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Supporting Information

Synergistic catalysis of CuO/In_2O_3 composites for highly selective electrochemical CO_2 reduction to CO

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Experimental section

Materials. All chemicals used in this work were of analytical grade and used as supplied. $Cu(Ac)_2 \cdot H_2O$, $InCl_3$, and KOH were obtained from Aladdin. High-purity (≥95%) carbon nanotubes (CNTs) were supplied by Bayer Material Science. The as-received CNTs were first oxidized via HNO_3 vapor treatment at 200 °C for 48 h. After cooling and repeated washing with distilled water, the CNTs were dried at 60 °C overnight. Then, 200 mg of the oxidized CNTs was subjected to heating in 10 vol% NH_3 in He at a flow rate of 25 sccm at 400 °C for 6 h to generate N-containing functional groups.

Synthesis of CuO-In_2O_3/NCNTs. Typically, a specific amount of $Cu(Ac)_2 \cdot H_2O$ and $InCl_3$ ethanol solutions (Table S1) were first mixed with 4 mg of NCNTs dispersed in 2 mL of ethanol and bath-sonicated for 1 h to form a uniform dispersion. Different amounts of 0.5 M KOH ethanol solution (Table S1) were then slowly added under vigorous magnetic stirring to ensure an appropriate pH value for the reaction system. The system was allowed to react for 6 h in an oil bath at 80 °C. After reaction, the solid products were repeatedly washed with ethanol and water, and then dried at 60 °C for use.

Characterization. X-ray powder diffraction (XRD) was performed with a D/MAX−RC diffractometer operated at 30 kV and 100 mA with Cu Kα radiation. X-ray photoelectron spectroscopy (XPS) experiments were carried out using Thermo Scientific ESCALAB 250Xi instrument. The instrument was equipped with an electron flood and a scanning ion gun. All spectra were calibrated according to the C 1s binding energy at 284.8 eV. HAADF-STEM was conducted using a JEOL ARM200 microscope with a 200 kV accelerating voltage. STEM samples were prepared by depositing a droplet of suspension onto a Cu grid coated with a Lacey Carbon film. Hydrogen temperature-programmed reduction (H_2-TPR) experiments were carried out in a quartz tube reactor equipped with a thermal conductivity detector (TCD) using a Micromeritics AutoChem HP 2950 instrument. Before each measurement, the sample was first pre-treated in pure Ar at 200 °C for 30 min. Subsequently, a certain amount of the pre-treated sample was heated in a gas flow (50 cm^3/min) of 10% H_2 in Ar from 50 to 750 °C at a ramp rate of 10 °C/min.

Cathode preparation

Typically, 1.2 mg of catalyst was dispersed in 241.2 μL of solution containing isopropanol, deionized water, and 5 wt% Nafion solution with a corresponding volume ratio of 120: 120: 1.2 by ultrasonicating for 30 min to form a homogeneous ink. The catalyst ink was then loaded onto a carbon paper electrode with an area of 1.2 cm × 1 cm and dried under ambient conditions. For linear sweep voltammograms in Ar- or CO_2-saturated 0.1 M $KHCO_3$ solution, 1 mg of a catalyst was dispersed in the mixture of 100 μL of ethanol, 100 μL of deionized water, and 100 μL of Nafion solution (1 wt%). Then the mixture was ultrasonicated for 30 min to form a homogeneous ink. 7.95 μL of the dispersion ink was then loaded onto glassy carbon electrode and dried under ambient conditions.

Electrochemical measurements. Controlled potential electrolysis of CO_2 was tested in an H-cell system, which was separated by a Nafion 117 membrane. Before ECR tests, the Nafion membrane was pretreated by heating in 5% H_2O_2 aqueous solution and 0.5 M H_2SO_4 at 80 °C for 1 h, respectively. Then the Nafion membrane was immersed in deionized water under ambient conditions for 30 min and then washed with deionized water. Toray Carbon fiber paper with a size of 1.2 cm × 1 cm was used as working electrode. Pt wire and Ag/AgCl electrodes were used as counter electrode and reference electrode, respectively. The potentials were controlled by an electrochemical working station (CHI 760E, Shanghai CH Instruments Co., China). All potentials in this study were measured against the Ag/AgCl reference electrode (in 3 M KCl solution) and converted to the RHE reference scale by

$$E\ (vs.\ \mathrm{RHE}) = E\ (vs.\ \mathrm{Ag/AgCl}) + 0.21\ \mathrm{V} + 0.0591 \times \mathrm{pH} \quad \text{(Eq. S1)}$$

Electrocatalytic CO_2 reduction was conducted in CO_2-saturated 0.1 M $KHCO_3$ solution at room temperature and atmospheric pressure. When saturated with CO_2, the pH of the electrolyte was 6.8. CO_2 was purged into the $KHCO_3$ solution for at least 30 min to remove residual air in the reservoir, then controlled potential electrolysis was performed at each potential for 60 min.

