

Preparation of copper oxide anchored on surfactant-functionalized macroporous carbon composite and its electrochemical applications

Experimental Section

Materials

Copper nitrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$) and Sodium dodecyl sulphate (SDS) were obtained from Beijing Chemical Co. Ltd. N,N'-dimethylformamide (DMF) (HPLC grade) and aminoethanol ($\text{NH}_2\text{CH}_2\text{CH}_2\text{OH}$) (AE) were purchased from Sigma–Aldrich. Hydrous hydrazine ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$, 80%) was obtained from Tianjin, China. The 0.1 M phosphate buffer solution (PBS pH 7.0), which was made up from NaH_2PO_4 , Na_2HPO_4 and H_3PO_4 , was employed as a supporting electrolyte. All other chemicals were at least of analytical grade. Aqueous solutions were prepared with doubly distilled water and stored in the shade.

Apparatus

All the electrochemical experiments were carried out on a computer-controlled CHI 830B electrochemical Analyzer (CH Instruments, Shanghai Chenhua Instrument Corporation, China). A conventional three electrode cell was used; bare or the modified glassy carbon electrode (GCE) was used as working electrodes, a platinum electrode was applied as the counter electrode and an Ag/AgCl (KCl-saturated) electrode served as a reference electrode. In this study, all the sample solutions were purged with purified nitrogen for 20 min to remove oxygen prior to the beginning of a series of experiments and all experiments were carried out at laboratory temperature. Scanning electron microscopy (SEM) images and energy dispersive X-ray

spectroscopy (EDX) were determined with a Philips XL-30 ESEM operating at 3.0 kV. Transmission electron microscope (TEM) images were obtained using a JEM-2100F transmission electron microscope JEOL (Japan) operating at 200 kV. Nitrogen adsorption-desorption isotherms were measured on ASAP 2020 Micromeritics (USA) at 77 K. X-Ray diffraction (XRD) patterns were obtained on an X-ray D/max-2200vpc (Rigaku Corporation, Japan) instrument operated at 40 kV and 20 mA using Cu K α radiation ($k = 0.15406$ nm). X-ray photoelectron spectroscopy (XPS) was measured using Thermo ESCA LAB X-ray photoelectron spectrometer (USA). Electrochemical impedance spectroscopy (EIS) was conducted using a Par 2273 Potentiostats-Electrochemistry Workstation.

Preparation of the modified electrodes

Prior to the modification, GCE (model CHI104, 3 mm diameter) was polished before each experiment with 1, 0.3 and 0.05 μm alumina power, respectively, rinsed thoroughly with doubly distilled water between each polishing step, and then sonicated successively in 1 : 1 nitric acid, absolute alcohol, double distilled water. The cleaned electrode was dried with a high-purity nitrogen steam for the next modification. To prepare the modified electrodes, 2 mg of the as-prepared samples were dispersed into 1 mL DMF to give homogeneous suspension upon bath sonication. A 5 μL of the suspension was dip-coated onto GCE and the electrode was then dried at room temperature.

Preparation of MPC

The SiO₂ template was prepared by the typical Stöber's method¹. The carbon was

introduced into the interstices of the template using the modified method of Jun et al². In a typical synthesis, 2.0 g of sucrose was dissolved in 10 mL aqueous solution containing 0.15 mL of 98% H₂SO₄. 2.0 g of SiO₂ template was immersed into sucrose solution and kept in vacuum for 3 hours at room temperature for thorough impregnation. Then the mixture was heated at 100 °C for 6 hours, followed by heating at 160 °C for a further 6 hours for polymerization of sucrose. The solid was subsequently carbonized at 900 °C in N₂ for 3 hours in a tube oven. The SiO₂ template was then etched away by overnight dissolution in 10% aqueous HF to leave behind a macroporous carbon.

Preparation of CuO/SMPC

First, 100 mg of the MPC was dispersed in 100 mL of deionized water with sonication in the form of 40-kHz ultrasonic waves at 100-W output power. Second, 11.2 mg of SDS was added as a surfactant with magnetic stirring at 50 °C for 1 h. Third, 50 mL, 4 mM of Cu(NO₃)₂·3H₂O was added and dissolved with magnetic stirring at 50 °C for 1 h. Then 50 mL, 4 mM of AE was added dropwise into this suspension. Then, after vigorous stirring at room temperature for 2 days, the preformed Cu(OH)₂/MPC nanocomposite was collected by filtration. The Cu(OH)₂/MPC precipitate was washed with deionized water, and dried in a vacuum oven at 60 °C for 24 h. Finally, Cu(OH)₂/MPC nanocomposite was transferred to a clean quartz boat and inserted into a tube furnace for heat treatment. The temperature of the furnace was raised from room temperature to 160 °C at the ascending rate of 2 °C min⁻¹ in air, and kept at 160 °C for 4 h to complete the dehydration. For

comparison, the CuO/MPC composite was prepared in the same way, except the MPC was functionalized by SDS.

