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Fabrication of 2D–2D Heterojunction Catalyst with Covalent Organic Framework (COF) and MoS₂ for Highly Efficient Photocatalytic Degradation of Organic Pollutants

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ABSTRACT: In this work, for the first time, we fabricated a novel covalent organic framework (COF)-based 2D–2D heterojunction composite MoS_2/COF by a facile hydrothermal method. The results of photocatalytic degradation of TC and RhB under simulated solar light irradiation showed that the as-prepared composite exhibited outstanding catalytic efficiency compared with pristine COFs and MoS_2 . The significantly enhanced catalytic efficiency can be ascribed to the formation of 2D–2D heterojunction with a well-matched band position between COF and MoS_2 , which can effectively restrain the recombination of charge carriers and increase the light absorption as well as the specific surface area. Moreover, the fabricated 2D–2D layered structure can effectively increase the contact area with an intimate interface contact, which greatly facilitates the charge mobility and transfer in the interfaces. This study reveals that artful integration of organic (COFs) and inorganic materials into a single hybrid with a 2D–2D interface is an effective strategy to fabricate highly efficient photocatalysts.

1. INTRODUCTION

Anthropogenic pollutions such as antibiotics and organic waste in bodies of water have arisen serious threats to the environment, human health, and ecosystems.^{1,2} Various techniques such as membrane separation, adsorption, chemistry methods, and photocatalysis have been applied to eliminate these pollutants.^{3–7} Compared to other techniques, photocatalysis is recognized to be attractive methods due to it being environmentally-friendly, solar energy utilization, and cost-effective.^{8–11} However, plenty of developed catalysts are limited in practical applications due to their drawbacks such as poor visible-light absorption, rapid charges carrier recombination rate, and low quantum yield.^{12,13} Thus, it is imperative to develop novel photocatalysts with strong visible-light absorption and outstanding photoactivity. Recently, two-dimensional covalent organic frameworks (COFs), as an emerging class of porous crystalline materials assembled with organic molecules through covalent bonds, have attracted much attention. COFs have been testified to be ideal candidates employed in catalysis, gas adsorption and separation, proton conductivity, optoelectronics, and energy applications^{14–19} due to their chemically and mechanically robust, inherent porosity, uniquely ordered channel structure,

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Scheme 1. Schematic Diagram of the Synthesis Process for 2D-2D Heterojunction Composite MoS₂/COF

high surface area, and tunable light harvesting properties.^{20–22} More recently, COFs have been recognized as a new type of photocatalysts and some of the COFs have exhibited fascinating properties for visible-light H₂ production.²³ The excellent photocatalytic properties of COFs should be attributed to their porous structure, wide light-harvesting ability, and strong $\pi - \pi$ interactions between the adjacent layers.²⁴ Moreover, crystalline COFs have emerged as ideal platforms to be used as an effective support matrix for stabilizing the homogeneously semiconducting materials to synthesize versatile photocatalysts in terms of their high surface area, porosity, and high stability.^{24,25} Particularly, the 2D crystalline feature of COFs can enhance the charge mobility and transfer between the interfaces, owing to its $\pi - \pi$ conjugation along the layers.²⁶ Although COFs-based photocatalysts have been used for H₂ production with considerable efficiency, their potential for pollutant removal remains hardly explored. Moreover, in most of the studies, noble metals as cocatalysts are inevitably employed in COFs-based photocatalysis to realize a high catalytic efficiency, owing to their high recombination rate of photoinduced electrons and holes.²⁷ Thus, it is crucial to seek an alternative to noble metal cocatalysts that match well with COFs, suppress the recombination of charge carrier, and consequently promote the photocatalytic activity. Usually, the fabrication of a 2D heterojunction is an efficient method to improve chargeseparation efficiency of a semiconductor and consequently improve its photocatalytic activity. For example, Y. J. Yuan et al. reported the $g-C_3N_4/graphene/MoS_2$ two-dimensional nanojunction, which exhibited a much higher photocatalytic H₂ production activity than the optimized Pt-loaded g-C₃N₄.²⁸ F. M. Zhang et al. reported that when 2D TpPa-1 COF was combined with NH₂-UiO-66 MOF to form heterojunction, its photocatalytic H₂ evolution rate was enhanced 20 times.²⁶ Z. B. Han et al. reported a heterojunction catalyst PCN-222-Co@

