

## Supporting Information

### Constructing Z-scheme heterojunction of Zr-MOF/g-C<sub>3</sub>N<sub>4</sub> for highly efficient photocatalytic H<sub>2</sub> production under visible light

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#### Characterizations

Powder X-ray diffraction (PXRD, Rigaku Ultima IV diffractometer) with  $\lambda = 1.5418 \text{ \AA}$  (Cu K $\alpha$  radiation),  $2\theta$  angle from  $5^\circ$  to  $60^\circ$ , scanning rate of  $5^\circ \cdot \text{min}^{-1}$ . Transmission electron microscope (TEM, JOEL JEM-2100 electron microscope). X-ray photoelectron spectroscopy (XPS, Thermo VG Scientific Escalab 250 spectrometer), using a monochromatic Al K $\alpha$  excitation source, calibrate binding energy according to C1s peak of 284.6 eV. UV-Vis diffuse reflection spectrum (DRS, UV-visible near-infrared spectrophotometer), with BaSO<sub>4</sub> as a reference. N<sub>2</sub> adsorption-desorption tests were carried out using ASAP2020 volumetric adsorption analyzer. Surface photovoltage spectroscopy (SPV) was performed by a light source monochromator locking in detection technique, using sandwich cells (FTO/mica/sample/FTO), with a testing range of 300-600 nm. Photoluminescence spectra (PL, Shimadzu RF-5301PC fluorescence photometer) and emission decays (TRPL Eidingberg FS920 photoluminescence lifetime system). Gas chromatography (GC, GC-2014C), with 5  $\text{\AA}$  molecular sieve column, thermal conductivity detector.

#### Photocatalytic H<sub>2</sub> production

Using a 300 W xenon lamp ( $420 \text{ nm} < \lambda < 780 \text{ nm}$ ), its photocatalytic activity was studied in a sealed quartz photoreactor. Put 5 mg of photocatalyst into 25

mL of pre-regulated 0.1 M ascorbic acid solution (pH=4.0). A 1.0 wt% Pt cocatalyst was deposited on the surface of the photocatalyst, which was obtained by directly dissolving H<sub>2</sub>PtCl<sub>6</sub> in the above reaction solution. Soak high-purity nitrogen in the dark for 30 minutes to remove the air, then turn on the xenon lamp. The above solution is continuously stirred under visible light irradiation. Extract 0.2 mL of gas per hour and analyze hydrogen by gas chromatography. The determination of apparent quantum yield (AQY) is consistent with our previous literature.<sup>1</sup> Typically, the wavelength of the light source is concentrated at 450 nm (300 W Xe lamp with a band-pass-filter), ultraviolet visible spectrophotometry (Shimadzu UV-3600) is used for measuring the number of photons of light. Place 25 mL (0.01 M) of K<sub>3</sub>Fe(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>·3H<sub>2</sub>O solution (V<sub>0</sub>) in a photocatalytic reactor and stir, After 60 seconds of irradiation, 5 mL of solution (V<sub>1</sub>) was taken and added into a 50 mL brown volumetric flask; then 10 mL of (0.01 M) 1,10-phenanthroline monohydrate (0.01 M) and 10 mL buffer solution of acetic acid/sodium acetate (pH = 5.0) are added, then diluted to 50 mL (V<sub>2</sub>), placed in dark condition for 30 min. Then the absorbance was measured at 510 nm (A<sub>t</sub>). The value of AQY can be calculated using the following equations:

$$n' = (A_t - A_0) N_0 V_0 V_2 / \epsilon L V_1 \varphi_{Fe^{2+}} t \quad (1)$$

$$AQY = 2nN_0 / n' \times 100\% \quad (2)$$

Where  $n'$  is the number of the photons emitted from light source in per unit time (s<sup>-1</sup>);

$A_0$  is the absorbance of the sample at 510 nm before the irradiation;

$A_t$  is the absorbance of the sample at 510 nm taken after the 60 s irradiation;

$N_0$  is the Avogadro's constant;

$\epsilon$  is the molar extinction coefficient of [Fe(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>]<sup>2-</sup> (1.11 × 10<sup>4</sup> L·mol<sup>-1</sup>·cm<sup>-1</sup>);

$L$  is the thickness of the cuvette;

$\varphi_{Fe^{2+}}$  is the quantum efficiency of Fe<sup>2+</sup> (1.11,  $\lambda = 450$  nm);

$t$  is the irradiation time of the light source (20 s);

$n$  is the amount of hydrogen generated in one hour (mol/h).

