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Supplementary Information

The Critical Role of Isolated Ti^{3+} Sites in MIL-125 for Photocatalytic Nitrate Reduction: Performance Enhancement and Deactivation Mechanism

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Characterizations

The powder X-ray diffraction (XRD) patterns were recorded using a Rigaku SmartLab SE X-ray diffractometer with a Cu Kα X-ray source (λ = 1.5406 Å). Scanning electron microscopy (SEM) images were obtained with a Hitachi Regulus 8220 SEM, operating at 200-30 kV and a maximum current of 22 A during measurement. Transmission electron microscopy (TEM) was performed using a JEOL JEM-F200 microscope. UV-vis diffuse reflectance spectra (UV-Vis DRS) were collected on a PerkinElmer Lambda 1050+ spectrometer. Nitrogen adsorption-desorption isotherms were measured with a Micromeritics ASAP 2460 instrument, using the Brunauer–Emmett–Teller (BET) method. X-ray photoelectron spectroscopy (XPS) was performed using an ESCALAB Xi+ electron spectrometer (Thermo Fisher) equipped with a monochromatic X-ray source. Electron paramagnetic resonance (EPR) spectra were recorded using a Bruker EMXplus spectrometer. Mott-Schottky measurements of the samples were performed with a CHI 760E electrochemical workstation (Shanghai Chenhua Co., Ltd.), using a three-electrode setup and 0.2 M sodium sulfate as the electrolyte. Thermogravimetric analysis (TGA) profiles were recorded over a temperature range of 30-600 °C using a NETZSCH Thermal Analyzer (STA449 F3), with a heating rate of

5°/min in air flow.

Photocatalytic nitrate reduction to ammonia

Typically, 100 mg $NaNO_3$ was dissolved in 50 mL ultrapure water in a 100 mL quartz reactor. Then, 25 mg of catalyst was added to the above solution. The suspension was ultrasonically treated for 5 min before light irradiation by a 500 W Xenon Lamp (CEL-S500, Beijing China Education Au-light Co., Ltd.). The temperature of the reactant suspension was maintained at 25 °C during the experiment using a water cooling system. 5 mL of the reaction mixture was sampled from the reactor at intervals of 15 min, and the catalyst particles were removed using a syringe filter. The concentrations of NH_4^+ in the reactant liquids were measured by Nessler's reagent test using a UV-9000 UV-Vis spectrometer from Shanghai Metash Instruments Co., Ltd. The obtained sample after 1 h reaction was washed with distilled water (DI) and methanol for at least 3 times, respectively, to remove the residual nitrate. The obtained sample was dried in an oven at 60 °C. For the cycling test, 100 mg $NaNO_3$, 25 mg MIL-125 catalyst, and 50 mL ultrapure water were mixed in a 100 mL quartz reactor and reacted for 1 h under full-spectrum light irradiation by a 500W Xenon Lamp. Then, 5 mL reactant liquid was collected for the NH_4^+ test after each cycle, while the used catalysts were also collected and redispersed in fresh reactant containing 100 mg of $NaNO_3$ and 50 mL ultrapure water for the subsequent cycles. Five cycling reactions were performed, with each cycle lasting 1 h.

DFT calculations

All calculations were performed with periodic DFT using the Gaussian plane wave method implemented in CP2K's Quickstep module. The explorative studies of the catalysts structure were performed using the molecularly optimized basis set DZVP-MOLOPT-SR-GTH for each atom with a Goedecker-Teter-Hutter (GTH) pseudopotential. The calculations were conducted using the generalized gradient approximation and the Perdew-Burke-Ernzerhof (PBE) functional with DFT-D3 correction. An energy convergence for the self-consistent field (SCF) calculation was set to 3×10^{-6} Hartree. An energy cutoff of 400 Ry was used throughout the calculations. The different coordinator defect was crated via removing the BDF molecular in model. The input file was generated by Multiwfn.

The adsorption energies (E_{ads}) are calculated using the follow equation:

$$E_{ads} = E_{model+sub} - E_{model} - E_{sub}$$

where $E_{model+sub}$, E_{model}, and E_{sub} stand for the energy of adsorption configurations, the energy of

model, and the energy of adsorption molecular, respectively.

