

## Supplementary material

### **In-situ fabrication of MIL-68(In)@ZnIn<sub>2</sub>S<sub>4</sub> heterojunction for enhanced photocatalytic hydrogen production**

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## 1. Characterization

The crystal structure of photocatalysts was analyzed by X-ray diffraction (XRD, Rigaku Ultima IV, Japan) using Cu K $\alpha$  radiation (40 kV, 40 mA). The microscopic morphology was observed by field-emission scanning electron microscope (FE-SEM, SUPRA 55, Zeiss) and transmission electron microscope (TEM, JEM-2200FS, JEOL). Energy-dispersive X-ray spectroscopy (EDS) mapping was also obtained by TEM. The X-ray photoelectron spectra (XPS) were determined by an AXIS ULTRA DLD spectrometer using a monochromatic Al K $\alpha$  radiation ( $h\nu = 1486.6$  eV). The texture properties of samples were characterized by Brunauer-Emmett-Teller (BET, ASAP 2460). The Ultraviolet-visible diffuse reflectance spectra (UV-vis DRS) were measured with Shimadzu UV-2550. The steady-state photoluminescence (PL) spectra and time-resolved photoluminescence (TRPL) decay plots were implemented on the spectrophotometer (FLS980) with an excitation wavelength of 314 nm. A typical three-electrode cell using the CHI660E electrochemical workstation was employed to determine the photoelectrochemical performance. The photocatalysts (5 mg) were dispersed in an ethanol solution containing 10 vol% Nafion reagents. The mixed solution was uniformly deposited on a 1 cm  $\times$  1 cm FTO conductive glass as a working electrode, while the Pt sheets and Ag/AgCl electrodes were used as counter and reference electrodes, respectively, and 0.5 M Na<sub>2</sub>SO<sub>4</sub> aqueous solution was used as the electrolyte. The electron paramagnetic resonance (EPR) characterization: Endor spectrometer (JES-FA300, JEOL) was used for the characterization of EPR with 300 W Xenon lamp and a 420 nm cutoff filter at room temperature. For the test of  $\cdot\text{O}_2^-$ , 5 mg sample was dispersed into methanol (1 mL). Then, 5,5-dimethyl-1-pyrroline N-oxide (DMPO) was added to the mixture. Under light irradiation, the signals at 0 and 10 min were

collected. For the test of  $h^+$ , 5 mg sample was dispersed into acetonitrile (1 mL), and then 2,2,6,6-tetramethylpiperidinoxy (TEMPO) was added into the mixture. Under light irradiation, the signals at 0 min and 10 min were collected.

## 2. Tables and Figures

Table S1. The AQEs of MIL-68(In)-20@ZIS at different wavelengths.

<b>Wavelength (nm)</b>	<b>400</b>	<b>420</b>	<b>450</b>	<b>500</b>	<b>550</b>
<b>AQE (%)</b>	0.702	0.44	0.22	0.019	0.002

Table S2. Exponential decay-fitted parameters of fluorescence lifetimes for ZIS and MIL-68(In)-20@ZIS.

<b>Sample</b>	<b><math>\tau_1</math> (ns)</b>	<b><math>A_1</math> (%)</b>	<b><math>\tau_2</math> (ns)</b>	<b><math>A_2</math> (%)</b>	<b><math>\tau_A</math> (ns)</b>
<b>ZIS</b>	0.63	30.10	2.20	69.90	2.03
<b>MIL-68(In)-20@ZIS</b>	1.48	63.94	4.97	36.06	3.76

