

**Metal doped black In₂O₃ for atmospheric pressure CO₂ photothermal reduction
with high efficiency and selectivity**

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DFT calculations

Spin-polarized DFT calculations were performed using the Vienna ab initio simulation package (VASP).^{1,2} The generalized gradient approximation proposed by Perdew, Burke, and Ernzerhof (GGA-PBE) is selected for the exchange-correlation potential.³ The pseudo-potential was described by the projector-augmented-wave (PAW) method.⁴ To accurately describe the dispersion interaction, we use DFT-D3 method with Becke-Jonson damping for dispersion correction.⁵ The geometry optimization was performed until the Hellmann–Feynman force on each atom is smaller than 0.02 eV·Å⁻¹. The energy criterion was set to 10⁻⁴ eV in the iterative solution of the Kohn-Sham equation. The Brillouin zone was sampled with 2×2×1 Monkhorst-Pack k-point mesh, and a Gaussian smearing of 0.05 eV was applied to speed up electronic convergence. Based on a computational hydrogen electrode (CHE) model proposed by Nørskov and co-workers,^{6,7} the Gibbs reaction free energy (ΔG) for CO₂ reduction was defined as,

$$\Delta G = \Delta E + \Delta ZPE - T\Delta S$$

where ΔE is the change of electronic energy, ΔZPE is the change of zero point energy, T is the system temperature (298.15 K), ΔS is the change of entropy, respectively. Under the potential of 0 V vs. RHE, the CHE method relates the chemical of proton-

electron pairs ($H^+ + e^-$) as $1/2 H_2$ (g). A vacuum height of 15 Å along the vertical direction was selected to avoid the unwanted interaction between the slab and its period images.

The dimension of the optimized cubic In_2O_3 model consist of 72 O atoms and 48 In atoms, and the $Cu-In_2O_{3-x}$ model consist of 65 O atoms, 48 In atoms and 3 Cu atoms. distributed in three In-O-In tri-layers. In the calculation, the oxygen vacancy near the Cu atom is used as the active site for the $Cu-In_2O_{3-x}$ system, and In is used as the active site for the In_2O_3 system.

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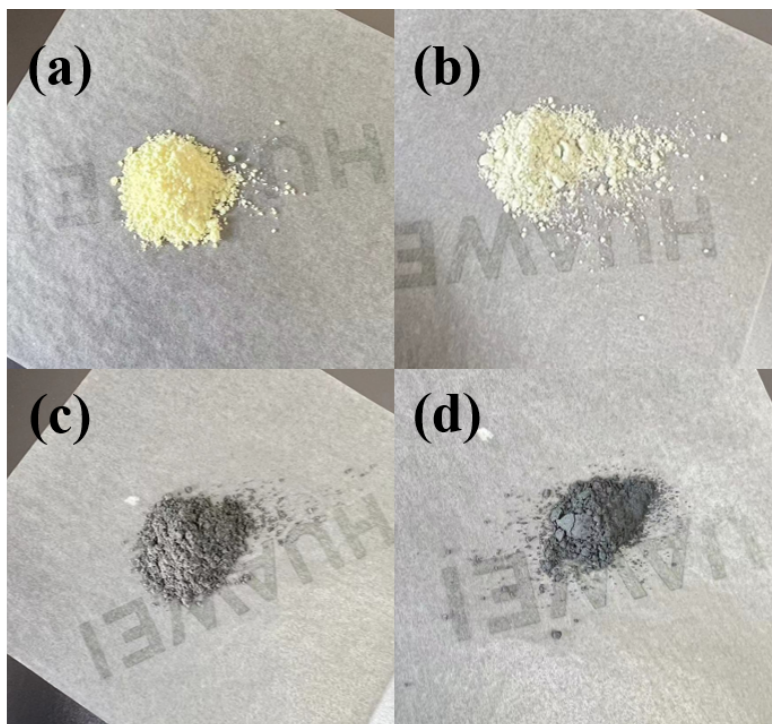


Fig. S1 Digital pictures of $\text{In}_2\text{O}_{3-x}$ treated with H_2 at (a) 25°C , (b) 200°C , (c) 300°C and (d) 400°C .

