

Enhanced photocatalytic CO₂ reduction by constructing In₂O₃-CuO heterojunction with CuO as cocatalyst

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1. Experimental section

1.1 Materials

Sodium sulfate (Na₂SO₄, >99%) were purchased obtained from Sigma-Aldrich. Sodium sulfite anhydrous (Na₂SO₃, >98%), ammonium hydroxide solution (NH₃·H₂O, AR, 25-28%) hexamethylenetetramine (C₆H₁₂N₄, ≥99%) and copper nitrate hydrate (Cu(NO₃)₃·3H₂O, AR) were purchased from Shanghai Macklin Biochemical Co., Ltd. Ethanol (C₂H₅OH) was gained from Sinopharm Chemical Reagent Co., Ltd. Sodium citrate tribasic dihydrate (Na₃C₆H₅O₇·2H₂O, ≥99%) and indium nitrate hydrate (InCl₃·4H₂O, >99.99) was obtained from Beijing Innochem Co., Ltd. All chemicals were used directly as received without further purification.

1.2 Experimental procedure

1.2.1 Preparation of In₂O₃ sphere.

In a typical procedure, 0.005 mol InCl₃·4H₂O and 0.005 mol Na₃C₆H₅O₇·2H₂O was added into a solution of 15 mL H₂O. After vigorous stirring for 30 min, The pH value of the solution was adjusted to 6.4-6.6 by 0.5 mol/L NH₃·H₂O. The mixture was transferred into a 25-mL Teflon-lined autoclave, sealed and heated at 130 °C for 24 h. The system was allowed to cool down to room temperature naturally, and the final product was collected by centrifuging the mixture, washed with H₂O and ethanol for three times, and then dried at 65 °C for 6 h. The product was further annealed at 500 °C in air for 3 h and cool down to room temperature naturally.

1.2.2 Preparation of CuO flowers.

In a typical procedure, 0.05 mol C₆H₁₂N₄ was added into a solution of 50 mL H₂O (Solution A) and 0.0025 mol Cu(NO₃)₃·3H₂O was added into a solution of 50 mL H₂O (Solution B). After vigorous stirring for 30 min, add solution A drop by drop to solution B. Then, the mixed solution was heated at 70 °C for 3 hours. The system was allowed to cool down to room temperature naturally, and the final product was collected by centrifuging the mixture, washed with H₂O and ethanol for three times, and then dried at 65 °C for 6 h.

1.2.3 Preparation of CuO flowers/In₂O₃ sphere Heterostructures.

In a typical procedure, 0.05 mol C₆H₁₂N₄ was added into a solution of 50 ml H₂O (Solution A) and 0.0015 mol In₂O₃-sphere 0.0025 mol Cu(NO₃)₃·3H₂O was added into a solution of 50 ml H₂O (Solution B). After vigorous stirring for 30 min, add

solution A drop by drop to solution B. Then, the mixed solution was heated at 70°C for 3 hours. The system was allowed to cool down to room temperature naturally, and the final product was collected by centrifuging the mixture, washed with H₂O and ethanol for three times, and then dried at 65°C for 6 h. The other In₂O₃-CuO sample was synthesized in the same way by different input of In₂O₃-sphere (0.0045mol In₂O₃ (IC-2-1); 0.0035mol In₂O₃ (IC-3-2); 0.0025mol In₂O₃ (IC-1-1); 0.0015mol In₂O₃ (IC-2-3); 0.0005mol In₂O₃ (IC-1-2)).

1.3 Material characterization

The morphology and structure of the samples were characterized by field emission scanning electron microscopy (FE-SEM, JSM-7001F, Japan) and transmission electron microscopy (TEM; jeol, JEM-2010). The crystalline phases of the samples were determined by X-ray diffraction (XRD, PANalytical X'Pert Powder, Netherlands) at room temperature. The X-ray diffraction pattern was described in the scanning range of 10°-80° with the scanning rate of 10° min⁻¹. The elemental states of samples were analyzed by X-ray photoelectron spectroscopy (VG ESCALABMK II).

The Ultraviolet-visible (UV-vis) diffuse reflectance spectra (UV-vis DRS) were obtained on a UV-vis spectrophotometer (HITACHI, U-3900) with pure BaSO₄ as a reflectance standard. Brunauer-Emmett-Teller (BET) surface area and CO₂ adsorption tests was measured by nitrogen adsorption and desorption isotherms with a Quantachrome ASiQwin-Autosorb Station 1.. Photoluminescence (PL) spectra were acquired on a fluorescence spectrophotometer (Hitachi, F-4600) with a xenon lamp as

an excitation source (excitation wavelength: 300 nm).

