Supporting Information

Aerobic Oxidation of Covalent Organic Framework Facilitating Photocatalytic CO₂ Reduction with Water

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1. Experimental procedures

1.1 Materials and Characterizations

Unless otherwise specified, all raw materials and solvents are purchased from commercial analytical purity. All the chemicals and reagents are analytically pure without further purification. A Rigaku Mini Flex 600 X-ray diffractometer and a Nicolet 5700 instrument, Invia Reflex Raman spectra were used to gain the Powder Xray diffraction (PXRD) and the Fourier transform infrared (FTIR) data and Raman data, respectively. ZEISS SUPRA 55 Scanning electron microscopy (SEM) and FEI Talos F200i transmission electron microscopy (TEM) were used to gain the sample morphology. The N₂ and CO₂ adsorption-desorption isotherms were conducted by a Micromeritics ASAP 2460 system. Quenched solid density functional theory (QSDFT) method was employed for the calculation of the pore size distribution. UV-vis diffuse reflectance spectra (DRS) were carried out with Agilent Cary 5000 UV-Vis-NIR spectrophotometer. Time-resolved fluorescence spectroscopy (TRPL) spectra were obtained using a FLS 980-STM with an excitation wavelength set as 380 nm. CO₂-TPD measurement was obtained using a Altamira Instruments AMI 300 Lite Chemisorption Analyzers. The chemical states of the elements in the samples were investigated by K-Alpha X-ray Photoelectron Spectrometer (XPS) System using nonmonochromatic Al Kα X-rays as the excitation source and choosing C 1s (284.6 eV) as the reference line. Ultraviolet photoelectron spectroscopy (UPS) measurements of the as-prepared samples were performed with HeI (21.22 eV) as monochromatic light source and a total instrumental energy resolution of 100 mV. A homemade IR cell using Thermo Scientific Nicolet IS50 was carried out to test the In-situ FTIR. In-situ Raman was obtained using a Edinburgh Instrument RMS 1000. The EPR measurements were performed on a Bruker A300 ESR spectrometer. The CO gas produced from ¹³CO₂ and the O_2 gas produced from $H_2^{18}O$ isotope experiments was examined by a gas chromatograph-mass spectrometer (GC-MS, Agilent 7890B-5977B).

1.2 Photocatalytic reduction of CO₂

In a typical reaction, 10 mg of N_3 -COF/MoS₂ is placed in a 32 mm diameter quartz dish. Deionized water (1 mL) is added to disperse the sample, which is then heated to remove the water. Subsequently, 10 mL of deionized water is added to the bottom of a special glass reactor to generate water vapor for the photocatalytic reaction. The quartz dish containing the catalyst is positioned at the top of the reactor. After evacuating the reactor, high-purity CO₂ is introduced for 30 minutes to ensure a gas-free environment. A 300 W Xe lamp equipped with a 420 nm filter is used to simulate natural light. During the photocatalytic reaction, circulating cooling water maintains the system's reaction temperature at 30 °C. Gas products are analyzed using gas chromatography (Agilent 7890B).

1.3 Photoelectrochemical Measurement

The photocurrent response was recorded with a CHI650E electrochemical workstation (Chen Hua Instruments, Shanghai, China) equipped with a conventional three-electrode cell. The platinum plate electrode and the Ag/AgCl electrode was used as counter electrode and reference electrode, respectively. The working electrodes were prepared as follow: 5 mg sample mixed with 0.5 mL solution (Nafion: DMF=1:2, 1% Nafion in ethanol) were sonicated for 1h to make it dispersible, and then dropping 40 μ L of the suspension onto the FTO glass to cover the area of 1.0 cm². The electrodes were immersed in 0.2 M Na₂SO₄ aqueous solution which severed as electrolyte solution. Visible-light irradiation was provided by a xenon lamp (300 W) with a 420 nm cut-off filter to illuminate the working electrode.

The Mott-Schottky plots were measured by a IM6 electrochemical workstation (ZAHNER, Germany) in the similar process to the photocurrent measurement. The Mott–Schottky analysis was carried out in a 0.2 M Na₂SO₄ aqueous solution. Electrochemical impedance spectroscopy (EIS) plots were performed by a CHI650E electrochemical workstation (Chen Hua Instruments, Shanghai, China). The EIS analysis was carried out in a 5 mM K₃[Fe(CN)₆]/ 5 mM K₄[Fe(CN)₆]/ 0.1 M KCl mixed aqueous solution.

