

Cu Nanowires paper interlinked Cobalt Oxide films for Enhanced Sensing and Energy Storage

1. Experimental Section

1.1 Materials and Method. The ultra-long Cu@CoO_x nanowires were synthesized by a two-step water-bath preparation and a heat treatment process. All reactants are analytic reagents.

Synthesis of ultra-long copper nanowires. The copper nanowires were synthesized by an aqueous-related method. Primarily, a 200 mL aqueous solution containing 120 g NaOH was prepared and heated to 60 °C in the water bath. Then, 10 mL 0.1 mol/L Cu(NO₃)₂ solution, 1.6 mL ethylenediamine (EDA) and 0.25 mL hydrazine hydrate (85%) was added dropwise into the solution, respectively. After keeping the solution in 60 °C water bath for 100 minutes, the product was washed by water and ethanol for several times and freeze-dried for 48 hours.

Synthesis of Cu@CoO_x. In a typical procedure, 20 mg as-prepared Cu nanowires, 0.45 g Co(NO₃)₂·6H₂O, 0.7 g hexamethylenetetramine and 14.5 mg sodium citrate were dispersed in 80 mL deionized water and ultrasonic-treated by 30 minutes. Then, the solution was kept in a 90 °C water bath for 60 minutes. Finally, the product is collected by centrifugation and heated at 350 °C in N₂ atmosphere for 90 minutes, with a heating rate of 2 °C/min.

Synthesis of ultra-thin CoO_x. For the purpose of comparison, the sole CoO_x was prepared by a similar process with Cu@CoO_x: 0.45 g Co(NO₃)₂·6H₂O, 0.7 g hexamethylenetetramine and 14 mg sodium citrate were dispersed into 80 mL pure water. With a 30-min ultrasonic process, the solution was kept in a 90 °C water bath for 60 minutes. Finally, the product is collected by centrifugation and heated at 350 °C in N₂ atmosphere for 90 minutes, with a heating rate of 2 °C/min.

1.2 Characterization. The phase structure and surface chemical states of nanomaterials were identified by X-ray diffraction (XRD) (X'Pert ProMPD ($\lambda_{\text{Cu-K}\alpha} = 1.5418 \text{ \AA}$)) and X-ray photoelectron

spectroscopy (XPS) (PHI-5400, USA, with monochromatic Cu-K α radiation ($h\nu = 1486.6$ eV)). Transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED) (FEI Tecnai F30G2) and field emission scanning electron microscopy (FESEM, FEI Nano SEM 450) were used to analyze the morphology and microstructure.

1.3 Electrochemistry Measurements. The CS310 electrochemical workstation (Corrtest, China) was used to investigate materials' electro-sensing and supercapacitor performances, at room temperature, in three-electrode cells with different electrolytes. In the cell for all tests, an Ag/AgCl (saturated with KCl) electrode and a platinum electrode (dia. 3mm) are used as the reference electrode and counter electrode, respectively. For the investigation of bio-sensing, a modified glass carbon electrode (dia. 3 mm) was used as the working electrode, the cyclic voltammograms (CVs) were put into action with the potential of -0.2 – 0.7 V, and the amperometric responses of the Cu@CoO $_x$ and CoO $_x$ were measured at +0.38 V and +0.60 V, respectively, under stirring. For the evidence of energy storage behavior, the working electrode was fabricated by following two steps: (1) mixing as-prepared materials, polytetrafluoroethylene (PTFE) and carbon black at a weight ratio of 80:1:1; (2) coating the above mixture on to the nickel foam (1 cm 2) and pressing that into a thin flake at a pressure of 10 MPa. The specific capacitance was calculated based on the mass of the active materials. The specific

capacitance was calculated by the equation
$$C_s = \frac{2i_m \cdot \int v dt}{v^2 \Big|_{v_i}^{v_f}}$$
, in which C_s is the specific capacitance, i_m (A g $^{-1}$) the mass normalized current, t (s) the time, v (V) the applied potential with v_i and v_f being the initial and final potential values, respectively. The electrochemical impedance spectrometry (EIS) was carried out in an aqueous solution containing 1 mmol/L KCl, 5 mmol/L K $_3$ [Fe(CN) $_6$] and 5 mmol/L K $_4$ [Fe(CN) $_6$].

