

Supporting Information

High surface area mesoporous CuO: A high-performance electrocatalyst for non-enzymatic glucose biosensing

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Experimental section

Materials

$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, glucose, H_2SO_4 (98 %), NaOH, HCl, sucrose, chitosan, acetic acid, ethanol, ascorbic acid (AA), and uric acid (UA) were purchased from Beijing Chemical Comp. Tetraethyl orthosilicate (TEOS) was purchased from Tianjin Chemical Co. Pluronic P123 ($\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$, $M = 5800$) was purchased from Aldrich. All chemicals were used as received without further purification. The water used throughout all experiments was purified through a Millipore system.

Preparation of SBA-15

SBA-15 was prepared by using P123 as soft template and TEOS as silica source

according to our previous report.¹ In a typical run, 1 g of P123 was dissolved in 25 mL of HCl solution (2 M). After that, the mixture was heated to 45 °C, followed by addition of 4.5 mL of TEOS. After further stirring for 12 h, the gel was transferred into a Teflon-lined autoclave and heated at 100 °C for 48 h. After filtration, drying at room temperature, and calcination in air at 550 °C for 3 h, SBA-15 was obtained.

Preparation of CMK-3

CMK-3 was prepared by using SBA-15 as hard template according to previous report.² In a typical run, 1 g of SBA-15 was added into 5 mL of H₂O, followed by addition of 1.25 g of sucrose and 0.14 g of H₂SO₄. After stirring for 5 h, the result viscous mixture was placed in a drying oven at 100 °C for 6 h and subsequently the increasing the oven temperature to 160 °C and maintaining for 6 h. After that, the mixture was mixed with 5 mL of H₂O consisting of 0.75 g of sucrose, 0.09 g of H₂SO₄, followed by heating at 160 °C again. Then, the obtained mixture was pyrolyzed at 900 °C under a nitrogen atmosphere for 4 h. Finally, the carbon/silica composite obtained after pyrolysis was washed with 1 M NaOH solution (an EtOH-H₂O mixture) to remove the silica template.

Preparation of mesoporous CuO

Mesoporous CuO was prepared by the nanocasting method using CMK-3 as hard template according to the published report.³ In a typical synthesis, 1 g of CMK-3 was dispersed in 10 mL of H₂O, followed by addition of 0.97 g of Cu(NO₃)₂·3H₂O. Then the mixture was heated to 100 °C and stirred for 2 h. The resultant sample was dried under vacuum to give a fine and completely dry powder. After that, the mixture was

heated in a tube furnace under nitrogen to 300 °C at a constant rate of 1 °C min⁻¹ and maintained for 4 h to convert the Cu(NO₃)₂·3H₂O within the pores to CuO. This procedure was repeated twice. Finally, the sample was calcined in air at 500 °C for 10 h to remove the carbon.

Characterizations

Powder X-ray diffraction (XRD) data were recorded on a RigakuD/MAX 2550 diffractometer with Cu-K α radiation ($\lambda=1.5418$ Å). Nitrogen isotherm was obtained at -196 °C on a Micromeritics Tri-star. Samples were prepared for measurement by treating at 150 °C under nitrogen atmosphere for 12 h. Pore size distributions were calculated using Barrett-Joyner-Halenda (BJH) method. The morphology of the samples was observed by field emission scanning electron microscopy (FE-SEM) on a JSM-6700F electron microscope (JEOL, Japan). Electrochemical measurements were performed with a CHI 660D electrochemical analyzer (CH Instruments, Inc., Shanghai). A conventional three-electrode cell was used, including a glassy carbon electrode (GCE, geometric area = 0.07 cm²) as the working electrode, a Ag/AgCl (saturated KCl) electrode as the reference electrode, and platinum foil as the counter electrode. The potentials are measured with a Ag/AgCl electrode as the reference electrode. All the experiments were carried out at room temperature.

