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Supporting Information

Engineering Valence State of ZIF-67 by Cu_2O for Efficient Nonenzymatic Glucose Detection

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Experimental sections

Reagents and materials

Copper(II) chloride dehydrate ($CuCl_2 \cdot 2H_2O$, Fengyue, Tianjin, China, ≥99%), Sodium dodecyl sulfate ($CH_3(CH_2)_{11}OSO_3Na$, SDS, Sixth Factory Branch, Tianjin, China, ≥59%), Sodium hydroxide (NaOH, Damao, Tianjin, China, ≥96%), Potassium hydroxide (KOH, Shuangshuang, Yantai, China, ≥85%), Hydroxylammonium chloride ($NH_2OH \cdot HCl$, Kermel, Tianjin, China, ≥98.5%), Ethanol (CH_3CH_2OH, Rionlon, Tianjin, China, ≥99.7%), Anhydrous methanol (CH_3OH, Rionlon, Tianjin, China, ≥99.5%), Polyvinylpyrrolidone (PVP, Kermel, Tianjin, China), Cobalt nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$, Xilong, Shantou, China, ≥98.5%), 2-Methylimidazole ($C_4H_6N_2$, Zhanyun, Shanghai, China, ≥99%), Glucose ($C_6H_{12}O_6 \cdot H_2O$, Kermel, Tianjin, China), Fructose ($C_6H_{12}O_6$, Kermel, Tianjin, China), Lactose monohydrate ($C_{12}H_{22}O_{11} \cdot H_2O$, Zhongqin, Shanghai, China), Uric acid ($C_5H_4N_4O_3$, Sigma, ≥99%), L-Ascorbic acid ($C_6H_8O_6$, Keshi, Chengdu, China, ≥99.7%), Sodium sulfate anhydrous (Na_2SO_4, Keshi, Chengdu, China, ≥99%), Potassium hexacyanoferrate ($K_3[Fe(CN)_6]$, Guangfu, Tianjin, China, ≥99.5%), Potassium hexacyanoferrate trihydrate ($K_4[Fe(CN)_6] \cdot 3H_2O$, Keshi, Chengdu, China, ≥99.5%) were of analytical grade and used as supplied without further purification. The deionized water (DI-water) was used throughout experiments.

Apparatus

Scanning electron microscopy (SEM) images were acquired through a thermoscientific Apero S microscope. Transmission electron microscopy (TEM) and energy dispersive X-ray spectroscopy (EDS) analysis were achieved using a Philips Tecnai G2 F30 machine. Powder X-ray diffraction (XRD) was performed on a Rigaku D/max 2400 X-ray diffractometer. X-ray photoelectron spectroscopy (XPS) was carried out on a PHI-5702 instrument.

Electrochemical Measurements

Electrochemical measurements were accomplished on a CHI660d electrochemical workstation (Chenhua, Shanghai, China) using 1.0 M KOH as electrolyte solution. A three-electrode configuration was set up: the working electrode (a glassy carbon electrode, Ø 5.0mm), the reference electrode (a Hg/HgO electrode with 1.0 M KOH), the counter electrode (a graphite rod). The catalyst ink was acquired by adding 5 mg catalyst into 1 mL ethanol under sonication treatment for several minutes. Then 20 μL suspension and 5 μL ethanol solution of Nafion (10% v/v) were dropped onto GCE surface followed by drying under ambient condition.

Preparation of samples

(a) Synthesis of Cu_2O nanocubes

According to a reported literature[1], $CuCl_2$ solution (5 mL, 0.1 M) and SDS powder (0.87 g) were added into 89.2 mL deionized water in a round-bottom flask, which was put in a water bath (33℃). After SDS powders dissolved, the round bottom flask was moved to ultrasonic water bath followed by introducing NaOH solution (1.8 mL, 1.0 M) drop by drop. Then, $NH_2OH \cdot HCl$ (4 mL, 0.1 M) was rapidly added to the mixture and kept it in the ultrasonic water bath for 60 minutes. The product was obtained by centrifugation and washing with the mixture of ethanol and water (1:1 volume ratio) for two times and only ethanol was used in the third washing step.

(b) Synthesis of Cu_2O@ZIF-67

In a typical procedure[1], 10.0 mg as-prepared Cu_2O nanocubes and 1.0 g PVP were added into 20 mL methanol solution followed by sonicating the mixture for several minutes to get a homogeneous solution (denoted as solution A). $Co(NO_3)_2 \cdot 6H_2O$ (0.7 g) and PVP (0.25 g) were dissolved in 20 mL methanol (denoted as solution B). 2-methylimidazole (0.26 g) and PVP (0.25 g) were dissolved in 20 mL methanol (denoted as solution C). Solution B was introduced into solution A drop by drop with stirring. Then solution C was added into the mixture of A and B. The final mixture was kept stirring under ambient condition for 24 hours. The product was collected by centrifugation and washing with methanol for three times followed by dried under vacuum overnight.

