Supporting Online Material for

Rational Design of CuO@Cu Nanostructure with Tuneable Morphology and Electrochemical Properties

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Experimental Section

Chemicals and Materials: Sodium hydroxide (NaOH, ≥96.0%), Potassium peroxydisulfate ($K_2S_2O_8$, ≥99.5%), Anhydrous sodium sulfate (Na_2SO_4, ≥99.0%), Sodium dodecyl sulphate (SDS), Hexadecyltrimethyl ammonium Bromide (CTAB, 99.0%), Octylphenoxypolyethoxy ethanol (TrironX-100, ≥99.0%), Hydrochloric acid (HCl, w% 36.0%-38.0%), and Nitric acid (HNO_3, w% 65.0%-68.0%) were purchase from Sigma-Aldrich and used without any treatment.

Synthesis of nanostrucuted CuO on Cu foil: A Cu foil (3.0 cm × 2.5 cm) was cleaned by consecutive ultrasonication in acetone, ethanol and pure water for 30 mins, respectively. Then, the foil was acidized in diluted HCl (5.0 M) solution for 30 mins under stirring. For the chemical-etching process, the starting solution was firstly prepared by mixing 6.40 g of NaOH in 32 mL of water under stirring. When the solution was cooled to room temperature, 1.30 g of $K_2S_2O_8$, 0.09 g of Na_2SO_4 and 0.46 g of SDS was introduced into the NaOH aqueous solution, respectively. Taking SDS as the example, when the surfactant was completely dissolved in NaOH solution, the mixture was quickly transferred into a 40 mL of Teflon-lined stainless steel autoclaves. Then, the cleaned Cu foil was immersed in the solution. The autoclaves were sealed and maintained at 160 °C for 3.5 h. The Cu foil was taken from the solution after the autoclaves were cooled to room temperature, and rinsed with distilled water for several times. The obtained sample was noted as CuO-3.5h.

Characterization: The morphology and elemental mapping of the CuO were characterized by using a scanning electron microscopy (SEM, QUANTA FEG 250 with energy dispersive spectrometer). Powder X-ray diffraction (XRD) patterns were obtained (D8 Focus, Bruker instrument, Germany) with Cu Kα radiation ($\lambda = 1.5406$ Å) in the 2θ range from 10° to 80° with a step size of 0.02° s^{-1}. The samples used for XRD was collected by scratching the black powders from the Cu foils.

Electrochemical Measurements: The electrochemical measurements were carried out on a CHI660D electrochemical working station (CHI, China), controlled by a personal computer with CHI software. A conventional three-electrode system used in the measurements consists of a CuO@Cu electrode as the working electrode, a saturated calomel electrode (SCE) as the reference electrode, and a Pt wire as the counter electrode. The amperometric responses of the CuO@Cu electrode to H_2O_2 was recorded at a constant potential of 0.25 V with a successive addition of H_2O_2 into phosphate buffer solution (PBS, pH 7.0) under stirring. The Linear sweep voltammetries (LSVs) were recorded in the solution of NaOH (0.1 M) containing MeOH (1.0 M) at a scan rate of 10 mV s^{-1}. The electrochemical impedance spectrum (EIS) of the different electrodes was measured in the potassium ferricyanide solution (1 mM) in a range from 0.01 Hz to 100 kHz. The cyclic voltammograms (CVs) of the different electrodes in the potassium ferricyanide solution (1 mM) was carried out at a scan rate of 50 mV s^{-1} in a potential range of -0.4 to 0.3 V.

