## **Electronic Supplementary Information (ESI) for**

# Defect-enrichment in porous interface of ultrathin CuO nanobelts

## realizes a novel CO<sub>2</sub> photoreduction pathway

Qiang Wang,<sup>a</sup> Yanan Zhou,<sup>b</sup> Kaifu Zhang,<sup>\*a,c</sup> Yu Yu,<sup>a</sup> Qiquan Luo,<sup>\*d</sup> Shan Gao,<sup>\*a</sup> and Yi Xie<sup>\*b</sup>

<sup>a</sup>Anhui Province Key Laboratory of Chemistry for Inorganic/Organic Hybrid Functionalized Materials, Key Laboratory of Structure and Functional Regulation of Hybrid Materials of Ministry of Education, School of Chemistry and Chemical Engineering, Anhui University, Hefei, 230039, China. E-mail: shangao@ahu.edu.cn; kfzhang@ahu.edu.cn <sup>b</sup>Hefei National Research Center for Physical Sciences at Microscale, University of Science & Technology of China, Hefei, 230026, China. E-mail: yxie@ustc.edu.cn <sup>c</sup>Key Laboratory of Advanced Energy Materials Chemistry (Ministry of Education), Nankai

University, Tianjin 300071, China.

<sup>d</sup>Institutes of Physical Science and Information Technology, Anhui University, Hefei, 230039, China. E-mail: qluo@ustc.edu.cn

## **Experimental Section**

## Chemicals

Two hydrated cupric chloride (CuCl<sub>2</sub>·2H<sub>2</sub>O), sodium hydroxide and (NaOH), cyclohexane and absolute ethanol were obtained from commercially purchased and used directly. Ultrapure water (18.25 M $\Omega$  cm) was used in all experiments. 5% Nafion-117 solution was purchased from Sigma-Aldrich.

## Methods

**Synthesis of Cu(OH)**<sub>2</sub> **nanobelts**: In a typical procedure, 0.8 mmol CuCl<sub>2</sub>·2H<sub>2</sub>O was added into 95 mL water under vigorous stirring. Then, 5 mL 16 M NaOH aqueous solution was added to CuCl<sub>2</sub> aqueous solution drop by drop under stirring for 30 min. The final product was collected by centrifuging the mixture, washed with cyclohexane and ethanol for several times, and then dried in vacuum freezing drier overnight for further characterization.

**Synthesis of CuO nanobelts with controllable defects**: In a typical procedure, the asobtained Cu(OH)<sub>2</sub> nanobelts were directly heated at 250 °C and then cooled to room temperature. CuO nanobelts with different amount of defect could be obtained by varying the heating time (1, 5, 10 and 15 min), named as Air-1, Air-5, Air-10, Air-15, respectively. The obtained powders were collected for further characterization.

## Characterization

The crystal structures of the samples were analyzed by using an X-ray powder diffractometer (XRD, SmatrLab9kW, Japan) equipped with Cu K $\alpha$  radiation ( $\lambda$ = 0.15418 nm). Transmission electron microscope (TEM) and high-resolution transmission electron microscope (HRTEM) images of the samples were obtained using a transmission electron microscope (JEM-2100F, JEOL, Japan) operated at an accelerating voltage of 200 kV. The photoluminescence spectra were measured in a F-4500 FL Spectrophotometer with an exciting wavelength of 290 nm, and decay curves for the samples were recorded on a FLUORMAX-4P Spectrophotometer. The chemical composition and state in detail were examined by X-ray photoelectron spectroscopy

(XPS) conducted by ESCALAB 250 Xi model. Typically, the hydrocarbon C1s line at 284.8 eV from adventitious carbon was used for energy referencing. The absorbance data of spectrophotometer were acquired on UV-3600 UV-vis spectrophotometer. Raman spectra were performed on a Raman spectrometer (Horiba Xplora Plus, France) spectrometer with a 532 nm laser. The specific surface area was obtained by the Brunauer-Emmett-Teller (BET) method and measured by using a Micromeritics ASAP 2020 at 77 K with N<sub>2</sub> physical adsorption. Automatic microporous gas adsorption analyzer (ASAP 2020) was used to conduct CO<sub>2</sub> adsorption measurements. Temperature-programmed desorption (TPD) experiments of CO<sub>2</sub> and CO were carried out using a Micromeritics Autochem model 2920 instrument.

