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Supporting information

Dual engineering of pores and surfaces in metal-organic frameworks via precision etching for enhanced photocatalytic performance

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1. Materials and Characterizations

All reagents and solvents were purchased from Aladdin Scientific as analytical grade products and do not require further purification for use. Powder X-ray diffraction (PXRD, PANalytical X'pert PRO), scanning electron microscopy (SEM, COXEM EM-3AX), Fourier transform infrared spectroscopy (FTIR, Thermo Scientific Equipment Nicolet iS10) and thermogravimetric analysis (TGA, Netzsch TG 209 F1 Libra) were used to characterize the structure of the prepared catalysts. Thermogravimetric analysis was carried out in the temperature range of 50 to 700 °C, heated under air conditions with a ramp rate of 10 °C/min. Adsorption-desorption isotherms were tested using a BSD-PS1 (beishide instrument) and the specific surface area of the materials was calculated using the Bruno Emmett Taylor (BET) method. The states of the elements were analyzed by X-ray photoelectron spectroscopy (XPS, Thermo Scientific Nexsa). The concentration of leached metal ions was measured by flame atomic absorption spectroscopy (Thermo Scientific, iCE 3000). Sample contact angles were tested using a dataphysics contact angle meter. Free radicals and single linear state oxygen signals were recorded by an electron paramagnetic resonance spectrometer (EPR, Magnettech ESR 5000). UV-visible spectra were measured using a MAPADA UV-1800PC spectrophotometer.

2. Single-crystal X-ray crystallographic experiment

For JOU-20, the single-crystal X-ray diffraction (SCXRD) data were tested using a Bruker apex CCD diffractometer with Mo- $K\alpha$ radiation ($\lambda = 0.71073$ Å). The structures were solved by the direct method of SHELXS-2018, and refined by the full matrix least square method using SHELXL-2018 program.¹ All hydrogen atoms were added in geometrically ideal positions. The disordered guest molecules in the structure were removed using the SQUEEZE routine. The selected bond lengths and bond angles were listed in Table S2 and S3, respectively. The CCDC number for JOU-20 is 2220461.

3. Photoelectrochemical experiments

To prepare the photoelectrodes, 2 mg of MOF powder was dispersed into 2 mL of ethanol and the mixture was sonicated for 1 h to ensure uniform dispersion of the sample. Subsequently, 30 μ L of the mixture was dropped onto ITO glass with an exposed area of 1 cm² and dried at 50 °C. This process was repeated three times to

ensure uniform coverage of the ITO substrate. Electrochemical impedance spectroscopy (EIS) and photocurrent response tests were performed using a threeelectrode system with an electrolyte of $0.5 \text{ M} \text{ Na}_2\text{SO}_4$ solution (pH = 6). The prepared electrodes were used as working electrodes, platinum sheets were used as counter electrodes and Ag/AgCl electrodes were used as reference electrodes.

4. Calculation of free radical contribution²

The contribution of SO_4^{-} , O_2^{-} , OH, and 1O_2 in MOF/PDS system were calculated according to the following equations.^[1]

$$\lambda(\cdot OH) = [(k_0 - k_1) / k_0] \times 100\%$$

$$\lambda(SO_4^{-}) = [(k_1 - k_2) / k_0] \times 100\%$$

$$\lambda(^1O_2 + O_2^{-}) = 1 - \lambda(\cdot OH) - \lambda(SO_4^{-})$$

Where $\lambda(\cdot OH)$, $\lambda(SO_4^{-})$, $\lambda(O_2^{-}+1O_2)$ are the contributions of $\cdot OH$, SO_4^{-} , and $O_2^{-}/1O_2$ to R6G degradation, respectively. k_0 , k_1 , k_2 , are the rate contents with the addition of no quenching agent, isopropanol, methanol, respectively.

5. Fe(IV) analysis

To a 0.1 mmol solution of methyl phenyl sulfoxide (PMSO) was added the appropriate amount of PDS and 10 mg of JOU-20-H₄. After 1 hour of xenon irradiation, 1 mL of the solution was withdrawn by syringe and filtered through a 0.22 μ m membrane. Then, 10 μ L of 1.0 mol/L sodium thiosulfate was added to the filtrate to quench the residual reactive radicals in the solution. The concentration of the generated methyl phenyl sulfoxide (PMSO₂) was subsequently determined using a liquid chromatograph. The detection wavelength was 230 nm, and the eluent was CH₃CN and H₂O in the ratio of 1:4 (both containing 0.1% formic acid) at a flow rate of 1 mL/min.