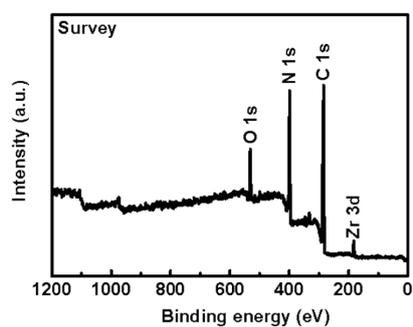
### **The trapping experiments of active species**

20 mg of photocatalyst was added into 50 mL of RhB (10 mg/L) solution. Then added  $N_2$ , 5 mL of isopropanol (IPA) and triethanolamine (TEOA) to the suspension, respectively. After stirring in the dark for 30 minutes to achieve adsorption desorption equilibrium, irradiate with a 300W xenon lamp. Take 3-4 mL of reaction solution every 10 minutes for centrifugation. Observe the concentration change of Rhodamine B (RhB) dye at an absorption wavelength of 554 nm.

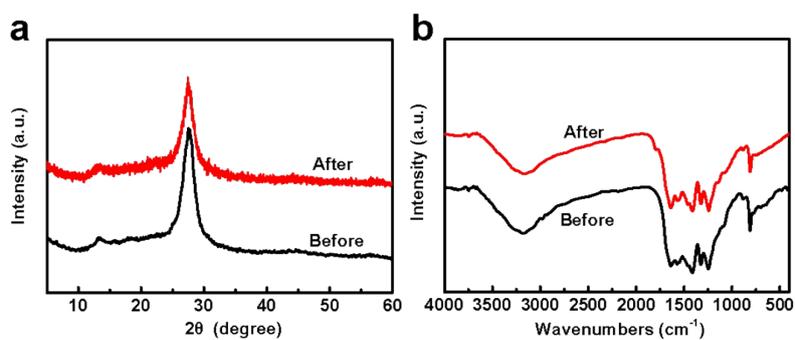
### **Photoelectrochemical studies**

All photoelectrochemical measurements are measured by the CHI 660E electrochemical system, with three standard electrodes: reference electrode (Ag/AgCl), counter electrode (Pt), working electrode (sample). The preparation method of the working electrode is as follows: 2 mg of photocatalyst is mixed with 10  $\mu$ L nafion in 1.0 mL of ethanol and sonicate the mixture for 2 hours. Add 200  $\mu$ L suspension to the surface of ITO conductive glass, dried at 80 °C. Using 0.2 M  $Na_2SO_4$  (pH=6.8) as an electrolyte, under visible light ( $420\text{ nm} < \lambda < 780\text{ nm}$ ). The photoresponse signals of the photocatalyst was measured at 420nm. Electrochemical impedance spectroscopy (EIS), with an amplitude variation of 5 mV and a frequency range of 0.01 to  $10^5$  Hz. Mott Schottky experiment, frequency 1000 Hz, dark conditions. Cyclic voltammetry (CV) used saturated calomel electrode as reference electrode, Pt plate as counter electrode, sample as working electrode, 0.5 M  $Na_2SO_4$  (pH=7.0) as the electrolyte. The current density was obtained according to the average value of anodic current density and cathodic current density at the central potential in the scanning range.<sup>2</sup> The slope of the fitted line is double layer capacitance ( $C_{dl}$ ).

