

## Supporting Information

### 1. Experimental detail

#### 1.1 Synthesis of MIL-68-In hexagonal micro-rods precursor

In a typical synthesis,  $\text{In}(\text{NO}_3)_3 \cdot 4\text{H}_2\text{O}$  (0.078 g, 0.21 mmol) and 1,4-benzenedicarboxylic acid (0.03 g, 0.18 mmol) were dissolved in 10 mL of N,N-dimethylformamide (DMF). After stirring by ultrasonic concussion for 10 minutes, the mixture was transferred to a 50 mL Teflon-lined steel autoclave and placed in an oven at 100 °C for 4 hours. After reaction, the product was collected via centrifugation and washed several times with ethanol, then dried at 60 °C overnight.

#### 1.2 Preparation of MIL-68-In@Cu-BDC precursor

In a typical synthesis, MIL-68-In precursor (0.0108 g) and 1,4-benzenedicarboxylic acid (0.015 g, 0.09 mmol) were weighed and placed in a small beaker of 50 mL, and then 10 mL N,N-dimethylformamide (DMF) was added. After stirring continuously at 120 °C for 30 min, copper nitrate hexahydrate (0.024 g, 0.1 mmol) was added to the small beaker. After stirring at 120 °C for another 30 min, the product was centrifuged to obtain.

#### 1.3 Synthesis of $\text{In}_2\text{O}_3/\text{CuO}@N\text{-C}$ hierarchical pagoda-like micro-rods

$\text{In}_2\text{O}_3/\text{CuO}@N\text{-C}$  was synthesized via calcination of the obtained at 390 °C for 55 min in Ar gas atmosphere with heating rate of 2 °C·min<sup>-1</sup>.

#### 1.4 Synthesis of DNCPH

In a typical synthesis of dodecahedral Cu/In-rho-ZMOFs, indium nitrate hexahydrate (0.015g, 0.040 mmol), copper nitrate trihydrate (0.0078g, 0.017 mmol), 4,5-imidazoledicarboxylic acid (0.04g, 0.256 mmol), and benzimidazole (0.1g, 0.846 mmol) were dissolved in DMF (8 mL). After stirring by ultrasonic concussion for 10 min, the mixture was heated at 120 °C under stirring conditions for 4 h. After the reaction, the product was collected via centrifugation and washed several times with water and ethanol, and then dried at 60 °C overnight.

DNCPH was synthesized via the calcination of the obtained dodecahedral Cu/In-rho-ZMOFs at 500 °C in an Ar gas atmosphere with heating rate of 2 °C·min<sup>-1</sup> for 1 h.

### **1.5 Synthesis of In<sub>2</sub>O<sub>3</sub>/CuO**

In<sub>2</sub>O<sub>3</sub>/CuO was synthesized via the calcination of the obtained MIL-68-In@Cu-BDC precursor at 330 °C for 6 h in O<sub>2</sub> gas atmosphere with heating rate of 5 °C·min<sup>-1</sup>.

### **1.6 Synthesis of CuO@N-C**

In a typical synthesis of Cu-BDC precursor, copper nitrate trihydrate (0.024 g, 0.1 mmol) and 1,4-benzenedicarboxylic acid (0.017 g, 0.09 mmol) were dissolved in 10 mL of methanol. After stirring by ultrasonic concussion for 10 minutes, the mixture was transferred to a 25 mL Teflon-lined steel autoclave and placed in an oven at 100 °C for 4 h. After reaction, the product was collected via centrifugation and washed several times with ethanol, then dried at 60 °C overnight.

CuO@N-C was synthesized via calcination of the obtained at 600 °C for 4 h in an Ar gas atmosphere with heating rate of 5 °C·min<sup>-1</sup>.

### **1.7 Synthesis of In<sub>2</sub>O<sub>3</sub>@N-C**

In<sub>2</sub>O<sub>3</sub>@N-C was synthesized via the calcination of the obtained In-MIL-68 at 450 °C for 120 min in an Ar gas atmosphere with heating rate of 2 °C·min<sup>-1</sup>.

### **1.8 Characterizations**

The composition and phase of the as-prepared products were acquired by powder X-ray diffraction (XRD) using a Panalytical X-pert diffractometer with CuK $\alpha$  radiation. The morphology and crystal structure of as-prepared products were observed by scanning electron microscopy (SEM, SU8100) and high-resolution transmission electron microscopy (HRTEM, FEI Tecnai-F20) with an acceleration voltage of 200 kV. All TEM samples were prepared by depositing a drop of diluted suspension in ethanol on a carbon film coated copper grid. PHI QUANTUM2000 photoelectron spectrometer (XPS) was used to characterize the surface compositions of products. The surface areas of these samples were measured by the Brunauer-Emmett-Teller (BET) method using nitrogen adsorption and desorption isotherms on a Micrometrics ASAP 2020 system.

### **1.9 Photoelectric measurements**

Photoelectrochemical measurements were performed in a CHI-760E workstation. A Pt plate was used as the counter electrode, and Hg/HgCl<sub>2</sub> electrode was used as the reference electrode. The working electrode was prepared on fluorine-doped tin oxide (FTO) glass that was cleaned

by ultrasonication in a mixture of ethanol for 10 min and dried at 60 °C. Typically, 10 mg of the sample powder was ultrasonicated in 0.2 mL of ethanol to disperse it evenly to get a slurry. The slurry was spread onto FTO glass. Then, the working electrode was further dried at 150 °C for 2 h to improve adhesion. The exposed area of the working electrode was 2.5 cm<sup>2</sup>. The electrochemical impedance spectroscopy (EIS) measurement was carried out using a CHI-760E workstation, in the three electrode cell the electrolyte were 0.025 M Na<sub>2</sub>HPO<sub>4</sub> standard buffer solution (25 °C, pHs = 6.864) without an additive under open circuit potential conditions. The visible light irradiation source was a 300 W Xe arc lamp system. The cathodic polarization curves were obtained using the linear sweep voltammetry (LSV) technique with a scan rate of 100 mV s<sup>-1</sup>. Linear sweep voltammetry (LSV) was measured in the range of -0.8 to 0.8 V bias (vs saturated calomel electrode), and the transient photocurrent responses with time (i-t curve) was measured at a bias potential of +0.16 V during repeated ON/OFF illumination cycles.

