Supporting Information For

Superaerophilic Copper Nanowires for Efficient and Switchable CO_2 Electroreduction

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EXPERMENTIAL DETAILS

Materials: $CuSO_4$ and NaOH were purchased from Beijing Chemical Works; Ethylenediamine was purchased from Alfa Aesar; N_2H_4 was purchased from Sinopharm Chemical Reagent; $KHCO_3$ was purchased from Aladdin. All the materials were used without further purification.

Synthesis of Copper Nanowires: In a typical synthesis, NaOH (15 M, 20 mL), $CuSO_4$ (0.1 M, 1 mL) and EDA (1.6 mmol) were mixed in a beaker and stirred for 5 min to form a homogeneous precursor solution. N_2H_4 (35 wt %, 0.12mmol) was then added at a preheated temperature (60 °C) under stirring at 700 rpm and kept stirring for another 2 min. Afterwards, the beaker was sealed and heated at 60 °C for 1 h. A layer containing the Cu NWs products consequently were accumulated at the top of the suspension and washed with water and ethanol for several times.

Characterization: The size and morphology of the products were characterized by field-emission SEM (Zeiss SUPRA 55) operating at 20 kV and a high-resolution TEM system (JEOL 2100) operating at 200 kV. The crystal structures were examined by X-ray powder diffractometer (XRD, Rigaku D/max 2500) at a scan rate of 10°/min. Chemical compositions were tested using X-ray photoelectron spectroscopy (Thermo Electron ESCALAB 250, X-ray source: Al). The bubble and drop contact angle was measured by the optical CA measurement (Dataphysics OCA20) and the volume of the carbon dioxide bubble and electrolyte was about 2 μL and 1 μL, respectively. All experiments were repeated for >5 times.

Preparation of the Working Electrode: The Cu NWs were firstly dispersed into anhydrous ethanol to prepare a homogeneous dispersion (4 mg/mL) by sonication for at least 20 min. Electrodes modified by PTFE were prepared by adding certain amount of PTFE solution into Cu NWs ethanol solution. The amount (mass ratio) of PTFE on Cu NWs was evaluated to be about

0% (0 μL), 20% (8 μL), 40% (15.7 μL), 60% (23.5 μL) and 80% (31.3 μL), respectively. Afterwards, 200 μL of the catalyst suspension was drop-casted on the carbon paper, and then heated at 350 °C for 30 min in air to solidification. Finally, the electrode was electrochemical reduced at -0.3 V vs. RHE in 0.1 M $KHCO_3$ for 30 min.

Electrochemical measurements: The CO_2RR electrochemical measurements were carried out using a Bio-Logic VMP3 electrochemistry workstation. A homemade gas-tight H-type electrochemical cell separated by a cation exchange membrane (Nafion N115, DuPont) was used. The CO_2 gas flow rate was 20 sccm. The electrolyte was 0.1 M $KHCO_3$ aqueous solution which had been electrochemically purified for 24 h before use. A graphite rod and an Ag/AgCl electrode were used as the counter electrode and the reference electrode, respectively. The reference electrode was periodically calibrated, and the potential applied on the working electrode was corrected using the IR compensation function of the electrochemistry workstation.

Product quantification: Gas products were analyzed by a GC (SRI Multiple Gas Analyzer #5) equipped with molecular sieve 5A and HayeSep D columns with N_2 as the carrier gas. Hydrogen was analyzed by a thermal conductivity detector, while carbon monoxide, methane, and ethylene were determined using a flame ionization detector. The peak areas were converted to gas volumes using calibration curves. Liquid products were quantified after electrocatalysis by ^{1}H NMR (V600a Varian VNMRS 600 MHz NMR). Electrolyte collected after electrolysis (700 μl) was mixed with 35 μl of 10 mM dimethyl sulfoxide and 50 mM phenol as internal standards in D^2O for the ^{1}H NMR analysis. The ^{1}H NMR spectrum was recorded with a water suppression function by a pre-saturation method. The relaxation time was 5 s.

The calculation of Faradaic efficiency for CO_2RR products: The FE of CO_2RR products were calculated using the following equation: FE = moles of product (measured by GC) × nF / I (A) × t (s), where n represents the number of electrons; F is the Faraday's constant (96485.3 C/mol), I is the reaction current, and t is the time used for electrolysis.