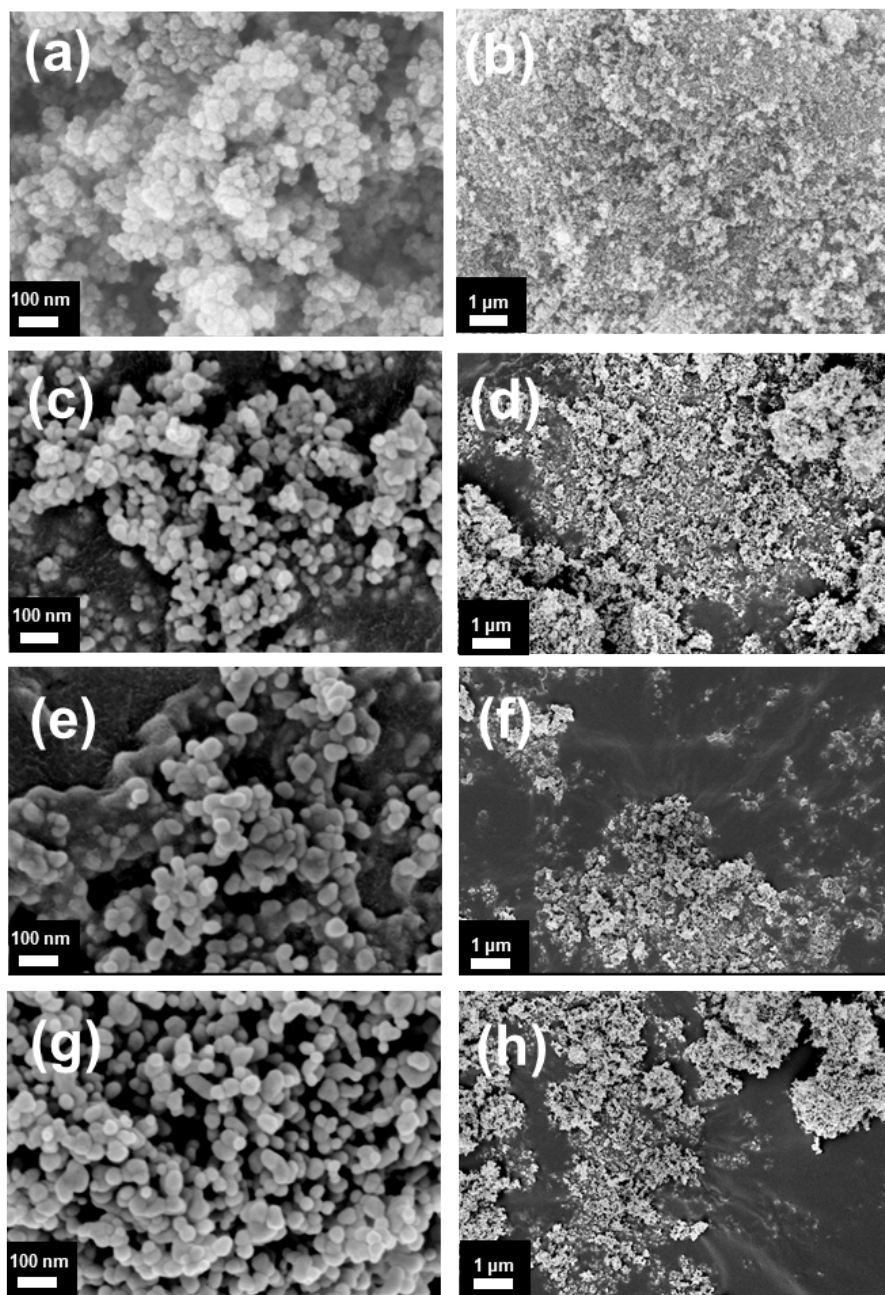


Fig. S2 SEM images of $\text{In}_2\text{O}_{3-x}$ treated with H_2 at (a-b) 25°C, (c-d) 200°C, (e-f) 300°C and (g-h) 400°C.

