Supplementary Information

NH₂-MIL-125(Ti) with transient metal centers via novel electron

transfer routes for enhancing photocatalytic

NO removal and H₂ evolution

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Section 1. Materials and Characterization

Materials

N, *N*-Dimethylformamide (Adamas, 99%), 2-Aminoterephthalic acid (Adamas, 98%), Titanium isopropoxide (Aladdin, 99%), Ytterbium nitrate pentahydrate (Aladdin, 98%). All reagents were of analytical grade and could be used without further purification.

Characterization

The microstructure and morphology of the Yb-NM-X composite materials were characterized by X-ray powder diffraction (XRD-6100, Shimadzu, Japan), scanning electron microscope (SEM) micrograph (ZEISS MERLIN Compact), energy Dispersive X-ray spectroscopy (EDX) (X-MAX-20mm² Oxford), X-ray photoelectron spectroscopy (XPS) (Thermo Scientific K-Alpha), BET measurement (ASAP 2020, USA). The photocatalytic performance and mechanism were studied through ultraviolet-visible diffuse reflectance spectroscopy (UV-vis DRS) (Shimadzu, Japan), photoluminescence spectrum (PL spectrum) (F-7000, HITACHI, Japan), transient photocurrent response curve (PEC 1000), electrochemical impedance spectroscopy (EIS) (PEC 1000), cyclic voltammetry (CV) (PEC 1000), Mott-schottky (M-S) (PEC 1000), electron spin resonance spectroscopy (DRIFTS) (Bruker, Germany).

Section 2. Experimental procedure

Synthesis of NH₂-MIL-125(Ti):

Firstly, 2-aminoterephthalic acid (2.86 g, 15.8 mmol) was added into a mixture solution of 10 mL anhydrous methanol and 40 mL anhydrous N, N-dimethylformamide and stirred at room temperature until 2-aminoterephthalic acid was completely dissolved. Next, titanium isopropoxide (2.86 mL, 9.7 mmol) was added to the above mixture solution and then transferred into a 100 mL PTFE lined autoclave with heating at 110 °C for 72 h. After cooling down to room temperature,

the solid product formed was centrifuged and immersed in DMF and methanol twice, respectively. The synthesized NH_2 -MIL-125(Ti) was finally dried overnight at 100 °C in a vacuum oven.

Synthesis of MIL-125(Ti):

Terephthalic acid (2.49 g, 15 mmol) was enchased into a mixture solution of 5 mL anhydrous methanol and 45 mL anhydrous *N*, *N*-dimethylformamide, then stirred at room temperature until terephthalic acid was completely dissolved. Next, titanium isopropoxide (2.66 mL, 9 mmol) was added to the above compounds and then transferred into a 100 mL PTFE lined autoclave autoclave with heating at 150 °C for 16 h. After cooling down to room temperature, the solid product was centrifuged and washed three times with DMF and methanol, respectively. The synthesized MIL-125(Ti) was finally dried overnight at 100 °C in a vacuum oven. The obtained NH2-MIL-125(Ti) was marked as NM

Synthesis of Yb-NH₂-MIL-125(Ti) and Yb-MIL-125(Ti):

According to the literature, Yb-NH₂-MIL-125(Ti) and Yb-MIL-125(Ti) were obtained. As-prepared NH₂-MIL-125(Ti) or MIL-125(Ti) (0.35 g) was dispersed into a deionized water (35 mL) of Yb(NO₃)₃ \cdot 5H₂O (1, 6, 12 and 20 mM) at room temperature and stirred vigorously for 2 h. Then the sample was centrifuged, washed three times with H₂O, and dried for 12 h at 80 °C in an oven. The obtained Yb-NH₂-MIL-125(Ti) samples synthesized with different concentrations (1, 6, 12 and 20 mM) of Yb(NO₃)₃ \cdot 5H₂O were labeled as Yb-NM-X (X=1, 6, 12, 20).

NO removal experiments

The synthesized catalyst (0.2 g) was put into two glass dishes (diameter: 12 cm), and then 10 mL of ethanol was added for ultrasonic dispersion. Afterward, the glass dishes were dried at 60 $^{\circ}$ C until all the solvent evaporated. After cooling to room temperature, these two dry dishes were used for further photocatalytic NO removal

experiment. Photocatalytic NO oxidation was tested by NO-NO₂-NO_x analyzer (Thermo Scientific, 42iTL). The reaction was carried out in a continuous flow reactor with two ordinary LED lights (12 W) vertically above the reactor. During each test, NO (initial concentration was 100 ppm) was introduced at first, and then the air generator was opened to dilute NO concentration to 530 ppb. After the gas reached adsorption-desorption equilibrium, the lamp was turned on to start the light reaction. The NO removal rate (η) was calculated by the following formula: η (%)=(1-C/C₀) × 100%, where C and C₀ were the concentration of NO in the outlet and feed stream, respectively.