According to Nernst equation : $E_{NHE}(V) = E_{Ag/AgCl}(V) + E_{Ag/AgCl}^{0}$.

Here, $E_{Ag/AgCl}^{0} = 0.197$ V at 25 °C, where $E_{Ag/AgCl}$ (V) represents the experimentally measured potential on the Ag/AgCl reference electrode, and E_{NHE} denotes the converted potential relative to the NHE.

1.4 Cyclic testing

During the cyclic stability test, one cycle was performed every 4 hours. After each cycle, the photocatalyst was recovered and washed with methanol and acetone to remove impurities from the catalyst surface. It was then dried in a vacuum at 60 °C overnight, dispersed in a quartz reaction dish, and purged with CO_2 for 30 minutes to ensure a gas-free environment in the reaction system. A 0.2 mL sample of gas was extracted from the catalytic system using an airtight syringe. The gas composition following the photocatalytic reaction was analyzed by gas chromatography, and the sample's cyclic stability was evaluated.

1.5 In-situ FTIR

In-situ FTIR measurements were conducted using a Thermo Nicolet iS50 spectrometer equipped with an MCT detector. In a typical procedure, N₃-COF/MoS₂ was placed in the chamber, which was then sealed and purged with Ar gas for 5 minutes. Typical signals of intermediates were captured after introducing a flow of CO₂ (g), O₂ (g), and H₂O (g) under dark conditions for 10 minutes, followed by visible light irradiation for 0 to 30 minutes.

1.6 In-situ Raman

In situ Raman experiments were performed on a confocal Raman microscope (Edinburgh Instruments RMS1000) with an in situ spectroelectrochemical cell. A Raman laser with 532 nm wavelength was utilized as the excitation source. In a typical procedure, N₃-COF/MoS₂ is loaded onto a silicon substrate and then purged with Ar gas for 5 minutes. Afterward, CO₂ (g) and O₂ (g) are introduced. The in-situ reaction is achieved by irradiating from the in-situ cell window using a 300W Perfect Light PLS-

SXE 300 xenon lamp equipped with a 420 nm filter.

1.7 EPR

EPR measurements were conducted using a Bruker A300 ESR spectrometer, with 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) serving as the trapping agent. The typical procedure for detecting $\cdot O_2^-$ radicals involves the following steps: dispersing the catalyst in a methanol solution via ultrasonication, adding DMPO as a trapping agent and shaking to ensure thorough mixing, drawing the solution into a capillary tube, sealing the bottom with paraffin wax, and irradiating the sample with a xenon lamp equipped with a 420 nm filter for 10 minutes. The capillary tube is then placed into the paramagnetic tube for testing.

The method for \cdot OH radical testing is essentially the same as that for \cdot O₂⁻, except that the test solution is replaced with deionized water.

2. Catalyst preparation

2.1 Preparation of N₃-COF

TFPT-azine-COF was prepared by solvothermal method as previously reported. Typically, 1,3,5-tris-(4-formylphenyl) triazine (0.06 mmol, 23.6 mg) and 85% hydrazine (0.45 mmol, 24 μ l) hydrate was added to 5 ml Pyrex tube, and then 1 ml 1,4-dioxane and mesitylene (v/v=1:1) mixed solution was added. After ultrasonic dispersion of the above mixed solution for 30 min, 0.1 ml of 6 mol/L acetic acid aqueous solution was added to the tube as acid catalyst. After that, use a long handle spoon to probe into the mixed solution for physical stirring to mix the monomer, solvent and catalyst evenly to form a yellow mixed solution. The mixture was then heated and reacted (120 °C, 72 h). Then, the product was filtered and washed with methanol, dichloromethane, DMF and acetone for three times, and then purified by methanol Soxhlet extraction method overnight. Finally, the obtained material was vacuum dried overnight at 60 °C, and then collected and grinded to obtain TFPT-azine-COF (defined as N₃-COF).

2.2 Preparation of MoS₂

 MoS_2 was prepared by a slightly modified solvothermal method as previously reported¹. 80 mg (NH₄)₆Mo₇O₂₄·4H₂O, 150 mg thiourea and 30 ml DMF respectively and put them into a 100 ml polytetrafluoroethylene high-pressure reactor, stir them for 3h, then put them into a steel shell for 200 °C heating for 24h, and then cool them naturally. The obtained black samples are washed with water and alcohol respectively. Finally, put the samples in a 60 °C vacuum drying oven overnight, collect and grind them to obtain MoS₂ nanoflowers (recorded as MoS₂).