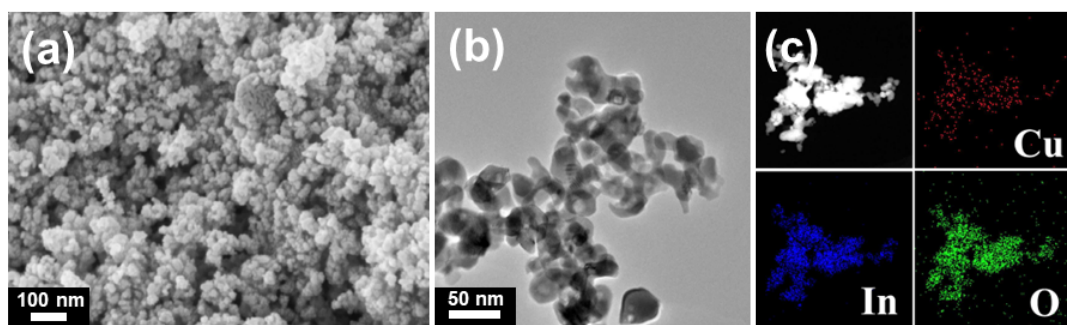


Fig. S3 (a) SEM image of $\text{Cu-In}_2\text{O}_{3-x}$. (b) and (c) are TEM and the corresponding mapping images of $\text{Cu-In}_2\text{O}_{3-x}$.

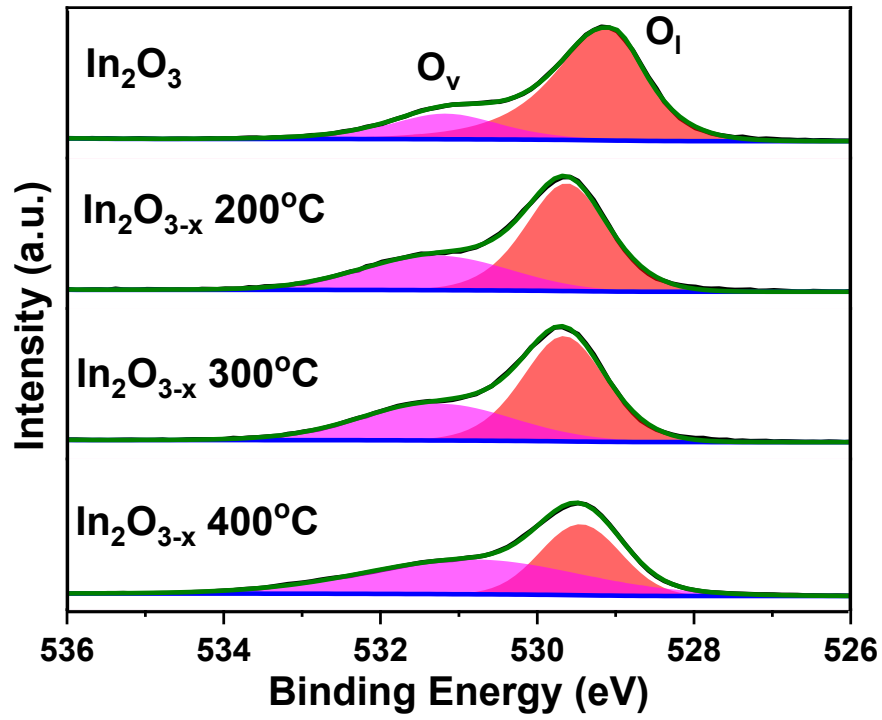


Fig. S4 XPS spectra of O 1s of $\text{In}_2\text{O}_{3-x}$ treated with H_2 at different temperatures.