#### **1.10 Photocatalysis: Cross dehydrogenative coupling (CDC) reaction**

The photocatalyst (5 mg), tetrahydroisoquinolines (0.05 mmol) and indoles (0.1 mmol) were added into 1 mL CD<sub>3</sub>CN. The mixture solution was stirred and irradiated by blue LEDs ( $\lambda=450$  nm, 3W) for 12 h under atmosphere at room temperature. The average light density was ca. 3.85 mW·cm<sup>-2</sup> and the irradiation area was 2.46 cm<sup>2</sup>. <sup>1</sup>H NMR was employed to determine the yield. To carry out recycle reactions, the photocatalyst was recycled by centrifuging at 5000 rpm for 3 min and washed by ethanol three times. Finally, the recycled catalysts were dried at 60 °C overnight.

#### **1.11 Density functional calculations**

All of the density functional calculations were performed using plane-wave pseudopotential method, as implemented in the Cambridge Sequential Total Energy Package (CASTEP) code<sup>1</sup>. The local density approximation (LDA)<sup>2</sup> and ultrasoft pseudopotential<sup>3</sup> were used to describe the exchange-correlation effects and electron-ion interactions, respectively. A Monkhorst-Pack mesh<sup>4</sup> of *k*-points,  $\Gamma$  and 1×1×2 points, was used, respectively, to sample the two-dimensional Brillouin zone for geometry optimization and for calculating electronic properties of reactants adsorbed graphite (001) surfaces. The self-consistent convergence accuracy was set at 2×10<sup>-5</sup> eV/atom, the convergence criterion for the force between atoms was 5.0×10<sup>-2</sup> eV/Å, and the

maximum displacement was  $2 \times 10^{-3}$  Å. The cutoff energy was set to 240 eV.

The adsorption energies for 2-phenyl-1,2,3,4-tetrahydroisoquinoline and indole on graphite (001) surface were calculated by

$$E_{ad} = E_{(R+G)} - E_{(R)} - E_{(G)}$$

where  $E_{(R+G)}$  was the total energy of the graphite (001) surface containing the adsorbed 2-phenyl-1,2,3,4-tetrahydroisoquinoline or indole,  $E_{(R)}$  was the energy of 2-phenyl-1,2,3,4-tetrahydroisoquinoline or indole, and  $E_{(G)}$  was the energy of graphite (001) surface.

## 2. Experimental results

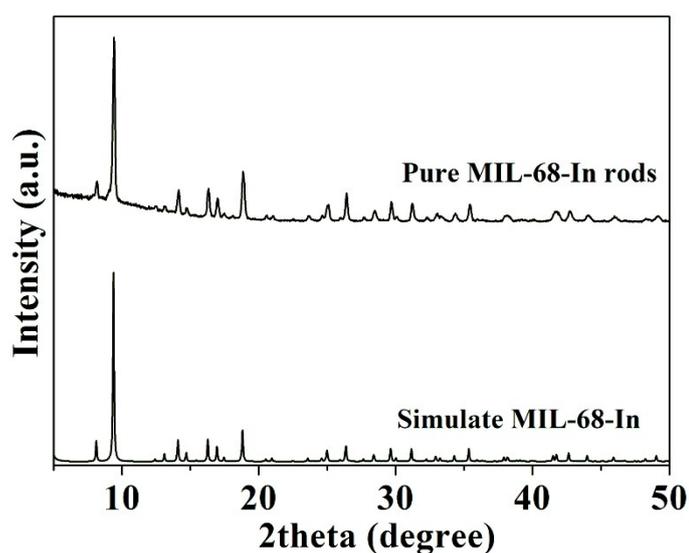


Figure S1 The XRD pattern of MIL-68-In rods.

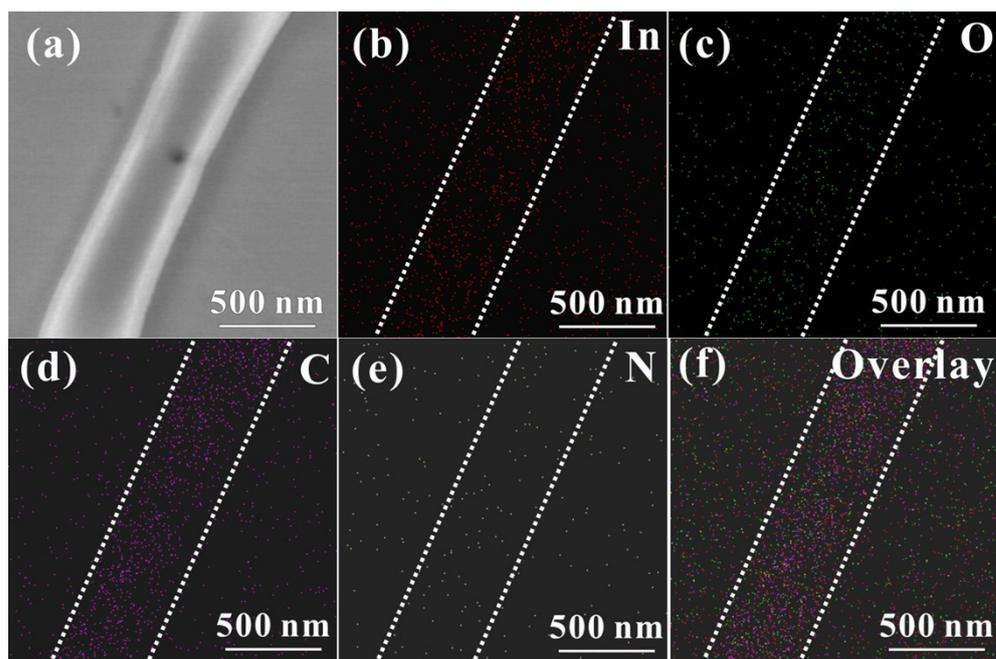


Figure S2 The EDX mapping of MIL-68-In micro-rod.

