Supplementary Information

Rational design of hierarchical $CuO/Cu_2O/SnO_2$ branched supernanowires for high-sensitive non-enzymatic glucose sensors

Peng Luo[a], Qing-Qing Zhou[a], Ying-Li Shi[c], Yang-Biao Xue[b], Zuo-Shan Wang[a*], Min Zheng[b*], Ming-Peng Zhuo[b*]

[a] College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou, Jiangsu 215123, China.

[b] National Engineering Laboratory for Modern Silk, College of Textile and Clothing Engineering, Soochow University, Suzhou Jiangsu 215123, China.

[c] Department of Electrical and Electronic Engineering, School of Advanced Technology, Xi'an Jiaotong-Liverpool University, Suzhou, Jiangsu 215123, China.

Correspondence and requests for materials should be addressed to Z.-S. Wang (zuoshanwang@suda.edu.cn), M.-P. Zhuo (mpzhuo@suda.edu.cn), and M. Zheng (zhengmin@suda.edu.cn).

Experimental details

1. Materials

Cupric acetate monohydrate ($Cu(Ac)_2 \cdot H_2O$), polyethylene glycol 200 (PEG200), sodium hydroxide (NaOH), Stannic chloride pentahydrate ($SnCl_4.5H_2O$) were purchased from Sinopharm Chemical Reagent Co., Ltd. All the reagents used here were analytically pure except for PEG200 which was of chemical grade. They were used directly without any further purification, and deionized water was used throughout the experimental procedure.

2. Synthesis of porous $Cu(OH)_2$ nanorods

$Cu(OH)_2$ nanorods were fabricated by a simple precipitation method. The preparation process is as follows: Configure the same volumes of 0.3 mol L^{-1} $Cu(Ac)_2$ and 3 mol L^{-1} NaOH aqueous solutions, respectively, and stir for a few minutes. Then $Cu(Ac)_2$ solution was added dropwise to NaOH solution under rapid magnetic stirring. At the end of the reaction, the reaction was immediately centrifuged and washed with deionized water and ethanol, and dried at 60°C for 12 h.

3. Synthesis of barnyardgrass-like $CuO/Cu_2O/SnO_2$ (B-$CuO/Cu_2O/SnO_2$) nanowires and $CuO/Cu_2O/SnO_2$ nanorods

B-$CuO/Cu_2O/SnO_2$ nanowires and $CuO/Cu_2O/SnO_2$ nanorods nanowires were synthesized by a microwave method. The entire experimental procedure is as follows: Firstly, 24 mg of porous $Cu(OH)_2$ nanorod powder was weighed and added to 100

mLPEG200 and ultrasonically dispersed into a homogeneous solution. Then 0.5 mL of 5 mM NaOH solution and 800 μL of 5 mM $SnCl_4$ solution were added successively. After stirring uniformly, transfer the solution to a 250 mL three-necked flask for microwave reaction with reaction conditions set to 700 W, 180 °C, and obtain a dark green solution after 10 min. Finally, the solution was centrifuged, washed, and dried at 60 °C for 6 h to obtain a dark green powder. Notably, the products synthesized by this method are B-$CuO/Cu_2O/SnO_2$ nanowires, and when NaOH is added in smaller amounts or not, the products are $CuO/Cu_2O/SnO_2$ nanorods.

4. Preparation of electrodes

4.1 Pretreatment of glassy carbon electrode

Before the modification, the surface of the glassy carbon electrode (Φ=3 mm) was polished to a mirror surface with $A1_2O_3$ powders of 1.0 μm, 0.3 μm and 0.05 μm in turn, and then ultrasonically cleaned in anhydrous ethanol and distilled water in turn. Electrochemical pretreatment of electrode: The glassy carbon electrode was placed in 1.0 M H_2SO_4 solution, and cyclic voltammetric scanning was performed at a sweep rate of 100 mV s^{-1} and a voltage sweep range of -1.0 V to +1.0 V until stability.

4.2 Preparation of B-$CuO/Cu_2O/SnO_2$ nanowires and $CuO/Cu_2O/SnO_2$ nanorods modified electrodes

1 mg of B-$CuO/Cu_2O/SnO_2$ nanowire powder was weighed and dispersed in 2 mL of distilled water and sonicated, followed by pipetting 30 μL drops onto the surface of the pretreated glassy carbon electrode, which was dried naturally at room temperature.

Before each test, the surface of the modified electrode is rinsed with secondary water to wash away the impurities on the surface. And the $CuO/Cu_2O/SnO_2$ nanorods modified electrodes were prepared by repeated methods.