TpPa-1 that can effectively catalyze the deacetalization-Knoevenagel condensation reaction (yield of 99.3%).²⁹

In this work, for the first time, a typical TpPa-1 COF was synthesized and it was integrated with MoS_2 to form a 2D–2D heterojunction composite by a facile hydrothermal method. The photocatalytic properties of the as-prepared products were assessed via the degradation of tetracycline (TC) and rhodamine B (RhB). The prepared MoS_2/COF 2D–2D heterojunction can greatly facilitate the charge mobility and transfer between the interface and effectively suppress the recombination of charge carriers, resulting in a remarkably enhanced photocatalytic efficiency.

2. EXPERIMENTAL SECTION

2.1. Materials. 2,4,6-Trihydroxy-benzene-1,3,5-tricarbaldehyde $(C_9H_6O_6)$, *p*-phenylenediamine $(C_6H_8N_2)$, 1,4-dioxine, 1,3,5-trime-thylbenzene, acetic acid, sodium molybdate dihydrate, thiourea, sodium sulfate (Na_2SO_4) , 1,4-benzoquinone (BQ), triethanolamine (TEOA), and isopropanol (IPA) were purchased from Sinopharm Chemical Reagent Corp. Tetracycline (TC) was obtained from Tianjin Seans Biochemical Technology Co., Ltd.

2.2. Synthesis of TpPa-1 COF. The TpPa-1 COF was synthesized according to the reported method with a slight change.³⁰ One milliliter of acetic acid (3 mol/L), 3 mL of 1,3,5 trimethylbenzene, and 3 mL of dioxane with a volume ratio of 1:3:3 were mixed in a round-bottom flask. Then, 63 mg of 1,3,5-triformylphloroglucinol (0.3 mmol) and 48 mg of paraphenylenediamine (0.45 mmol) were added into the mixture. The mixture was continuously sonicated for 15 min until a homogeneous dispersion was obtained. Then, the mixture was bubbled with N₂ for 15 min and heated at 120 °C for 3 days under a nitrogen atmosphere. After cooling down to room temperature, the resultant product was, respectively, washed with tetrahydrofuran, acetone, and hot DI water three times. The obtained product was dried at 120 °C for 10 h in a vacuum oven.

2.3. Synthesis of 2D–2D heterojunction composite MoS₂/ COF. As shown in Scheme 1, 2D–2D heterojunction composite



Figure 1. (a) XRD patterns of the as-prepared samples and (b) enlarged view of XRD patterns for the as-prepared samples.

 MoS_2/COF was prepared by a facile hydrothermal method. Typically, 8 mg of as-prepared COF, 48.4 mg of sodium molybdate dihydrate ($Na_2MoO_4.2H_2O$), and 30.5 mg of thiourea were mixed in 60 mL of DI water with magnetic stirring for 1 h. The resulting mixture was put into Teflon-lined stainless steel autoclave and heated at 200 °C for 12 h. After cooling down to the room temperature, the resulting product was collected by centrifugation, washed with DI water three times, and finally was dried in a vacuum oven at 80 °C overnight. Different weight ratios of MoS_2/COF ranging from 10% to 30% (referred to COF proportion) were synthesized. The obtained MoS_2/COF composites with different weight ratios including 10, 20, and 30 wt % were donated as MoS_2/COF (10), MoS_2/COF (20), and $MoS_2/$ COF (30), respectively. The MoS_2/COF (20) was chosen for characterizations. Pure MoS_2 was prepared with the same experimental method but without the addition of COF.



Figure 2. FTIR spectra of the as-prepared samples.