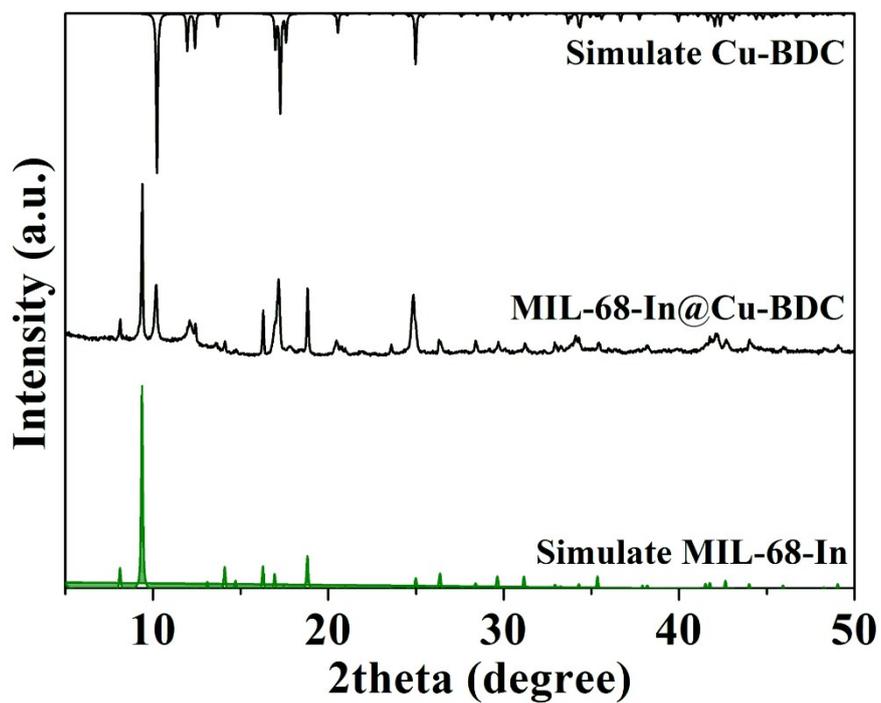


Figure S3 The XRD pattern of MIL-68-In@Cu-BDC precursor.

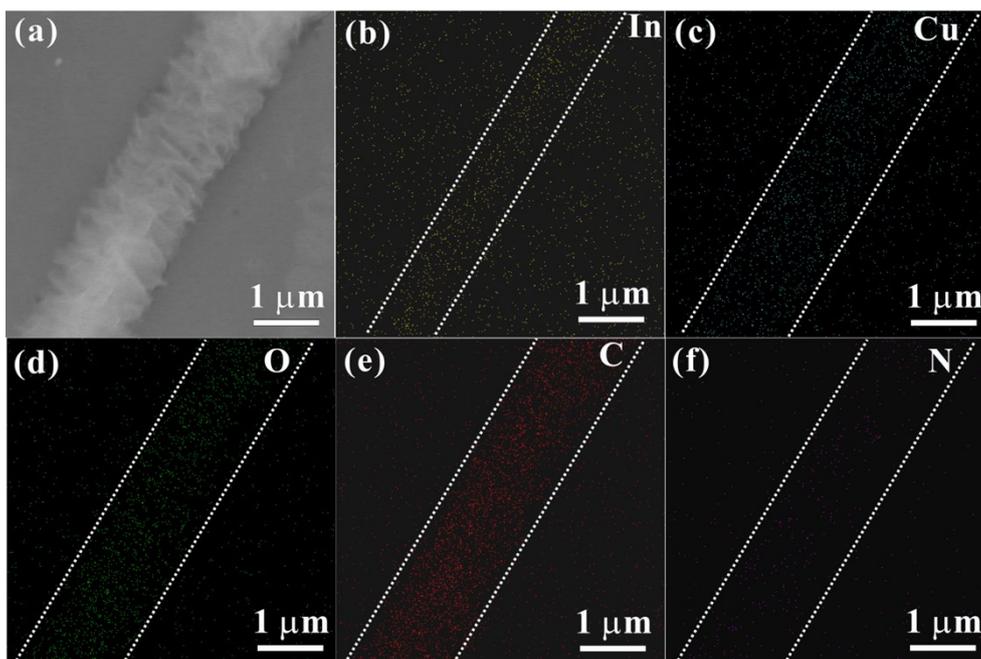


Figure S4 The EDX mapping of MIL-68-In@Cu-BDC precursor.