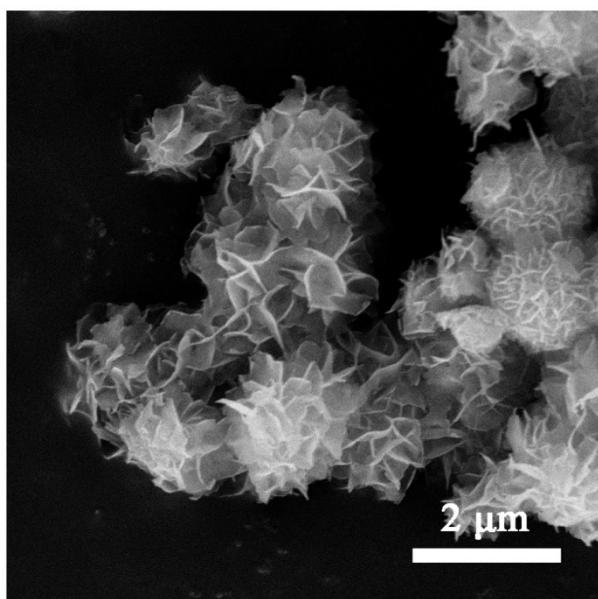


Fig. S1. The SEM image of pure ZIS.

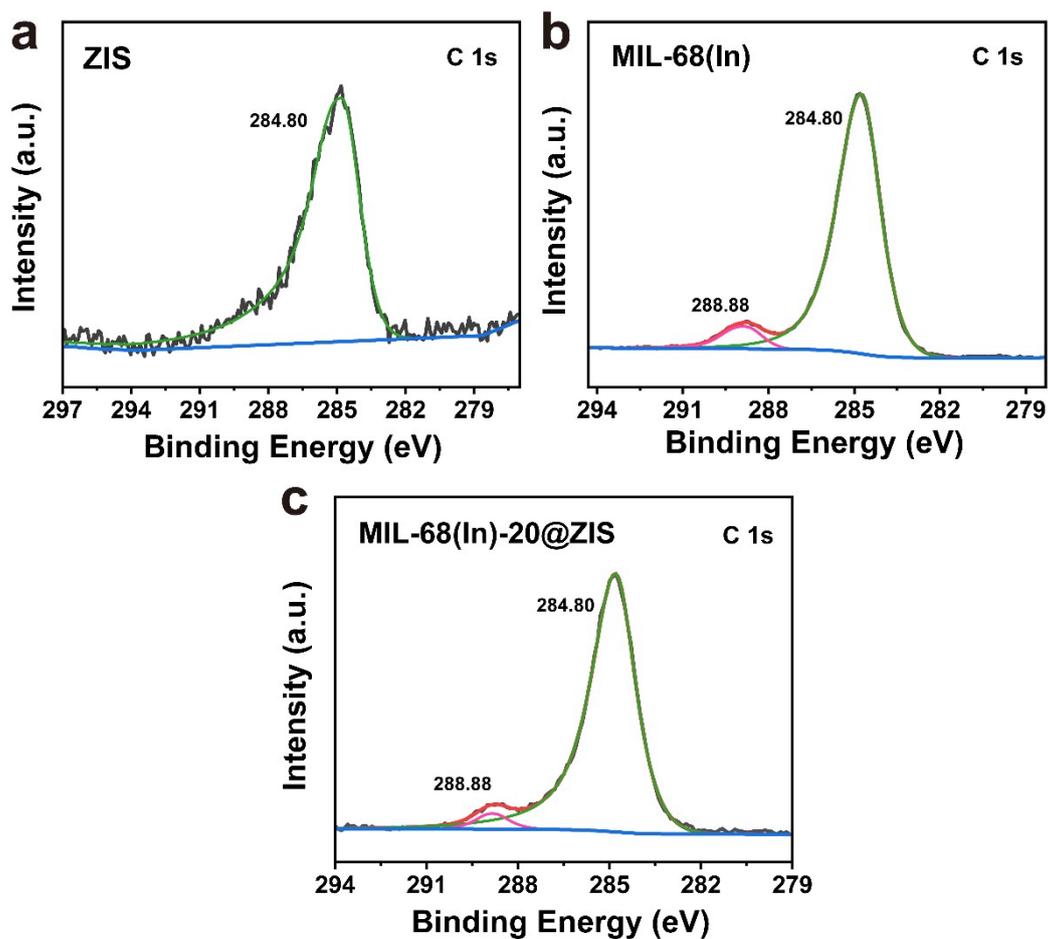


Fig. S2. The high-resolution XPS spectra of C 1s for ZIS, MIL-68(In) and MIL-68(In)-20@ZIS.