The NO_3RR process was calculated as fellow element step:

$$* + NO_3 \rightarrow *NO_3$$

$$*NO_3 + 2H^+ + 2e^- \rightarrow *NO_2 + H_2O$$

$$*NO_2 + 2H^+ + 2e^- \rightarrow *NO + H_2O$$

$$*NO + H^+ + e^- \rightarrow *NOH$$

$$*NOH + H^+ + e^- \rightarrow *N + H_2O$$

$$*N + H^+ + e^- \rightarrow *NH$$

$$*NH + H^+ + e^- \rightarrow *NH_2$$

$$*NH_2 + H^+ + e^- \rightarrow *NH_3$$

$$*NH_3 \rightarrow * + NH_3$$

Table S1. Comparison of the photocatalytic ammonia synthesis efficiency between MIL-125 in this work and recently reported photocatalysts.

Photocatalyst	**Light source**	**Sacrificial agent**	**Optimal ammonia synthesis rate (μmol g_{cat}^{-1} h^{-1})**	**Reference**
BaO_{NC}-TiO_2	300 W Xe lamp, full-spectrum	Ethylene glycol	3500	[1]
JRC-TIO-6	2 kW Xe lamp (λ >300 nm)	Formic acid	16	[2]
Ag_2O/P25	300 W Hg lamp (365 nm)	Formic acid	450	[3]
Ru/g-C_3N_4	300 W Xe lamp, full-spectrum	Formic acid	150	[4]
$V_{Cu\text{-}S}$ rich $CuIn_2S_4$	300 W Xe lamp	Ethylene glycol	975.9	[5]
CuO_x/TNS	300 W Xe lamp	Formic acid	6360	[6]
Ni/H_xWO_{3-y}	300 W Xe lamp, full-spectrum	Ethylene glycol	10500	[7]

Cu-NM-1.5	300 W Xe lamp, full-spectrum	Ethylene glycol	1929	[8]
NVCN475	300 W Xe lamp (λ >420 nm)	Formic acid	8.83	[9]
AgCu-CN	300 W Xe lamp (λ >420 nm)	Ethylene glycol	630.5	[10]
D-PDI	Not available	None	149.6	[11]
Pt SAs/$Ti_{0.87}O_2$ NSs	LED (275 nm)	None	ca. 35	[12]
Cu-TiO_2	2 kW Xe lamp, AM 1.5G	None	1.07	[13]
β-FeOOH(Cl_T)-OVs	2 kW Xe lamp (λ >300 nm)	None	9.5	[14]
Au_2-COF	Xe lamp (AM 1.5)	None	382.48	[15]
Ru/MoO_{3-x}	300 W Xe lamp	None	370	[16]
MIL-125	500 W Xe lamp, full-spectrum	None	738.3	This work

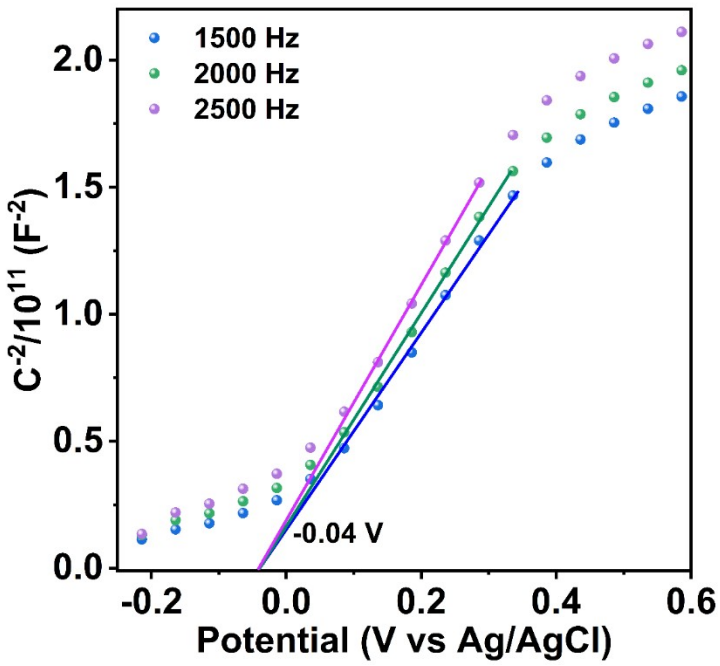

Figure S1. Mott-Schottky curves of MIL-125 after 1 h photocatalytic nitrate reduction reaction.