2.3 Preparation of N₃-COF/MoS₂

The N₃-COF/MoS₂ composites were prepared by in-situ hydrothermal method. Generally, MoS₂ (24 mg) was dispersed in 20 ml mesitylene/1,4-dioxane (v: v=1: 1), sonicated for 30 minutes, and then 1,3,5-tris-(4-formylphenyl) triazine (0.06 mmol, 23.6 mg), hydrazine (0.45 mmol, 24 μ L) and acetic acid (6 mol/L, 0.2 ml) were added dropwise. Thereafter the suspension stirs continuously in an oil bath at 120 °C for 72 h. After cooling to room temperature, the solid was filtered and washed three times with methanol, dichloromethane, N, N-dimethylformamide, and acetone. Then the composites were gathered after dry under vacuum (60 °C, 12 h).

The preparation of N_3 -COF/MoS₂ composites with different components was carried out by adjusting the amount of MoS₂ added in the in-situ hydrothermal reaction. For instance, in the composite denoted as N_3 -COF/MoS₂ (1:6), 6 mg of MoS₂ was incorporated, while in N_3 -COF/MoS₂ (2:6), the addition of MoS₂ was increased to 12 mg. Other composite samples with different ratios were also prepared by adjusting the amount of MoS₂ added in the in-situ hydrothermal reaction accordingly.

For comparison, a physical mixture of N_3 -COF and MoS_2 with the same ratio as N_3 -COF/MoS₂ (4:6) was prepared by mechanical grinding.

3. DFT Calculations

All density functional theory (DFT) calculations of molecular models were carried out using the Gaussian 16 software package². All geometries were optimized using the M06-2X hybrid functional³ and Grimme's D3(BJ) dispersion correction (GD3)⁴ with a basis set of def2-svp⁵ for all atoms. Vibrational frequency calculations were performed for all the stationary points to confirm if each optimized structure is a local minimum on the respective potential energy surface or a transition state structure with only one imaginary frequency. The simulation of periodic COF structure was conducted using the Vienna ab initio Simulation Package (VASP) code⁶, Perdew-Burke-Ernzerhof exchange-correlation functional⁷. An energy cutoff (400 eV) for describing the wave function and Monkhorst pack k-point mesh ($3 \times 3 \times 1$) were set. The vacuum space 5 thickness was set to 15 Å for eliminating the interaction of layers for all COFs. All atoms were allowed to converge to 0.01 eV Å⁻¹. For hydrogen evolution reaction, two coupled protons and electrons transfer are involved⁸.

4. Supporting Figures



Fig. S1 Schematic diagram of N_3 -COF/MoS₂ synthesis.



Fig. S2 FTIR spectra of (a) 1,3,5-tris-(4-formylphenyl) triazine and N₃-COF (b) MoS_2 , N₃-COF and N₃-COF/MoS₂.

The chemical structure of 1,3,5-tris-(4-formylphenyl) triazine and N₃-COF were characterized by FTIR, the characteristic peak of C=O at 1706.7 cm⁻¹ disappeared, and the characteristic peak of C=N at 1621 cm⁻¹ appeared, which proved the successful preparation of N₃-COF. On the one hand, the infrared signal of MoS₂ is weak, on the other hand, the outer layer of the composite is wrapped by N₃-COF, so N₃-COF/MoS₂ it mainly presents the characteristic signal of N₃-COF. (Fig. S2).



Fig. S3 (a) Raman spectra of N_3 -COF/MoS₂ in 350-2000 cm⁻¹ and (b) Raman spectra of N_3 -COF, MoS₂ and N_3 -COF/MoS₂ in 350-450 cm⁻¹.

Raman spectra clearly show that there are Mo-S, C=N, N-N characteristic signals in the heterostructure (Fig. S3)⁹.



Fig. S4 FESEM image of (a) N_3 -COF, (b)-(c) MoS_2 and (d) N_3 -COF/ MoS_2 .



Fig. S5 STEM-HAADF and EDS mapping images of N_3 -COF/MoS₂.



Fig. S6 STEM-HAADF line scanning of N_3 -COF/MoS₂.

Energy Dispersive X-ray Spectroscopy (EDS) indicates a clear interaction between N_3 -COF and MoS_2 (Fig. S5 and S6).