#### The photoelectrochemical measurements

The photoelectrochemical tests of the catalysts were evaluated in a typical threeelectrode system using the electrochemistry workstation (CHI 760E). The catalyst ink was spread on the fluorine-doped tin oxide (FTO) glass as working electrodes. For a typical procedure, 5 mg catalyst and 50  $\mu$ L Nafion-117 solution were dispersed in a mixed solution of 0.1 mL of ethanol and 0.5 mL ultrapure water to form the homogeneous catalyst ink. Then, 100  $\mu$ L catalyst ink was spread on the FTO glass and dried naturally at room temperature. The Ag/AgCl electrode and Pt foil were used as the reference electrode and counter electrode, respectively. The photocurrent response tests were conducted under a 300 W Xenon light (PLs-SXE300+, Perfect light, China) illumination. Chronoamperometry tests were conducted at 0.33 V vs. Ag/AgCl. Electrochemical impedance spectroscopy (EIS) was carried out in Swagelok in the frequency range of 0.01 to 1×10<sup>6</sup> Hz at a scan rate of 0.1 mV s<sup>-1</sup>. The Mott-Schottky plots were tested at the frequency of 100 Hz.

#### Photocatalytic performance tests

10.0 mg CuO nanobelts was dispersed in 0.1 mL ethanol to form uniform ink and then was spread on the round quartz slide. The quartz slide with CuO nanobelts was dried under room temperature overnight. In the photocatalytic conversion of CO<sub>2</sub>, the dried quartz slide with CuO nanobelts was flatly placed in the middle of the reactor of

Labsolar-6A system (Beijing Perfect light Technology Co. Ltd). Before the photocatalytic test, the reactor was filled with the ultrapure  $CO_2$  by aerating  $CO_2$  for 0.5 h, and 5.0 mL water was added in the bottom of reactor as the proton source. The 300 W Xenon light was used as the light source. The reaction system temperature was controlled at 278 K through recycle cooling water system. The gas products were quantified online by the gas chromatograph (Agilent GC 8860) using argon as the carrier gas. In addition, the CO reduction experiment was under similar conditions, except that the reaction gas was changed to 80 Kpa argon mixed with 10  $\mu$ L CO.

#### In-situ FT-IR measurements

*In-situ* FT-IR results was obtained using a Thermofisher Nicolet iS50. The sample was placed in the reaction cell, and then the argon gas was injected into the reaction cell for removing the impurities on the surface of the CuO nanobelts. One hour later, the high-purity  $CO_2$  was injected into the reaction cell. After 0.5 h in  $CO_2$  atmosphere, turn on the Xenon lamp, and then record after a certain time interval.

#### Quantum efficiency calculations

The apparent quantum efficiency of Air-10 was determined at 334 nm. The catalyst was measured under a 300W Xe lamp irradiation. The average intensity of irradiation was determined to be 1.291 mW cm<sup>-2</sup> by an PL-MV2000 spectroradiometer (Perfectlight) and the irradiation area was measured to be 12.56 cm<sup>2</sup>. The number of incident photons (N) was  $6.13 \times 10^{19}$  according to the following equation. The yields of CH<sub>4</sub> and CH<sub>3</sub>OH molecules within 1 h were 1.32 µmol g<sup>-1</sup> and 2.26 µmol g<sup>-1</sup>, respectively. The quantum efficiency was calculated by the following equations:

$$N = \frac{E\lambda}{hc} = \frac{8.07 \times 10^{-4} \times 12.56 \times 3600 \times 334}{6.626 \times 10^{-34} \times 3 \times 10^{17}} = 6.13 \times 10^{19}$$

 $QE = \frac{\text{the number of reacted electrons}}{\text{the number of incident photons}} \times 100\%$ 

$$=\frac{\left(8\times1.32\times10^{-6}+6\times2.26\times10^{-6}\right)\times6.02\times10^{23}\times8\times10^{-3}}{6.13\times10^{19}}\times100\%=0.19\%$$