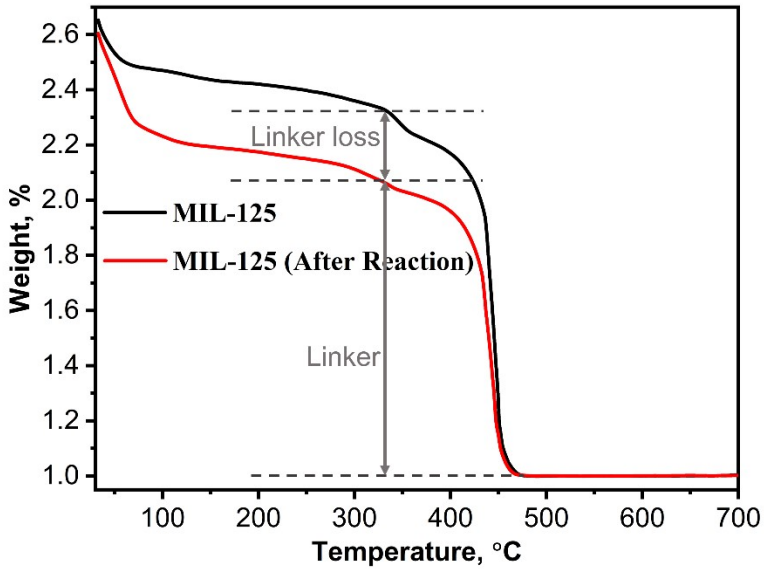

Figure S2. TGA curves of pristine MIL-125 and the MIL-125 after 1 h photocatalytic nitrate reduction reaction.

References

1. J. Li, R. Chen, J. Wang, Y. Zhou, G. Yang and F. Dong, *Nat. Commun.*, 2022, **13**, 1098.
2. H. Hirakawa, M. Hashimoto, Y. Shiraishi and T. Hirai, *ACS Catal.*, 2017, **7**, 3713-3720.
3. H.-T. Ren, S.-Y. Jia, J.-J. Zou, S.-H. Wu and X. Han, *Appl. Catal. B: Environ.*, 2015, **176-177**, 53-61.
4. D. Hao, J. Ren, Y. Wang, H. Arandiyan, M. Garbrecht, X. Bai, H. K. Shon, W. Wei and B.-J. Ni, *Energy Mater. Adv.*, 2021, **2021**, 9761263.
5. H. Liang, C. Ye, Y. Wu, J. Xiong, P. Zhang, X. Cao, G. Hao, W. Jiang and J. Di, *Appl. Catal. B: Environ. Energy*, 2025, **362**, 124776.
6. S. Shen, R. Chen, X. Li, J. Wang, S. Yu, J. Li and F. Dong, *Environ. Sci. Technol.*, 2024, **58**, 7653-7661.
7. Y. Wang, H. Yin, X. Zhao, Y. Qu, A. Zheng, H. Zhou, W. Fang and J. Li, *Appl. Catal. B: Environ.*, 2024, **341**, 123266.
8. Y. Zhao, J. Shen, J. Yuan, H. Mao, X. Cheng, Z. Xu and Z. Bian, *Nano Energy*, 2024, 109499.
9. I. Hong, H. S. Moon, B. J. Park, Y.-A. Chen, Y.-P. Chang, B. Song, D. Lee, Y. Yun, Y.-J. Hsu, J. W. Han and K. Yong, *Chem. Eng. J.*, 2024, **484**, 149506.
10. Z. Lian, D. Luo, J. Yang, Y. Yang, S. Tang, H. Li, D. Zhang and H. Li, *Angew. Chem. Int. Ed.*, 2026, **65**, e202516964.
11. H. Peng, Y. Liu, Y. Wang, M. Song, H. Song, P. Chen and S.-F. Yin, *ACS Catal.*, 2024, **14**, 2971-2980.
12. H. Jung, G. Cha, H. Kim, J. Will, X. Zhou, E. Spiecker, J. Breu and P. Schmuki, *J. Am. Chem. Soc.*, 2025, **147**, 9049-9055.
13. W. Hiramatsu, Y. Shiraishi, S. Ichikawa, S. Tanaka, Y. Kawada, C. Hiraiwa and T. Hirai, *J. Am. Chem. Soc.*, 2025, **147**, 1968-1979.
14. Y. Shiraishi, S. Akiyama, W. Hiramatsu, K. Adachi, S. Ichikawa and T. Hirai, *JACS Au*, 2024, **4**, 1863-1874.

15. X. Sun, J. Liu, Q. Li, C. Wang and B. Jiang, *Chin. J. Catal.*, 2025, **73**, 358-367.
16. L. Zhang, R. Li, L. Guo, L. Cui, X. Zhang, Y. Wang, Y. Wang, X. Jian, X. Gao, C. Fan, J. Wang and J. Liu, *ACS Catal.*, 2024, **14**, 5696-5709.