Fig. S7 PXRD patterns of MoS_2 , Physical mixing (MoS_2+N_3 -COF), N_3 -COF/ MoS_2 and N_3 -COF.

The PXRD patterns of N₃-COF showed a strong diffraction peak at $2\theta = 3.5^{\circ}$, which could be the characteristic diffraction peak of N₃-COF at the (100) crystallographic plane, as well as peaks at $2\theta = 6.3^{\circ}$ and 26.4° , which were the characteristic diffraction peaks of (110) and (001) crystallographic planes, respectively. The PXRD patterns of MoS₂ exhibited diffraction peaks at $2\theta = 9.8^{\circ}$, 18.9°, 23.5°, 32.7° and 57.4°, which could be associated with the (002), (004), (005), (100) and (110) planes. In addition, the PXRD pattern of N₃-COF and MoS₂ matched well with the simulated patterns and previous literature. Normally, it can be found that the characteristic diffraction peaks of N₃-COF/MoS₂ composite originate from N₃-COF and MoS₂. Moreover, the PXRD results showed a decrease in the crystallinity of N₃-COF with increasing MoS₂ incorporation. This phenomenon can likely be attributed to the in-situ growth strategy, in which with increasing MoS₂ in the hybrid, the enhanced interactions between the COF and MoS₂ would interfere the self-healing process during the COF formation, leading to a relatively decreased crystallinity of N₃-COF. These observations confirmed the successful synthesis of the N₃-COF/MoS₂ (x:6) composite materials (Fig. S7).



Fig. S8 Experimental and simulated PXRD patterns of (a) N₃-COF, (b) MoS₂, (c) Structural models of the C axis enlarged interlayer spacing and the pristine 2H-MoS₂.

As shown in Figure 2b, the PXRD pattern of the synthesized MoS₂ with broaden peaks exhibits some discrepancy with the standard reference card. This may arise from its hexagonal crystal structure with expanded interlayer spacing along the c-axis. By using the Bragg equation, the interlayer distance of as-prepared MoS₂ is calculated to 9.4 nm, consistent with the measured interlayer distance from the TEM image (Figure 2c). Further, XRD pattern has been simulated from the as-built structural model of MoS₂ with enlarged interlayer spacing (Figure S8). It is consistent with the obtained patterns. The broaden diffraction peaks positioned near 10°, 18°, and 25° can well be indexed to (002), (004), and (005) planes of MoS₂. Similar structural modifications have been previously reported (Nat. Commun. 2015, 6, 7493; J. Am. Chem. Soc. 2013, 135, 17881-17888; J. Mater. Chem. A 2015, 3, 12631-12635). These results revealed the successful synthesis of MoS₂. And the hybrid of N₃-COF/MoS₂.



Fig. S9 TEM images of N₃-COF.





d (002) = 4.703/5= 0.941 nm= 9.41 Å; According to the Bragg equation: $2d\sin\theta = n\lambda$ d (002) = Cu Ka/2×sin 4.9°= 1.54 Å/ 2×0.08= 9.63 Å. Here, 4.9° is converted based on the 2 θ =9.8° of the (002) crystal plane in MoS₂ XRD pattern.



Fig. S11 TEM images of N₃-COF/MoS₂.

Transmission electron microscopy (TEM) images reveal a distinct interface between MoS_2 and the N_3 -COF framework.



Fig. S12 Qst of CO_2 adsorption for N_3 -COF, MoS_2 and N_3 -COF/ MoS_2 .



Fig. S13 (a) N_2 adsorption-desorption curves at 77K, and (b) Pore size distribution for N_3 -COF, MoS₂ and N₃-COF/MoS₂.



Fig. S14 (a) CO_2 adsorption/desorption measurements at 273K, (b) at 298K of CO_2 adsorption for N₃-COF, MoS₂ and N₃-COF/MoS₂.



Fig. S15 CO₂-TPD curves of N_3 -COF, MoS_2 , N_3 -COF/ MoS_2 .

The desorption temperature of N_3 -COF/MoS₂ was higher than N_3 -COF and MoS₂, suggesting the more potent CO₂ adsorption of N_3 -COF/MoS₂.



Fig. S16 UV-vis DRS spectra of N_3 -COF, MoS_2 and N_3 -COF/ MoS_2 (a), and N_3 -COF/ MoS_2 with different mixture ratio of MoS_2 and N_3 -COF (b).