(c) Synthesis of ZIF-67

2-methylimidazole (5.5g) and $Co(NO_3)_2 \cdot 6H_2O$ (0.45 g) were dissolved in 20 mL and 3 mL water respectively. Then the two solutions were mixed and the mixture stayed stirring for 6 h followed by washing with ethanol for three times. Finally, the product was obtained after drying at vacuum overnight[2].

Supplementary Figures

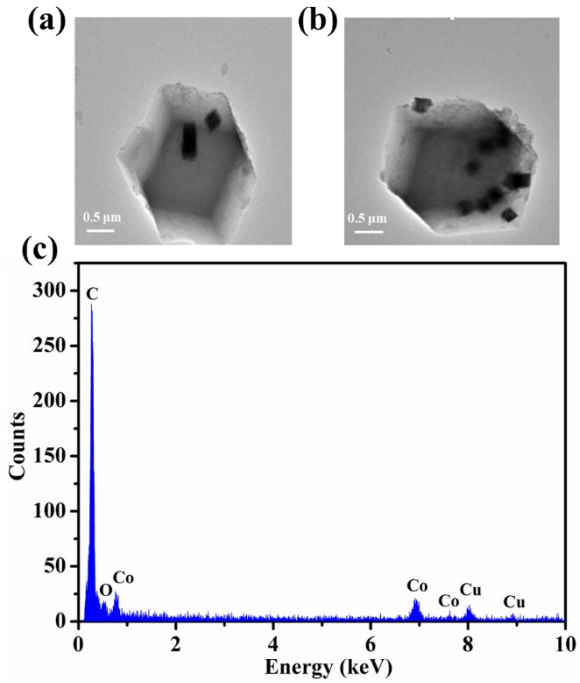

Figure S1. (a, b) TEM images and (c) EDS spectrum of Cu_2O@ZIF-67.

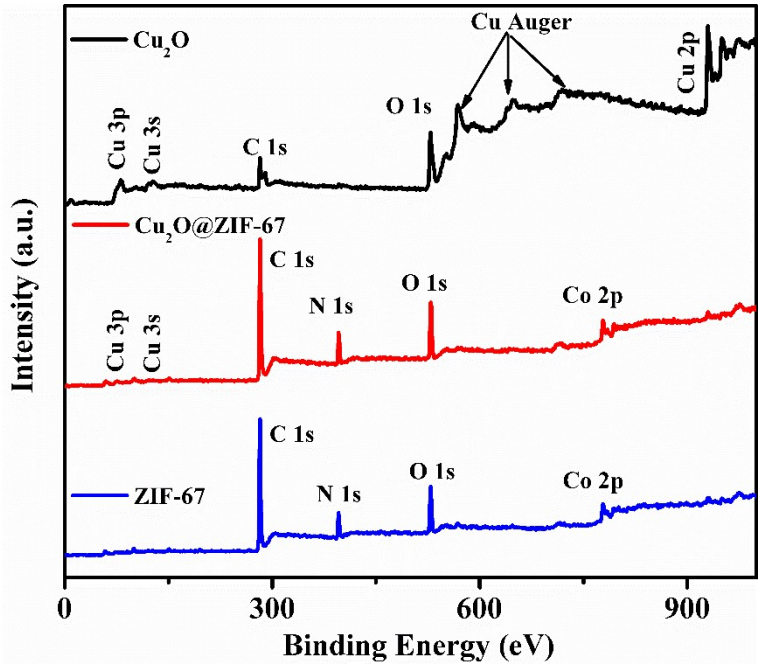

Figure S2. XPS survey scans of Cu_2O, ZIF-67 and Cu_2O@ZIF-67.