Detection of glucose

The modified electrodes were prepared by a simple casting method. Prior to the surface coating, the GCE was polished with 1.0 and 0.3 μm alumina powder, respectively, and rinsed with water, followed by sonication in ethanol solution and

water successively. Then, the electrode was allowed to dry in a stream of nitrogen. After that, 1.5 μL of mesoporous CuO aqueous dispersion (5 mg/mL) and 1 μL of chitosan solution (in 1 % acetic acid aqueous solution) were dropped on the clean surface of GCE, and dried at room temperature. The amperometric measurements were carried out in a glass cell containing a buffer solution (5 mL) with constant stirring (500 rpm).

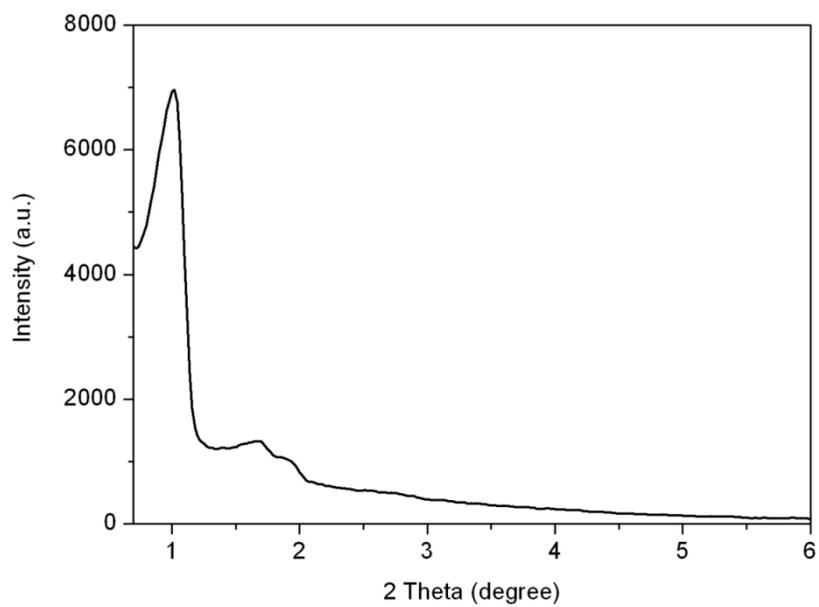


Fig. S1 Small-angle XRD pattern of SBA-15 after calcination in air at 550 °C for 3 h.

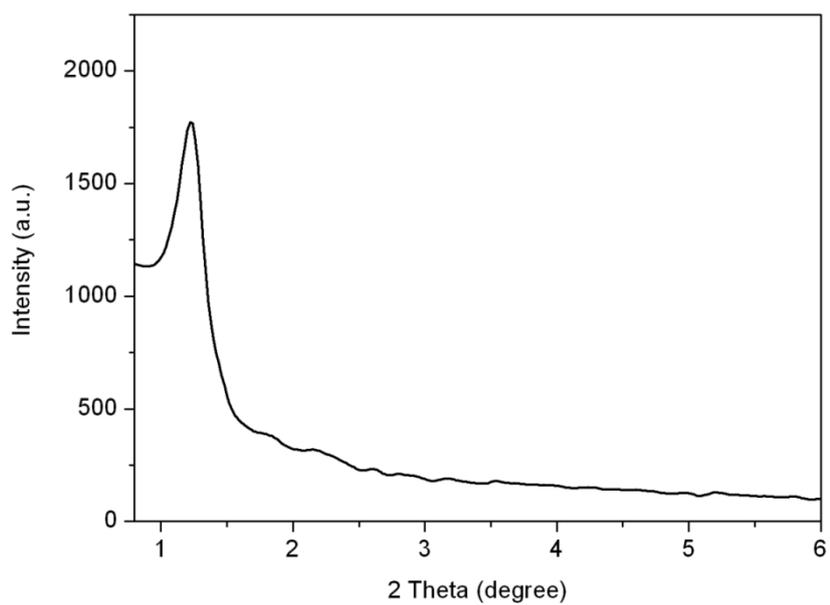


Fig. S2 Small-angle XRD pattern of CMK-3 calcination in N₂ at 900 °C for 4 h.

