

## Supporting information

### CuS Nanotube for Ultrasensitive Nonenzymatic Glucose Sensors

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### Experimental Procedures

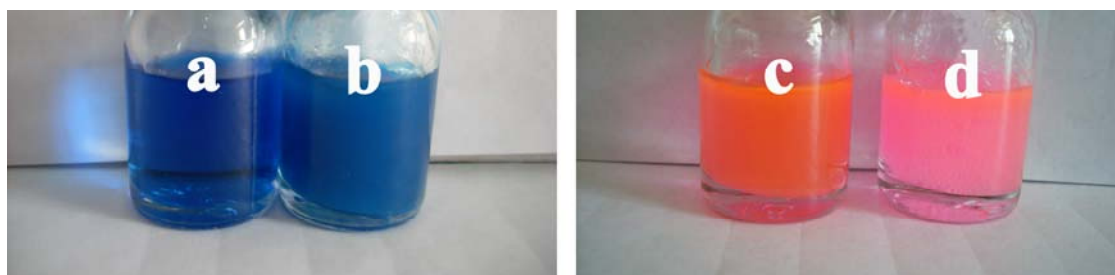
**Chemicals.**  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ , oleic acid, sodium thiosulfate, poly(vinylpyrrolidone) (PVP), ethanol, and  $\text{K}_3[\text{Fe}(\text{CN})_6]$  were purchased from Shanghai Chemical Corp, and D(+)-glucose (97%) and Nafion (5 wt %) were purchased from Sigma-Aldrich. All chemicals were used as received without any further purification. Distilled water was used in all experiments.

**Synthetic Procedures.** In a typical synthesis process, 0.24 g of copper nitrate, 0.3 g sodium thiosulfate and 0.2 g of poly(vinylpyrrolidone) were mixed with distilled water, and then the oleic acid was added. The mixture was stirred vigorously to homogeneity and then transferred into a 60 mL steel autoclave. The autoclave was sealed, maintained at 150 °C for 12 h, and then cooled naturally to room temperature. The product was washed with distilled water and ethanol several times to remove impurities before characterization.

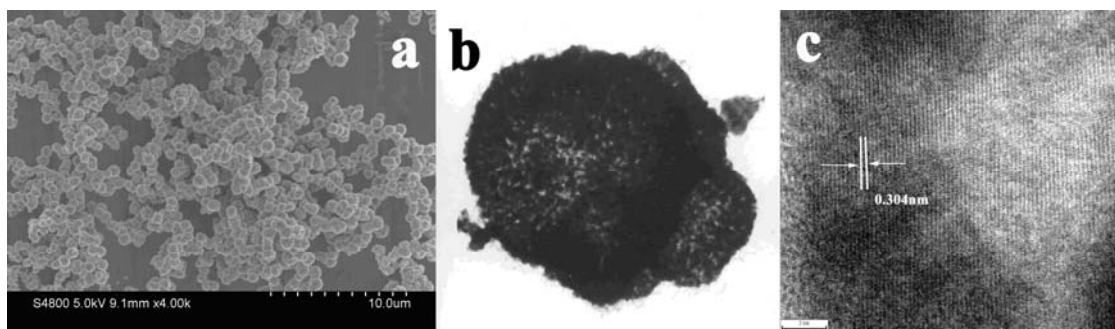
**Electrochemical Measurements.** The modified electrode was prepared as follows: GC electrodes (3 mm diameter) were carefully polished with a diamond pad/3  $\mu\text{m}$  polishing suspension, rinsed with distilled water and ethanol, and then dried under ambient nitrogen gas. CuS nanotubes (10 mg) were dissolved in a mixture of 0.1 mL of Nafion perfluorosulfonated ion-exchange resin and 0.9 mL of distilled water. Approximately 60 min of ultrasonication was necessary to obtain uniformly dispersed CuS nanotubes. After

dropping 10  $\mu\text{L}$  of the CuS nanotubes solution onto the electrode surface, the electrode was dried in air. Electrochemical measurements were performed on a model CHI660B electrochemical analyzer (ChenHua Instruments Co. Ltd., Shanghai, China) controlled by a personal computer. Using the modified GC working electrode, the CV and CA data were measured in a mixture of 1  $\text{mmol L}^{-1}$  glucose and 20  $\text{mmol L}^{-1}$  phosphate buffer solution (PBS, pH 9.2). The CA measurements required operation of the electrode at a constant applied potential of 0.20 V versus SCE. Once the current reached a baseline in the absence of glucose, glucose was added every 40 s thereafter. The CV and CA measurements were carried out in 50  $\text{mmol L}^{-1}$  PBS (pH 9.2).