From UV-vis DRS, N₃-COF/MoS₂ exhibited an almost full spectrum light harvesting (Fig. S16).



Fig. S17 The band gap of N_3 -COF.



Fig. S18 Mott-Schottky plots of (a) N_3 -COF and (b) MoS_2 .



Fig. S19 UPS spectra of N_3 -COF (a) $E_{\text{cut off}}$, (b) E_{VBM}

and MoS_2 (c) $E_{cut off}$, (d) E_{VBM} .

Further elaborate on the energy band and work function of materials using ultraviolet photo-electron spectroscopy (UPS) test (Fig. S19). The secondary cutoff edge of N₃-COF and MoS₂ was determined to be 18.01 and 17.01 eV, respectively. And the valance band maximum energies (E_{VBM}) of N₃-COF and MoS₂ were calculated to be 0.55 and 1.23 eV. According to the formula: $W_f = hv + E_{VBM}$ - E_{cutoff} , the work function of N₃-COF and MoS₂ were 3.8 and 5.44 eV (vs. vacuum level). Due to the difference of work function, electrons will flow from N₃-COF with small work function to MoS₂ with large work function until the Fermi energy level at the interface reaches balance, and finally form a built-in electric field at the interface.



Fig. S20 (a) The averaged charge density difference for N_3 -COF/MoS₂. Yellow and blue region represent electron accumulation and depletion, respectively. C (dark gray), N (blue), H (light gray), Mo (pink) and S (yellow).



Fig. S21 (a) XPS survey spectra for N_3 -COF, MoS_2 and the N_3 -COF/MoS_2. In situ and ex situ XPS spectra for N 1s (b), Mo 3d (c), C 1s (d), S 2p (e) in N_3 -COF, MoS_2 and N_3 -COF/MoS_2.

The chemical composition and surface chemical states of N_3 -COF, MoS_2 and N_3 -COF/MoS_2 heterostructures were discussed by applying XPS analysis (Fig. S21). The XPS survey spectra showed that the N_3 -COF/MoS_2 heterostructure consists of C, N, S and Mo elements (Fig. S21 a). For the N 1s spectra (Fig. S21 b), the peaks at 399.56 and 398.77 eV in pure N_3 -COF were assigned to the C=N-N=C and C-N=C bonds,

respectively. Meanwhile, the Mo 3d peaks observed for MoS₂ at 228.63, 231.97, 232.71, 235.8 eV are assigned to ^{IV}Mo $3d_{5/2}$, ^{IV}Mo $3d_{3/2}$, ^VMo $3d_{5/2}$ and ^VMo $3d_{3/2}$ doublets, respectively (Fig. S21 c). In the high-resolution spectrum of C 1s spectra (Fig. S21 d) the peaks at 284.60 and 286.55 eV in pure N₃-COF were assigned to the C=C and C=N bonds. In addition, the S 2p peaks for MoS₂ observed at 161.61 and 162.87 eV are assigned to S $2p_{3/2}$, S $2p_{1/2}$ (Fig. S21 e). As shown in Fig. S20, compared with N₃-COF, the binding energies of N 1s in N₃-COF/MoS₂ composite obviously shift toward higher binding energies in darkness. Nevertheless, compared with MoS₂, the binding energies of Mo 3d, S 2p in N₃-COF/MoS₂ clearly shifted to lower binding energies in darkness, electrons have migrated from N₃-COF to MoS₂. However, when in situ light irradiated XPS measurements were performed, compared with samples in darkness, the binding energies of C 1s and N 1s in the N₃-COF/MoS₂ composite under light irradiation markedly moved to lower binding energies. In contrast, the binding energies of Mo 3d and S 2p in the composite significantly shifted to higher binding energies, suggesting the photogenerated electrons transferred from MoS_2 to N_3 -COF under light irradiation.



Fig. S22 (a) Transient photocurrent response spectra of N_3 -COF/MoS₂, N_3 -COF and MoS₂, (b) Electrochemical impedance spectra of N_3 -COF, MoS₂ and N_3 -COF/MoS₂.

The transient photocurrent response intensity of N_3 -COF/MoS₂ is much higher than MoS₂ and N₃-COF (Fig. S22 a), while the electrochemical impedance spectroscopy (EIS) shows a relatively lower interface charge transfer resistance of N_3 -COF/MoS₂ (Fig. S22 b).