2.4. Characterizations. The crystal phases of the samples were characterized by powdered X-ray diffraction (XRD) on a Rigaku D/ max-2500 diffractometer (Rigaku) using Cu K α radiation operated at 18 kV and 80 mA in the range from 4° to 85°. The morphologies of the samples were investigated by a transmission electron microscope (TEM) with a HT7700 electron microscope (HITACHI) and by a scanning electron microscope (SEM) (Hitachi S-4800). The structure specification and chemical states of the sample were investigated by XPS spectra analysis on a Thermo ESCALAB 250XI spectrometer. UV–vis diffused reflectance spectra were recorded on a Cary-5000 Ultraviolet–visible near-infrared spectrophotometer by using BaSO₄ as a reference. The specific surface area was calculated by the Brunauer–Emmett–Teller (BET) method according to a N₂

adsorption-desorption isotherm, which was collected by using Quantachrome instruments (Autosorb-iQ-MP-AG). Photoluminescence spectra (PL) of samples were recorded on a FS5 fluorescent spectrophotometer (Edinburgh Instruments). FTIR spectra were conducted on a Nicolet iS10 spectrophotometer.

2.5. Photoelectrochemical Measurements. The photocurrent of the as-prepared samples was recorded by a CHI 660A workstation with a three-electrode cell, where a Pt wire electrode was regarded as the counter electrode, the as-prepared sample as the working electrode, and a saturated calomel electrode as the reference electrode. A Na_2SO_4 (0.2 M) solution was employed as the supporting electrolyte. A 300W Xe lamp was used as the light source.

2.6. Evaluation of Photocatalytic Activity. Photocatalytic performances of as-prepared catalysts were evaluated by the degradation of tetracycline (TC) and Rhodamine B (RhB). The photocatalytic degradation experiments were carried out at room temperature using a SGY-IB multifunction photochemical reactor (Hao Bin Co. Ltd., Nanjing, China) equipped with a 300W Xeon lamp. In a typical experiment, 10 mg of as-prepared sample and 20 mL of TC (20 mg/L) or RhB (20 mg/L) aqueous solution were mixed in a quartz cuvette. The suspension was first stirred in the dark for 30 min to get an adsorption-desorption equilibrium between the catalyst and dye. Then, the photoreaction vessels were exposed to Xenon lamp irradiation with continuous stirring. The wavelength distribution of the 300 W Xe lamp (PL-X500D) is similar to that of solar light. After the photodegradation started, 1 mL of the sample was taken at a given time intervals and filtered with 0.22 μ m PVDF disposable filters. The sample was analyzed by measuring UV-visible absorption at the maximum absorption bands of RhB ($\lambda_{max} = 554 \text{ nm}$) and TC ($\lambda_{max} = 357$ nm) with a TU-1810DPC UV-vis spectrophotometer.

3. RESULTS AND DISCUSSION

3.1. Characterizations. The X-ray diffraction patterns of pure MoS₂, COF, and MoS₂/COF are shown in Figure 1. The diffraction peaks of MoS₂ at 14.4°, 33.45°, 39.54°, and 58.35° can be assigned to (002), (101), (103), and (110) planes of the hexagonal phase of MoS₂ (JCPDS 75-1539).^{31,32} The intense peak at 4.7° for COF corresponds to the reflection of its (100) plane.^{26,30} The peak at a 2 θ value ~27° of COF corresponds to its (001) plane ascribed to their π – π stacking structure.^{33,34} The obtained pattern is similar to a previous report.²⁶ As shown in Figure 1a, the composites display similar diffraction patterns of MoS₂, suggesting that the coupling with COF does not change the crystal structure of MoS₂. However, its diffraction peak at 39.54° slight decreases after coupling with COF and with an increasing amount of COF due to their



Figure 3. TEM images of (a) COF, (b) MoS₂, and (c) MoS₂/COF.



Figure 4. (a-e) EDX elemental mapping and (f) EDX spectrum of MoS₂/COF (20).



Figure 5. (a) UV-vis diffuse reflectance spectra and (b) band gap energies for the as-synthesized samples.

interaction (Figure 1b). No obvious diffraction peaks of COF can be detected in the hybrids, owing to its inherently poor diffraction peak intensity in comparison to that of MoS_2 .