5. Characterization

The samples were observed morphologically using transmission electron microscopy (TEM, FEI Tecnai G20), high resolution transmission electron microscopy (HRTEM, HitachiH600A-G) and selected area electron diffractogram (SAED) to confirm the morphology and crystalline surface of the samples. The crystalline phase of the synthesized samples was ascertained through powder X-ray diffraction (XRD) on a Rigaku D/max-III C X-ray diffractometer with Cu-Kαradiation (k = 0.154 nm), scanning from 10° to 80° with a scanning voltage of 40 kV, aS-3scanning current of 100 mA. The elemental composition and valence states were confirmed by x-ray photoelectron spectrometry (XPS, ESCALAB 250). The specific surface area and pore size distribution were analyzed by the Brunauer-Emmett-Teller (BET) method. Electrochemical experiments were performed on CHI-6611D electrochemical workstation with a three-electrode system, which includes working electrode, counter electrode (platinum wire) and reference electrode (saturated chromium alloy electrode).

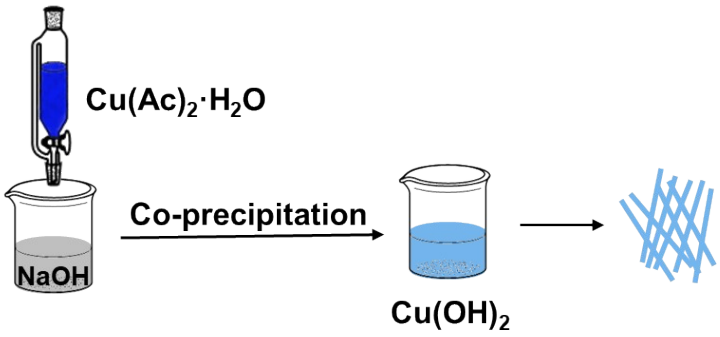

Fig. S1. The flow chart of the preparation of porous $Cu(OH)_2$ nanorods.

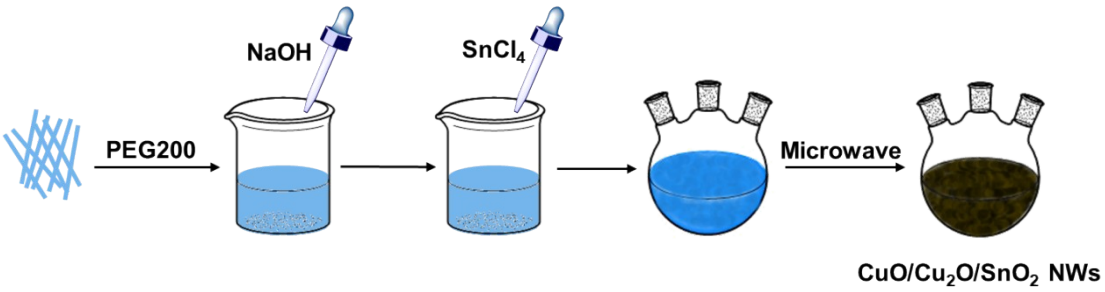

Fig. S2. The flow chart of the preparation of B-$CuO/Cu_2O/SnO_2$ nanowires.

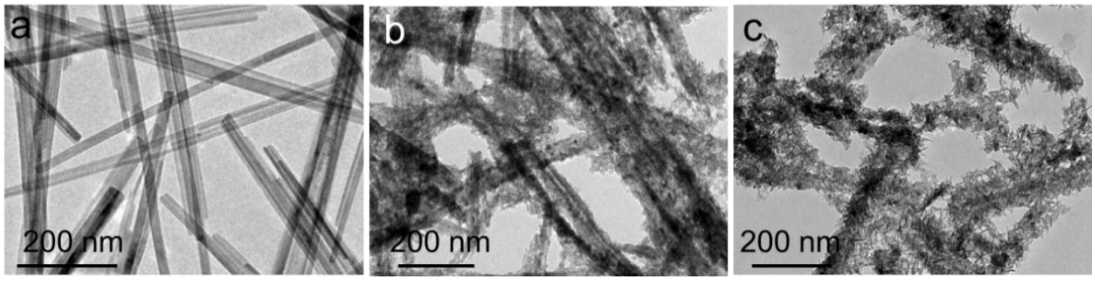

Fig. S3. (a) TEM images of porous $Cu(OH)_2$ nanorods with scale bar of 200 nm. (b)TEM images of $CuO/Cu_2O/SnO_2$ nanorods with scale bar of 200 nm. (c) TEM images of B-$CuO/Cu_2O/SnO_2$ nanowires with scale bar of 200 nm.