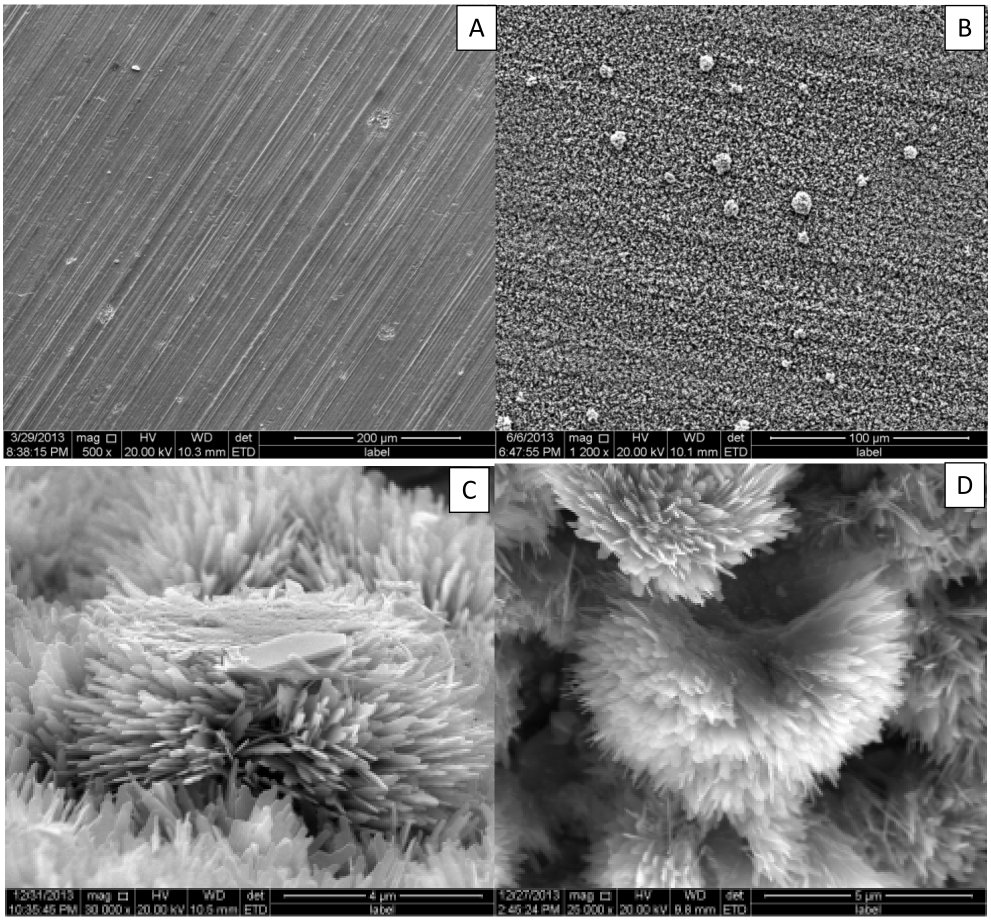


Fig. S1 SEM images of (A)Cu foil and (B) CuO@Cu prepared without surfactant.(C) and (D) shows the SEM images of the Cuo@Cu owning semisphere with nanoplates.

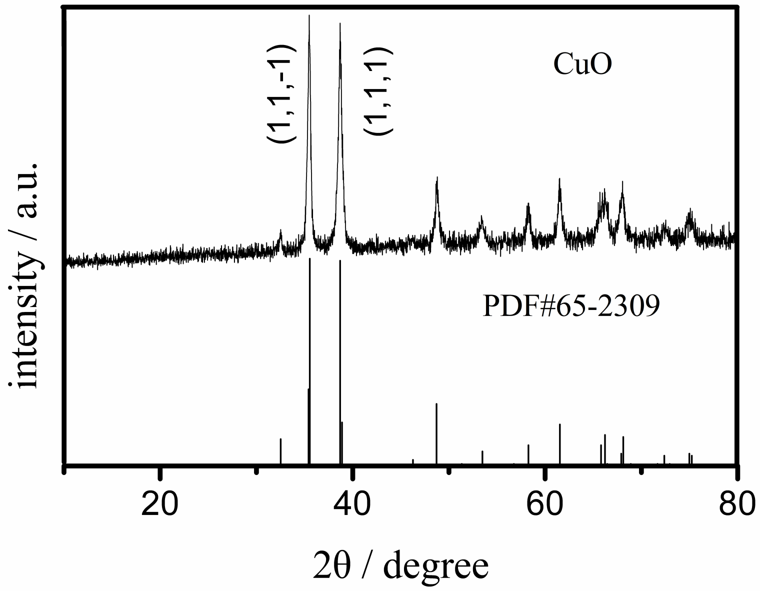
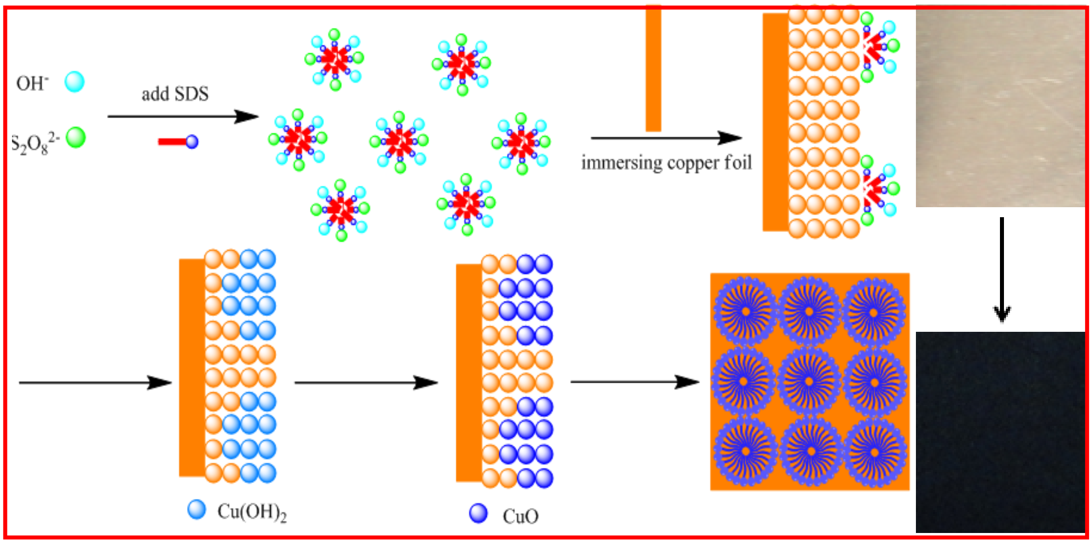


Fig. S2 XRD pattern of the CuO powder collected from the CuO@Cu samples.