In the Fourier transform infrared (FTIR) spectrum of COF (Figure 2), the peaks at 1580 and 1250 cm⁻¹ are assigned to the characteristic peaks of C=C and C-N bonds, respectively.³⁴ These characteristic peaks remain unaltered after hybrid formation, indicating that the COF is highly stable to the hydrothermal conditions on the course of the formation

of heterojunction. MoS_2 shows its characteristic peaks at 1400 and 473 cm⁻¹, which are attributed to the bridging Mo—S bond (Mo—S) vibration perpendicular to the basal plane.^{35,36} All the patterns of the MoS₂/COF hybrids exhibit the characteristic peaks of both MoS₂ and COF, indicating that the composites are successful assembled. Moreover, the characteristic diffraction peak intensities (1400 cm⁻¹) of MoS₂ increase with increasing of the mass ratios of MoS₂/



Figure 6. XPS survey spectra of (a) whole spectrum, (b) C 1s spectra, (c) N 1s spectra, (d) O 1s spectra, (e) Mo 3d spectra, and (f) S 2p spectra for MoS₂/COF (20).

COF, which is in good accordance with the rising MoS_2 contents in the synthesis process.

The morphologies of the samples were detected by TEM images. As shown in Figure 3a, the COF displays an irregular sheet-like structure, which can be ascribed to the $\pi-\pi$ stacking of COF layer. Interestingly, the morphology of MoS₂ is similar to that of the COF, with a sheet-like two-dimensional layer structure (Figure 3b). Figure 3c shows that the composite MoS₂/COF (20) displays a 2D–2D heterojunction structure with an intimate interfacial contact. It is worth noting that the 2D–2D structure can effectively increase the contact area with the intimate interface contact, which can greatly facilitate the

charge transfer in the interfaces and consequently contribute to the enhancement of photocatalytic activity. As shown in Figure S1, the SEM image of the TpPa-1-COF displays a kind of flower-like cluster consisting of nanorods, while the SEM image of MoS_2/COF (20) shows that MoS_2 nanosheets are distributed on the TpPa-1-COF. Furthermore, the elemental mapping analysis (Figure 4a–e) displays that Mo, S, C, and N are evenly distributed. EDX spectroscopy was also applied to confirm the chemical composition of the product. As shown in Figure 4f, all of the elements including C, O, N, Mo, and S are detected in the composite. All of the above results confirm that the 2D–2D heterojunction composite MoS_2/COF is successfully prepared.

The light absorptions of the samples were measured by the UV–vis diffuse reflectance spectra (DRS). As shown in Figure 5a, the COF exhibits a broad absorption band over the visible region with an edge around 620 nm, while the MoS₂ displays a full absorbance range from 200 to 1200 nm. When the COF is coupled with MoS₂, its absorbance edge has a remarkable red shift and its light absorption in visible-light region exhibits an obvious enhancement. In addition, the red shift and enhanced light absorption in the visible-light region raise with increasing of MoS₂ contents. The red shift and enhanced visible-light absorption suggest that the composite can absorb more visible light to generate more electron–hole pairs. The band gap energies (E_g) of pure MoS₂, COF, and MoS₂/COF are determined according to the following equation:³⁷

$$(\alpha h\nu) = A(h\nu - E_{\sigma})^{n/2}$$

Where, α , hv, $E_{g'}$ and A are the absorption coefficient, photon energy, band gap energy, and Planck's constant, respectively. The values of n is 1 for the direct and 4 for indirect transitions of semiconductor, respectively.³⁸ Therefore, the E_{g} values for MoS_2 , COF, MoS_2/COF (10), MoS_2/COF (20), and $MoS_2/$ COF (30) are calculated to be approximately 1.1, 2.11, 1.42, 1.59, and 1.72 eV, respectively. Compared with bare COF, the band gap of MoS₂/COF shows an obvious reduction. The narrowing band gap of MoS₂/COF is consistent with the enhanced optical absorption (Figure 5b). The band gap energy of the hybrid increases with an increase in COF mass content. The results of Mott-Schottky measurements indicate that the flat band position $(V_{\rm fb})$ of TpPa-1-COF is approximately -0.88 eV vs that of the saturated calomel electrode (SCE). Generally, the bottom of the CB in many n-type semiconductors is more negative by about 0.10 V than the $V_{\rm fb}$, ^{26,39} thus the CB of TpPa-1-COF was estimated to be -0.78 eV. Combined with the band gap energy, the VB position of TpPa-1-COF was calculated as 1.33 eV.