6. Determination of PMS concentration³

0.1 mL of sample was added to a mixture containing 0.5 mL of 2 mM 2,2'azobis(3ethylbenzothiazoline-6 sulfonic acid) diammonium salt (ABTS), 1 mL of pH = 4 acetate buffer solution, and 1.5 mM of sodium iodide solution. Then, the mixture was diluted to 10 mL with water. The yielded ABTS•⁺ was detected at 415 nm.

7. Apparent activation energy test

The apparent activation energy of PMS activation was calculated using the Arrhenius equation $Lnk = LnA - E_a/RT$, where E_a is the activation energy, k represents the degradation rate constant, R is the gas constant 8.314 J/(K/mol), T is the thermodynamic temperature (K), and A is the pre-power coefficient. The concentration of PMS was determined by the above ABTS method. The relationship between the reaction temperature and the activation of PMS was determined by fitting Lnk with 1/T. The E_a values of PMS activation in the JOU-20/PMS, JOU-20-A₁/PMS, and JOU-20-H₄/PMS systems were calculated to be 55.23, 26.71, and 20.28 kJ/mol, respectively.



Fig. S1. FT-IR spectra of different MOFs.



Fig. S2. PXRD patterns of etched MOFs prepared with different concentrations of H_2O_2 .



Fig. S3. PXRD patterns of etched MOFs prepared with different concentrations of HCl.



Fig. S4. N_2 adsorption-desorption isotherms of H_2O_2 etched MOFs.



Fig. S5. N₂ adsorption-desorption isotherms of HCl etched MOFs.



Fig. S6. XPS spectra of different MOFs.



Fig. S7. TGA curves of H₂DMTDC and TPT.



Fig. S8. Phenanthroline colorimetric experiment indicates that more iron ions are released under HCl etching process.



Fig. S9. The structural model used for DFT calculations.



Fig. S10. Solid UV-Vis absorption spectra for different MOFs.



Fig. S11. Mott-Schottky curves for JOU-20.



Fig. S12. Mott-Schottky curves for JOU-20-A₁.



Fig. S13. Mott-Schottky curves for JOU-20-H₄.



Fig. S14. Fluorescence spectra of JOU-20, JOU-20- A_1 , and JOU-20- H_4 .



Fig. S15. Electrical impedance spectroscopies of different MOFs.



Fig. S16. CV curves of JOU-20 at different scan rates (From inner to outer: 20, 40, 60, 80, 100, 120, and 140 mV s⁻¹).



Fig. S17. CV curves of JOU-20-H₄ at different scan rates (From inner to outer: 20, 40, 60, 80, 100, 120, and 140 mV s⁻¹).



Fig. S18. CV curves of JOU-20-A₁ at different scan rates (From inner to outer: 20, 40, 60, 80, 100, 120, and 140 mV s⁻¹).



Fig. S19. Effects of PMS concentrations on R6G degradation.



Fig. S20. Photocatalytic performance of H_2O_2 etched MOFs.



Fig. S21. Photocatalytic performance of HCl etched MOFs.



Fig. S22. Kinetics of R6G degradation in the presence of different MOFs.



Fig. S23. PXRD patterns of JOU-20-H₄ after photocatalytic reaction.



Fig. S24. XPS curves of iron in JOU-20-H₄ before and after photocatalytic reactions.



Fig. S25. N_2 adsorption and desorption isotherms of JOU-20-H₄ before and after photocatalytic reactions.



Fig. S26. R6G degradation kinetics in the presence of different catalysts.



Fig. S27. PXRD pattern of JOU-20-H₄@PU.



Fig. S28. Comparison of adsorption energies of PMS in intact and defective MOFs.



Fig. S29. Reaction rate contents of R6G degradation after adding different quenchers.



