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Supporting Information

Construction of BiOBr-Vo/MIL-101(Fe)-F microsphere heterostructure for

photocatalytic nitrogen fixation

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1. Experimental Section.

Synthesis of BiOBr. In the beginning, two separate solutions were formulated. Solution A: 1.5 mmol Bi(NO₃)₃ 5H₂O was dissolved in 30 mL methanol solution and continuously stirred until it was evenly dispersed. Then 1.5 mmol NaBr was dissolved in 6 mL deionized water and recorded as solution B. Subsequently, the A solution was slowly injected into the B solution under vigorous stirring. After further stirring for 30 min, the pH of the above solution was adjusted to 11.5 with 2 M NaOH solution. Transfer the mixture to a 50 mL teflon-lined autoclave and heat it in an oven at 160 °C for 24 h. The solution after the reaction is centrifuged by a high-speed centrifuge. The precipitate was collected and washed three times with deionized water and methanol, respectively. The treated samples were dried in a vacuum oven at 80 °C.

Synthesis of BiOBr-Vo/MIL-101(Fe)-F composites. A novel BiOBr-Vo/MIL-101(Fe)-F composite (BMF) was constructed through thermal calcination and solvothermal methods. At first, oxygen vacancy-rich BiOBr (BiOBr-Vo) was prepared via thermal calcination in a tube furnace, in which the pre-synthesized BiOBr was calcined at 400 °C for 2 hours under a H₂/Ar atmosphere with a heating rate of 2 °C/min. The BiOBr-Vo/MIL-101(Fe)-F composite (BMF) was synthesized using a solvothermal method. Firstly, a specific amount of BiOBr-Vo was dispersed in 15 mL of N,N-dimethylformamide (DMF) via ultrasonication until dispersed completely. Subsequently, a DMF solution containing a predetermined amount of 2-fluoroterephthalic acid (H₂BDC-F) and an aqueous solution of FeCl₃ $6H_2O$ were sequentially added to the BiOBr-Vo suspension. The resulting solution was transferred into a Teflon-lined autoclave and maintained at 110 °C for 20 hours. The final product was washed three times with DMF and ethanol, then dried in an oven at 80 °C.

To investigate the effect of MIL-101(Fe)-F content on the pNRR effect, BiOBr-Vo/MIL-101(Fe)-F composites with different mass ratios of MIL-101(Fe)-F (5, 10 and 15 wt% doping) were synthesized. The composites were designated as BMF-1 (5 wt%), BMF-2 (10 wt%) and BMF-3 (15 wt%) based on the weight percentage of MIL-101(Fe)-F. To evaluate the impact of fluorinated ligand modification on nitrogen fixation efficiency, we synthesized a BiOBr-Vo/MIL-101(Fe) composite with the addition of 10 wt% MIL-101(Fe), designated as BM-2.

Determination of NH₄⁺**.** The generation of NH₄⁺ was detected by nuclear magnetic internal standard method and indophenol blue method.

Nuclear magnetic internal standard method. After the reaction, all the solution of the photoreaction tube was centrifuged, and the supernatant was filtered with a 0.22 μ m membrane filter. A certain amount of hydrochloric acid was added to the rotary evaporator to adjust the pH to 2 and spin dry 0.5 mL DMSO-d₆ was added as a deuterium reagent and 5 μ L 0.1 M maleic acid was used as an internal standard. The ¹H NMR detection was performed on a nuclear magnetic resonance spectrometer (NMR, 500 MHz), and the amount of NH₄⁺ generated was quantified based on the internal standard.

Indophenol blue method. After the reaction, a portion of the supernatant was centrifuged and passed through a 0.22 µm membrane filter. After diluting the filtrate with water to a certain ratio, 2 mL filtrate was transferred to colorimetric tube, followed by the addition of 2 mL of 1M NaOH solution (containing 5 wt% salicylic acid, 5 wt% sodium citrate), 0.2 mL of 1 wt% sodium nitroprusside solution, and 1 mL of 0.05 mol/L sodium hypochlorite solution. Following mixing, a color reaction developed after one hour, and a UV-visible spectrophotometer was employed to measure at a wavelength of 655 nm. The concentration of bound nitrogen was then determined based on the sample's absorbance.

Determination of apparent quantum efficiency (**AQE**). The catalytic experiment used to measure AQE was carried out in pure water without the use of any sacrificial reagents, with 10 mg of BiOBr-Vo/MIL-101(Fe)-F as the photocatalyst. To obtain the AQE value, the reaction solution was irradiated with a 300 W xenon lamp, using different wavelength bandpass filters (405, 420 nm). The AQE value was calculated according to the following formula:

$$AQE(\%) = \frac{N_{reacted}}{N_{incident}} \times 100\% = \frac{3 \times N_a \times M_{NH_3}}{\frac{P \times s \times t \times \lambda}{h \times c}} \times 100\%$$

Where $N_{reacted}$, $N_{incident}$ represent the quantities of reacted electrons, incident photons. M_{NH3} represents the molar number of generated ammonia molecules during the irradiation time, respectively. Additionally, P, t, s and λ refer to the light intensity, illumination time, light incident area and the wavelength of the monochromatic light, respectively. c denotes the speed of light in a vacuum, h is Planck's constant, and N_a represents Avogadro's constant. 2. Characterizations of Catalysts.