The structure specification and chemical states of asprepared sample were investigated by XPS spectra analysis. Figure 6a displays the XPS spectra of $MoS_2/COF(20)$, which confirm the presence of C, N, O, Mo, and S in the prepared sample. In the C 1s region (Figure 6b), the peak at 284.58 eV can be attributed to the C—C of $COF^{40,41}$ and the peaks at 286.6 and 288.32 eV can be ascribed to the MoC=O and C-OH (C=O) bonds, respectively.^{39,42,43} The N 1s spectra shown in Figure 6c can be resolved into three peaks at 394.5, 396.99, and 398.9 eV, respectively. The peak at 394.5 eV corresponds to Mo_2N ($3p_{3/2}$), which may be caused by the coordination between the Mo phase from MoS₂ and N in COF.⁴⁴ The two other N 1s peaks at 396.99 and 398.9 eV refer to a Mo-N bond and sp²-hybridized nitrogen C=N-C, respectively.⁴³⁻⁴⁹ The O 1s spectra (Figure 6d) can be deconvoluted into three peaks at 531.1, 532.6, and 533.3 eV, which are ascribed to the C=O, C-O/H-O, and Mo-O bonds, respectively.⁴² As shown in Figure 6e, the Mo 3d spectra can be resolved into three peaks at 229.02, 232.18, and 235.9 eV, respectively. Two strongest peaks centered at 229.02 and 232.18 eV are attributed to the Mo $3d_{5/2}$ (divulges from Mo-N bond) and Mo 3d_{3/2} orbits of Mo⁴⁴.^{32,48,50} Furthermore, the peak centered at 235.9 eV can be assigned to the Mo $3d_{3/2}$ orbit of characteristics state of Mo⁶⁺, which may come from the slight partial oxidation of Mo atoms at the

defects or edges of MoS_2 .⁴² The weak peak located at 226.18 eV can be ascribed to a S 2s band.⁵¹ The S 2P spectra (Figure 6f) can be resolved into two peaks at 161.8 and 163.04 eV, corresponding to S $2p_{3/2}$ and S $2p_{1/2}$ of S²⁻ in MoS₂, respectively.^{40,42} The XPS results verified that the MoS₂/COF composite is successfully synthesized.

TG analysis was carried out to determine the stabilities of assynthesized photocatalysts (Figure 7). According to the TGA



Figure 7. TGA curves of MoS₂, COF, and MoS₂/COF (20).

curves, both the COF and MoS_2/COF (20) show high thermal stability up to 300 °C. The little weight loss around 100 °C can be assigned to the absorbed water. The weight loss from 300 °C corresponds to the decomposition of COF and MoS_2 . The mass ratio of COF in the MoS_2/COF (20) was calculated to be about 19.29 wt %, which is comparable to the experimental value (20 wt %).

The surface areas and porous structure of the products were measured by N_2 adsorption-desorption experiments. As shown in Figure 8 and Figure S2, all of the samples exhibit type IV isotherms with hysteresis loops, suggesting a mesopore



Figure 8. N₂ adsorption-desorption isotherm of the samples.

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structure of the materials. The calculated Brunauer–Emmett– Teller surface areas (S_{BET}) of the MoS₂ and MoS₂/COF (20) were 3.159 and 18.984 m²/g, respectively. It is clear that the S_{BET} of MoS₂/COF (20) is six times higher than that of pure MoS₂, suggesting that the formation of 2D–2D heterojunction could increase specific surface area. As shown in Figure 8 and Table 1, the S_{BET} and pore volume of the composite increase

Table 1. Surface Areas, Pore Sizes, and Pore Volumes of thePrepared Samples

sample	surface area (m²/g)	pore size (nm)	pore volume (cm³/g)
MoS ₂	3.159	4.001	0.019
COF	474.5	1.52	0.2
MoS_2/COF (10)	10.87	3.983	0.023
MoS_2/COF (20)	18.984	3.906	0.062
MoS_2/COF (30)	31.385	2.64	0.091

with an increase in the content of COF. It is well-known that a larger surface area can provide more active sites for photocatalytic reactions, resulting in enhanced photocatalytic activity. Surface area, pore size, and pore volume for MOS_2 and MOS_2/COF heterojunctions are displayed in Table 1.