1.4 Photocatalytic CO₂ reduction Measurement

As shown in Figure S1, the equipment for photocatalytic CO₂ reduction reaction is a closed vacuum glass reaction system, which is composed of reaction chamber, constant temperature condensate cooling reaction system and circulating pump.



Figure S1. Schematic diagram of the photocatalytic reduction CO₂ system.

Typically, 30 mg of photocatalyst, 20mL of 0.01 mol·L⁻¹ Na₂SO₃ were added into a gas-closed glass reactor (400 mL in capacity). Then, high purity CO₂ was introduced into the reactor with a partial pressure of 0.4 atm. A 300W Xe lamp was used as the light source and the wavelength of the lamp source is 200-780 nm in the reaction process. During the photocatalytic process, the reaction system was vigorously stirred by a magnetic stirrer. After each reaction, the generated products were quantified by GC (GC2019, 7920-TF2A, China). Other reaction conditions were the same as those of the typical reaction.

1.5 Photoelectrochemical characterizations

1.5.1 Transient photocurrent

The transient photocurrent experiment was carried out using a domestic three electrode system in light (3w, perfectlight LS sxe300 +, China) at electrochemical workstation (CHI 760E, Chenhua Instrument, China)

1.5.2 Electrochemical impedance spectroscopy (EIS)

The Nyquist plots were measured on a frequency response analyzer (gamery interface 5000, UK). The working electrode was CuO / In₂O₃ (similar to In₂O₃), the counter electrode was platinum mesh, and the reference electrode was Ag / AgCl (3M KCl). Na₂SO₄ (0.1 M, pH = 7) was used as electrolyte.

1.5.3 Mott–Schottky experiment

A Mott–Schottky experiment was in progress in 0.1 M Na₂SO₄ with the potential window ranged from - 0.5 to + 0.5 eV, using 1000 Hz and an AC amplitude of 10 mV at each of the potentials.

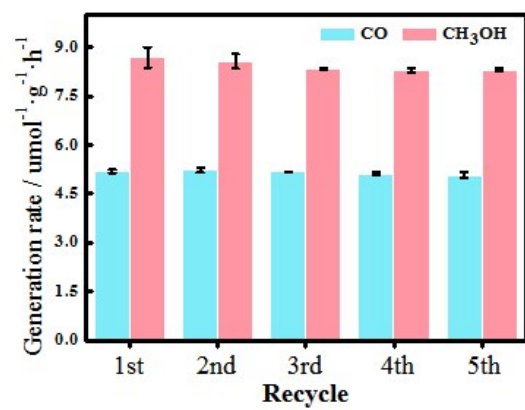


Figure S2. CO₂ photoreduction activities of different proportions of In₂O₃-CuO.

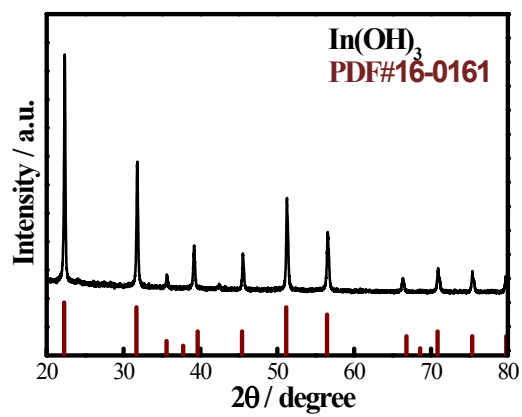


Figure S3. XRD pattern of In(OH)_3 .

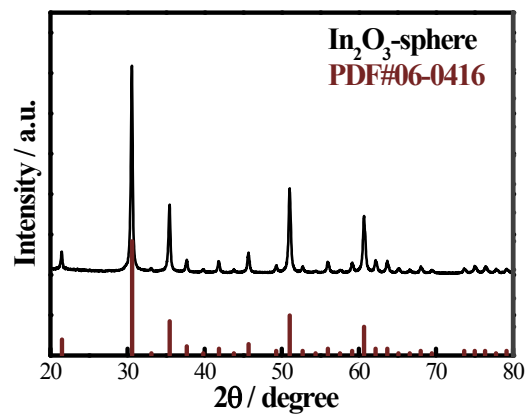


Figure S4. XRD pattern of In₂O₃ sphere.