SUPPLEMENTARY FIGURES

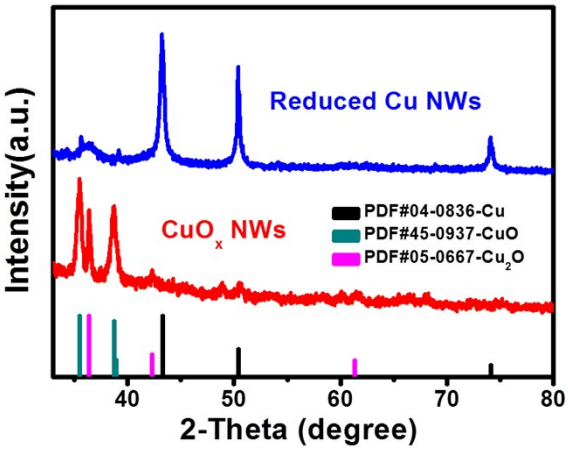

Figure S1. XRD patterns of CuO_x NWs before and after electrochemical reduction. After reduction, the electrode was named as Cu NWs.

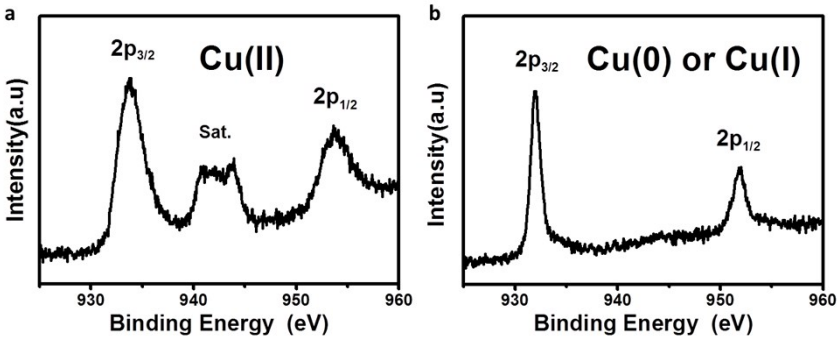

Figure S2. XPS analysis of CuO_x NWs (a) before and (b) after electrochemical reduction.

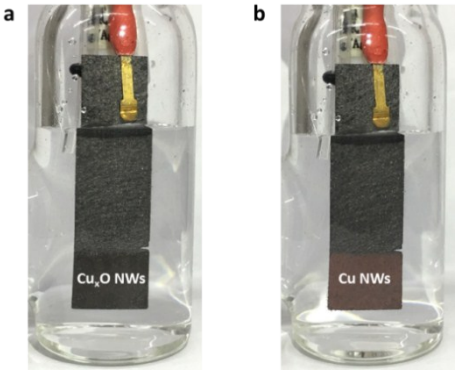

Figure S3. Digital images of CuO_x NWs electrode (a) before and (b) after electrochemical reduction.

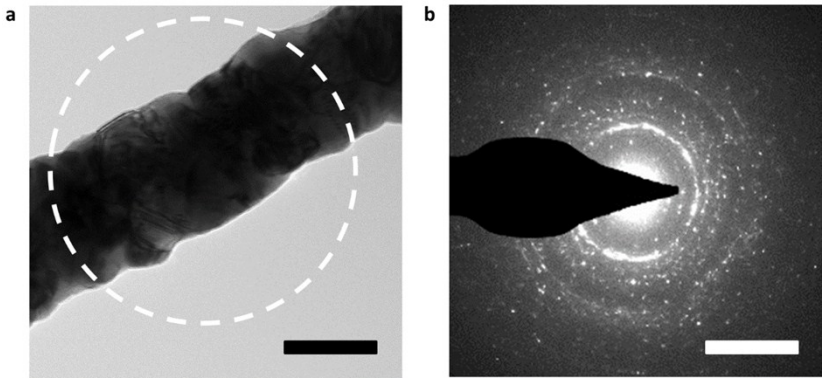

Figure S4. (a) HRTEM and (b) SAED pattern of as-prepared Cu NWs, scale bars: 100 nm in (a) and 5 1/nm in (b).