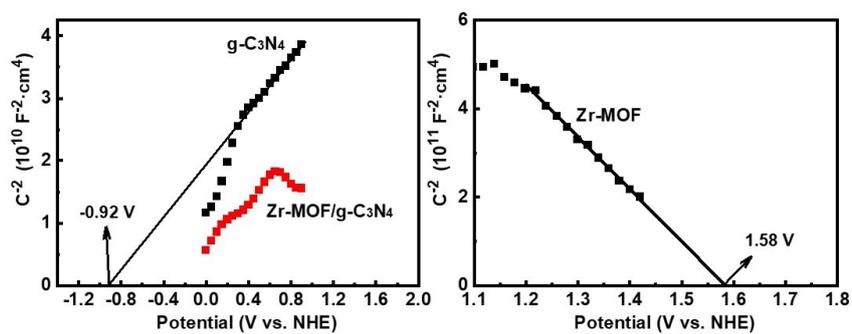
## Results and discussion



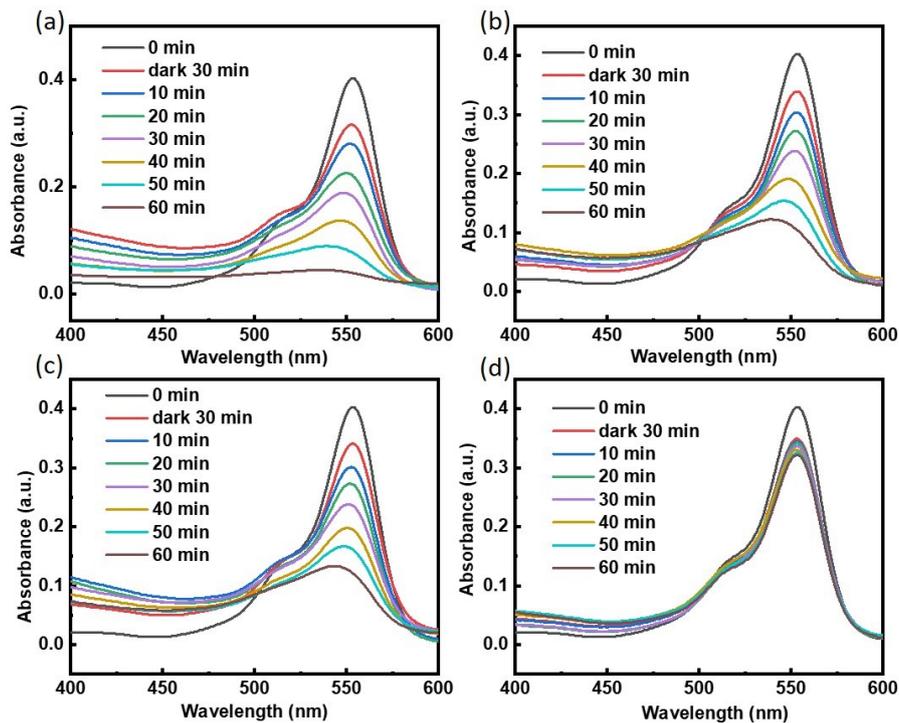
**Fig. S1** XPS survey spectrum of Zr-MOF/g-C<sub>3</sub>N<sub>4</sub> heterojunction photocatalyst.



**Fig. S2** (a) PXRD and (b) FTIR spectra of Zr-MOF/g-C<sub>3</sub>N<sub>4</sub> heterojunction before and after photocatalytic H<sub>2</sub> production reaction.



**Fig. S3** Mott Schottky curves of (a) g-C<sub>3</sub>N<sub>4</sub> and Zr-MOF/g-C<sub>3</sub>N<sub>4</sub>, (b) Zr-MOF.



**Fig. S4** UV–Vis absorbance spectra of Zr-MOF/g-C<sub>3</sub>N<sub>4</sub> photocatalyst for the photodegradation of RhB: (a) no sacrificial agent, (b) N<sub>2</sub>, (c) IPA, (d) TEOA.

## References

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- 2 X. Y. Lian, S. H. Chen, F. Y. He, S. Dong, E. Z. Liu, H. Li, K. Z. Xu, *Separation and Purification Technology*, 2022, **286**, 120449.