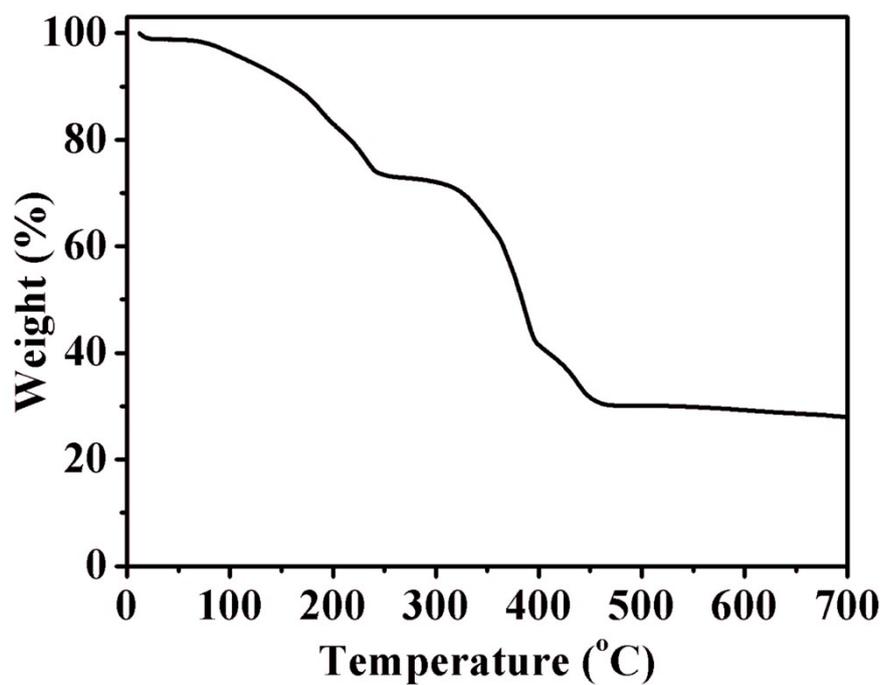


Figure S5 TGA curves of the as-obtained MIL-68-In@Cu-BDC precursor.

As shown in the TGA curve (Figure S5), the initial weight loss below 240 °C was

attributed to the removal of adsorption solvent molecule. The major weight loss between 240~390 °C could be ascribed to the carbonization of MIL-68-In@Cu-BDC precursor. Thus, the annealing condition of MIL-68-In@Cu-BDC was set to 390 °C for 1h in Ar atmosphere with a ramping rate of 2 °C·min<sup>-1</sup> to convert the MIL-68-In@Cu-BDC precursor into In<sub>2</sub>O<sub>3</sub> and CuO.

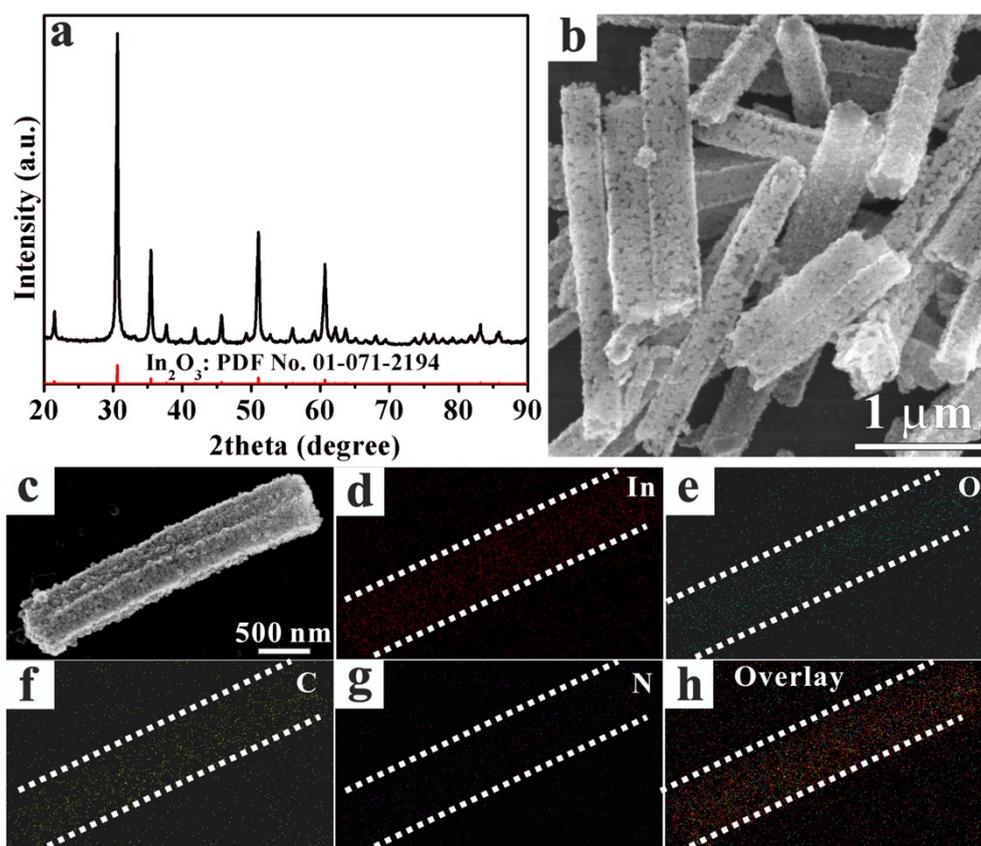


Figure S6 (a) XRD pattern of In<sub>2</sub>O<sub>3</sub>@N-C, (b, c) FESEM image of In<sub>2</sub>O<sub>3</sub>@N-C, (d-h) the corresponding EDX mapping of In<sub>2</sub>O<sub>3</sub>@N-C.