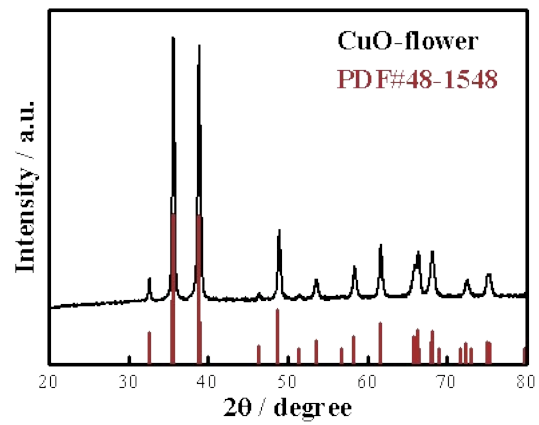


Figure S5. XRD pattern of CuO flower.

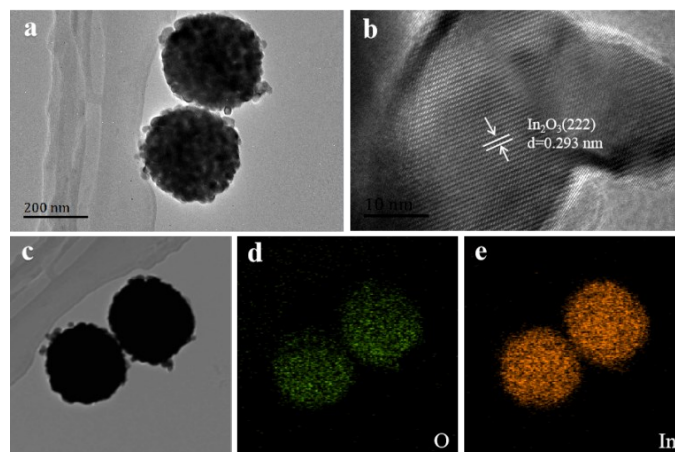


Figure S6. (a) TEM images, (b-c) HRTEM image (d-e) EDX mappings of In_2O_3 sphere.

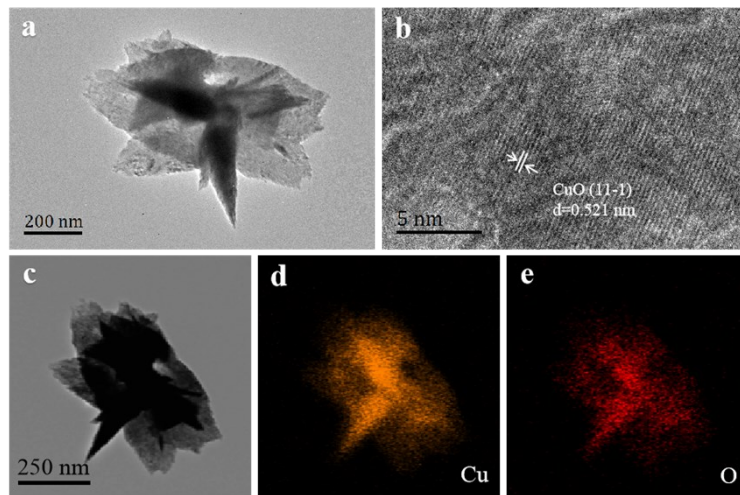


Figure S7. (a) TEM images, (b-c) HRTEM image (d-e) EDX mappings of CuO flower

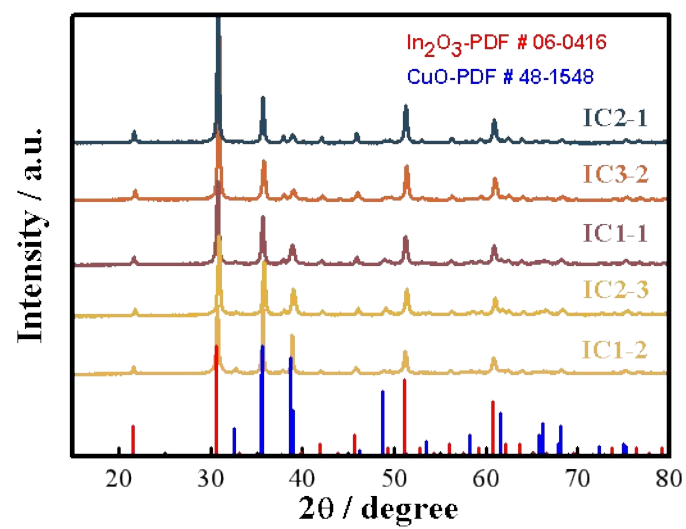


Figure S8. XRD pattern of different proportions of In₂O₃-CuO.