Fig. S23 Control experiments of CO₂ reduction.



Fig. S24 Photocatalytic CO $_2$ conversion rates of $N_3\text{-}COF,\,MoS_2$ and $N_3\text{-}COF/MoS_2$

with different mass ratio.



Fig. S25. ¹H-NMR of rinsing solution of N_3 -COF/MoS₂ after photocatalytic CO₂

reduction reaction.



Fig. S26 Apparent Quantum Yield (AQY) of N_3 -COF/MoS₂ in CO₂

and CO₂ (80%) + O₂ (20%) atmosphere.



Fig. S27 Conversion of photocatalytic CO_2 reduction under different oxygen concentrations of N₃-COF/MoS₂.

To simulate the oxygen levels found in natural atmospheric conditions, the photocatalytic performance was evaluated under various atmospheric settings, specifically with an oxygen concentration of 20% (Fig. S27). It can be clearly observed that the activity of the material has been significantly improved after the addition of O_2 . At the same time, to further evaluate the photocatalytic CO_2 reduction performance of the heterostructure under the condition of low CO_2 concentration, a series of control experiments were carried out. The catalytic activity decreased with the decrease of CO_2

concentration (Fig. S27 a-e), and still maintained an average of 18.3 μ mol·g⁻¹·h⁻¹ at only 40% CO₂ concentration. To illustrate the effect of O₂ on the performance, a 70% CO₂+30% Ar control group was set (Fig. S27 f). As compared with Fig. S27 b and S27 d, the introduction of O₂ significantly promoted the photocatalytic CO₂ reaction when the CO₂ concentration and Ar concentration were kept constant, respectively.



Fig. S28 PXRD patterns of N_3 -COF/MoS $_2$ before and after cyclic reaction.



Fig. S29 SEM images of N_3 -COF/MoS₂ (a), (b) before and (c), (d) after cyclic reaction.



Fig. S30 TEM image (a), STEM-HAADF (b), element line scanning (c), chemical composition (d) of N₃-COF/MoS₂ after cycling reaction.



Fig. S31 FTIR spectra of N_3 -COF/MoS₂ before and after cyclic reaction without O₂ (a), with O₂ (b).



Fig. S32 In-situ FTIR experiment over N₃-COF/MoS₂ under light irradiation in CO₂+H₂O+O₂ condition. In-situ FTIR spectra in 2000-800 cm⁻¹ (a), in 1750-1640 cm⁻¹ (b), in 2500-2200 cm⁻¹ (c), in 3620-3580 cm⁻¹ (d).



Fig. S33 In-situ FTIR experiment over N_3 -COF/MoS₂ under light irradiation in CO₂+H₂O condition. In-situ FTIR spectra in 2000-800 cm⁻¹ (a), in 1750-1640 cm⁻¹ (b), in 2500-2200 cm⁻¹ (c), in 3620-3580 cm⁻¹ (d).



Fig. S34 In-situ FTIR experiment over N₃-COF/MoS₂ under light irradiation in O₂+H₂O condition. In-situ FTIR spectra in 2000-800 cm⁻¹ (a), in 1750-1640 cm⁻¹ (b), in 2500-2200 cm⁻¹ (c), in 3620-3580 cm⁻¹ (d).



Fig. S35 In-situ FTIR experiment over N₃-COF/MoS₂ in CO₂ (without H₂O, under light irradiation) condition (a), CO₂+H₂O (dark) condition (b), CO₂+O₂ (without H₂O, under light irradiation) condition (c), CO₂+H₂O+O₂ (dark) condition (d).



Fig. S36 (a) XPS survey spectra, (b) C 1s, (c) Mo 3d, (d) S 2p XPS spectra of N_3 -COF/MoS₂ under different photocatalytic reaction conditions.

The binding energies of Mo and S elements almost unchanged before and after the photocatalytic reaction.



Fig. S37 (a) EPR DMPO- \cdot O₂⁻ signal in methanol (b) EPR DMPO- \cdot OH signal in aqueous solution of N₃-COF, MoS₂, and N₃-COF/MoS₂.



Fig. S38 (a) CO₂ and O₂ adsorption energies on triazine and azine units of N₃-COF. (b)(e) calculated structural model with Gaussian.