2. Electrochemical Measurements

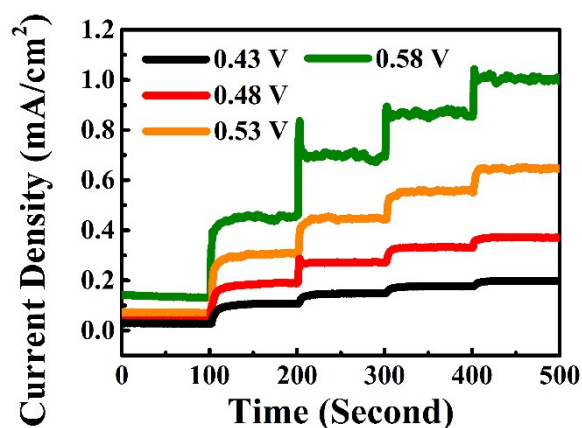


Fig. S1 Current responses of the Cu@CoO_x-modified electrode to 0.2 mmol/L glucose with potentials of +0.43 V, +0.48 V, +0.53 V and +0.58 V.

Comparing the I-t curves at different voltage, +0.53 V is the best choice, as the curve at +0.53 V is most stable and the response current is biggest, which is preferable for deviation control.

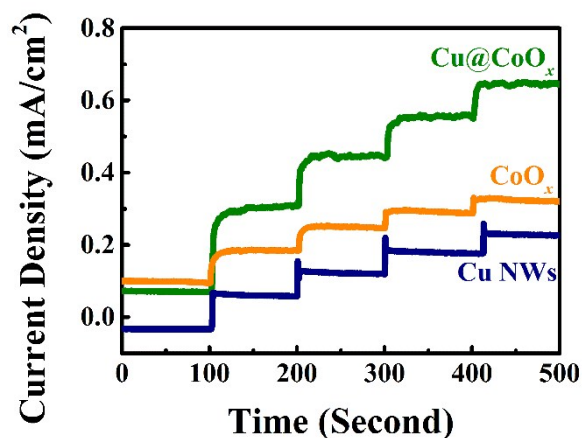


Fig. S2 Amperometric responses of the Cu@CoO_x-, CoO_x- and Cu NWs-modified electrodes to every 0.2 mmol/L glucose. Electrolyte: 0.1 mol/L NaOH aqueous solution.

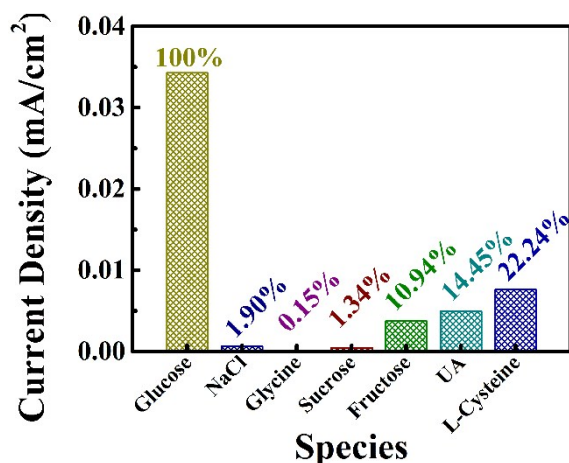


Fig. S3 Current densities caused by active terms and their percentages compared to glucose.

For NaCl, glycine and sucrose, they rarely interfere this electrode. The current responses, inspired by them with half of the glucose concentration, are all under 2% of those brought by glucose. As for fructose, L-Cysteine and UA, responses of current density are imperceptible until concentrations reach 0.05 mol/L.