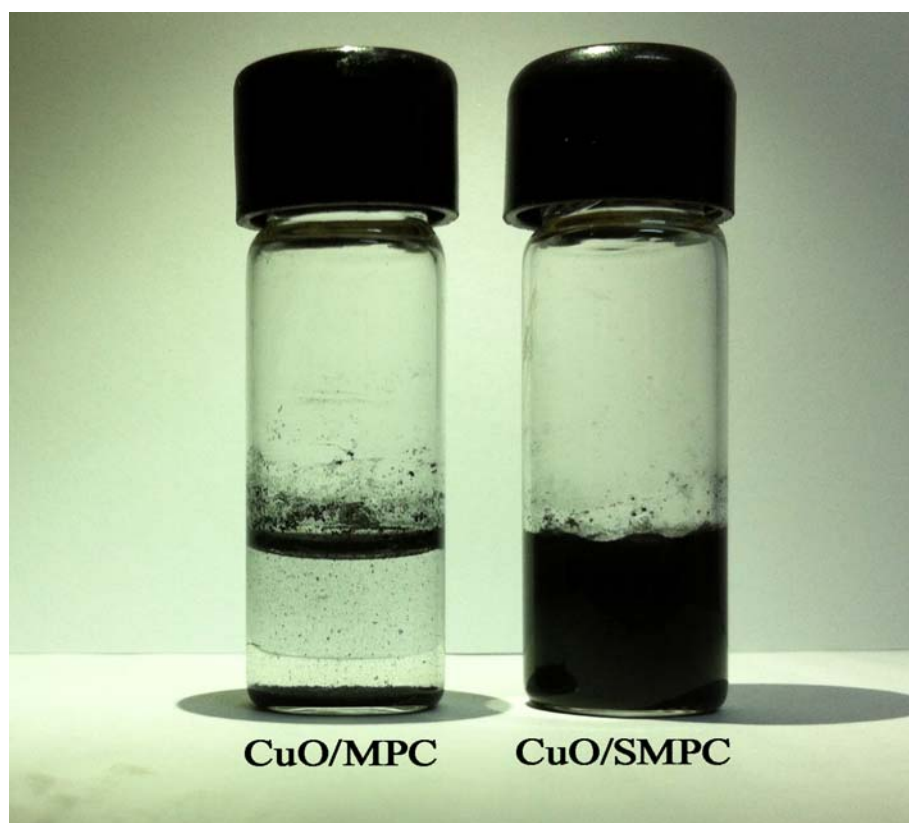


Fig. S1 Photographs of MPC and SMPC dispersed in aqueous solution taken two days later.

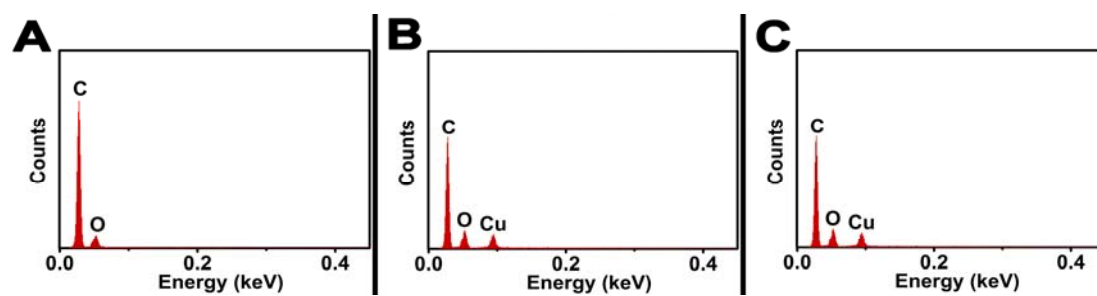


Fig. S2 EDX spectra of MPC (A), CuO/MPC (B), and CuO/SMPC (C).