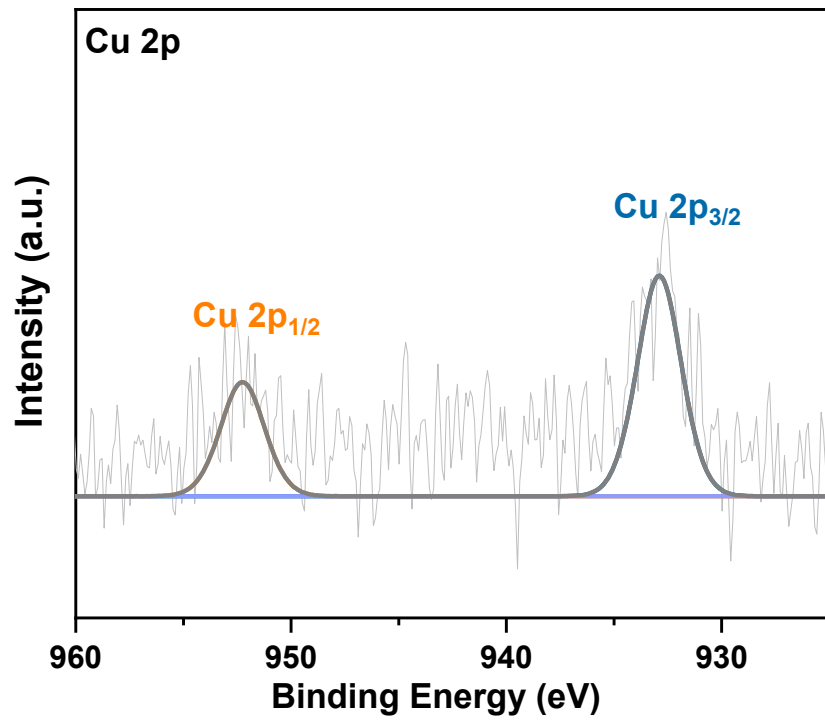


Fig. S5 XPS spectra of Cu 2p of Cu-In₂O_{3-x}.

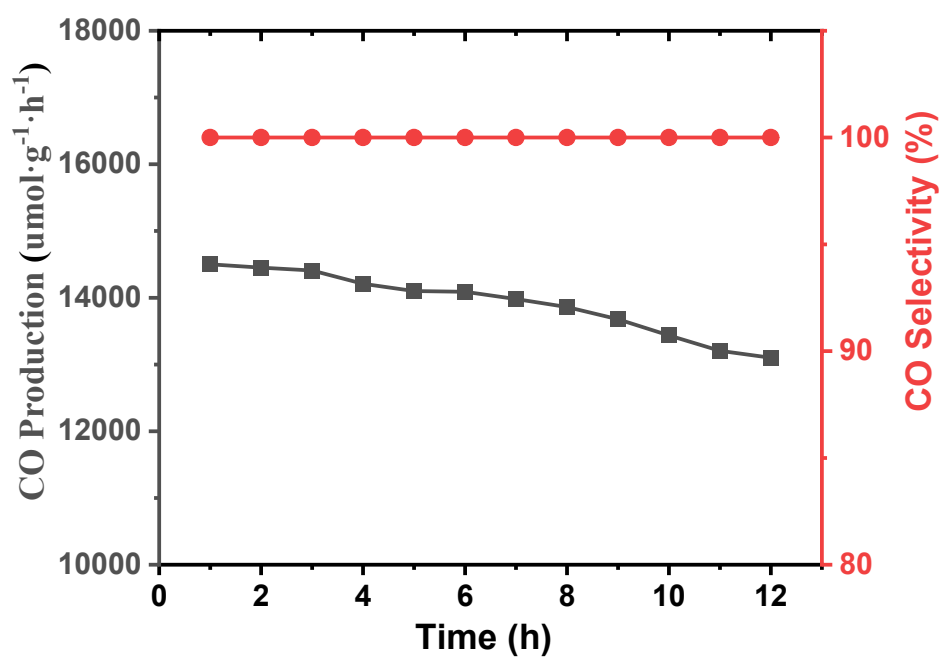


Fig. S6 CO yield and selectivity of Cu-In₂O_{3-x} at 300°C for 12 h.