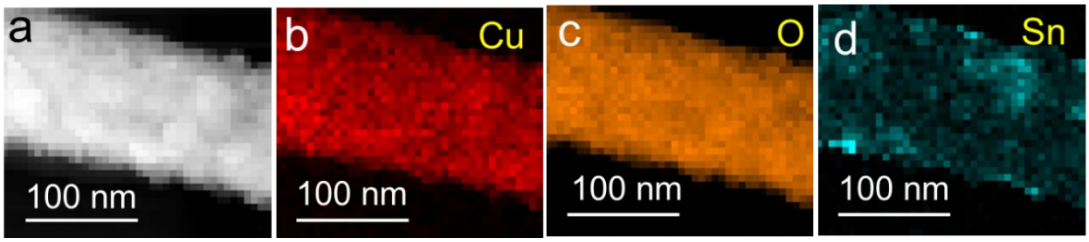

Fig. S4. The Mapping images of the $CuO/Cu_2O/SnO_2$ nanorod with scale bar of 100 nm.

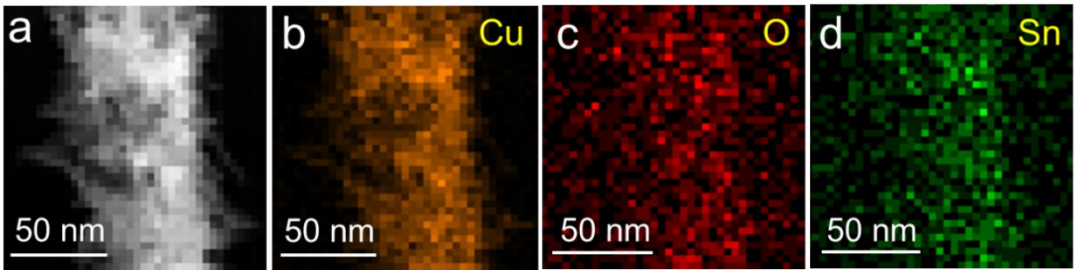

Fig. S5. The Mapping images of the B-$CuO/Cu_2O/SnO_2$ nanowire with scale bar of 50 nm.

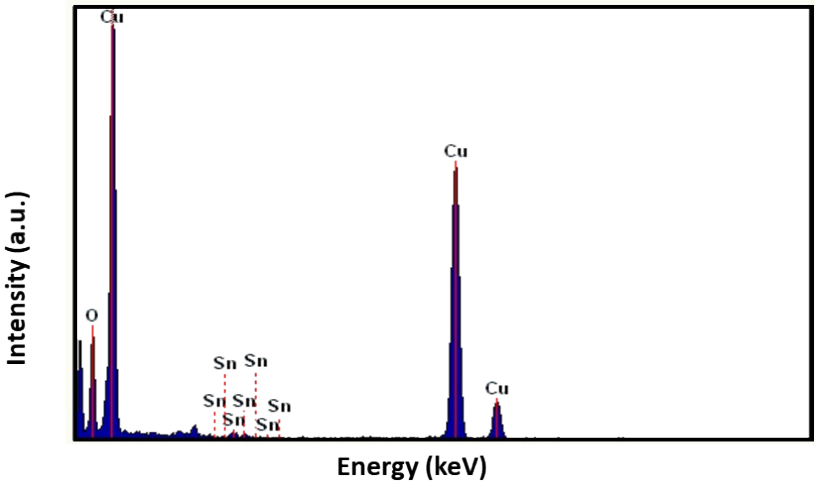

Fig. S6. The EDX pattern of the B-$CuO/Cu_2O/SnO_2$ nanowires.