## **Computational details**

All density functional theory (DFT) calculations were performed by using Vienna ab initio Simulation Package (VASP)<sup>1,2</sup>. The projector augmented wave (PAW) potentials were explored to describe ion-electron interaction<sup>3</sup>. The electronic exchange and correlation effects were described by the generalized gradient approximation (GGA)<sup>4</sup> with the Perdew-Burke-Ernzerhof (PBE)<sup>5</sup> functional. The kinetic energy cutoff of 450 eV was used. All the structures were fully relaxed, the convergence criteria for force and energy were set to be 10<sup>-5</sup> eV and 10<sup>-2</sup> eV/Å, respectively. The Brillouin zones were sampled at 3x3x1 by Monkhorst-Pack meshes due to the large systems<sup>6</sup>. The vacuum space of 15 Å was set to avoid the interaction between adjacent images. The semiempirical dispersion-corrected DFT-D3 scheme proposed by Grimme<sup>7</sup> was used to describe the van der Waals interaction. The Gibbs free energy change ( $\Delta G$ ) of every elemental step was calculated by equation:  $\Delta G = \Delta E + \Delta Z P E - T \Delta S$ . The  $\Delta E$  is the adsorption energy of adsorbed intermediates and can be directly obtained from the DFT calculations.  $\Delta ZPE$  and  $\Delta S$  are the zero-point energy and the entropy change between the adsorbed state and the gas phase, respectively. T is the temperature (298.15 K, in this work).



Figure S1. Digital photo demonstrating the gram-scale synthesis of Air-10.



Figure S2. (a) TEM image, (b) XRD pattern of the  $Cu(OH)_2$  nanobelts.



**Figure S3.** (a) Atomic force microscopy image, (b) the corresponding height profiles of Air-10.



Figure S4. (a) TEM image, (b) HRTEM image, (c) HAADF-STEM image, (d) EDX elemental mappings of Air-1.



**Figure S5.** The molar fraction of uniformly distributed Cu and O elements in Air-1 and Air-10, respectively.



Figure S6. (a) XPS survey spectra, (b) Cu2p XPS diagrams of Air-1 and Air-10, respectively.



Figure S7. Gas chromatogram profiles of (a) CH<sub>4</sub>, (b) CO, (c) O<sub>2</sub>, and (d) H<sub>2</sub>.



**Figure S8.** <sup>1</sup>H-NMR spectra of liquid products under (a) CO<sub>2</sub> and (b) Ar, respectively. The CH<sub>3</sub>OH was generated under CO<sub>2</sub> atomosphere while no detectable product generation when Ar was used as the gas source.



Figure S9. Stability tests of photocatalytic CO<sub>2</sub>RR over Air-1.



Figure S10. Stability tests of (a)  $O_2$  and (b)  $H_2$  generated from photocatalytic  $CO_2RR$  over Air-1 and Air-10, respectively.



Figure S11. O1s XPS diagrams of Air-5 and Air-15, respectively.



Figure S12. (a) The yields of  $CH_3OH$  and  $CH_4$ , and (b) CO for Air-10 and Air-1 under different wavelength irradiation, respectively.



Figure S13. The yields of CH<sub>3</sub>OH and CH<sub>4</sub> of Air-10 under different test conditions.



**Figure S14.** (a) O1s XPS spectra, (b) EPR spectra, (c) and XRD patterns of Air-10 before and after photocatalysis. (d) TEM image of Air-10 after photocatalysis.



Figure S15. Nitrogen adsorption and desorption isotherms of different CuO catalysts.



Figure S16. CO-TPD spectra of Air-1 and Air-10, respectively.



Figure S17. Photocatalytic activity of CO reduction over Air-1 and Air-10, respectively.