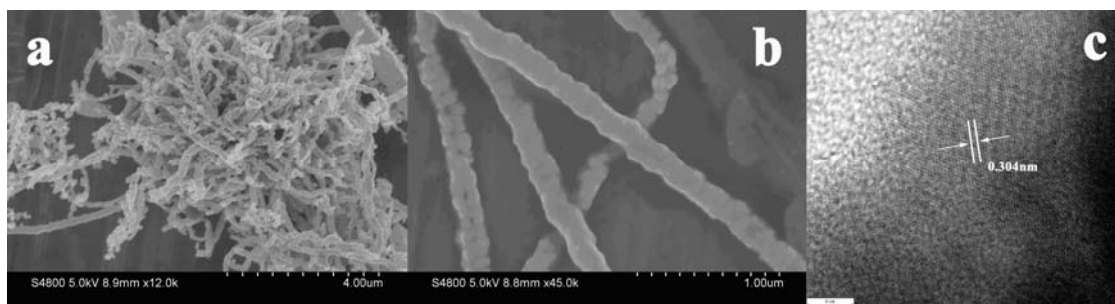
**Characterization.** XRD patterns of the products were recorded on a Shimadzu XRD-6000 X-ray diffractometer at a scanning rate of  $0.05^\circ/\text{s}$  with a  $2\theta$  range from 10 to  $80^\circ$ , with high-intensity Cu  $K\alpha$  radiation ( $\lambda = 0.154178 \text{ nm}$ ). Field emission scanning electron microscopes and energy dispersive X-ray analyses were obtained using a JEOL JSM-6700 FESEM (operating at 10 kV). The HRTEM analysis used a JEOL 2010 instrument with an accelerating voltage of 200 kV.



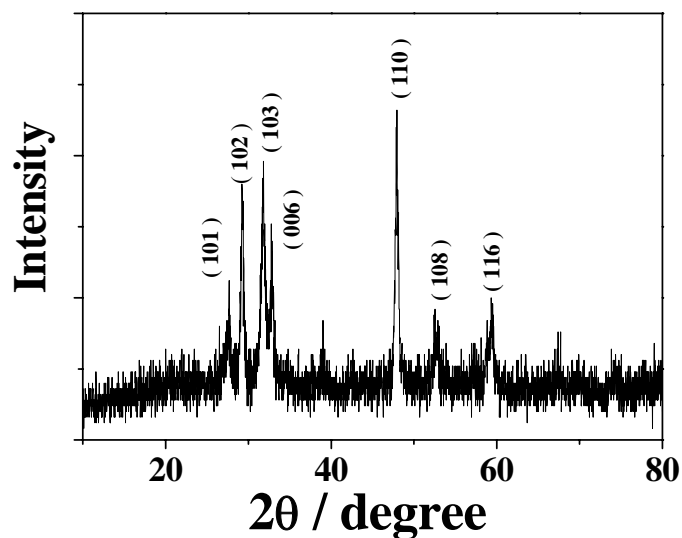
**Figure S1.** Methylene blue (Water-solubility dye) in water (a), O/W microemulsion (b); Sudan III (Oil-solubility dye) in oleic acid (c), O/W microemulsion (d).



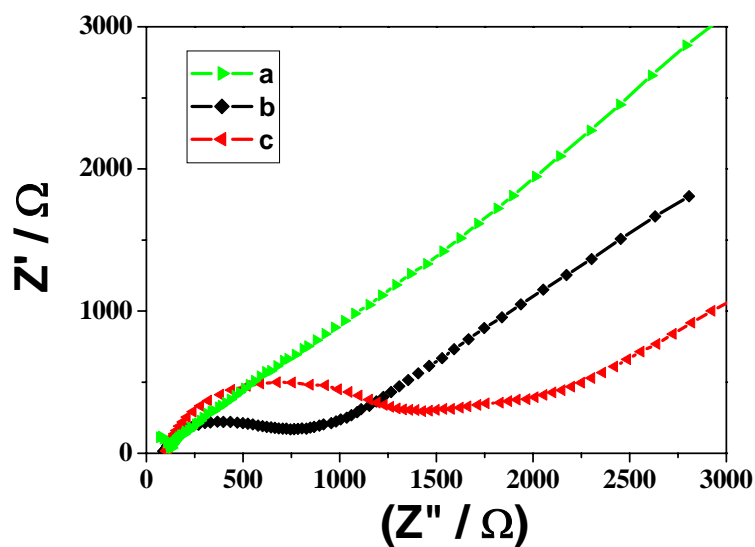
**Figure S2.** (a) SEM image of the hollow CuS nanospheres, (b) TEM image of the single hollow CuS nanospheres, (c) HRTEM image of the hollow CuS nanospheres.



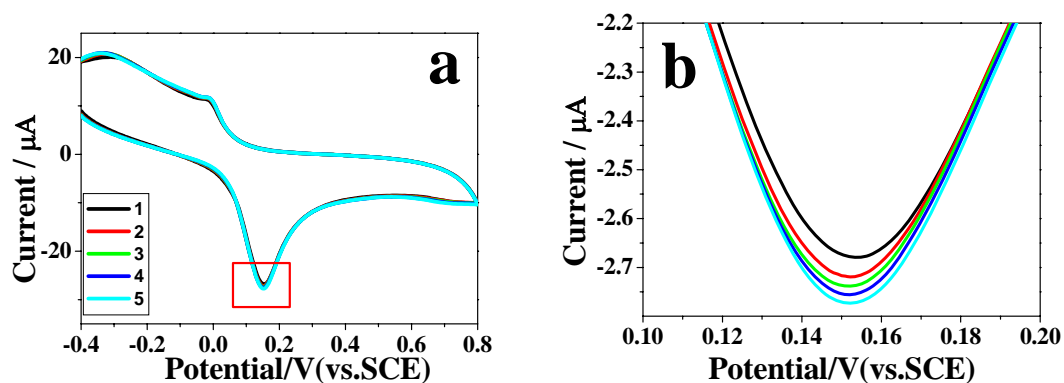
**Figure S3.** (a) Low magnified and (b) high magnified FESEM images of the CuS nanotubes, (c) HRTEM image of the nanotube.



