Supporting Information

Synergistic Advantages of In-MOF/Bi₂MoO₆ Composite in Photocatalytic CO₂ Reduction: Enhanced Light Absorption, Charge Separation and Reactivity

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1. Experimental

2.1. Materials

The bismuth nitrate pentahydrate , sodium molybdate, N, N' -dimethylformamide (DMF), Terephthalic acid (H₂BDC) was purchased from Shanghai Macklin Biochemical Co., Ltd. Deionized (DI) water was used in all the experiments. All reagents were used directly as received without further purification.

2.2. Preparation of Bi₂MoO₆

In a typical solvothermic synthesis process, 2 mmol of $Bi(NO_3)_3 \cdot 5H_2O$ and 1 mmol of Na_2MoO_4 are slowly added to 30 mL of deionized water and stirred for 1 h to completely dissolve. The solution was then transferred into a Teflon lined reactor and kept at 160 °C for 12 h. Finally, anhydrous ethanol and deionized water were washed repeatedly to remove the unreacted ions. The yellow powder, Bi₂MoO₆, was obtained by vacuum drying overnight at 60 °C.

2.3. Preparation of In-MOF/Bi₂MoO₆

3 mmol In(NO3)₃·5H₂O was added into 18 mL DMF and dissolved by stirring to form liquid A. A certain amount of Bi₂MoO₆ was added into liquid A for ultrasonic dispersion. 3.6 mmol H₂BDC was added into 18 mL DMF and dissolved by stirring to form B solution. After that, the two completely dissolved solutions were mixed together, continued to stir for 10 min, and transferred to a Teflon-lined reactor at 100 °C for 24 h. Centrifuge and wash with DMF and ethanol. After drying, the In-MOF/Bi₂MoO₆ complex is obtained, denoted as IB-Y (Y is the mass proportion of Bi₂MoO₆). Pure In-MOF was prepared without adding Bi₂MoO₆.

2.4. Material characterization

The morphology and structure of all films were characterized by scanning electron microscopy (SEM, ZEISS Sigma 500, Germany) and energy dispersive spectroscopy (EDS). Energy dispersive spectroscopy (EDS) and transmission electron microscopy (TEM, FEI-Tecnai G2, USA) at 200 kV. In the 2θ range of 10°-90°, the crystal structure was characterized by Cu Kα radiation and X-ray powder diffractometer (XRD, Bruker D8 Advance). The diffuse reflectance spectrum was detected on an UV-visible spectrophotometer (UV-2600, Shimazu, Japan). The surface chemical states were analyzed by X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha, USA). Time-resolved photoluminescence (TRPL) spectroscopy were obtained by fluorescence spectrophotometer (FLS-980). The test range of photoluminescence (PL) spectroscopy is controlled between 330 nm-500 nm. All electrochemical tests are performed on an electrochemical workstation (CHI-760), using a three-electrode system. For samples with an

effective area of 1 cm *1 cm, platinum sheet and Ag/AgCl electrodes are used as opposite and reference electrodes, respectively. 0.5 M sodium sulfate solution was used as the supporting electrolyte. Electrochemical impedance spectroscopy (EIS) was performed the measured frequency range was from 0.1 to 100 kHz. Mott-schottky test frequency is selected as1000 Hz, 2000 Hz and 3000 Hz. The transient photocurrent response is tested in a cycle of 50 s on/off light within 400 s.

2.5. Photocatalytic CO₂ reduction test

The 50 mg photocatalytic powder is evenly dispersed and placed on a circular tray. The whole system is in a customized quartz container (effective volume of about 250 mL). The sample was placed flat on a tray using a special quartz support. 1 mL of deionized water was placed at the bottom of the container in advance. In order to remove the dissolved gas contained in the ultrapure water to the maximum extent, vacuum operation was carried out. Then strict nitrogen operation was carried out. This stage was repeated three times, and after the last full of nitrogen, 1 mL of high-purity CO₂ (purity = 99.99%) was injected with a specific standard gas syringe, and stirring was started. Continue for 5 min to ensure that the gas in the reaction vessel is completely mixed evenly. The 300 W Xe lamp (CEL-HXF300, China) was used as the energy source of CO₂ reduction driven by optical drive. 1 mL of mixed gas was extracted from the reaction vessel every 1 h and injected into the gas chromatograph (HF-900, Shandong Hui Fen Instrument Co., LTD, China). The flame ionization detector (FID) was used for qualitative analysis and quantitative detection of gas products.



Fig. S1 TEM, HRTEM and EDS elemental mapping images of images of IB-30.



Fig. S2 Cyclic stability test of IB-30 complex under light.



Fig. S3 Comparison of XRD patterns of IB-30 composite catalyst before and after cyclic reaction.

Table. S1 The textural properties of the In-MOF, ${\rm Bi}_2{\rm MoO}_6$ and IB-30.

Material	S _{BET} (m²/g)	Pore Volume (cm ³ /g)	Average Pore Size (nm)
In-MOF	130.75	0.41	7.18
Bi ₂ MoO ₆	17.22	0.05	1.45
IB-30	83.08	0.38	5.36