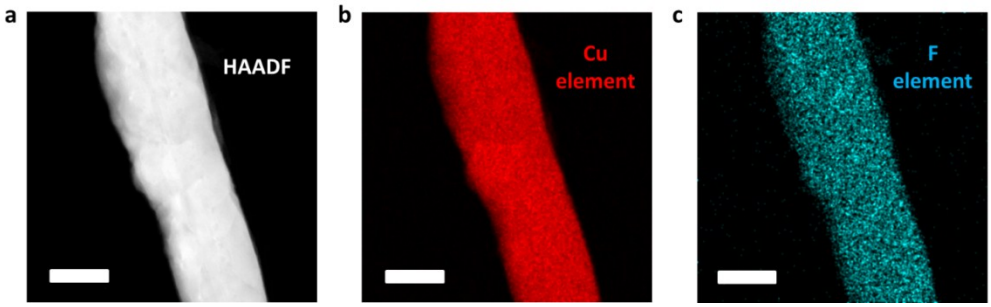

Figure S5. (a) HAADF image, (b) Cu and (c) F EDS mapping results of 40% PTFE-Cu NWs, scale bars: 100 nm.

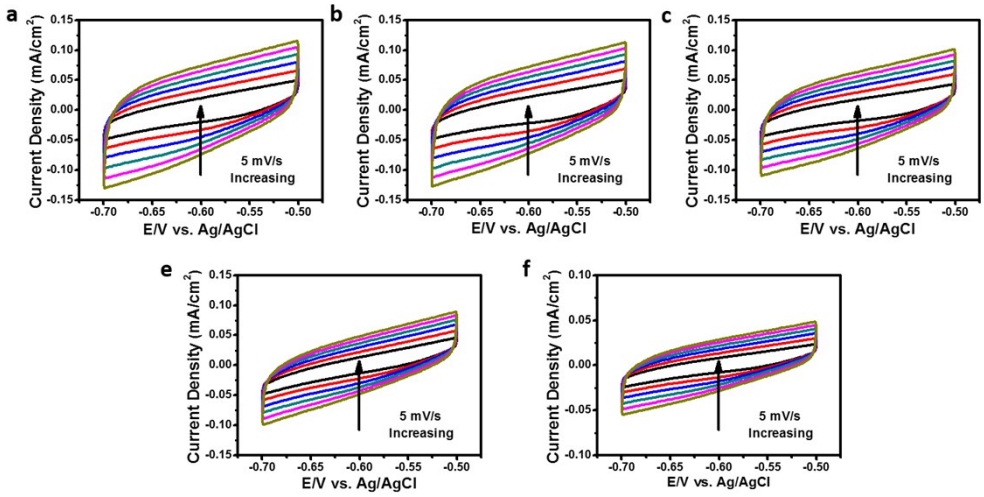

Figure S6. ECSA measurements of Cu NWs with different amount of PTFE : (a) 0%; (b) 20%; (c) 40%; (d) 60% and (e) 80%.

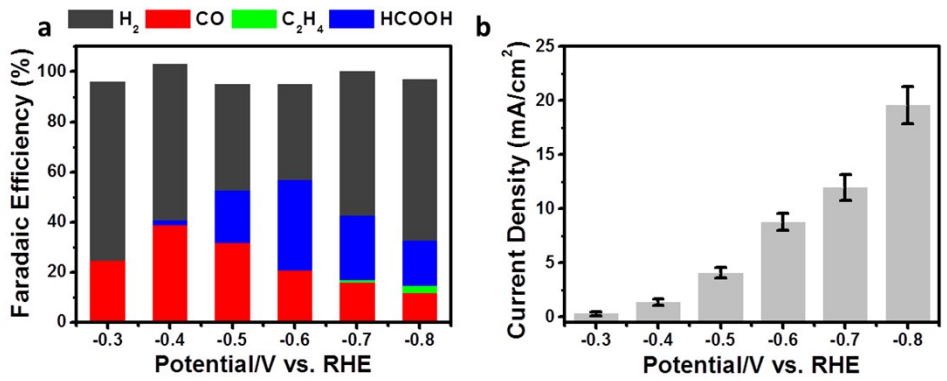

Figure S7. (a) Product distribution and (b) total current density using 20% PTFE-Cu NWs electrode.

