Supporting Information

UV-Laser-Induced Oxygen Vacancy Engineering of $In(OH)_3$ for Boosted CO_2 Photoreduction

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Sample characterization: The crystal structure of as-prepared samples were characterized by X-ray diffractometer (XRD) (Rigaku Ultima III, Japan) using Cu-Kα radiation (λ = 0.15406 nm) at 40 kV and 40mA with a scan rate of 5° min^{-1}).

The morphology was taken on scanning electron microscope (SEM, Zeiss Gemini 500) and transmission electron microscope (TEM, FEI Tecnai F20).

XPS measurement was performed on PHI-5702 multi-functional X-ray photoelectron spectrometer and standardizing according to the binding energy of the adventitious C 1s peak at 284.8 eV, which was used to inspect the chemical states.

The PL (PicoHarp300) were employed to detecte the PL spectra.

Electron paramagnetic resonance (EPR) spectra were recorded on a JEOL FA-200 EPR spectrometer at room temperature.

UV–vis spectra were measured on a PerkinElmer Lambda750 instrument at wavelengths of 200–800 nm by using $BaSO_4$ as a reference.

Photoelectrochemical measurements were performed in an electrochemistry workstation (CHI 660, CH Instrument, Austin, TX) with a three-electrode system using a three-compartment glass cell. Platinum electrode and Ag/AgCl electrode were used as the counter electrode and the reference electrode, respectively. A sample coated on ITO glass served as the working electrode. The experiments were operated at room temperature with Na_2SO_4 solution (0.1 $mol \cdot L^{-1}$) as electrolyte. A 300 W Xe lamp was used as the light source.

The Fourier transform infrared (FT-IR) spectra were recorded with Thermo Nicolet Nexus using the KBr disk method.

Photocatalysis testing: Photocatalytic reduction of CO_2 is a gas phase reaction. The reaction was carried out in a 170 mL stainless steel tank using a 300 W xenon lamp as the light source. 2 mg of the sample was evenly dispersed on a reactor with an area of about 4.2 cm^2, and 0.2 mL of deionized water was injected into the reaction system as a reducing agent. Before the irradiation, the reaction device was vacuum-treated several times, and then high-purity CO_2 gas (purity of 99.999%) was injected into the reaction device to reach 1.2 times the chamber pressure, and the temperature was raised to 180°C. During the photocatalytic reaction, about 5ml of gas was injected into the gas

chromatograph (Agilent-8890, USA) from the reaction chamber every 1h to analyze the photocatalytic CO_2 reduction products of the material.

The laser-treated sample exhibits not only a higher total CO_2 adsorption capacity but also a significantly higher desorption amount compared to the pristine sample. Specifically, under the same partial pressure conditions, the treated sample shows a greater CO_2 uptake, while its desorption branch also remains at a higher level, indicating that its surface not only exposes more active adsorption sites but also demonstrates a stronger CO_2 desorption capability.

The organic solvents were completely removed by repeated washing prior to the catalytic test. Nevertheless, to rigorously evaluate the potential impact of any residual organic solvents, we conducted two control experiments:

(1) Without $In(OH)_3$-L (only organic solvent and CO_2 reaction atmosphere) - no CO was detected, indicating that the organic solvent does not participate in the reaction.

(2) Without CO_2 reaction atmosphere (only $In(OH)_3$-L) - no CO was detected either, confirming that the carbon source of the produced CO originates entirely from CO_2.

Table S1. The band gap, the position of conduction band and valence band of $In(OH)_3$ and $In(OH)_3$-L

Catalysts	Band gap /(eV)	Defect energy /(eV)	$E_{FB}/(V\ vs.\ N$	$E_{CB}/(V\ vs.\ N$	$E_{VB}/(V\ vs.\ N$	$E_{VB-defect}/($
$In(OH)_3$	5.24		-0.85	-1.05	4.19	
$In(OH)_3$-L	4.62	2.73	-1.16	-1.36	3.26	0.53

Table S2. Performance and selectivity comparison of photocatalytic CO_2 reduction with other Indium-based material photocatalysts from previous reported works.

Catalyst	Light	Major product production	Ref.
$In(OH)_3$-L	300 W Xe lamp	CO (138.47μmol g^{-1}) Selectivity≥ 96%	This work
La–$In(OH)_3$	300 W Xe lamp	CO (56.56μmol g^{-1}) Selectivity~61.97%	1
ZIS/BC	300 W Xe lamp 320~780 nm	CO (20.7μmol g^{-1})	2
In_2O_3/BiOCl	300 W Xe lamp λ ≥ 320 nm	CO (96.11μmol g^{-1}) Selectivity≥96.7 %	3
$ZnIn_2S_4$/Pt	300 W Xe lamp	CO (14.8μmol g^{-1}) Selectivity~85%	4
$Cs_3Bi_2I_9/In_2S_3$	300 W Xe lamp	CO (10.4μmol g^{-1})	5
sulfur-doped $In(OH)_3$	300 W Xe lamp	CH_4(2.75μmol g^{-1}) Selectivity~ 80.75%	6
WO_3/In_2O_3	300 W Xe lamp	CH_4(5.4μmol g^{-1}) Selectivity~53.7%	7
In_2O_3/BiOI	300 W Xe lamp	CO (11.98μmol g^{-1})	8
Cu-doped In_2O_3	300 W Xe lamp with a 420 nm cut-off filter	CO (45.5μmol g^{-1}) Selectivity~100%	9
In_2S_3	300 W Xe lamp	CO (18.3μmol g^{-1})	10
rh/c-In_2O_3	300 W Xe lamp λ > 320 nm	CO (29.19μmol g^{-1}) Selectivity~94.47 %	11

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