Linear sweep voltammograms in Ar- or CO_2 atmosphere were carried out in a three-electrode system using Ag/AgCl as reference electrode, Pt wire as counter electrode, and glassy carbon as working electrode on a CHI 760E potentiostat (CHI 760E., Shanghai CH Instruments Co., China). Rotating disk electrode (RDE) experiments were run on an AFMSRCE RDE control system (Pine Inc., USA). The electrolyte is 0.1 M $KHCO_3$ solution with Ar or CO_2 purged for at least 30 min.

Gaseous products from the cell were analyzed using an Agilent 7890B GC system. Two thermal conductivity detectors and a flame ionization detector were applied to analyze and differentiate the injected samples. To characterize the gas product, 20 mL of the gas products in the dead volume of a gas bag (~1 L) was injected into the GC under identical experimental conditions (e.g., pressure, temperature, and time) using a sample lock syringe. CO and H_2 peaks were detected at 11.4 and 3.7 min, respectively. The liquid products such as formic acid were quantified by ^{1}H NMR using a solvent presaturation technique to suppress the water peak. FE was determined from the amount of charge passed to produce each product divided by the total amount of charge passed at a specific time or during the overall run.

Table S1. The recipes for synthesizing the CuO-In_2O_3/NCNTs materials.

Cu/In	CuO	60:1	40:1	30:1	20:1	15:1	3:1	1:1	1:3	1:15	In_2O_3
C_{InCl3}/M						0.02					
V_{InCl3}/μL	0	49	72	95	138	180	635	1095	1450	1660	1725
$C_{Cu(OAc)2}$/M						0.02					
$V_{Cu(OAc)2}$/μL	3000	2940	2880	2850	2800	2690	1900	1095	485	110	0
C_{NCNT}						2 mg/mL					
V_{NCNT}/mL						2					
C_{KOH}/M						0.5					
V_{KOH}/μL	300	300	300	300	300	300	300	300	300	300	300

Table S2. The ECR activity optimized by modulating the concentration and feeding sequence of the metal salt precursors.

$C_{\text{metal salt precursors}}$/M	FE_{CO}/%	Feeding sequence$_{\text{metal salt precursors}}$	FE_{CO}/%
0.005	71.7	In_2O_3@CuO/$NCNT_S$	75.9

0.01	93.0	In_2O_3-CuO/NCNTs	92.0
0.02	92.0	CuO@In_2O_3/NCNTs	71.2
004	70.4		

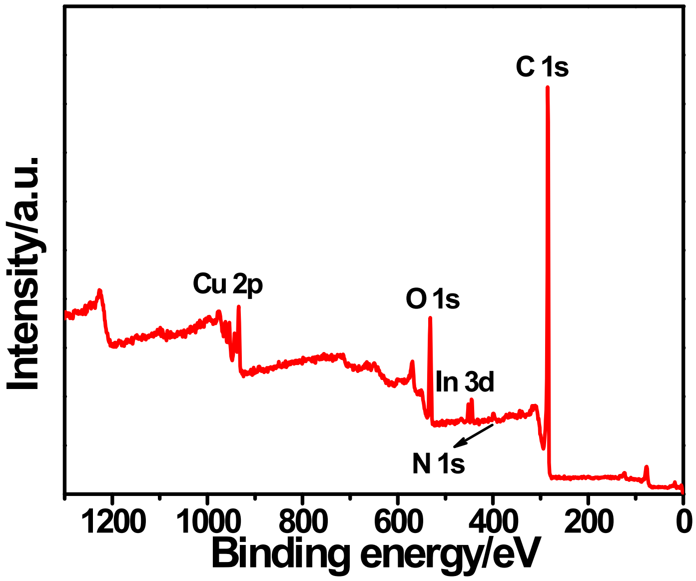

Fig. S1 Wide-survey XPS spectrum of CuO-In_2O_3/NCNTs (Cu-to-In mole ratio of 30:1).