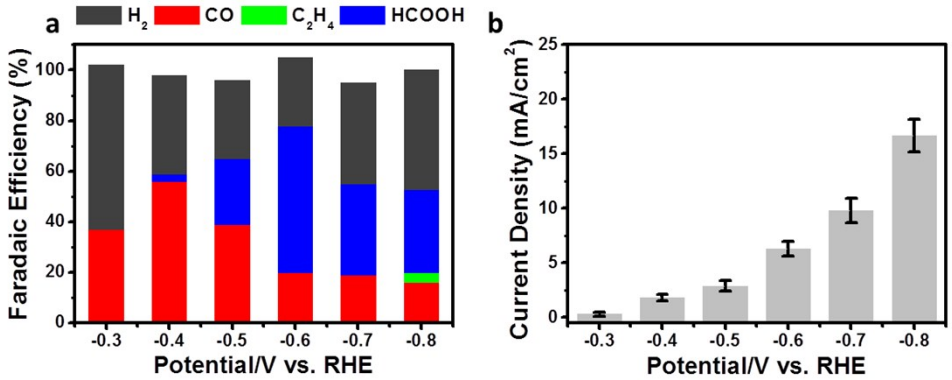

Figure S8. (a) Product distribution and (b) total current density using 60% PTFE-Cu NWs electrode.

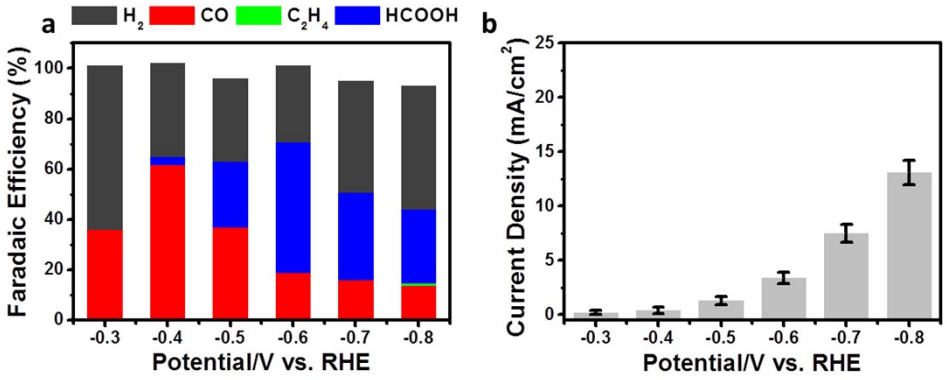

Figure S9. (a) Product distribution and (b) total current density using 80% PTFE-Cu NWs electrode.

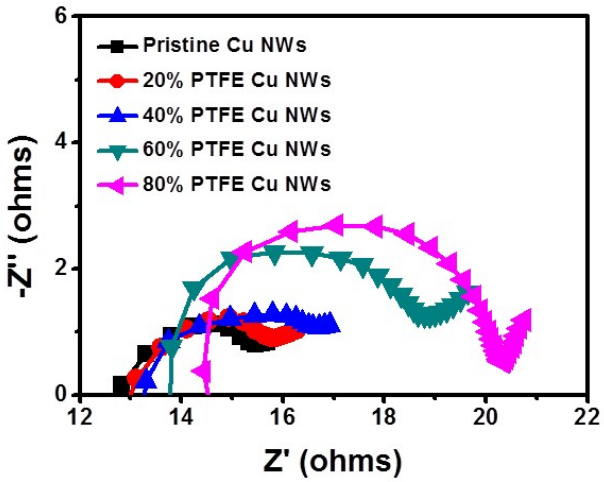

Figure S10. Nyquist plots of 0-80% PTFE-Cu NWs electrode.