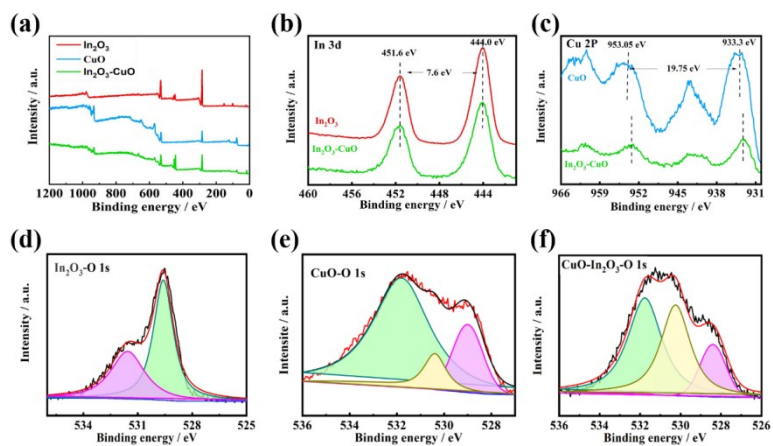


Figure S9. XPS spectra of (a) survey, (b) In 3d, (c) Cu 2p and O 1s of different samples.

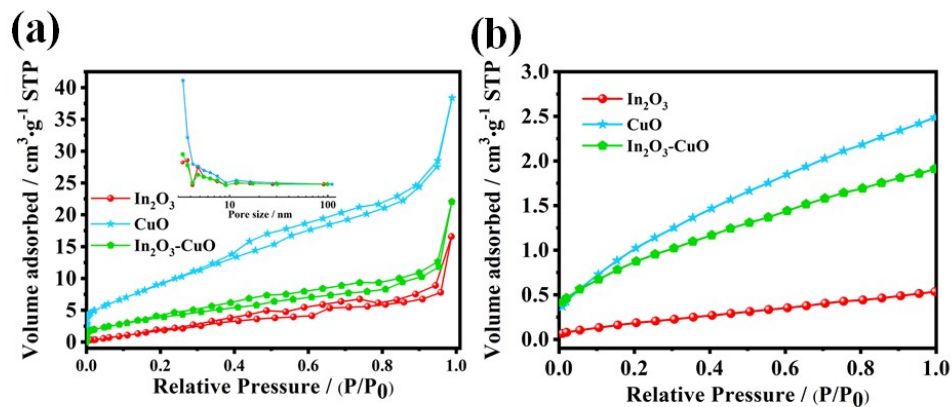


Figure S10. (a) N₂ adsorption-desorption isotherms, pore size distributions (inset) and (b) CO₂ adsorption curves of In₂O₃, CuO and In₂O₃-CuO.

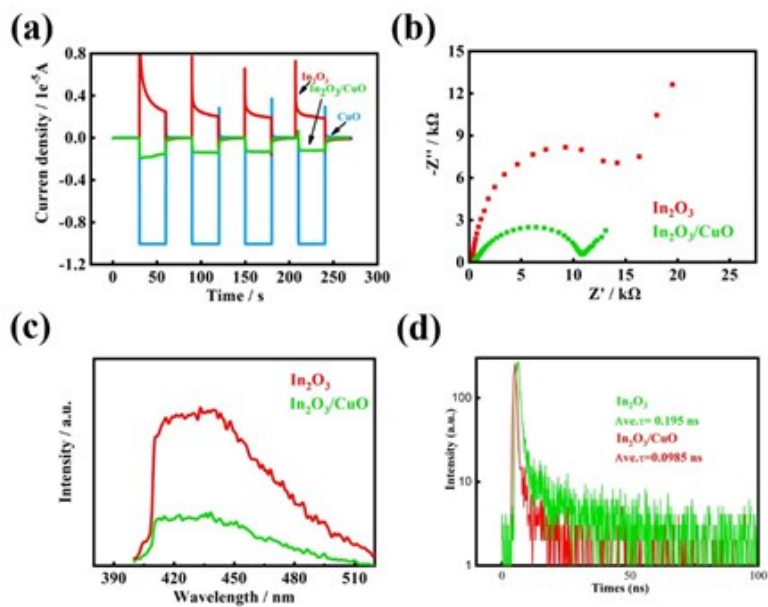


Fig. S11. (a) Transient photocurrent spectra, (b) EIS spectra of In_2O_3 and $\text{In}_2\text{O}_3/\text{CuO}$, and (c) steady-state PL spectra (d) Time-resolved transient PL decay of In_2O_3 , CuO and $\text{In}_2\text{O}_3/\text{CuO}$.