The photoluminescence (PL) emission spectra were conducted to determine the recombination rate of photoinduced charge carriers. As shown in Figure 9a, the PL intensity of MOS_2/COF is much weaker than that of pure COF and MOS_2 , indicating a great decrease of the recombination rate of the photoinduced charge carriers in the MOS_2/COF composite. In addition, the emission PL peaks shift toward a longer wavelength after the introduction of COF, due to their interaction and ring-strain of $COFs^{52,53}$

Transient photocurrent responses and electrochemical impedance spectroscopy (EIS) were conducted to further study the separation efficiency of the charge carriers. As shown in Figure 9b, the photocurrent density of MoS_2/COF is significant higher than that of the pure COF and MoS_2 , confirming the formation of heterojunction contributing to accelerating the separation of charge carriers. As shown in Figure 9c, the Nyquist semicircles diameter of the MoS_2/COF is smaller than that of the MoS_2 , indicating its lower interface charge transport resistance. All of these results demonstrate that the formation of 2D-2D MoS_2/COF heterojunction can effectively improve the interface charge transfer and separation.

3.2. Phocatalytic Performances and Mechanism. The photocatalytic performances of the prepared products were accessed via the degradation of RhB and TC (Figure 10). In Figure 10a, the removal efficiency of RhB is about 98% for MoS₂/COF (20) after simulated sun-light irradiation for 30 min, whereas it is only 37.5% and 35.6% for pure MoS₂ and COF, respectively. The apparent rate constant of MoS₂/COF (20) is 0.118 min^{-1} , which is about seven and eight times higher than those of the pristine MoS₂ and COF, respectively. For TC, its degradation ratio by MoS₂/COF (20) is 85.9% after 60 min irradiation, while it is only 47% and 37.8% for pure MoS₂ and COF, respectively. The apparent rate constant of the TC degradation for MoS₂/COF (20) is 0.0316 min⁻¹, which is about three and four times higher than those of the pristine MoS_2 (0.0103 min⁻¹) and COF (0.0083 min⁻¹), respectively.

The superior photocatalytic performance of the prepared MoS₂/COF composite should be ascribed to the formation of 2D-2D heterostructure, which facilitates the transfer and separation of the charge carriers and increases light absorption and specific surface area. The MoS_2/COF (20) exhibits the best photocatalytic performance of all of the samples. The mass ratio (MoS_2/COF) impacts the photocatalytic performance of the composites. The photocatalytic efficiency increases to a certain extent (up to 20 wt % COF) and then eventually decreases on a further increase of the amount of COF. The detriment of the photocatalytic activity is likely a consequence of shielding effect. Due to its relatively low visible-light absorption in contrast to MoS₂, an excess of COF covers the visible-light-active MoS₂, resulting in a decrease of photocatalytic activity. The results of degradation of TC is similar to that of RhB, further demonstrating that the as-prepared composite possesses high photocatalytic activity and exhibits potential capability for highly efficient degradation of organic pollutants.

A cycling experiment was conducted to explore the stability of the as-prepared photocatalyst. The used catalyst was collected after each cycle test by centrifuging, washing, and vacuum-drying at 60 °C overnight. As shown in Figure 11a, the degradation efficiency of the catalyst does not obviously decrease after three cycles, suggesting that the as-prepared catalyst MoS_2/COF (20) is quite stable and reusable in the photocatalytic degradation process. Furthermore, XRD of the hybrid after photocatalytic experiments was measured. As shown in Figure S3, the XRD patterns between the samples



Figure 9. (a) Photoluminescence (PL) emission spectra, (b) transient photocurrent responses, (c) and Nyquist plot of electrochemical impedance spectra (EIS) of MoS_2 and MoS_2/COF composites.