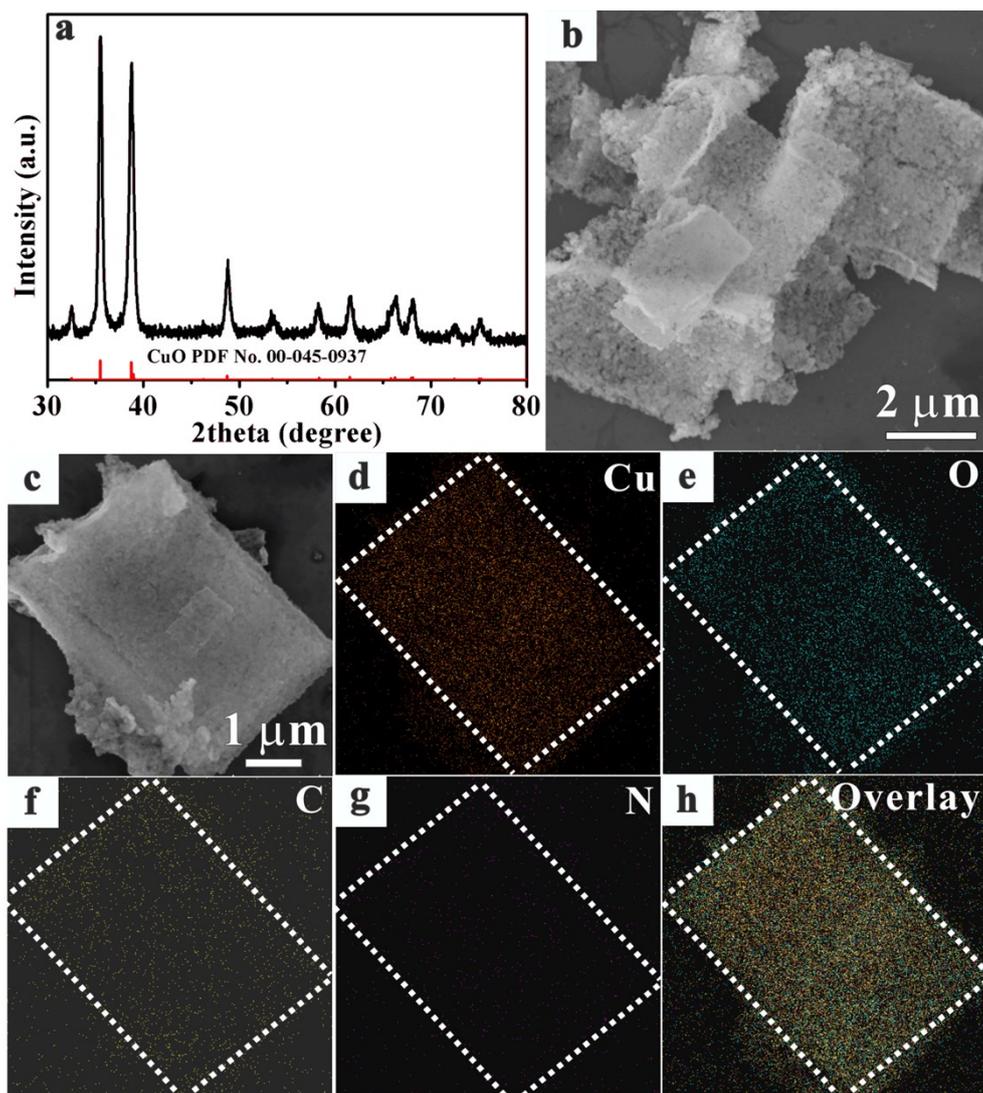


Figure S7 (a) XRD pattern of CuO@N-C, (b, c) FESEM image of CuO@N-C, (d-h) the corresponding EDX mapping of CuO@N-C.

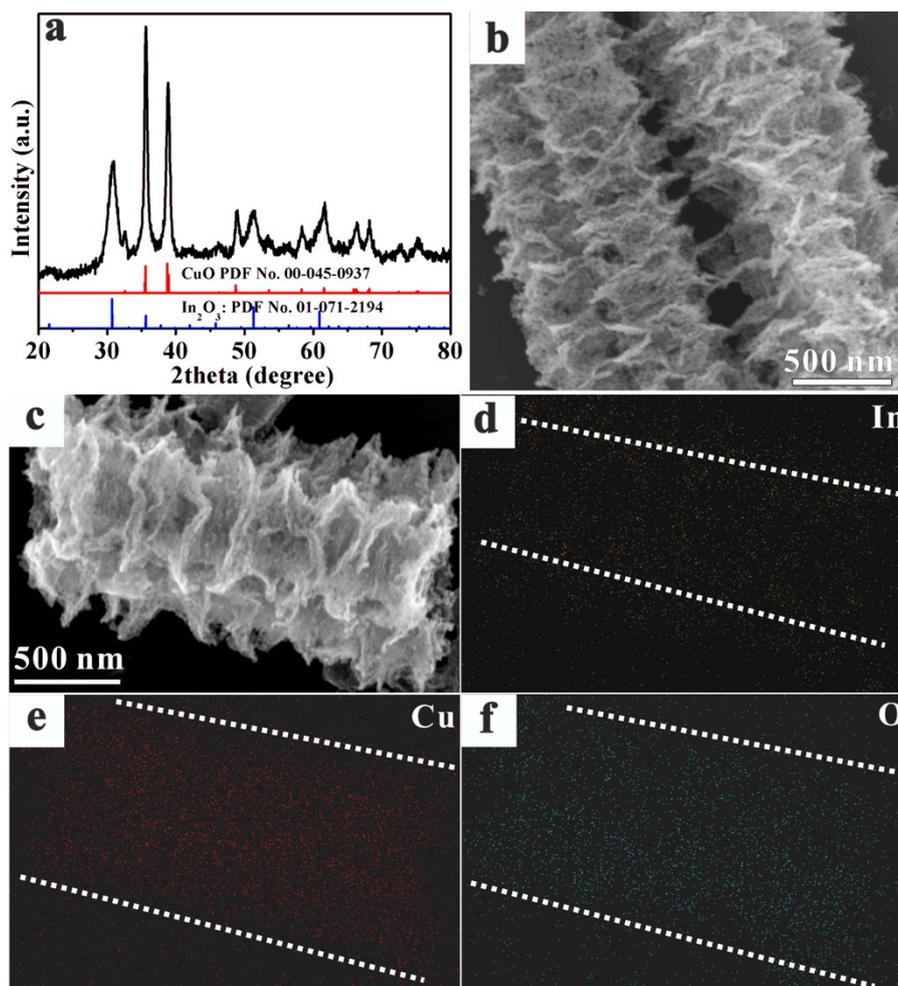


Figure S8 (a) XRD pattern of In<sub>2</sub>O<sub>3</sub>/CuO, (b, c) FESEM image of In<sub>2</sub>O<sub>3</sub>/CuO, (d-f) the corresponding EDX mapping of In<sub>2</sub>O<sub>3</sub>/CuO.