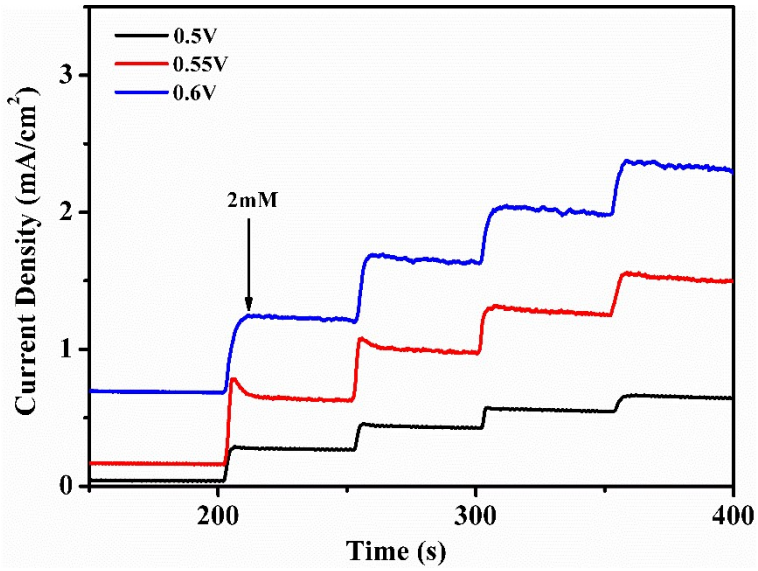

Figure S3. Amperometric response of Cu_2O@ZIF-67 at different potentials with successive addition of 2 mM glucose.

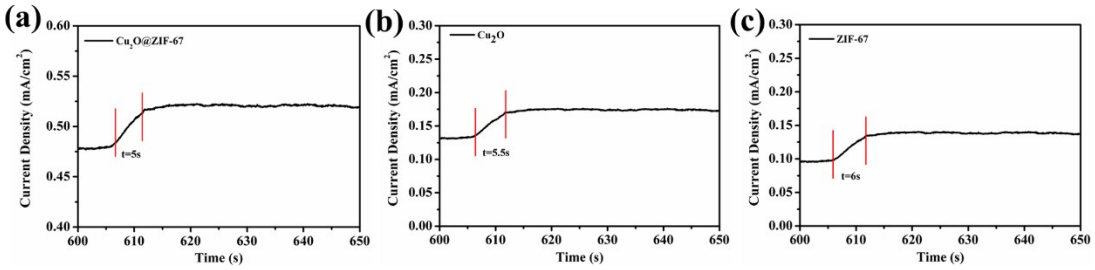

Figure S4. Current response time upon glucose addition of (a) Cu_2O@ZIF-67, (b) Cu_2O and (c) ZIF-67.

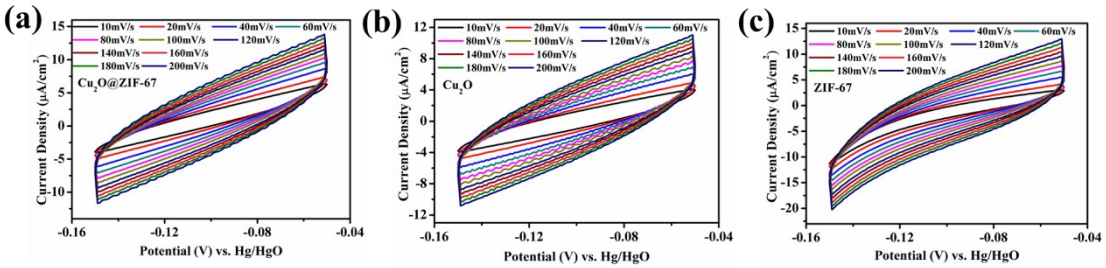

Figure S5. The CV curves at different scan rates from -0.15V to -0.05 V (vs. Hg/HgO) of (a) Cu_2O@ZIF-67, (b) Cu_2O and (c) ZIF-67.

Table S1. Comparison of electrocatalytic performance of Cu_2O@ZIF-67 with other copper and cobalt-based non-enzymatic glucose sensors.

Electrode	Linear range (mM)	Sensitivity ($\mu A\ cm^{-2}\ mM^{-1}$)	Limit of detection (μM)	Ref.
Octahedral Cu_2O	0.1-5	293.893	5.11	3
Nano-cubic Cu_2O-Ti	0.017–11.65	28.40	15.6	4
Cu_2O/AlOOH/rGO	0.005–14.47	155.1	2.6	5
Nafion/CuO Microspheres	2-9	26.59	20.6	6
Cu/Cu_2O/CS	0.01–0.69	63.8	5	7
	1.19–3.69	22.6		
MnO_2/Co_3O_4	Up to 7	127	0.03	8
ZIF-Air	0.1–0.5	21	25.8	2
ZIF-N_2	0.1-1.1	227	5.69	2
Co_3O_4 porous film	Up to 3	366.03	1	9
CoOx·nH_2O-MWCNTs	Up to 4.5	162.8	2.0	10
3D/Co_3O_4	0.001-1	180	0.046	11
Zn doped Co_3O_4	0.005-0.62	193	2	12
Cu_2O@ZIF-67	0.01-10	307.02	6.5	This work
	10-16.3	181.34		

References

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