Scheme S1 Schematic illustration of the in-situ formation of nanostructured CuO@Cu by chemical etching Cu foil in NaOH solution containing SDS.

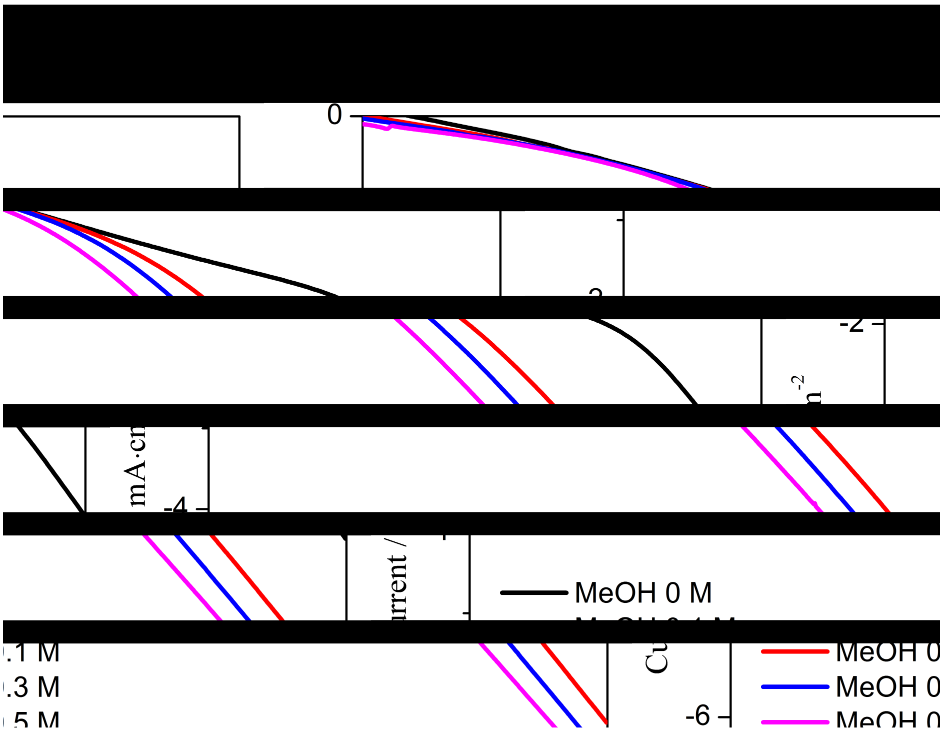


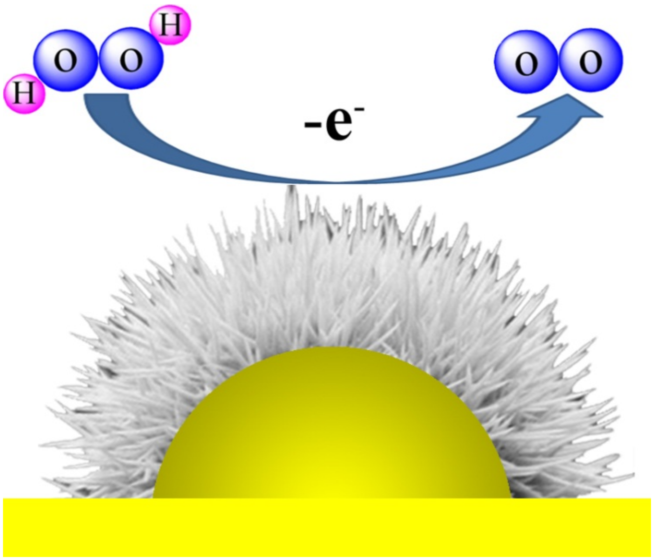
Fig. S3 LSVs observed at CuO@Cu electrodes in 0.1 M of NaOH containing different concentrations of MeOH at a scan rate of 10 mV s^{-1}.

Table S1 Relationship between the concentration of H_2O_2 and respond current and detection limits

Sample	respond current vs. concentration of H_2O_2	Sensitivity (μA mM^{-1})	Detection limit (μM)
CuO@Cu-0.5h	y=0.1063x+0.0079	110	37
CuO@Cu-2h	y=0.1653x+0.0077	170	29
CuO@Cu-3.5h	y=0.2424x+0.0273	240	11
CuO@Cu-6h	y=0.1814x+0.0268	180	18

Table S2 Electrochemical parameters calculated from CVs and EIS results.

Electrode	Cu foil	CuO 0.5h	CuO 2h	CuO 3.5h	CuO 6h
ΔE_p / V	0.261	0.362	0.371	0.385	0.392
Q / C	0.61	1.12	1.24	2.38	2.89
R_{ct} / (Ω)	183	56	89	460	486



Scheme S2 Schematic illustration of the electron transfer process for the oxidation of H_2O_2 at the CuO@Cu electrode.