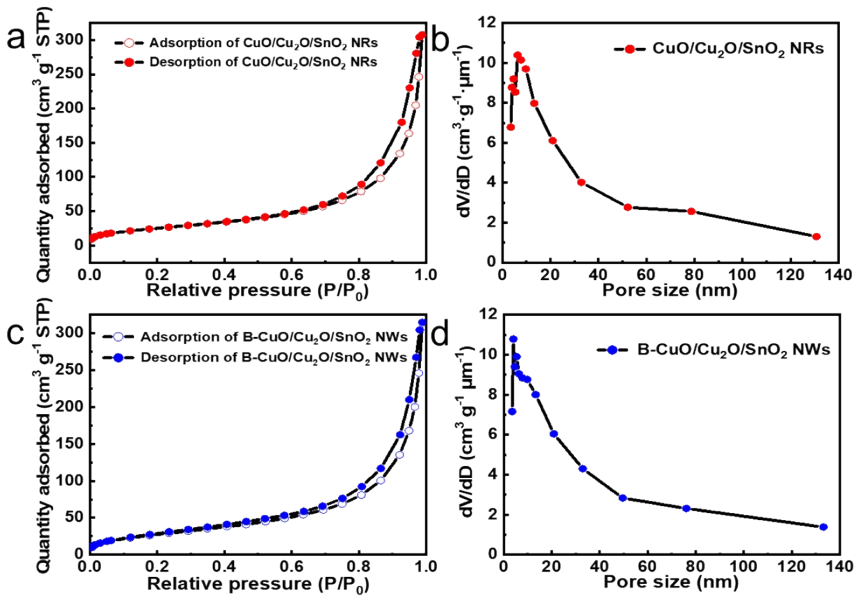

Fig. S7. (a) Nitrogen adsorption—desorption isotherm and (b) corresponding pore size distribution curves of CuO/Cu_2O nanorods and $CuO/Cu_2O/SnO_2$ nanorods. (c) Nitrogen adsorption—desorption isotherm and (d) corresponding pore size distribution curves of B-$CuO/Cu_2O/SnO_2$ nanowires.

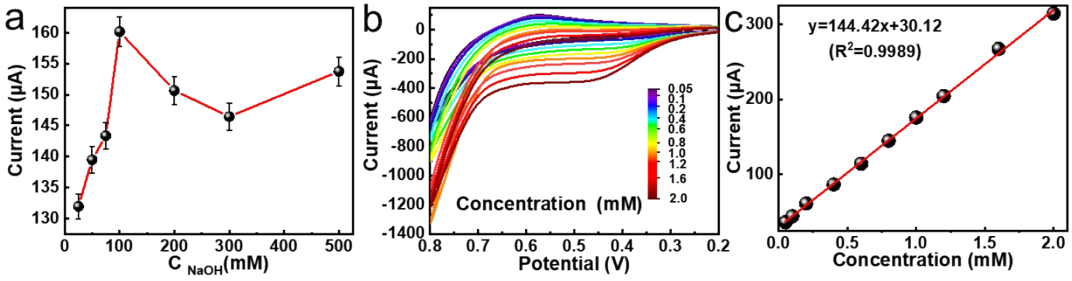

Fig. S8. (a) The effect of NaOH concentration on the peak current response of $CuO/Cu_2O/SnO_2$ nanorods electrodes containing 1 mM glucose (scan rate: 100mV s^{-1}). (b) CV curves of the $CuO/Cu_2O/SnO_2$ nanorods electrode in the 100 mM NaOH electrolyte with a concentration of glucose ranging from 0.05 to 2 mM at a scan rate of 100 mV s^{-1}. (c) The linear calibration plot between the oxidation peak current and glucose concentration.

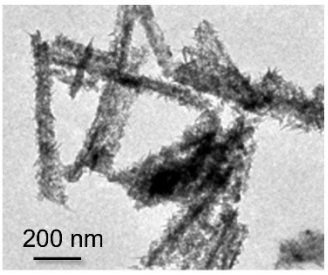

Fig. S9. The TEM images of B-CuO/Cu_2O/SnO_2 nanowires after 4 weeks.

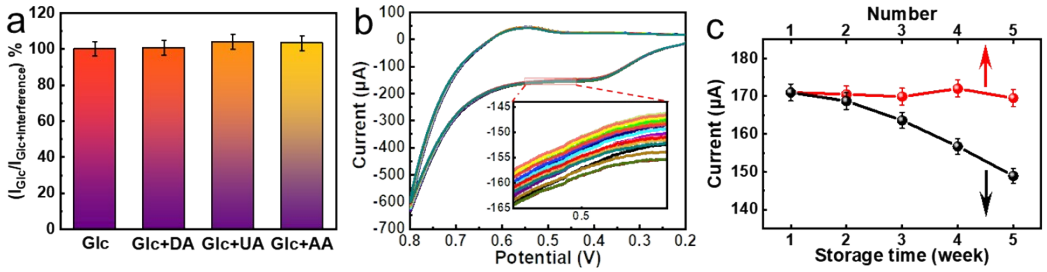

Fig. S10. (a) Selectivity study of the CuO/Cu_2O/SnO_2 nanorods modified electrodes in the determination of 0.1 mM glucose (with 0.15 mM DA, 0.15 mM UA, 0.15mM AA). (b) 20 cycles of CV curves of the CuO/Cu_2O/SnO_2 nanorods electrode. (c) Red and black point plots corresponding to 5 uniform CuO/Cu_2O/SnO_2 nanorods electrodes and the same CuO/Cu_2O/SnO_2 electrode measured over 4 weeks, respectively.

Table S1. The comparison of BET data for each sample.

Materials	**CuO/Cu_2O/SnO_2 NRs**	**B-CuO/Cu_2O/SnO_2 NWs**
specific surface area	92.83 m^2 g^{-1}	102.92 m^2 g^{-1}
pore size distribution	5-15 nm	5-10 nm