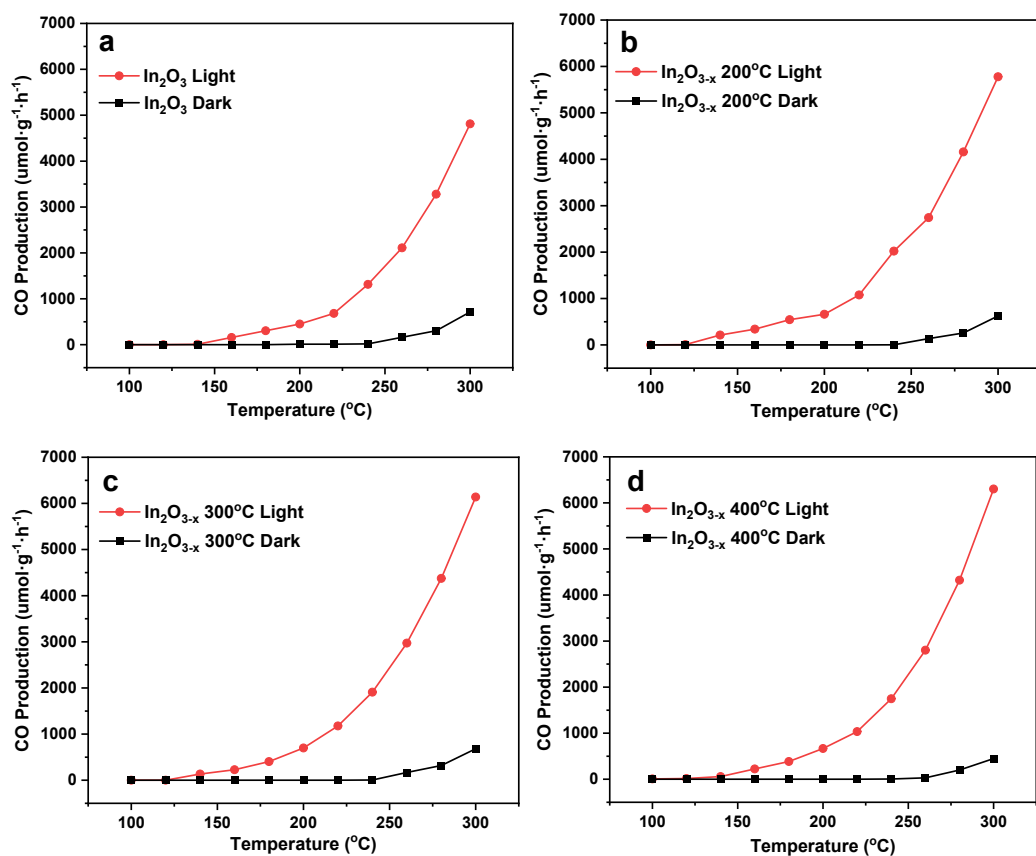


Fig. S7 Comparison of photothermal and thermal catalytic activities of $\text{In}_2\text{O}_{3-x}$ treated with H_2 at (a) 25°C, (b) 200°C, (c) 300°C, (d) 400°C.

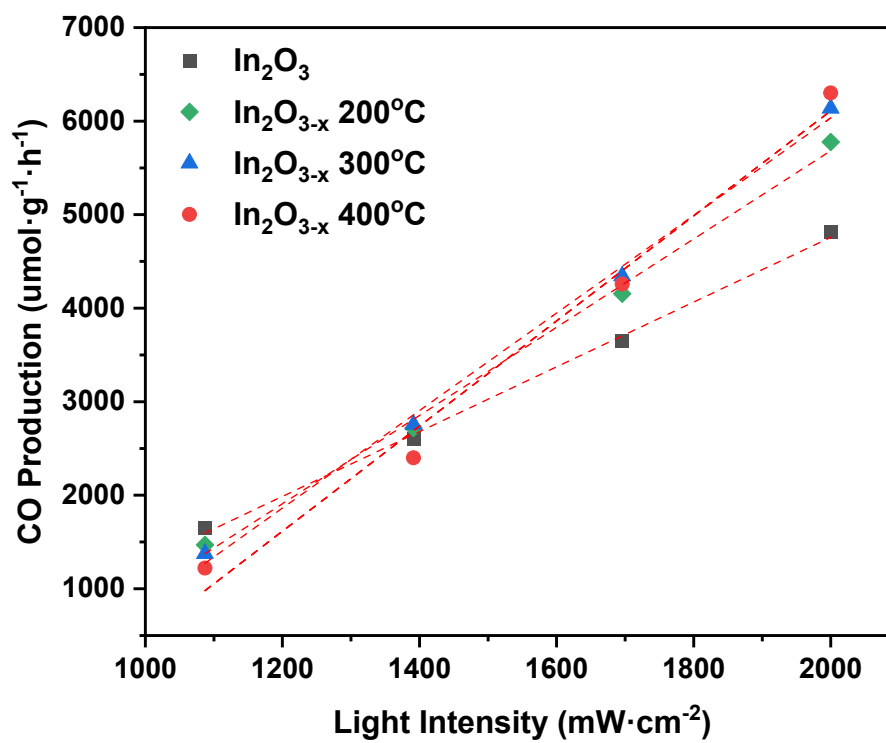


Fig. S8 Photothermal catalytic performance of In₂O_{3-x} treated with H₂ at different temperatures at reaction temperature of 300°C.