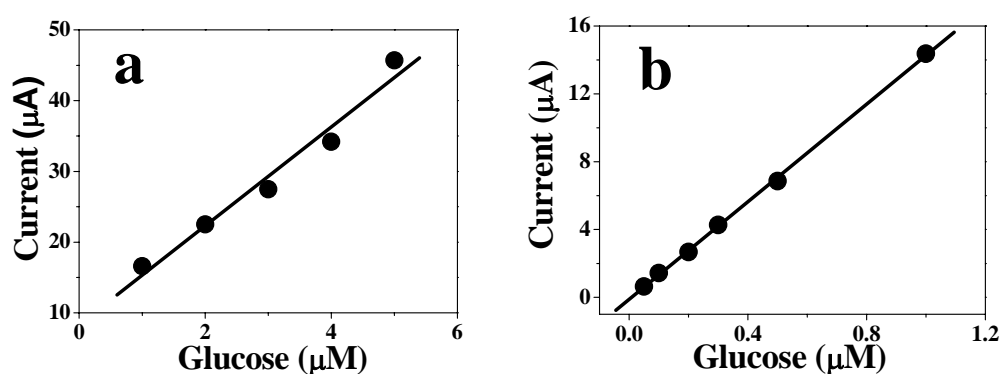
**Figure S4.** XRD pattern of the as-prepared products showing hexagonal phase of CuS nanotubes.



**Figure S5.** The electrochemical impedance spectroscopy of: (a) bare GC electrode; (b) CuS nanotube made up of CuS nanoparticles; (c) regular CuS nanotube modified GC electrode in  $2.5 \times 10^{-3} \text{ mol L}^{-1} [\text{Fe}(\text{CN})_6]^{4-/3-} + 0.1 \text{ mol L}^{-1} \text{ KCl} + 10 \times 10^{-3} \text{ mol L}^{-1} \text{ PBS}$  (pH = 7.2) at a bias potential of 0.20 V.



**Figure S6.** (a) CV performance of regular CuS nanotube/Nafion-modified GC electrodes in the presence of the same amount of the glucose in  $50 \text{ mmol L}^{-1}$  PBS (pH 9.2) at a scan rate of  $50 \text{ mV s}^{-1}$ . (1-5 means 1, 2, 3, 4, 5  $\mu\text{mol L}^{-1}$  glucose in  $50 \text{ mmol L}^{-1}$  PBS, respectively) (b) the enlargement of the peak part in a.



**Figure S7.** Linear response for glucose concentrations between (a) 1  $\mu\text{mol L}^{-1}$  and 5  $\mu\text{mol L}^{-1}$ ; (b) 0.05  $\mu\text{mol L}^{-1}$  and 1  $\mu\text{mol L}^{-1}$

Glucose ( $\mu\text{M}$ )	Current ( $\mu\text{A}$ )			Average Current $\pm$ SD ( $\mu\text{A}$ )
	1	2	3	
1	15.51	16.07	15.27	15.61 $\pm$ 0.4106
2	22.08	22.84	22.65	22.52 $\pm$ 0.3955
3	27.78	27.18	27.46	27.47 $\pm$ 0.3002
4	34.40	34.18	33.97	34.18 $\pm$ 0.2151
5	45.67	45.99	45.37	45.68 $\pm$ 0.3101

**Table S1** Glucose concentration (between 1  $\mu\text{mol L}^{-1}$  and 5  $\mu\text{mol L}^{-1}$ ) influence to Average Current  $\pm$  standard deviation (SD) determined by CV.

Glucose ( $\mu\text{M}$ )	Current ( $\mu\text{A}$ )			Average Current $\pm$ SD ( $\mu\text{A}$ )
0.05	0.6406	0.6570	0.6372	0.6449 $\pm$ 0.01059
0.1	1.429	1.422	1.443	1.431 $\pm$ 0.01061
0.2	2.676	2.622	2.714	2.671 $\pm$ 0.04623
0.3	4.144	4.228	4.428	4.267 $\pm$ 0.1459
0.5	6.858	6.982	6.715	6.852 $\pm$ 0.1336
1	14.50	14.37	14.19	14.35 $\pm$ 0.1557

**Table S2** Glucose concentration (between 0.05  $\mu\text{mol L}^{-1}$  and 1  $\mu\text{mol L}^{-1}$ ) influence to Average Current  $\pm$  standard deviation (SD) determined by CV.