Enhanced photocatalytic CO$_2$ reduction by constructing In$_2$O$_3$-CuO heterojunction with CuO as cocatalyst

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1. Experimental section

1.1 Materials

Sodium sulfate (Na$_2$SO$_4$, >99%) were purchased obtained from Sigma-Aldrich. Sodium sulfite anhydrous (Na$_2$SO$_3$, >98%), ammonium hydroxide solution (NH$_3$·H$_2$O, AR, 25-28%) hexamethylenetetramine (C$_6$H$_{12}$N$_4$, ≥99%) and copper nitrate hydrate (Cu(NO$_3$)$_3$·3H$_2$O, AR) were purchased from Shanghai Macklin Biochemical Co., Ltd. Ethanol (C$_2$H$_5$OH) was gained from Sinopharm Chemical Reagent Co., Ltd. Sodium citrate tribasic dihydrate (Na$_3$C$_6$H$_5$O$_7$·2H$_2$O, ≥99%) and indium nitrate hydrate (InCl$_3$·4H$_2$O, >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 In$_2$O$_3$ sphere.

In a typical procedure, 0.005 mol InCl$_3$·4H$_2$O and 0.005 mol Na$_3$C$_6$H$_5$O$_7$·2H$_2$O was added into a solution of 15 mL H$_2$O. After vigorous stirring for 30 min, The pH value of the solution was adjusted to 6.4-6.6 by 0.5 mol/L NH$_3$·H$_2$O. The mixture was transferred into a 25-mL Teflon-lined autoclave, sealed and heated at 130 ℃ 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 H$_2$O and ethanol for three times, and then dried at 65 ℃ for 6 h. The product was further annealed at 500 ℃ 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 C$_6$H$_{12}$N$_4$ was added into a solution of 50 mL H$_2$O (Solution A) and 0.0025 mol Cu(NO$_3$)$_3$·3H$_2$O was added into a solution of 50 mL H$_2$O (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 ℃ 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 H$_2$O and ethanol for three times, and then dried at 65 ℃ for 6 h.

1.2.3 Preparation of CuO flowers/In$_2$O$_3$ sphere Heterostructures.

In a typical procedure, 0.05 mol C$_6$H$_{12}$N$_4$ was added into a solution of 50 ml H$_2$O (Solution A) and 0.0015 mol In$_2$O$_3$-sphere 0.0025 mol Cu(NO$_3$)$_3$·3H$_2$O was added into a solution of 50 ml H$_2$O (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 H$_2$O and ethanol for three times, and then dried at 65°C for 6 h. The other In$_2$O$_3$-CuO sample was synthesized in the same way by different input of In$_2$O$_3$-sphere (0.0045mol In$_2$O$_3$ (IC-2-1); 0.0035mol In$_2$O$_3$ (IC-3-2); 0.0025mol In$_2$O$_3$ (IC-1-1); 0.0015mol In$_2$O$_3$ (IC-2-3); 0.0005mol In$_2$O$_3$ (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 BaSO$_4$ as a reflectance standard. Brunauer-Emmett-Teller (BET) surface area and CO$_2$ 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 CO$_2$ reduction Measurement

As shown in Figure S1, the equipment for photocatalytic CO$_2$ 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 CO$_2$ system.](image)

Typically, 30 mg of photocatalyst, 20mL of 0.01 mo·L$^{-1}$ Na$_2$SO$_3$ were added into a gas-closed glass reactor (400 mL in capacity). Then, high purity CO$_2$ 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 / In$_2$O$_3$ (similar to In$_2$O$_3$), the counter electrode was platinum mesh, and the reference electrode was Ag / AgCl (3M KCl). Na$_2$SO$_4$ (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 Na$_2$SO$_4$ 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. CO$_2$ photoreduction activities of different proportions of In$_2$O$_3$-CuO.
**Figure S3.** XRD pattern of In(OH)$_3$. 
Figure S4. XRD pattern of In$_2$O$_3$ sphere.
Figure S5. XRD pattern of CuO flower.
Figure S6. (a) TEM images, (b-c) HRTEM image (d-e) EDX mappings of In$_2$O$_3$ 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 In$_2$O$_3$-CuO.
Figure S9. XPS spectra of (a) survey, (b) In 3d, (c) Cu 2p and O 1s of different samples.
Figure S10. (a) N$_2$ adsorption-desorption isotherms, pore size distributions (inset) and (b) CO$_2$ adsorption curves of In$_2$O$_3$, CuO and In$_2$O$_3$-CuO.
Fig. S11. (a) Transient photocurrent spectra, (b) EIS spectra of $\text{In}_2\text{O}_3$ and $\text{In}_2\text{O}_3$-$\text{CuO}$, and (c) steady-state PL spectra (d) Time-resolved transient PL decay of $\text{In}_2\text{O}_3$, CuO and $\text{In}_2\text{O}_3$-$\text{CuO}$. 
**Figure S12.** DRS of In$_2$O$_3$, CuO and In$_2$O$_3$-CuO.
Figure S13. Tauc plots of (a) In$_2$O$_3$, (b) CuO and Mott-Schottky plots of (a) In$_2$O$_3$, (b) CuO.
Figure S14. Z-scheme model of In$_2$O$_3$-CuO photocatalyst and its charge transfer process under light irradiation.