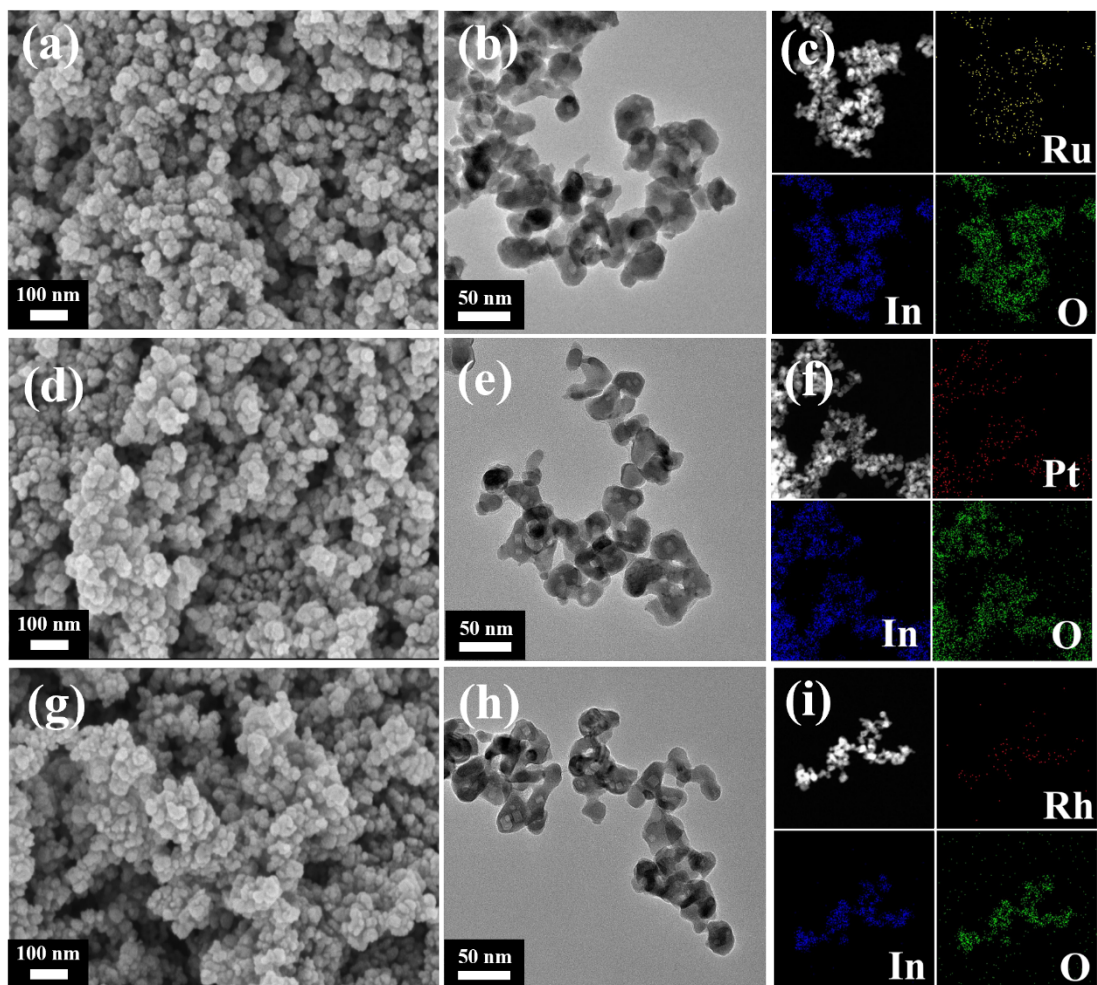


Fig. S9 (a) SEM image of Ru-In₂O_{3-x}, (b) and (c) are TEM and the corresponding mapping images. (d) SEM image of Pt-In₂O_{3-x}, (e) and (f) are TEM and the corresponding mapping images. (g) SEM image of Rh-In₂O_{3-x}, (h) and (i) are TEM and the corresponding mapping images.