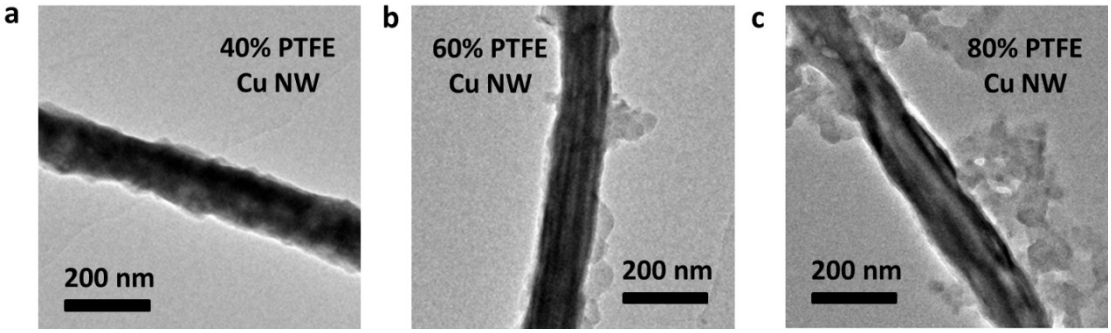

Figure S11. TEM images of (a) 40%, (b) 60%, and (c) 80% PTFE-Cu NWs.

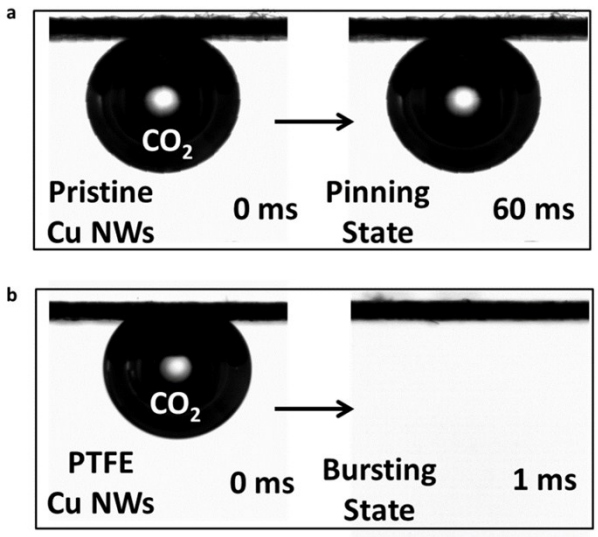

Figure S12. CO_2 gas bubble contact behaviors of (a) pristine Cu NWs and (b) PTFE-Cu NWs after stability test.

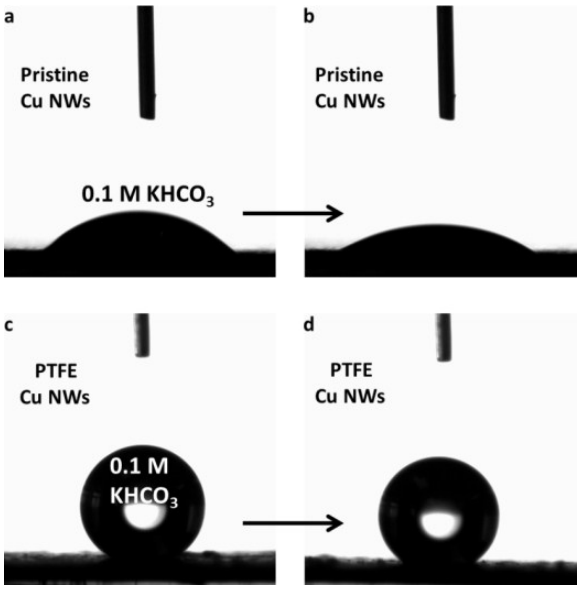

Figure S13. Electrolyte contact behaviors of pristine Cu NWs (a) before and (b) after stability test. Electrolyte contact behaviors of PTFE-Cu NWs (c) before and (d) after stability test.

SUPPLEMENTARY TABLES

Table S1. The C_{dl} calculation results of pristine Cu NWs electrode modified with different PTFE concentrations (R stands for the correlation coefficient of linear fitting).

PTFE percentage (%)	C_{dl}	R
0%	4.2 mF/cm^2	0.998
20%	3.9 mF/cm^2	0.996
40%	3.6 mF/cm^2	0.998
60%	2.4 mF/cm^2	0.998
80%	1.6 mF/cm^2	0.997

Table S2. The stability results of pristine Cu NWs and PTFE-Cu NWs electrodes.

Samples	Current density	FE of CO	FE of HCOOH
Pristine Cu NWs	69.7%	48.5%	31.6%
PTFE-Cu NWs	95.3%	90.9%	96.4%