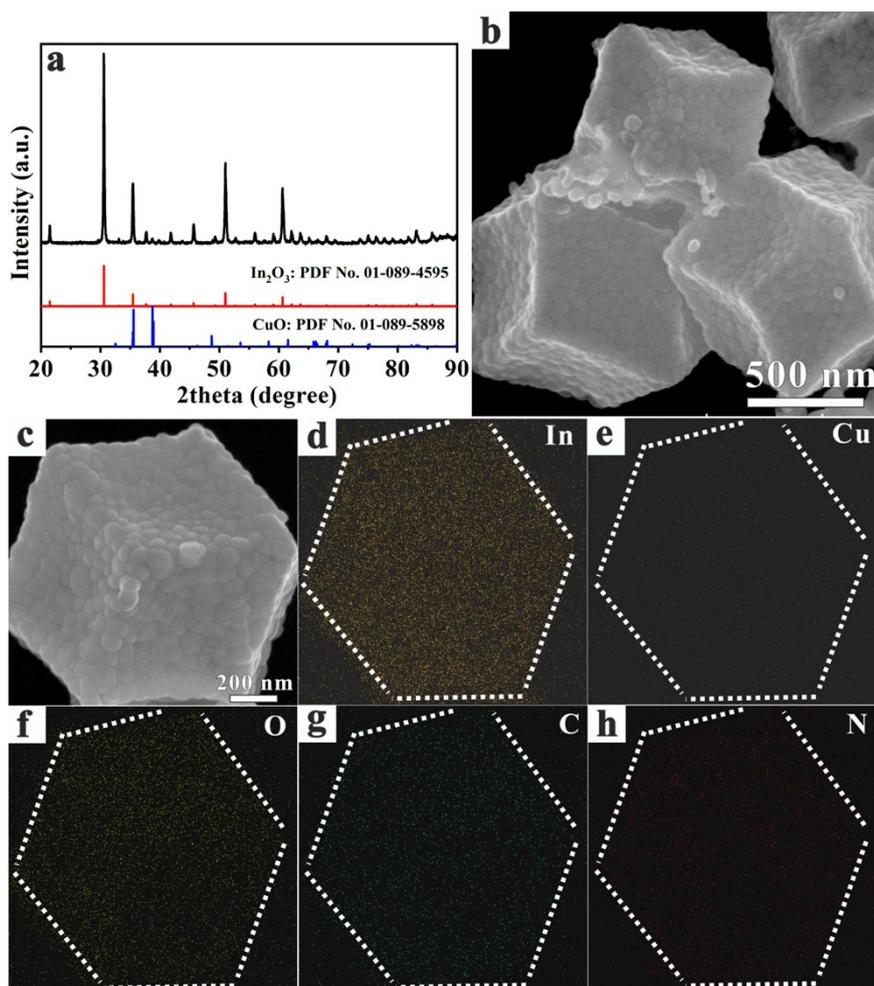


Figure S9 (a) XRD pattern of DNCPH, (b, c) FESEM image of DNCPH, (d-f) the corresponding EDX mapping of DNCPH.

Table S1. Catalyzed Cross-dehydrogenative Coupling Reaction in different Reaction Conditions

$h\nu$ (450nm, LED)	Catalyst (In <sub>2</sub> O <sub>3</sub> /CuO@N-C)	Reaction time	Conv (%)
Yes	No	12 h	No Product
No	Yes	12 h	No Product
Yes	Yes	12 h	98%

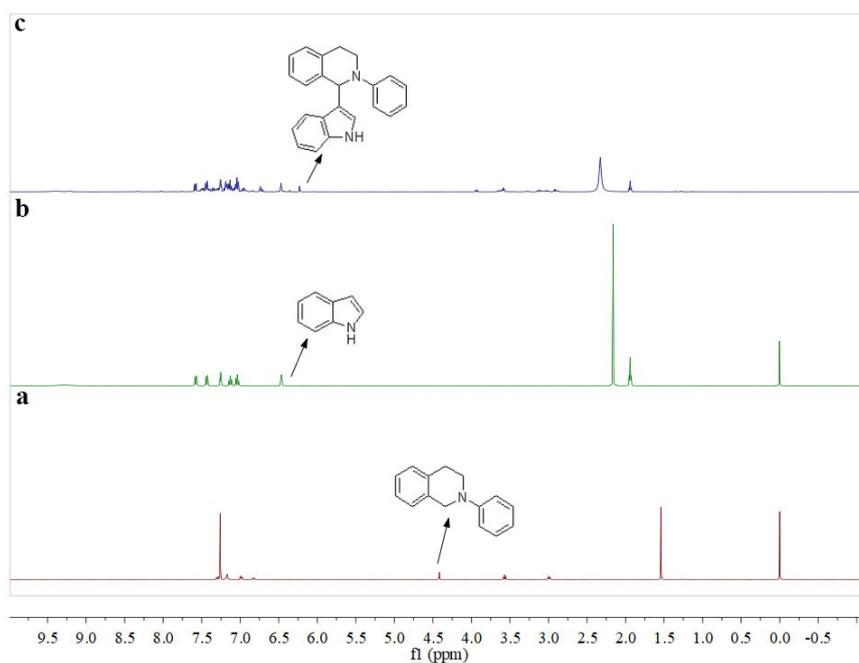


Figure S10 (a)  $^1\text{H}$  NMR spectrum of 2-phenyl-1,2,3,4-tetrahydroisoquinoline, (c)  $^1\text{H}$  NMR spectrum of product, (b)  $^1\text{H}$  NMR spectrum of indole.