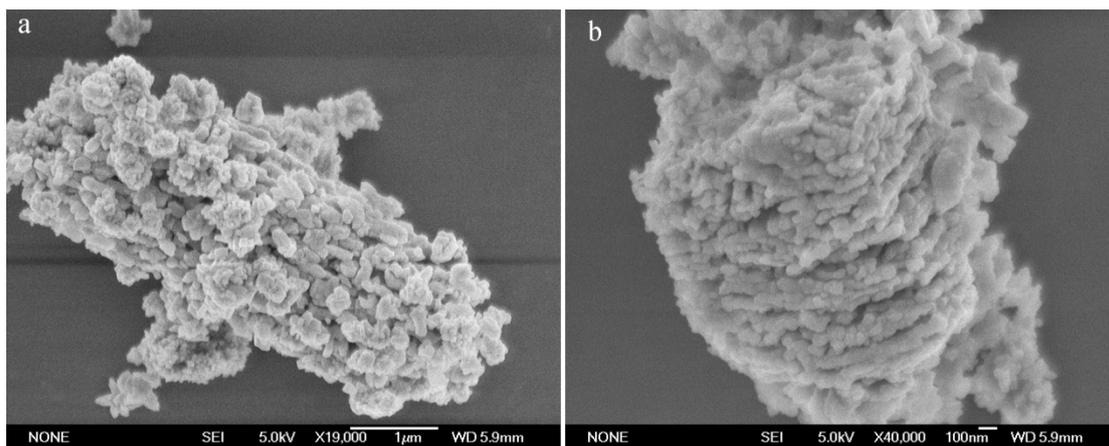


Fig. S3 (a) Low magnification and (b) high magnification SEM images of mesoporous CuO thus obtained.

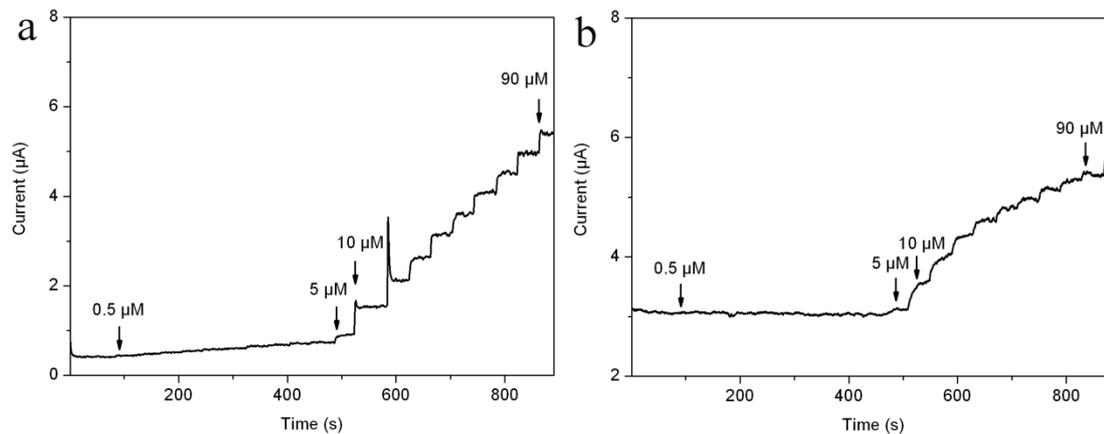


Fig. S5 Typical steady-state responses of the CuO/GCE to successive injection of glucose into the 0.1 M NaOH solution under stirring with applied potential at (a) +0.5 V and (b) +0.7 V.

References:

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- 2 L. Wang, S. Lin, K. Lin, C. Yin, D. Liang, Y. Di, P. Fan, D. Jiang and F.-S. Xiao, *Micropor. Mesopor. Mater.*, 2005, **85**, 136-142.
- 3 X. Lai, X. Li, W. Geng, J. Tu, J. Li and S. Qiu, *Angew. Chem. Int. Ed.*, 2007, **46**, 738-741.