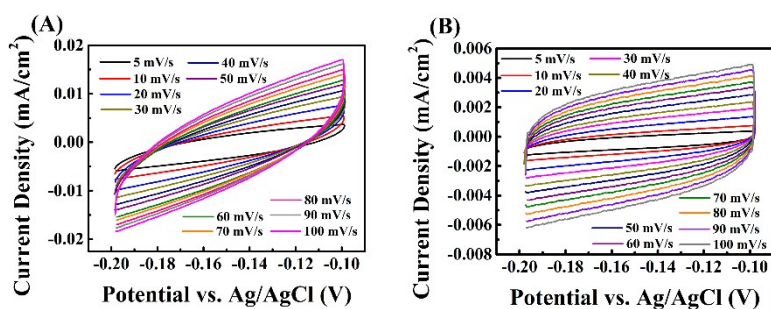


Fig. S4 (A) CVs for Cu@CoO_x-modified electrode with various scan rates. (B) CVs of CoO_x-modified electrode with different scan rates.

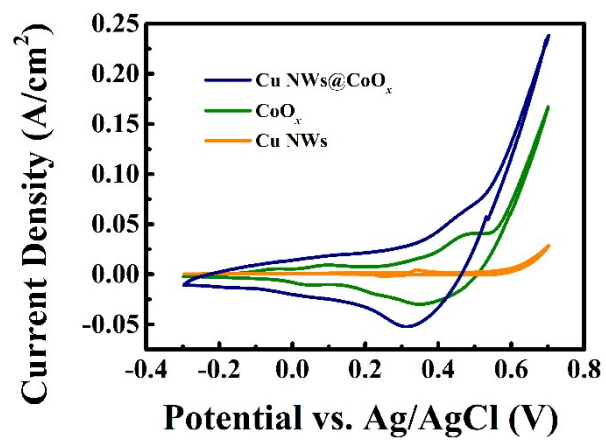


Fig. S5 CVs of Cu NWs, CoO_x and Cu@CoO_x at 10 mV/s.

Table S1. Compare of BET Surface area of different active nanomaterials

Electrode Material	BET Surface Area (m²/g)	Reference
Hollow SnO ₂	41.5	2
ZnCo ₂ O ₄ nanowires	29.36	3
NiCo ₂ O ₄ microtubes	98.4	4
Zn _{0.76} Co _{0.24} S nanoartichokes	67.8	5
NiO nanosheets	25.29	6
CoO _x	42	7
CoO/C@Ni Foam	20.8	8
Pomegranate-like CoO@N-C Sphere	45	9
Co/CoO Nanofiber	25.01	10
CoO _x	97.63	This Work
Cu NWs@CoO _x	168.40	This work

Table S2. Contract of electrochemical performances of different active nanomaterials to catalyze glucose oxidation.

Electrode materials	Detection limit (μM)	Linear range (μM)	Sensitivity ($\mu\text{A mM}^{-1} \text{cm}^{-2}$)	Reference
Co_3O_4 NFs	0.97	0.97 – 2040	36.25	11
$\text{Co}_3\text{O}_4/\text{Zn}$	2	5 – 620	193	12
$\text{Co}_3\text{O}_4/\text{rGO}$	0.14	1 – 380	29.5	13
Co_3O_4 nanowires	5	5-570	300.8	14
CoO_x -MWCNT	2	Up to 4500	162.8	15
Co_3O_4 film	1	1–3000	366.03	16
$\text{Co}(\text{OH})_2/\text{rGO}$	5	50 – 6000	242 ± 14	17
$\text{Co}_3\text{O}_4/\text{ZnO}$ p-n junction	1.38	10 – 5000	116.64	18
$\text{Cu}@\text{CoO}_x$	1	1-5000	396.57	This work

Table S3. Compare of performances of different electrode materials to electrochemical energy storage

Electrode materials	Current density	Specific capacitance	Reference
Co(OH)	2 A g ⁻¹	688	19
Co ₉ S ₈ /NS-C	1 A g ⁻¹	734	20
Co(VO ₃) ₂ -Co(OH) ₂	0.5 mA cm ⁻²	803	21
NiCo ₂ S ₄	5 mA cm ⁻²	494	22
Co-Ni-P	1.5 A g ⁻¹	227	23
Co ₃ O ₄ -NF	1 A g ⁻¹	278.4	24
Cu NWs@CoO _x	1 A g ⁻¹	797.7	This work

Reference

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