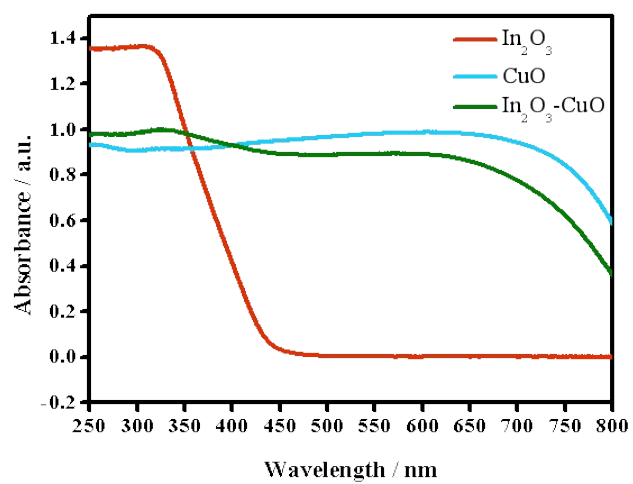


Figure S12. DRS of In₂O₃, CuO and In₂O₃-CuO.

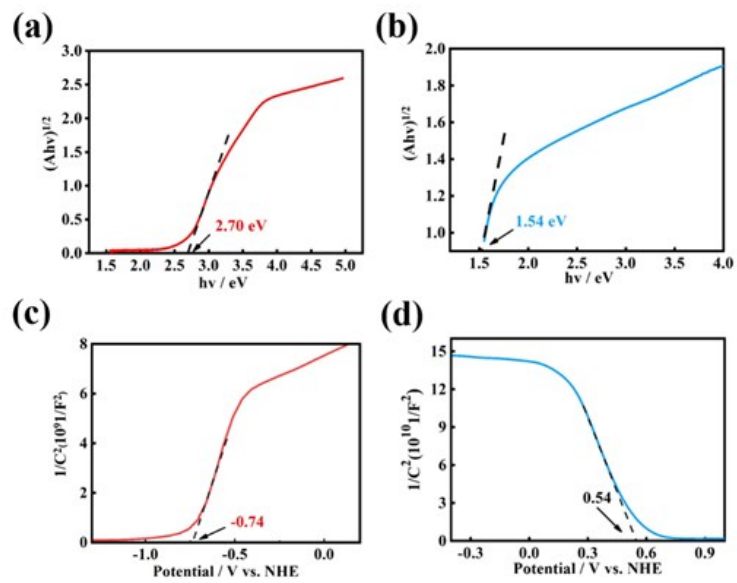


Figure S13. Tauc plots of (a) In_2O_3 , (b) CuO and Mott-Schottky plots of (a) In_2O_3 , (b) CuO .

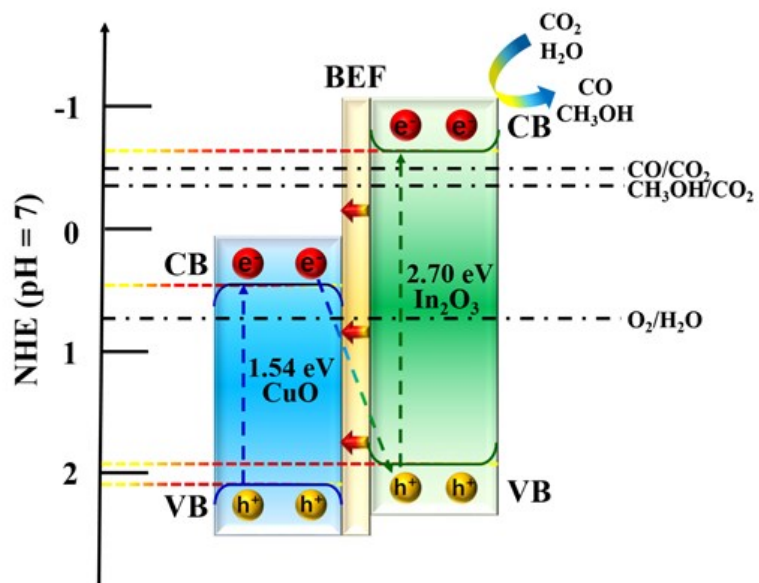


Figure S14. Z-scheme model of In_2O_3 - CuO photocatalyst and its charge transfer process under light irradiation.