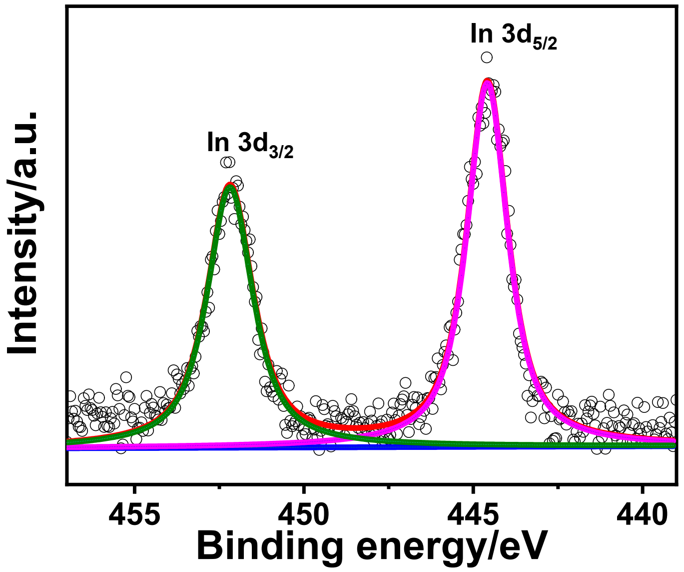

Fig. S2 In 3d XPS spectrum of CuO-In_2O_3/NCNTs (Cu-to-In mole ratio of 30:1).

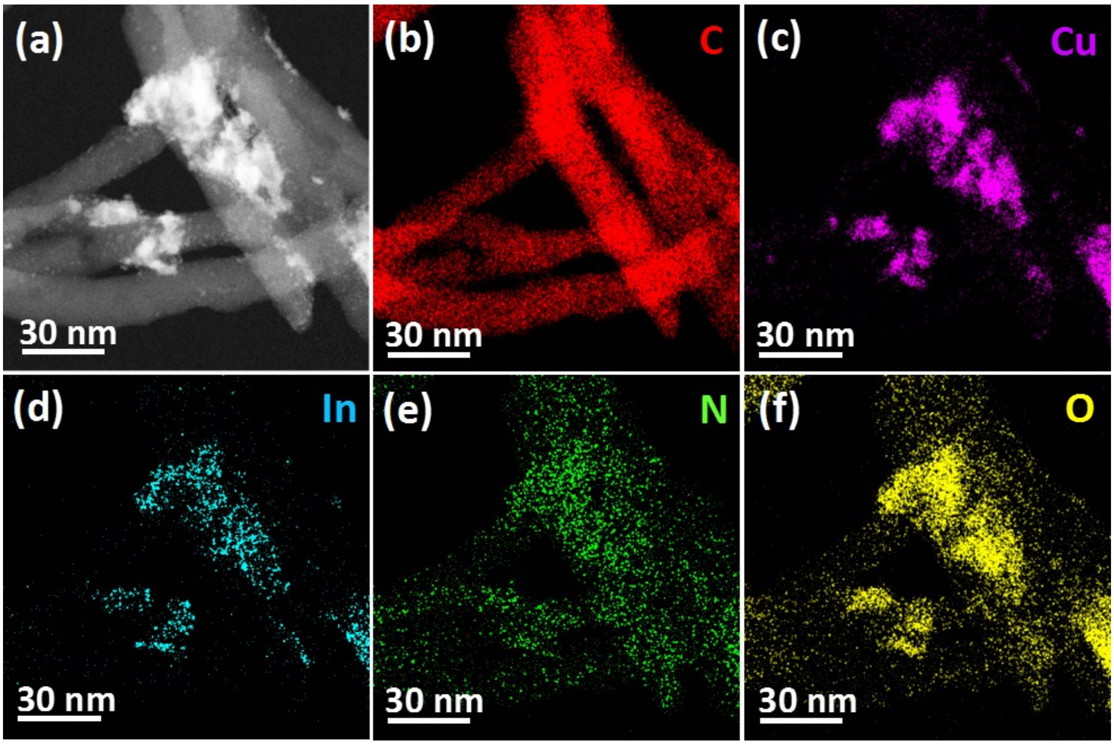

Fig. S3 (a) HAADF-STEM image of CuO-In_2O_3/NCNTs (Cu-to-In mole ratio of 30:1). EDS elemental maps of (b) C, (c) Cu, (d) In, (e) N, and (f) O over the region shown in image (a).

