0.05	0.22–10.89	33.63	[2]
CuO-G-GCE	0.59 V (vs.Ag/AgCl)	0.7	0.002-4	1360 μAmM ⁻¹ cm ⁻²	[3]
CuO/GCE	0.55 V (vs.Ag/AgCl)	0.5	0.005–2.3	1397 μAmM ⁻¹ cm ⁻²	[4]
CuO/graphene/ GCE	0.6 V (vs.Ag/AgCl)	4	0.004-8	709.52μAmM ⁻¹ cm ⁻²	[5]
Cu _x O/PPy/Au electrode	0.60 V(vs. SCE)	6.2	Up to 4.5	232.22μAmM ⁻¹ cm ⁻²	[6]
CuO nanocubes–graphene/GCE	0.55 V(vs. SCE)	0.7	0.002–4.0	1360μAmM ⁻¹ cm ⁻²	[7]
CuO–SWCNTs/ITO	0.45 V(vs. SCE)	0.05	0.00005–1.8	1610μAmM ⁻¹ cm ⁻²	[8]
Cu ₂ O NPs/graphite electrode	0.75 V(vs. Hg/HgO)	2.4	Up to 6.0	629μAmM ⁻¹ cm ⁻²	[9]
Cu–CuO/carbon electrode	0.75 V(vs. Hg/HgO)	5.0	Up to 3.0	598μAmM ⁻¹ cm ⁻²	[10]
Cu _x O/Cu _{NaClO4}	0.55 V (vs. SCE)	47.8	0.2-2.25	317.3	This work
Cu _x O/Cu _{CoCl2}	0.4 V (vs. SCE)	50.5	0.2-2.25	422.86	This work
Cu _x O/Cu _{NaClO4+CoCl2}	0.4 V (vs. SCE)	55.0	0.2-2.25	506.31	This work
Cu _x O/Cu _{NaClO4+CoCl2+SDS}	0.35 V (vs. SCE)	14.3	0.025-9.05	452.4	This work

Table S2 Detection of Glucose in Human Blood Serum.

Samples	Samples found (mM)	Added (mM)	Found (mM)	Recovery (%)	RSD (% ,n=3)
1	0.5	0.5	1.11	111.21	4.57
2	0.5	1.00	1.59	106.65	2.98
3	0.5	1.5	2.03	101.96	3.34
4	0.5	2	2.46	98.72	2.83

Reference

- 1 L. Wang, J. Fu, H. Hou, Y. Song, 2012, **7**, 12587-12600.
- 2 A-J. Wang, J-J. Feng, Z-H. Li, Q-C. Liao, Z-Z. Wang, J-R. Chen *CrystEngComm*, 2012, **14**, 1289
- 3 L. Luo, L. Zhu, Z. Wang, *Bioelectrochemistry*, 2012, **88**, 156-163.
- 4 Liu S et al. *Catalysis Science & Technology*, 2012, **2**, 813.
- 5 X. Wang, C. Hu, H. Liu, G. Du, X. He, and Y. Xi, *Sensors and Actuators B*, 2010, **144**, 220–225.
- 6 F. Meng, W. Shi, Y. Sun, X. Zhu, G. Wu, C. Ruan, X. Liu and D. Ge, *Biosens. Bioelectron.*, 2013, **42**, 141-147.
- 7 L. Luo, L. Zhu and Z. Wang, *Bioelectrochem.*, 2012, **88**, 156-163.
- 8 N. Q. Dung, D. Patil, H. Jung and D. Kim, *Biosens. Bioelectron.*, 2013, **42**, 280-286.
- 9 K.M. El Khatib and R.M. Abdel Hameed, *Biosens. Bioelectron.*, 2011, **26**, 3542-3548.
- 10 H. B. Hassan and Z. Abdel Hamid, *Int. J. Electrochem. Sci.*, 2011, **6**, 5741-5758.