Fig. S39 The Gibbs free energy calculated structural model (a) N₃-COF, (b) *CHOOH,
(c) *O, (d) *OCOOH, (e) *Hz, for the photocatalytic CO₂ reduction reaction (CO₂RR) by N₃-COF under CO₂ and O₂ atmosphere. Where the asterisk (*) indicated the adsorption state on the photocatalyst surface.



Fig. S40 The Gibbs free energy calculated structural model (a) N₃-COF, (b)
*CHOOH, (c) *O, (d) *OH, for the photocatalytic O₂ reduction reaction (ORR)
by N₃-COF under CO₂ and O₂ atmosphere. Where the asterisk (*) indicated the adsorption state on the photocatalyst surface.



Fig. S41 The Gibbs free energy calculated structural model (a) N₃-COF, (b) *CO₂,
(c) *COOH, (d) *CO, for the photocatalytic CO₂ reduction reaction (CO₂RR) by N₃-COF under CO₂ atmosphere. Where the asterisk (*) indicated the adsorption state on the photocatalyst surface.

Sample	$\tau_{1}\left(ns\right)$	τ_2 (ns)	A_1	A_2	$\tau_{ave}\left(ns\right)$
MoS_2	1.36	5.95	0.85	0.12	3.10
N ₃ -COF	0.55	8.93	1.15	0.01	2.22
N ₃ -COF/MoS ₂	0.53	3.75	0.97	0.11	1.98

Table S1 Fluorescence lifetime and average lifetime results for different samples.

The decay model of $f(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$ was used to fit the PL decay curves. The average lifetime τ_{ave} can be calculated by the formula: $\tau_{ave} = (A_1\tau_1^2 + A_2\tau_2^2) / (A_1\tau_1 + A_2\tau_2)$ The calculated results were listed in Table S1.

Photocatalysts	Reaction medium	Illumination	Performance (µmol·g ⁻¹ ·h ⁻¹)	Reference
N ₃ -COF/MoS ₂	Solid-gas phase	$\lambda \ge 420 \text{ nm} (300 \text{ W Xe})$	Pure CO ₂ : CO: 20.125 Aerobic environment: CO: 28.15	This work
TTCOF/NUZ	Solid-gas phase	$\lambda \ge 420 \text{ nm} (300 \text{ W Xe})$	CO: 6.56	[10]
$CeO_2/g-C_3N_4$	Solid-gas phase	Simulated sunlight (300 W Xe)	CH ₄ : 2.3	[11]
g-C ₃ N ₄ @CeO ₂	Solid-gas phase	$\lambda \ge 420 \text{ nm} (300 \text{ W Xe})$	CO: 5.6	[12]
BN (Porous)	Solid-gas phase	$\lambda \ge 400 \text{ nm} (300 \text{ W Xe})$	CO: 1.16	[13]
BiOI/g-C ₃ N ₄	Solid-gas phase	$\lambda \ge 400 \text{ nm} (300 \text{ W Xe})$	CO: 3.58	[14]
$MnO_2/g-C_3N_4$	Solid-gas phase	Simulated sunlight (300 W Xe)	CO: 9.6	[15]
$g-C_3N_4/Bi_2WO_6$	Solid-gas phase	$\lambda \ge 420 \text{ nm} (300 \text{ W Xe})$	CO: 5.19	[16]
TiO ₂ -g-C ₃ N ₄ /BiVO ₄	Solid-gas phase	$\lambda \ge 420 \text{ nm} (300 \text{ W Xe})$	CO: 5.18	[17]
(-CN)/g-C ₃ N ₄	Solid-gas phase	$\lambda \ge 420 \text{ nm} (300 \text{ W Xe})$	CO: 0.38	[18]
ZnIn ₂ S ₄ @TAz-COF	Solid-gas phase	$\lambda \ge 420 \text{ nm} (300 \text{ W Xe})$	CO: 12.625	[19]
CuWO4/TTCOF	Solid-gas phase	$\lambda \ge 420 \text{ nm} (300 \text{ W Xe})$	CO: 7.17	[20]
TT-COF-Zn	Solid-gas phase	$\lambda \ge 420 \text{ nm} (300 \text{ W Xe})$	CO: 2.06	[21]
ZnIn ₂ S ₄ /MOF-808	Solid-gas phase	$\lambda \ge 420 \text{ nm} (300 \text{ W Xe})$	CO: 8.21	[22]
$Au/g-C_3N_4$	Solid-gas phase	UV-vis light (300 W Xe)	CO: 6.59	[23]
DUT-67/RGO	Solid-gas phase	UV-vis light (300 W Xe)	CO: 42.41	[24]

Table S2 The catalytic performance of N_3 -COF/MoS₂ compared with other photocatalysts for photocatalytic CO₂ reduction with H₂O.