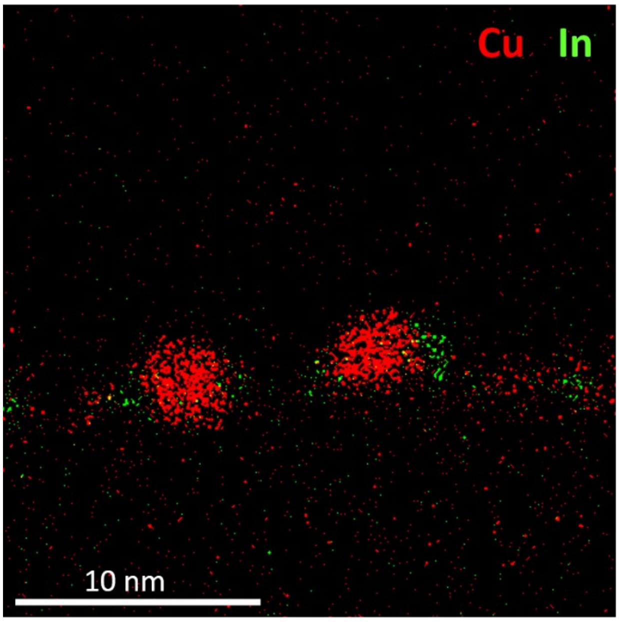

Fig. S4 EDS elemental map of overlay of Cu (red) and In (green) over the region shown in Fig. 2c.

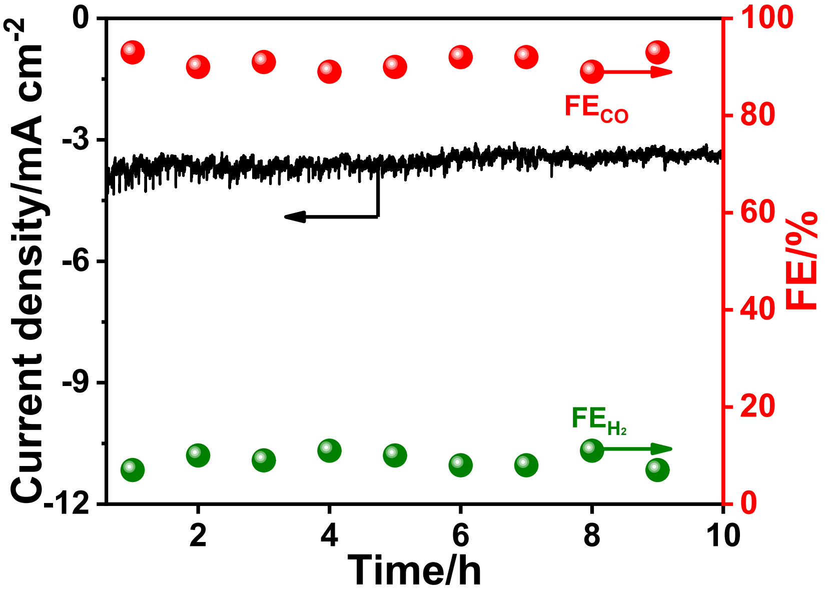

Fig. S5 Current, CO FE, and H_2 FE-time responses of CuO-In_2O_3/NCNTs (Cu-to-In mole ratio of 30:1) at -0.7 V (*vs*. RHE).

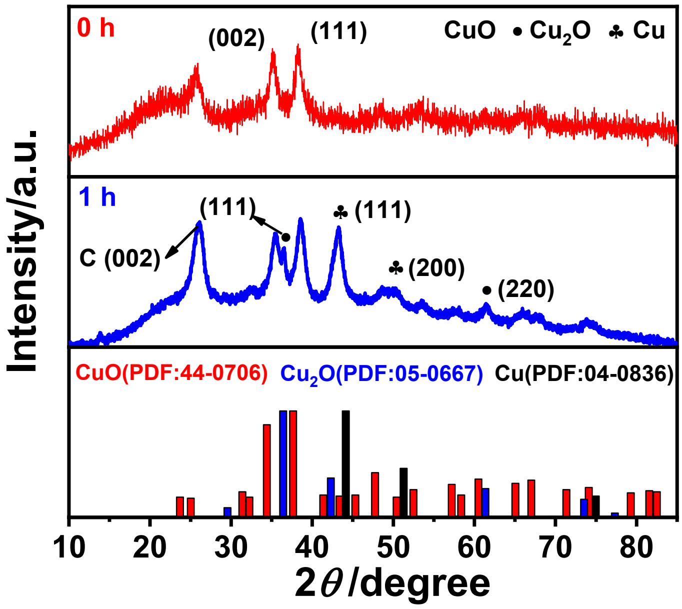

Fig. S6 XRD patterns of CuO-In_2O_3/NCNTs (Cu-to-In mole ratio of 30:1) after electrocatalysis at different times.