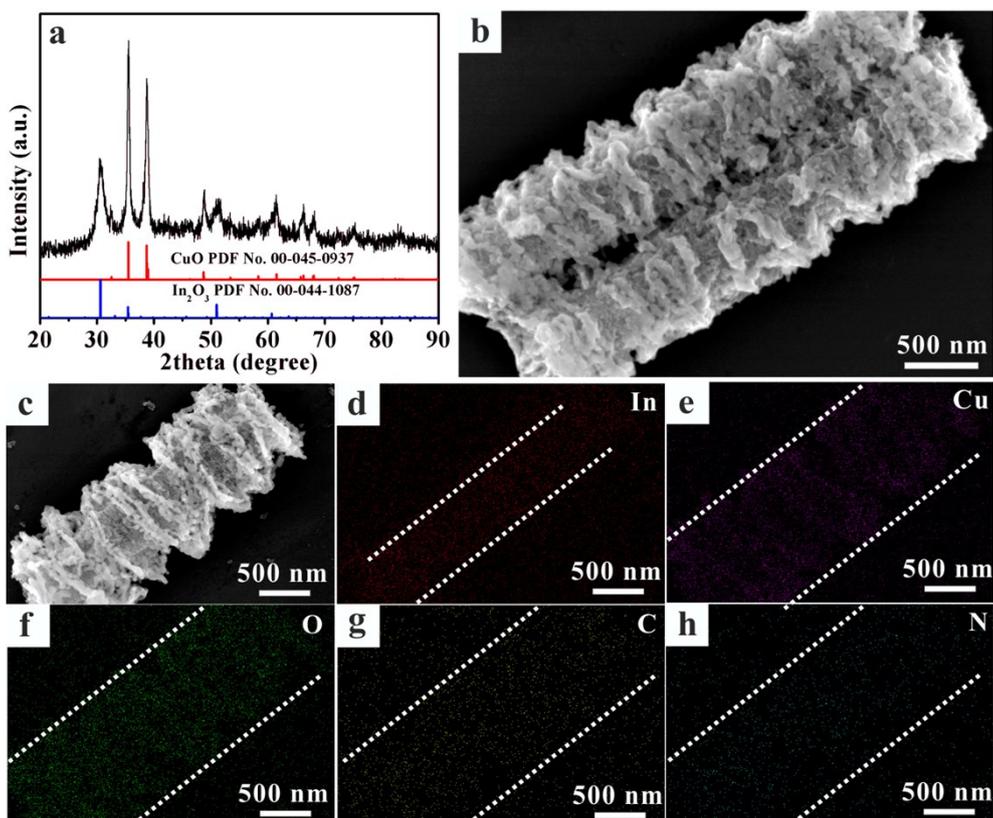


Figure S11 (a) XRD pattern of  $\text{In}_2\text{O}_3/\text{CuO}@N\text{-C}$ , (b, c) FESEM image of  $\text{In}_2\text{O}_3/\text{CuO}@N\text{-C}$ , (d-h) the corresponding EDX mapping of  $\text{In}_2\text{O}_3/\text{CuO}@N\text{-C}$  after four cycles of photocatalytic reaction.

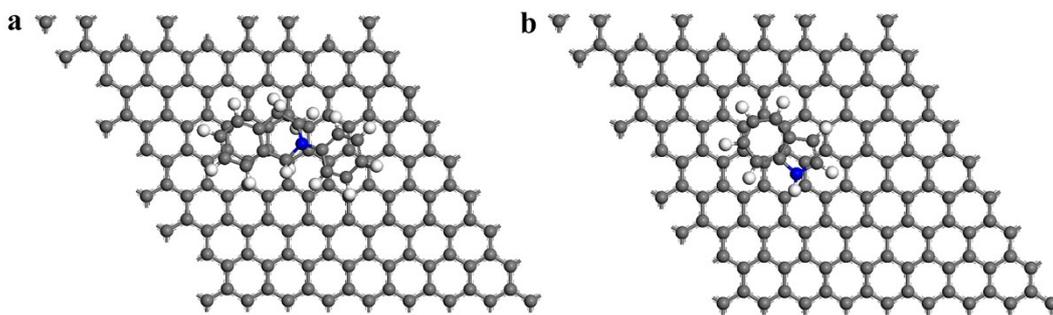


Figure S12 The geometric configurations of 2-phenyl-1,2,3,4-tetrahydroisoquinoline (a) and indole (b) adsorbed on graphite (001) surface.

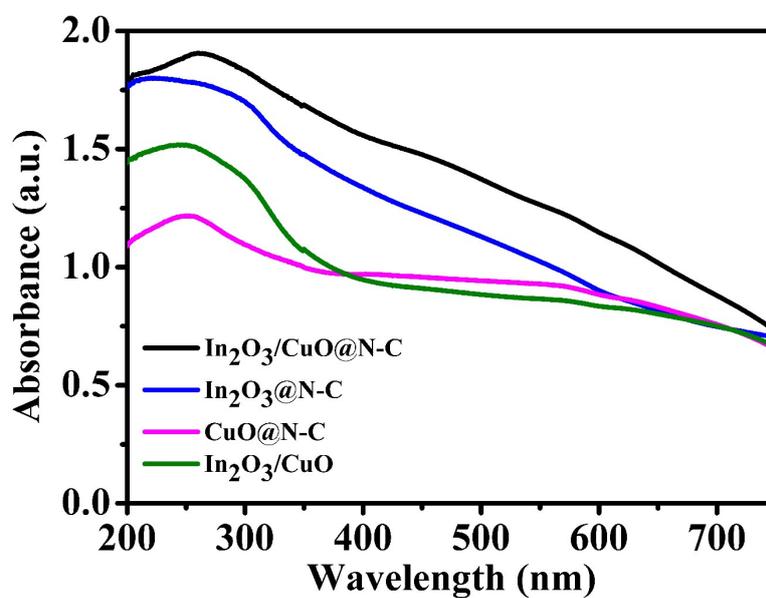


Figure S13 UV-vis spectra of  $\text{In}_2\text{O}_3/\text{CuO}@N\text{-C}$ ,  $\text{In}_2\text{O}_3@N\text{-C}$ ,  $\text{CuO}@N\text{-C}$  and  $\text{In}_2\text{O}_3/\text{CuO}$ .