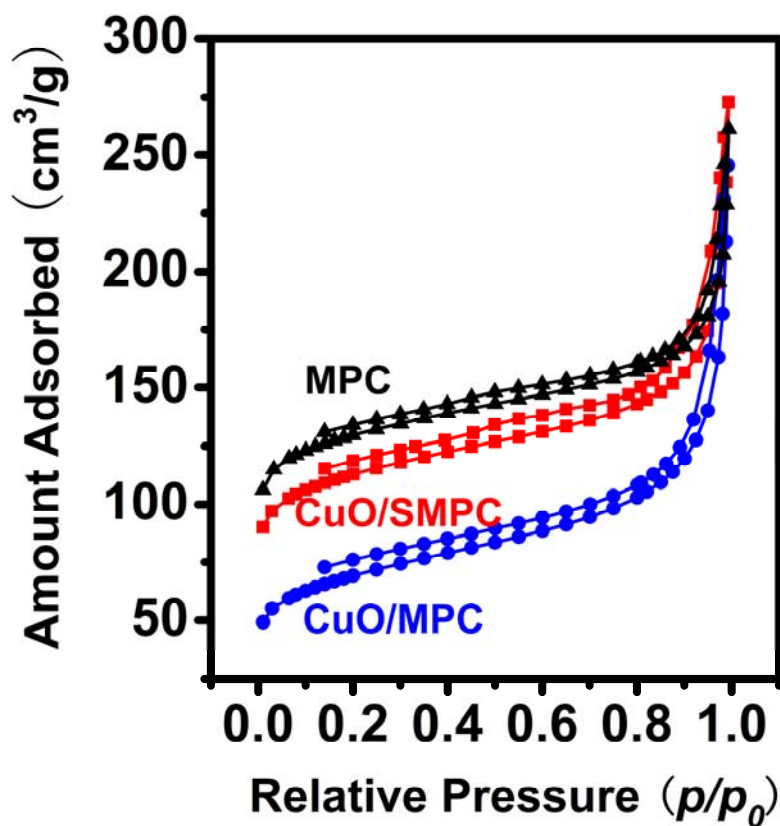


Fig. S3 Nitrogen adsorption–desorption isotherms of the MPC (black line), CuO/MPC (blue line), and CuO/SMPC (red line).

Table S1 BET surface areas of MPC, CuO/MPC, and CuO/SMPC

Samples	MPC	CuO/MPC	CuO/SMPC
S _{BET} (m ² g ⁻¹)	440.5	388.6	241.2

Table S2 Comparison of the performances of modified electrodes used in the electroanalysis of hydrazine

Working electrode	Applied potential (V)	Limit of detection (μM)	Linear range (μM)	sensitivity ($\mu\text{A } \mu\text{M}^{-1}$)	Reference
Manganese hexacyanoferrate	0.45	6.65	33.3-8180	47.53	3
Polypyridil and phosphine Ru (II)	0.75	1	6-1200	NO	4
CuO hollow sphere modified Si	0.7	0.25	1-5000	218	5
PNWs-Nafion/GCE					
GCE/ZnO/MWCNTs	0.4	0.18	0.6–250	17.47	6
PGE/nano-Rh/CNF	0.4	0.3	0.5–175	37.42	7
PCF	0.5	0.14	1–550	14.56	8
CPE/NiHCF/AuNP	0.3	0.1	0.5-900	52.99	9
Co-GE/GCE	0.3	0.1	0.25–370, 370–2200	39.93	10
CuO/MPC	0.6	2.82	10-1700	20.32	This work
CuO/SMPC	0.4	0.15	0.5-20 20-3000	1826.13 261.19	This work

References

1. S. Jun, J. Sang Hoon, R. Ryoo, M. Kruk, M. Jaroniec, Z. Liu, T. Ohsuna and O. Terasaki, *J. Am. Chem. Soc.*, 2000, **122**, 10712-10713.
2. W. Stöber, A. Fink and E. Bohn, *J. Colloid Interface Sci.*, 1968, **26**, 62-69.
3. Y. He, J. Zheng and S. Dong, *Analyst*, 2012, **137**, 4841-4848.
4. P. C. Pandey and A. K. Pandey, *Analyst*, 2012, **137**, 3306-3313.
5. M. Hadi, A. Rouhollahi and M. Yousefi, *Sens. Actuators, B*, 2011, **160**, 121-128.
6. G. Hu, Z. Zhou, Y. Guo, H. Hou and S. Shao, *Electrochem. Commun.*, 2010, **12**, 422-426.
7. B. Fang, C. Zhang, W. Zhang and G. Wang, *Electrochim. Acta*, 2009, **55**, 178-182.
8. A. Abbaspour, M. Shamsipur, A. Siroueinejad, R. Kia and P. R. Raithby, *Electrochim. Acta*, 2009, **54**, 2916-2923.
9. D. Jayasri and S. S. Narayanan, *J. Hazard. Mater.*, 2007, **144**, 348-354.
10. Z. Guo, M. L. Seol, M. S. Kim, J. H. Ahn, Y. K. Choi, J. H. Liu and X. J. Huang, *Nanoscale*, 2012, **4**, 7525-7531.