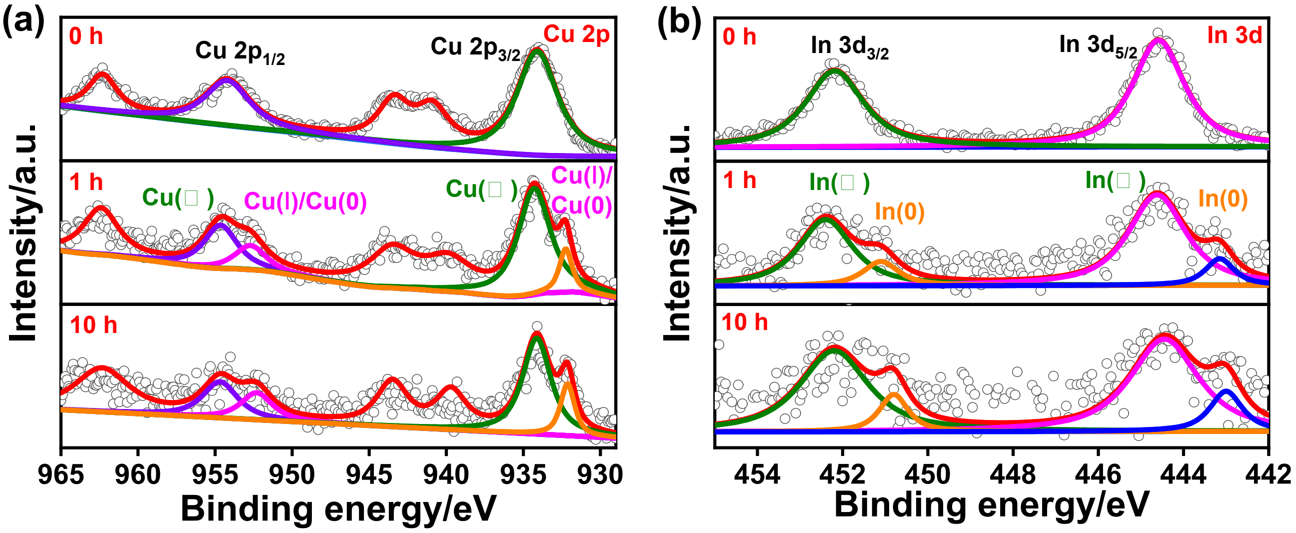

Fig. S7 (a) Cu 2p and (b) In 3d XPS spectra of CuO-In_2O_3/NCNTs (Cu-to-In mole ratio of 30:1) after electrocatalysis at different times.

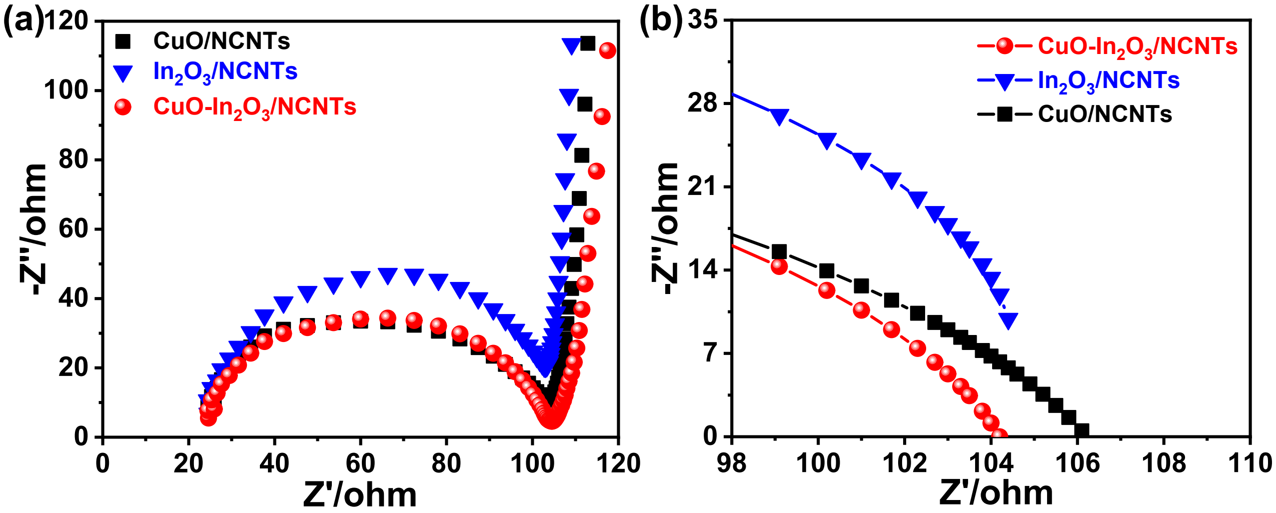

Fig. S8 (a) EIS plots of CuO-In_2O_3/NCNTs (Cu-to-In mole ratio of 30:1), CuO/NCNTs, and In_2O_3/NCNTs. (b) Enlarged fitting curves of (a).