Supporting Information

Lattice-matched MOF-on-MOF heterostructure for robust photocatalytic nitrogen fixation

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Experimental section

2.1 Chemicals and synthesis

Chemicals

Indium(III) trinitrate hydrate ($In(NO_3)_3·xH_2O$, 99.9%) was purchased from Tianjin Xiensi Biochemical Technology Co., Ltd. Sodium acetate (CH_3COONa, 99%) and H_2BDC (99%) were obtained from Aladdin Industrial Corporation. Cobalt(II) acetate tetrahydrate ($(CH_3COO)_2Co·4H2O$, 99%) was supplied by Chengdu Kelong Chemical Reagent Co., Ltd. 2,3,6,7,10,11-Hexahydroxytriphenylene (HHTP, 97%) was purchased from Shanghai Dibai Biotechnology Co., Ltd.; N, N-dimethylformamide (DMF) was obtained from Tianjin Fuyu Fine Chemical Co., Ltd. The Nash reagent was supplied by Jinan Longcheng Biotechnology Co.

Synthesis

The synthesis of MIL-68(In) was conducted as follows: Firstly, 2 mmol of $In(NO_3)_3·xH_2O$ and 2 mmol of BDC were dissolved in 20 mL of DMF, followed by stirring for 10 minutes and sonication for 5 minutes. Subsequently, 100 µL of 0.5 M CH_3COONa solution was added, and the mixture was further sonicated for 10 minutes. Finally, the resulting mixture was transferred into a capped glass bottle and heated in a preheated oil bath at 100°C for 30 minutes. Upon completion of the reaction, the product was washed thoroughly and dried in an oven at 90°C for 8 hours to obtain MIL-68(In).

The Co-HHTP/MIL-68(In) heterojunctions were fabricated via *in-situ* growth of Co-HHTP particles on the surface of MIL-68(In) under specific temperature and time conditions. Typically, 100 mg of MIL-68(In) was dispersed in 80 mL of deionized water and sonicated for 10 minutes to form a homogeneous suspension. Then, different masses of $(CH_3COO)_2Co·4H_2O$ (60 mg, 120 mg, 240 mg) and HHTP (70 mg, 140 mg, 280 mg) were added sequentially, and the mixture was sonicated for another 30 minutes. Finally, the suspension was transferred into a 250 mL round-bottom flask and maintained in an oil bath at 55 °C for 3 hours. After the reaction, the composite product was washed and dried in an oven at 80 °C for 9 hours. The as-prepared composites were termed **S1**, **S2**, and **S3** based on the increasing content of Co-HHTP in the MIL-68(In) matrix, with Co-HHTP to MIL-68(In) feeding molar ratios of approximately 2:3, 4:3, and 6:3, respectively. For comparison, pure Co-HHTP was also synthesized following the same procedure without the addition of MIL-68(In).

2.2 Characterization

Transmission electron microscopy (TEM) analysis was performed on a JEOL-2100F microscope with an accelerating voltage of 200 kV. Powder X-ray diffraction patterns were recorded on the D/max-2500PC (Rigaku, Japan) diffractometer equipped with Cu-$K\alpha$ radiation. The X-ray photoelectron data were collected using Thermo ESCALAB 250 XI (USA) with filtered Al-$K\alpha$ radiation at a voltage of 1486.6 TeV and calibrated with the C 1s binding energy of 284.8 eV. The UV-vis adsorption spectra and UV–vis DRS spectra were collected by UV-2600i ultraviolet-visible spectrophotometer of SHIMADZU (Japan) to analyze the band gap of the photocatalysts and products during the NRR process. The Mott-Schottky plots, electrochemical impedance spectroscopy (EIS), and photocurrent data were collected on a CHI 660E electrochemical workstation (Chenhua Shanghai, China). The photoluminescence spectra were measured using a fluorescence spectrophotometer (Edinburgh Instrument Ltd, FLS1000).

2.3. Photocatalytic N_2 fixation performance

The N_2 fixation performance of the catalyst was evaluated in a photocatalytic system without any sacrificial agents or cocatalysts. The detailed procedure was as follows: 20 mg of the catalyst was dispersed in a glass reactor containing 50 mL of ultrapure water, followed by stirring under sonication for 15 minutes. Subsequently, the reactor was sealed and purged with high-purity N_2 (99.999%) for 30 minutes. After that, the solution was irradiated using a 300 W xenon lamp equipped with a full-spectrum filter, with the N_2 outlet kept open throughout the process. Finally, the reaction solution was irradiated again using the xenon lamp. After each hour of reaction, 5 mL of the reaction mixture was sampled, centrifuged to obtain a clear supernatant, and subjected to NH_4^+ concentration detection via the Nash reagent method.