MTCN-H(Ys)	Solid-gas phase	$\lambda \ge 300 \text{ nm} (300 \text{ W Xe})$	CO: 16.87	[25]
COF-318/TiO ₂	Solid-gas phase	$\lambda \ge 380 \text{ nm} (300 \text{ W Xe})$	CO: 69.67	[26]
ZnSe/CdS	Solid-gas phase	400 nm LEDs (100 mW cm ⁻²)	CO: 11.3	[27]
UiO-66-NH ₂ /RGO-3	Solid-gas phase	300 W Xe lamp	CO: 23.54	[28]
Bi ₂ S ₃ /UiO-66	Solid-gas phase	The PLS-SXE300 Xe lamp	CO: 25.6	[29]
$\alpha\text{-}Fe_2O_3/g\text{-}C_3N_4$	Solid-gas phase	300 W Xe lamp	CO: 27.2	[30]
TiO ₂ /NH ₂ -UiO-66	Solid-gas phase	$\lambda \ge 325 \text{ nm} (150 \text{ W Xe})$	CO: 4.25	[31]
TiO ₂ /Co-ZIF-9	Solid-gas phase	200≤λ≤900 nm, 300 W Xe lamp	CO: 17.58	[32]
TAPBB-COF	Solid-gas phase	Xe lamp	CO: 24.6	[33]
CsPbBr ₃ QDs/UiO- 66(NH ₂)	Solid-gas phase	300 W Xe lamp	CO: 8.21	[34]
Co(II)/ZnO/rGO	Solid-gas phase	Simulated sunlight (300 W Xe)	CO: 26.15	[35]
g-C ₃ N ₄ /Ag-TiO ₂	Solid-gas phase	300 W xenon lamp	CH ₄ : 9.33 CO: 6.33	[36]
g-C ₃ N ₄ /NiAl-LDH	Solid-gas phase	300 W xenon lamp	CO: 27.02	[37]
Ti_3C_2/g - C_3N_4	Solid-gas phase	$\lambda \ge 420 \text{ nm} (300 \text{ W Xe})$	CH ₄ : 0.044 CO: 5.19	[38]
Pd-HPP-TiO ₂	Solid-gas phase	UV-vis light (300 W Xe)	Pure CO ₂ : CH ₄ : 48, CO: 34 Aerobic environment: CH ₄ : 12.2, CO: 4.9	[39]
ZnTCPP/g-C ₃ N ₄	Solid-gas phase	360≤λ≤800 nm, 300 W Xe lamp	Pure CO ₂ : CH ₄ : 3.2, CO: 16.7 Aerobic environment CH ₄ : 11.3, CO: 92.0	[40]

Sample	Reaction condition	Average CO yield (μmol g ⁻¹ h ⁻¹)	CO selectivity (%)
MoS_2	High-purity CO ₂	0.14	≈100%
N ₃ -COF	High-purity CO ₂	1.78	≈100%
N3-COF/MoS2	High-purity CO ₂	20.13	≈100%
	5% O ₂ +95% CO ₂	27.33	92.43 %
	10% O ₂ +90% CO ₂	29.60	91.13 %
	20% O ₂ +80% CO ₂	28.15	90.05 %
	30% O ₂ +70% CO ₂	25.11	89.47 %
	40% O ₂ +60% CO ₂	22.43	90.22 %
	50% O ₂ +50% CO ₂	17.76	90.36 %
	60% O ₂ +40% CO ₂	14.40	89.96 %
	20% O ₂ +70% CO ₂ +10% Ar	25.12	89.78 %
	20% O ₂ +60% CO ₂ +20% Ar	22.43	90.34 %
	20% O ₂ +50% CO ₂ +30% Ar	17.77	90.15 %
	20% O ₂ +40% CO ₂ +40% Ar	16.40	89.53 %
	70% CO ₂ +30% Ar	14.37	≈100 %

Table S3 The selectivity of the photocatalytic CO $_2$ reduction reaction for N $_3$ -COF, MoS $_2$, and N $_3$ -COF/MoS $_2$.

Average CO yield: the average yield of CO produced by the material through photocatalysis over a period of 6 hours under corresponding conditions.

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