Photocatalytic H₂ evolution experiments

The experiment of photocatalytic H_2 production was carried out in a 100 ml Pyrex reactor, and the opening of the flask was sealed with a quartz window. In a typical experiment, 10 mg of photocatalyst was suspended in a 20 mL mixed solution, which contained 17 mL of acetonitrile, 0.2 mL of deionized water, and 3 mL of TEOA as a sacrificial agent. Subsequently, 0.5 mL of acetonitrile solution of chloroplatinic acid was added as the precursor of platinum co-catalyst. Then, the suspension of the catalysts was dispersed by ultrasound for 10-15 min, and nitrogen was injected into the solution in reactor for 20 min to discharge oxygen. An uninterrupted magnetic stirrer was applied at the bottom of the reactor to keep the photocatalyst particles at suspension status during the experiment process. Finally, a 300 W Xe lamp was turned on to initiate the reaction to generate H_2 . After 30 min reaction, a 420 nm filter was added into the Xe lamp source. The gas product was detected and analyzed by a GC gas chromatograph (GC 7920, Beijing). The apparent quantum efficiency (AQE) of the synthesized photocatalyst was obtained by Equation:

$$AQE(\%) = \frac{number \ of \ reacted \ electrons}{number \ of \ incident \ photons} \times 100\%$$
$$= \frac{number \ of \ evolved \ H_2 \ molecules \ \times \ 2}{number \ of \ incident \ photons} \times 100\%$$

Active species trapping experiment

In previous reports, silver nitrate (AgNO₃), potassium iodide (KI), p-benzoquinone (BQ) and isopropanol (IPA) confirmed the existence of photo-generated electrons, photo-generated holes, hydroxyl radicals and superoxide radicals in the system. In the no removal system, 1% of different active species scavengers were added to carry out the capture experiment. In the hydrogen production system, different capture agents of 1 mm were added to carry out the capture experiment.

Electrode preparation

3 mg of catalyst were dispersed in 10 μ L Nafion, 250 μ L H₂O and 250 μ L CH₃CH₂OH. The 40 μ L as-prepared solution was dropped in an active area of ca. 2.25 cm² (1.5*1.5 cm) to achieve a uniform coverage of catalyst on ITO and then dried at 60 °C for further characterization.

Photoelectrochemical measurement

The photocurrents and electrochemical impedance spectroscopy (EIS) measurements were performed in a conventional three electrode system on an electrochemical station (CHI 660D). Samples with an active area of Ca. 2.25 cm² (1.5*1.5 cm) on ITO glass were served as working electrode. The platinum sheet and saturated calomel electrode (SCE) were the counter electrode and the reference electrode, respectively. Na₂SO₄ (0.2 M) aqueous solution was used as electrolyte. A 300 W Xe lamp with a wavelength at 420 nm was used as the light source.

Section 3. Characterization of the as-formed samples



Figure S1. XRD pattern of MIL-125(Ti).



Figure S2. The Elemental mapping images of Yb-NM-6.



Figure S3. The FTIR spectra of NM and Yb-NM-X.

The range of 400-800 cm⁻¹ was Ti-O-Ti vibration. The peak at 1255 cm⁻¹ was assigned to the C-N stretching absorption. The infrared absorption peaks at 1386 cm⁻¹, 1421 cm⁻¹ and 1532 cm⁻¹ belong to the stretching vibration of carboxylic acid functional groups. The peak of benzene ring skeleton vibration was 1573 cm⁻¹.



Figure S4. (a) N_2 adsorption-desorption isotherms for NM and Yb-NMI-6; (b)

Pore size distribution curves for NM and Yb-NM-6.

Sample	$S_{BET}(m^2 \cdot g^{-1})$	$V_p(cm^3 \cdot g^{-1})$	D _P (nm)
NM	1127.41	0.62	2.18
Yb-NM-6	910.35	0.50	2.16

Table S1. Structural parameters of different samples.

 S_{BET} = BET surface area, V_p = pore volume, D_P = pore diameter



Figure S5. The yield of NO₂ with light time.



Figure S6. (a) The photocatalytic NO oxidation performance of X-NM; (b) The photocatalytic NO oxidation performance of MIL-125(Ti) and Yb-MIL-125(Ti).



Figure S7. (a) the quantum efficiency of Yb-NM-X (X=1, 6, 12, 20) photocatalysts under visible light ($\lambda > 420$ nm); (b) Effect of different pH values on hydrogen production rate.



Figure S8. (a) Effect of different radical scavengers on NO removal over Yb-NM-6 photocatalyst; (b) Photocatalytic hydrogen evolution trapping experiment in the presence of Yb-NM-6.





The XRD pattern after the reaction was similar to that of NM, indicating that its crystal structure was maintained. In addition, it could be seen from the SEM image after the reaction that the geometric morphology of Yb-NM-6 was basically unchanged, but the surface became a little rough. The above results again proved that it had good stability.