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Figure 10. Photocatalytic degradation curves for (a) RhB and (b) TC over various as-prepared samples. The kinetic rate constants for degradation of (c) RhB and (d) TC.



Figure 11. (a) Cycle experiments for degradation of RhB over MoS_2/COF (20). (b) Trapping experiments by using different scavengers on the RhB degradation over MoS_2/COF (20).

before and after photocatalytic experiments showed no obvious differences, further confirming the high stability of the hybrid.

The trapping experiments were carried out to explore the photocatalytic mechanism. To test the role of these reactive species, triethanolamine (TEOA), isopropylalcohol (IPA), and ρ -benzoquinone (BQ) were employed as scavengers for h⁺, •OH, and •O₂⁻, respectively. As can be seen in Figure 11b, the

degradation ratios for RhB are all reduced after the addition of the three trapping reagents, indicating that the $h^{+, \bullet}OH$, and ${}^{\bullet}O_2^{-}$ are all responsible for the degradation process. When the TEOA is added into the reaction system, the degradation efficiency is remarkably decreased, suggesting that h^+ takes a crucial part in the degradation of organic pollutants. Figure 11b demonstrates that the influence sequence of the active radicals for RhB degradation is $h^+ > {}^{\bullet}OH > {}^{\bullet}O_2^{-}$.

Based on the experimental results, the tentative mechanism for the superior photocatalytic performance of MoS₂/COF is illustrated in Figure 12. Both COF and MoS₂ are excited and



Figure 12. Schematic diagram for the proposed photocatalytic reaction mechanism of MoS₂/COF.

engender photogenerated electron-hole pairs under the simulated solar-light irradiation. The generated electrons on the CB of COF rapidly transfer to the MoS₂ since the CB edge potential of COF is more negative than the MoS₂, meanwhile the holes on the VB of MoS₂ transfer to the COF since the VB edge potential of MoS₂ is more positive than the COF. This can effectively restrain the recombination of photoinduced electron-hole pairs for COF and MoS₂. The accumulated electrons on the CB of MoS₂ can react with the adsorbed O₂ to form ${}^{\bullet}O_2^{-}$ radicals, which react with H⁺ and e⁻ to generate H_2O_2 and finally result in the production of ${}^{\bullet}OH.$ The generated *OH and h+ are powerful to oxidize the organic pollutants into small molecules, e.g., CO₂ and H₂O. The photocatalytic reaction processes are illustrated below.

$$MoS_2 + h\nu = h^+ + e^-$$

$$COF + h\nu = h^+ + e^-$$

$$COF (e_{CB}^{-}) \rightarrow MoS_2 (e_{CB}^{-})$$

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 $MoS_2 (e^-) + O_2 = O_2^-$

$$O_{2}^{-} + 2H^{+} + e^{-} = H_{2}O_{2}$$

$$H_2O_2 + e^- = OH^- + OH^-$$

 $h^+ + {}^{\bullet}OH + {}^{\bullet}O_2^- + pollutants$

= $CO_2 + H_2O$ + degradation intermediate

4. CONCLUSION

In summary, a novel 2D-2D nanocomposite MoS₂/COF has been synthesized via a facile hydrothermal method. The prepared products are characterized in detail. The results of photocatalytic degradation of TC and RhB under simulated solar-light irradiation show that the MoS₂/COF composite with an optimized weight ratio of 4:1 exhibits a significantly enhanced catalytic efficiency in contrast to those of the pristine MoS₂ and COF. The enhanced catalytic activity can be assigned to the formation of band position well-matched

heterojunction and the 2D-2D layered structure. This work provides new insights into the fabrication of COF-based composites as high-performance photocatalysts and facilitates their application in environmental protection and hydrogen energy issues using solar light.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c00422.

Figures of SEM images, N2 adsorption-desorption isotherms, and XRD patterns (PDF)

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Notes

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