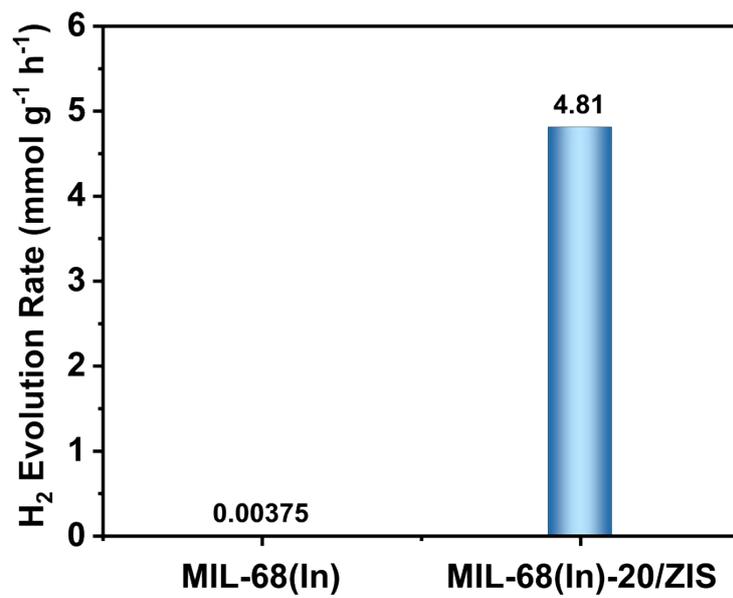


Fig. S3. The photocatalytic hydrogen evolution rates of MIL-68(In) and MIL-68(In)-20/ZIS.

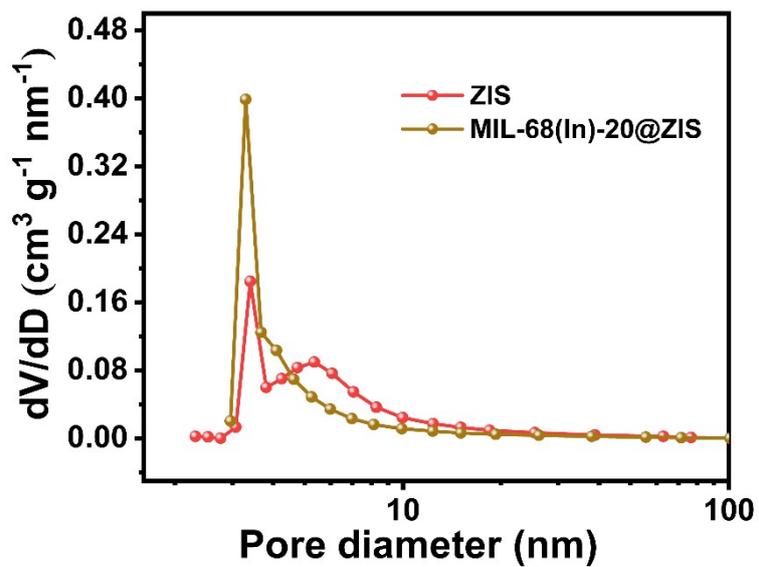


Fig. S4. The pore size distribution of ZIS and MIL-68(In)-20@ZIS.

Table S3. Textural properties of samples.

Samples	$S_{\text{BET}}$	Pore volume	Average pore size
	( $\text{m}^2 \text{g}^{-1}$ )	( $\text{cm}^3 \text{g}^{-1}$ )	(nm)
ZIS	209.82	0.7588	12.54
MIL-68(In)-20@ZIS	210.58	0.6129	10.18