Fig. S30. No PMSO₂ can be detected in JOU-20-H₄/PMS system after the light irradiation. Experimental conditions: $C_{R6G} = 10 \text{ mg/L}$, $C_{PMS} = 3 \text{ mmol/L}$, pH = 6, $m_{cat.} = 10 \text{ mg}$, V = 30 mL, Xe lamp (> 420 nm).



Fig. S31. Content of Fe^{3+} and Fe^{2+} before and after reaction.

Table S1. Comparison of the photocatalytic performance of different materials.

Material	C _{cat.}	pollutant	PMS	Removal efficiency	<i>k</i> (min ⁻¹)	Ref.
		concentration				
25%Co-MIL-53(Al)	0.2 g/L	30 mg/L	1.0 mM	60 min, 94.0%	0.039	4
Goethite/1.0BC500	0.05 g/L	30 mg/L	2.0 mM	60 min, 68.3%	0.0206	5
α -MnO ₂ nanowires (Mn ⁻¹)	0.25 g/L	20 mg/L	3.0 mM	100 min, 100%	0.023	6
Fe/Fe ₃ O ₄	0.5 g/L	5 mg/L	0.1 mM	120 min, 98.6%	0.0684	7
Natural titano magnetite	8.0 g/L	10 mg/L	5.0 mM	90 min, 92%	0.025	8
Bi2MoO6 nanosheets	0.6 g/L	2.5 mg/L	0.8 mM	60 min, 99%	0.064	9
JOU-20-H ₄	0.3 g/L	10 mg/L	3.0 mM	120 min, 95.6%	0.026	This work

Compounds	JOU-20		
Formula	$C_{48}H_{30}Fe_{3}N_{6}O_{13}S_{6}Cl$		
Formula weight	1294.19		
Crystal system	hexagonal		
Space group	P6 ₃ /mmc		
$a \text{ and } b (\text{\AA})$	16.8071(16)		
<i>c</i> (Å)	19.6138(18)		
$V(Å^3)$	4798.2 (10)		
Ζ	2		
Density (g cm ⁻³)	0.871		
μ / mm^{-1}	0.616		
<i>F</i> (000)	1276		
2θ (°)	26.05		
Reflections	0.0485(1264)		
Data/restraints/parameters	1804/12/88		
GOF on F ²	1.005		
$R_{1}, wR_{2} [I > 2\sigma (I)]^{a}$	$R_1 = 0.0485, wR_2 = 0.1592$		

Table S2. Crystallographic data and structure refinements of JOU-20.

 ${}^{a}\overline{R_{1}} = \sum ||F_{0}| - |Fc|| / \sum |F_{0}|; wR_{2} = \sum [w(F_{0}{}^{2} - Fc^{2})^{2}] / \sum [w(F_{0}{}^{2})^{2}]^{1/2}.$

Table S3. Selected bond lengths (Å) and angels (°) for JOU-20(Fe₃).

Fe ₁ -O ₁	1.9256(8)	Fe ₁ -O ₂	2.037(2)
$Fe_1-O_2^1$	2.037(2)	Fe_{1} - O_{2}^{2}	2.037(2)
$Fe_1-O_2^3$	2.037(2)	Fe ₁ -N ₁	2.204(5)
O_1 -Fe ₁ - O_2^1	95.26(7)	O_1 -Fe ₁ - O_2^2	95.26(7)
O_2^1 -Fe ₁ - O_2^2	90.73(14)	O_1 -Fe ₁ - O_2^3	95.26(7)
O_2^1 -Fe ₁ - O_2^3	88.30(14)	O_2^2 -Fe ₁ - O_2^3	169.47(13)
O ₁ -Fe ₁ -O ₂	95.26(7)	O_2^1 -Fe ₁ - O_2	169.47(13)
O_2^2 -Fe ₁ - O_2	88.30(14)	O_2^3 -Fe ₁ - O_2	90.73(14)
O ₁ -Fe ₁ -N ₁	180.00(5)	O_2^1 -Fe ₁ -N ₁	84.74(7)
O_2^2 -Fe ₁ -N ₁	84.74(7)	O_2^3 -Fe ₁ -N ₁	84.74(7)
O_2 -Fe ₁ -N ₁	84.74(7)		

Symmetry transformations: ¹ +X, +X-Y, 1/2-Z; ² +X, +X-Y, +Z; ³ +X, +Y, 1/2-Z.

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