Fig. S1 (a) SEM image of BMF-2. (b) TEM micrograph of BMF-2.



Fig. S2 The XPS survey spectra for BiOBr-Vo, MIL-101(Fe)-F and BMF-2 composite.



Fig. S3 The high resolution XPS of O 1s for MIL-101(Fe)-F, BiOBr-Vo and BMF-2 composite.



Fig. S4 Nitrogen adsorption-desorption isotherms (inset: the corresponding pore size distribution).



Fig. S5 Room-temperature EPR spectra of BMF-2 before and after irraiation.



Fig. S6 Mott-Schottky plots of MIL-101(Fe)-F at different frequencies.



Fig. S7 Mott-Schottky plots of BiOBr-Vo at different frequencies.



Fig. S8 The cyclic voltammetry (CV) curves of the BMF-2 catalyst under N_2 and Ar atmospheres.

3. Catalysis Details.



Fig. S9 Comparison of NH4⁺ yield of BiOBr-Vo/MIL-101(Fe)-F and

BiOBr/MIL-101(Fe)-F.



Fig. S10 Tauc plots of the MIL-101(Fe) catalyst.



Fig. S11 Comparison of NH4⁺ yield of MIL-101(Fe)-F, MIL-101(Fe), BMF-2 and

BM-2.



Fig. S12 Mott-Schottky plots of MIL-101(Fe) at different frequencies.



Fig. S13 In situ Raman spectra of BMF-2 under visible-light irradiation at 0, 10, 20, 30, 40 and 50 minutes. The increasing intensities of the peaks at 750 cm⁻¹ and 2900 cm⁻¹ are attributed to the formation of *NH species, while the peak at 1150 cm⁻¹ corresponds to *NH₂ intermediates, indicating the gradual activation of N₂ during the photocatalytic process.



Fig. S14 ¹H NMR spectrum of the solution after N₂ photoreduction with BMF-2.



Fig. S15 The Nessler method was absolutely calibrated with the known concentration

of NH₄Cl solution as the standard.



Fig. S16 The calibration curve for ammonium concentration vs. absorbance at 655 nm. $R^2 = 0.99866.$



Fig. S17 Apparent quantum efficiencies (AQEs) of BiOBr-Vo/MIL-101(Fe)-F for photocatalytic NH₃ synthesis under various monochromatic light wavelengths.



Fig. S18 Powder XRD pattern and FT-IR spectra of BMF-2 before and after 8 cycles of photocatalytic nitrogen fixation.



Fig. S19 SEM image and EDS elemental mappings of BMF-2 after 8 cycles of photocatalytic nitrogen fixation.



Fig. S20 High-resolution XPS spectra of Fe 2p in BMF-2 before and after 8 cycles of photocatalytic nitrogen fixation.

Photocatalyst	Light source	Sacrificial	NH4 ⁺ yields	Ref.
		agent	$(\mu mol g^{-1} h^{-1})$	
BiOBr-Vo/MIL-101(Fe)-F	$\lambda \ge 420 \text{ nm}$	No	80.9	This work
Bi-BiOBr	$\lambda \ge 420 \text{ nm}$	Na ₂ SO ₃	78.6	[1]
5-FTNFs	Full-spectrum	No	64.2	[2]
PMo10V2@MIL-88A	Full spectrum	No	50.82	[3]
In2O3/In2S3-ZnCdS	300W Xe	No	71.2	[4]
	Lamp			
BiOBr-Fe-S-1	$\lambda > 400 \text{ nm}$	No	46.1	[5]
UiO-66(SH) ₂	$\lambda > 400 \text{ nm}$	No	32.38	[6]
SA Fe-porous g-C ₃ N ₄	Full spectrum	No	62.42	[7]
Ru@MIL-125/MnOx	$\lambda \ge 420 \text{ nm}$	No	10.43	[8]
Fe-TiO ₂ -SiO ₂	Full spectrum	No	32	[9]
Ru ₁ /d-UiO-66	300W Xe	No	53.28	[10]
	Lamp			
Fe-sdc	Full spectrum	No	61.01	[11]
PMo10V2@MIL-88A	Full spectrum	No	50.82	[12]
W-doped Bi ₂ MoO ₆	$\lambda \ge 420 \text{ nm}$	No	56	[13]
WO _{3-x}	Full spectrum	CH ₃ OH	28.4	[14]

Table S1. Comparison of NH_4^+ production with other reported photocatalysts inrecent works.

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