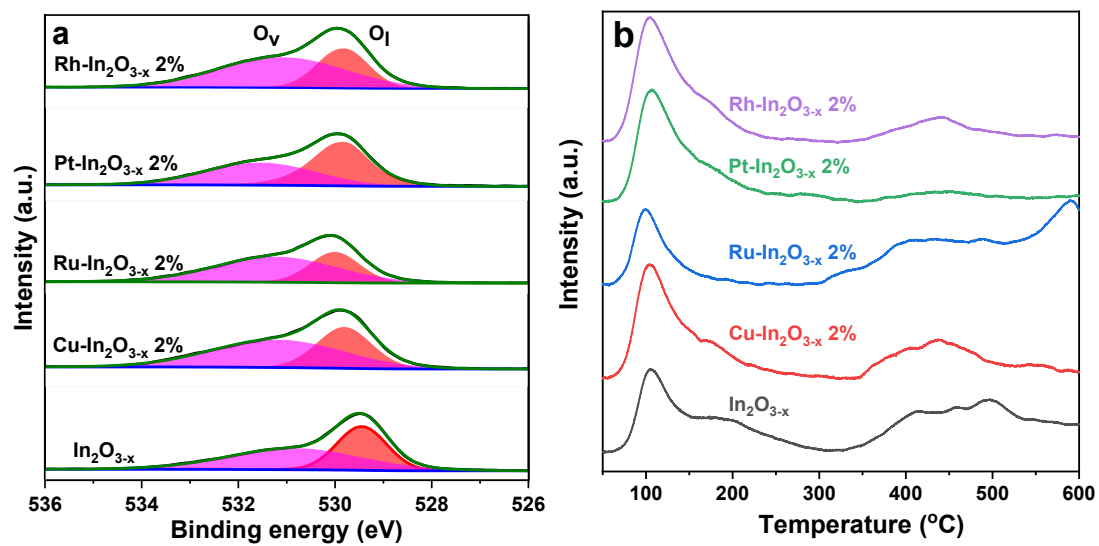


Fig. S10 (a) XPS spectra of O 1s of In₂O_{3-x} doped with different metals. (b) CO₂-TPD spectra of different metal doped In₂O_{3-x}.

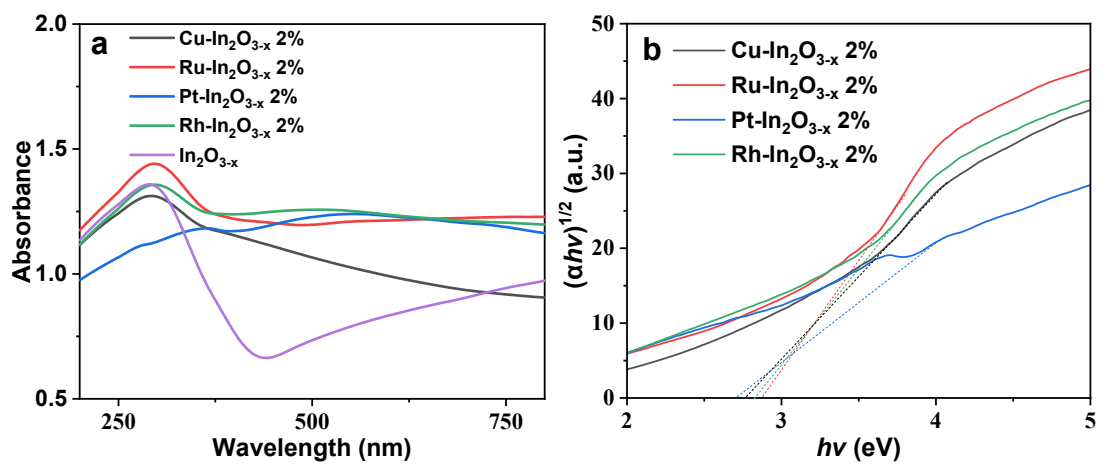


Fig. S11 UV-visible diffuse reflectance spectrums (a) and band gap (b) of different metal doped $\text{In}_2\text{O}_{3-x}$.