2.4. DFT calculations

The DFT calculations were carried out with the CP2K/Quickstep package at the density functional theory (DFT) level using the Perdew–Burke–Ernzerhof (PBE) functional.[1-3] A double-zeta polarized (DZVP) MOLOPT basis set and a plane-wave cutoff of 500 Ry were employed for all atomic species. Dispersion interactions were included via the DFT-D3 correction scheme.[4, 5] The input file preparation and result analysis were carried out using the Multiwfn program.[6]

Table S1 Representative MOF-based photocatalysts toward NRR.

Catalyst	**Light source**	**NH_3 production rate/μmol g^{-1} h^{-1}**	**Reference**
MIL-101(Fe)	Full spectrum	50.4	7

MOF-76(Ce)	Full spectrum	34.0	8
NH2-MIL-125(Ti)	≥400 nm	12.3	9
NJUZ-1	Full spectrum	140	10
Au@PCN-221(Fe)	Full spectrum	129.2	11
UiO-66-defect	Full spectrum	16.3	12
$W_{18}O_{49}$/UiO-66	Full spectrum	40.1	13
Al-PMOF(Fe)	Full spectrum	7.5	14
MIL-88A($Fe_{0.95}Cu_{0.05}$)	≥400 nm	68.6	15
MIL-68(In)@Co-HHTP	Full spectrum	76.1	This work

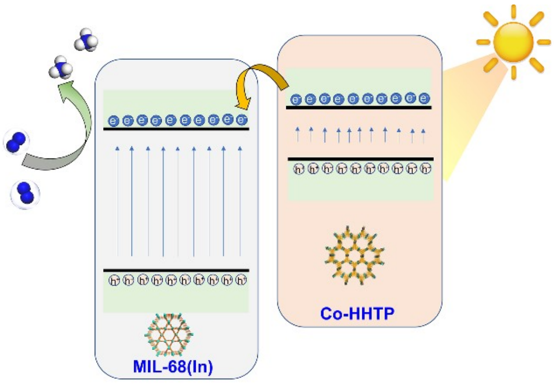

Figure S1 Proposed photocatalytic mechanism of the MIL-68@Co-HHTP heterostructure.

Reference

1. M. Ernzerhof and G. E. Scuseria, *J. Chem. Phys.*, 1999, **110**, 5029-5036.
2. J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865.
3. T. D. Kühne, M. Iannuzzi, M. Del Ben, V. V. Rybkin, P. Seewald, F. Stein, T. Laino, R. Z. Khaliullin, O. Schütt and F. Schiffmann, J. Chem. Phys., 2020, **152**.
4. S. Grimme, S. Ehrlich and L. Goerigk, *J. Comput. Chem.*, 2011, **32**, 1456-1465.
5. S. Grimme, A. Hansen, J. G. Brandenburg and C. Bannwarth, *Chem. Rev.*, 2016, **116**, 5105-5154.
6. T. Lu and F. Chen, *J. Comput. Chem.*, 2012, **33**, 580-592.
7. G. Li, F. Li, J. Liu, C. Fan, *J. Solid State Chem.*, 2020, **285**, 121245.
8. C. Zhang, Y. Xu, C. Lv, X. Zhou, Y. Wang, W. Xing, Q. Meng, Y. Kong, G. Chen, *ACS Appl. Mater. Interfaces.,* 2019, 11, 29917-29923.

9. H. Huang, X. S. Wang, D. Philo, F. Ichihara, H. Song, Y. Li, D. Lie, T. Qiu, S. Wang, J. Ye, *Appl. Catal. B-Environ.*, 2020, **267**, 118686.
10. Y. Xiong, B. Li, Y. Gu, T. Yan, Z. Ni, S. Li, J. Zuo, J. Ma, Z. Jin, *Nat. Chem.*, 2023, **15**, 286-293.
11. Q. Dong, X. Li, Y. Duan, X. He, X. Liang, F. Yu, C. Wang, *Appl. Catal. B-Environ.*, 2025, 366, 125042.
12. G. Ren, J. Zhao, Z. Zhao, Z. Li, L. Wang, Z. Wang, C. Li, X. Meng, Angew. Chem. Int. Ed., 2024, 63, e202314408.
13. J. Zhao, X. Chen, Q. Chu, Z. Chen, X. Meng, Z. Li, *J. Alloy. Compd.* 2025, **1042**, 184014.
14. S. Shang, W. Xiong, C. Yang, B. Johannessen, R. Liu, H. Y. Hsu, Q. Gu, M. K. H. Leung, J. Shang, *ACS Nano*, 2021, **15**, 9670-9678.
15. R. Liu, Q. Chen, J. Qiu, C. Liu, J. Wu, J. C. Yu, L. Wu, *J. Colloid. Interf. Sci.*, 2025, **692**, 137504.