Catalyst	Experimental condition	Yield of CH₃OH (µmol g <sup>-1</sup> h <sup>-1</sup> )	Selectivity of CH₃OH (%)	QE	References
Air-10	300W Xe lamp,	12.3	62.5	0.19% at	This work
	pure CO <sub>2</sub> gas			334 nm	
WO <sub>3-x</sub>	300W Xe lamp,	17.0	86.0	0.26% at	EES Catal., 2023, <b>1</b> ,
	pure CO <sub>2</sub> gas			334 nm	36-44.
CN-MRF	300W/Xelamn	9.9	89.8	5.50% at 380 nm	J. Am. Chem. Soc.,
	pure CO <sub>2</sub> gas				2022, <b>144</b> , 9576-
	pure 602,800				9585.
V-Bi <sub>19</sub> Br <sub>3</sub> S <sub>27</sub>	300W Xe lamn	3.43	36.6	-	J. Am. Chem. Soc.,
	nure (O <sub>2</sub> gas				2021, <b>143</b> , 6551-
	pure 602800				6559.
Cuº/CuO	300W Xe lamp,	2.6	37.1	-	ACS Sustain. Chem.
	15% CO <sub>2</sub> + 85%				Eng., 2021, <b>9</b> , 1754-
	Ar				1761.
mCD/CN	300W Xe lamp,	13.9	99.6	2.00% at	Nat. Commun.,
	pure CO <sub>2</sub> gas	13.3		420 nm	2020, <b>11</b> , 2531.
BiVO <sub>4</sub> /Bi <sub>4</sub> Ti <sub>3</sub> O <sub>1</sub>	300W Xe lamp,	16.6	55.5	-	Appl. Catal., B,
	pure CO <sub>2</sub> gas				2020, <b>270</b> , 118876.
Cu SAs/UiO-	300W Xe lamp.	5.33	38.7	-	J. Am. Chem. Soc.,
66-NH <sub>2</sub>	pure CO <sub>2</sub> gas				2020, <b>142</b> , 19339-
	puic 602803				19345.
CCN	350W Xe lamp,	3.85	23.3	-	Adv. Funct. Mater.,
	pure CO <sub>2</sub> gas				2019, <b>29</b> , 1900093.
Ti <sub>3</sub> C <sub>2</sub> /BiWO <sub>6</sub>	300W Xe lamp,	0.44	15.6	-	Adv. Funct. Mater.,
	pure CO <sub>2</sub> gas				2018, <b>28</b> , 1800136.
CuInS <sub>2</sub> /TiO <sub>2</sub>	350W Xe lamp,	0.86	20.5	-	Appl. Catal., B,
	pure CO <sub>2</sub> gas				2018, <b>230</b> , 194-202.
Pt/C-In <sub>2</sub> O <sub>3</sub>	300W Xe lamp	5.625	1.0	-	J. Am. Chem. Soc.,
	nure (O <sub>2</sub> gas				2017, <b>139</b> , 4123-
	pure eo <sup>2</sup> gus				4129.
NS g-C <sub>3</sub> N <sub>4</sub>	300W Xe lamp,	1.87	50.2	-	
	$CO_2$ reacted by				J. Mater. Chem. A,
	$H_2SO_4$ and				2017, <b>5</b> , 3230-3238.
	NaHCO <sub>3</sub>				
WO <sub>3</sub>	300W Xe lamp,	2.14	22.1	-	J. Mater. Chem. A,
	pure CO <sub>2</sub> gas				2016, <b>4</b> , 5314-5322.
Cu/GO-2	300W Xe lamp,	2.94	36.1	-	Nano Lett., 2014,
	pure CO <sub>2</sub> gas				<b>14</b> , 6097-6103.

**Table S1.** Comparison of  $CO_2RR$  performance of Air-10 with the reported catalysts.

Samples	Lattice oxygen (%)	Oxygen vacancy (%)				
Air-1	49.71	50.29				
Air-5	44.73	55.27				
Air-10	38.55	61.45				
Air-15	34.20	65.80				

**Table S2.** The peak area ratio of lattice oxygen and oxygen vacancy of different samples.

**Table S3.** Time-resolved transient PL decay of Air-1 and Air-10, respectively.

Samples	τ <sub>1</sub> (ns)	τ <sub>2</sub> (ns)	τ₃(ns)
Air-10	0.80	3.47	14.3
Air-1	0.67	2.87	12.3

## **References:**

[1] G. Kresse and J. Furthmüller, Comput. Mater. Sci., 1996, 6, 15-50.

[2] G. Kresse and J. Furthmüller, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1996, **54**, 11169-11186.

[3] G. Kresse and D. Joubert, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1999, **59**, 1758-1775.

[4] K. Perdew and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865-3868.

[5] J. Perdew, M. Ernzerhof and K. Burke, J. Chem. Phys., 1996, 105, 9982-9985.

[6] H. Monkhorst and J. Pack, Phys. Rev. B, 1976, 13, 5188-5192.

[7] S. Grimme, J. Antony, S. Ehrlich and H. Krieg, J. Chem. Phys., 2010, 132, 154104.