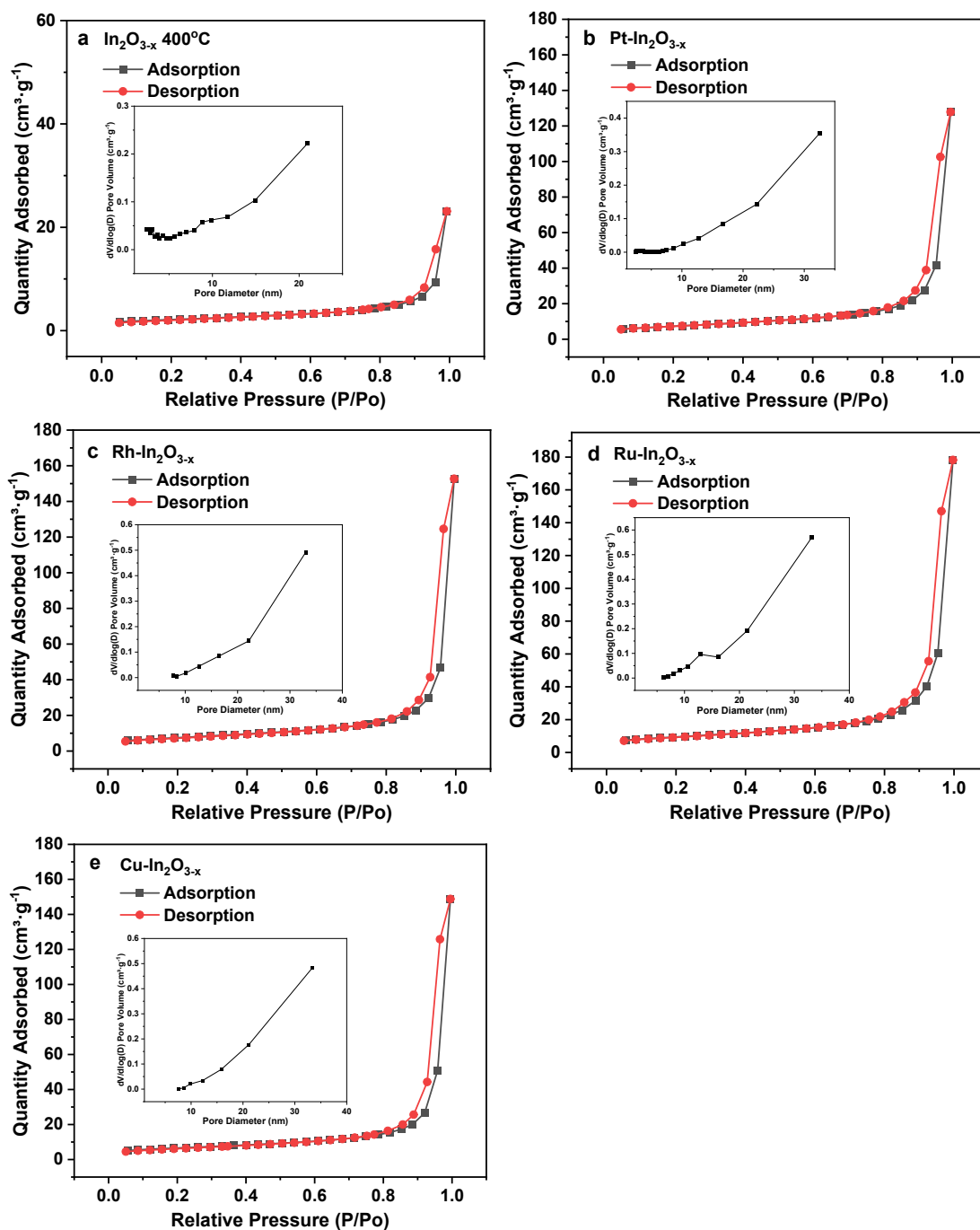


Fig. S12 N_2 adsorption-desorption curves of different metal doped $\text{In}_2\text{O}_{3-x}$.

Table S1 Specific surface area, pore characteristics and loading capacity of catalysts.

Samples	S _{BET} (m ² /g)	Pore volume (cm ³ /g)	Pore diameter (nm)	Loading (%)
In ₂ O _{3-x} 400°C	7.31	0.020	11.52	0
Cu-In ₂ O _{3-x}	23.75	0.230	38.76	2.06
Ru-In ₂ O _{3-x}	33.72	0.178	32.71	1.97
Pt-In ₂ O _{3-x}	26.06	0.198	30.36	1.99
Rh-In ₂ O _{3-x}	26.82	0.236	35.23	2.09