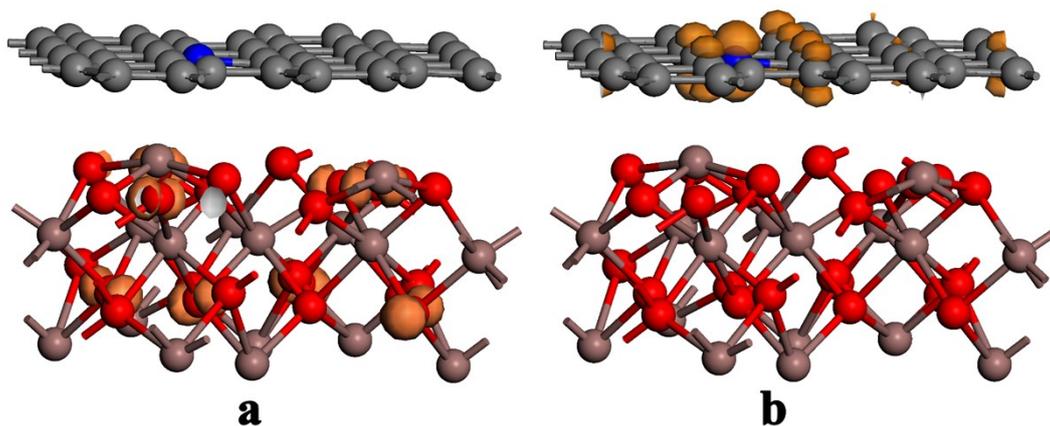


Figure S14 The  $\Gamma$ -point orbital-isoamplitude surface of the HOMO (a) and LUMO (b) for the  $\text{In}_2\text{O}_3$  (100)/N-doped graphite (001) interface. The red, brown, grey and blue balls represent O, In, C and N atoms, respectively.

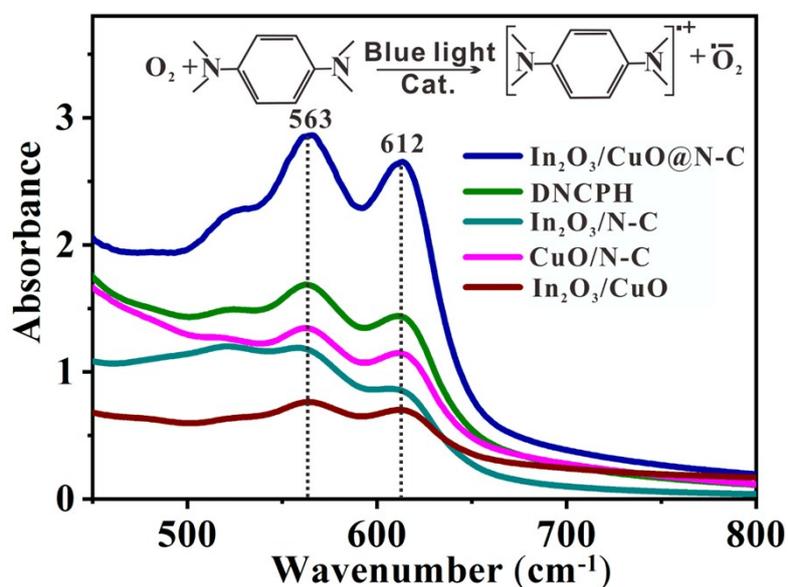


Figure S15 UV-vis absorption spectra for cationic radicals of TMPD treated by  $\text{In}_2\text{O}_3/\text{CuO}@N\text{-C}$ , DNCPH,  $\text{In}_2\text{O}_3/N\text{-C}$ ,  $\text{CuO}/N\text{-C}$ ,  $\text{In}_2\text{O}_3/\text{CuO}$  under blue LED light irradiation.

Table S2. Mulliken charge population on the C<sub>a</sub>, C<sub>b</sub> and bonding H atoms, and the bond lengths of corresponding C-H for 2-phenyl-1,2,3,4-tetrahydroisoquinoline and indole before and after adsorption on the graphite (001) surface.

Species	Charge population( <i>e</i> )				Bond lengths(Å)	
	C <sub>a</sub>	H <sub>1</sub>	C <sub>b</sub>	H	C <sub>a</sub> -H <sub>1</sub>	C <sub>b</sub> -H
2-phenyl-1,2,3,4-tetrahydroisoquinoline (before adsorption)	-0.46	0.31			1.11	
2-phenyl-1,2,3,4-tetrahydroisoquinoline (after adsorption)	-0.42	0.27			1.12	
Indole (before adsorption)			-0.40	0.33		1.08
Indole (after adsorption)			-0.39	0.32		1.09

**References:**

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2. Ceperley, D. M., Alder, B. J. *Phys. Rev. Lett.*, **45**, 566 (1980).
3. Rappe, A. M., Rabe, K. M., Kaxiras, E., Joannopoulos, J. D. *Phys. Rev. B*, **41**, 1227 (1990).
4. Monkhorst, H. J., Pack, J. *Phys. Rev. B*, **13**, 5188 (1976).