High-Efficiency Photocatalytic Degradation of Tannic Acid Using TiO₂ Heterojunction Catalysts
Ruixi Liu, Linzhen Wu, Hao Liu, Youkui Zhang, Jianjun Ma, Cairong Jiang,* and Tao Duan*

ABSTRACT: Photocatalysts have been extensively used for hydrogen evolution or organic degradation. In this work, two different heterojunction types of composite photocatalysts, 1T-MoS₂@TiO₂ with Schottky heterojunction and 2H-MoS₂@TiO₂ with type-II heterojunction, are synthesized via hydrothermal synthesis. These two composite materials exhibit excellent photocatalytic activity toward the degradation of tannic acid, which is a typical organic in nuclear wastewater. At an optimal loading of 16% 1T-MoS₂, the 1T-MoS₂@TiO₂ shows the highest degradation capacity of 98%, which is 3.2 times higher than that of pure TiO₂. The degradation rate of 16% 1T-MoS₂@TiO₂ is much higher than that of 13% 2H-MoS₂@TiO₂. The enhanced photocatalytic activity might be attributed to the improved charge transfer according to the mechanism investigation, supported by the X-ray photoelectron spectroscopy (XPS) and electrochemical impedance spectroscopy (EIS) analyses. This work provides new opportunities for constructing highly efficient catalysts for nuclear waste disposal.

1. INTRODUCTION
Nuclear energy is a nonrenewable alternative energy source with high energy density, environmental protection, and a small footprint. However, radioactive organic wastewater is produced in nuclear fuel production, operation of nuclear power plants, and decommissioning of nuclear facilities, which causes long-term harm to the ecological environment. Organic nuclear waste liquid mainly consists of the radioactive element uranium, organic matter tannic acid (TA), and tributyl phosphate. It has the characteristics of complex composition, intense radioactivity, poor safety and stability, and a high amount of heat generation. The presence of organic matter not only easily causes the blockage and regeneration of the ion exchange resin channel but also has potential safety hazards. Therefore, it is required to pretreat the organic matter before solidifying the radioactive waste liquid containing organic matter.

Traditional methods for removing organic matter include high-temperature oxidation, wet chemical reaction, physical adsorption, photocatalysis, etc. Among them, the semiconductor photocatalysis technology displays many advantages, for example, strong oxidizing ability, effective absorption of light, environment friendliness, mild reaction conditions, and stable chemical properties without secondary pollutants. It has become a research focus in energy and the environment. Anatase TiO₂ material used as a photocatalyst demonstrates high efficiency and excellent chemical stability. The main characteristics of anatase TiO₂ are its nontoxicity, low cost, and strong corrosion resistance. Therefore, it is widely used in the photocatalytic field. Solar energy, generated through photoelectricity and water photocatalysis over photocatalysts (e.g. TiO₂), can alleviate the environmental and energy crisis. TiO₂ wide band gap, high electron–hole recombination rate, and few active catalytic sites are the main obstacles hindering its wide application. It is therefore interesting to develop new photocatalytic materials with good photocatalytic activities or tailor the structure and particle size. It is found that nanoflower TiO₂ has better degradation ability toward methylene blue than pure TiO₂.

Developing heterojunction materials is another effective method to accelerate charge separation, activate the catalyst surface, and enhance photocatalytic active sites. New composite materials synthesized with metals or semiconductors contain the Schottky barrier heterojunctions. Therefore,
they are often used for photocatalytic hydrogen evolution. However, some metals are high-cost, and hence it is necessary to seek alternatives. The CdSe/graphene/TiO2 composite prepared shows high photocatalytic activity for methylene blue under visible light. Type-II heterojunctions have been proven to be promising excellent photocatalytic materials. The large exposed edge of MoS2 originates from the rich catalytic active sites on the sulfur edge of the crystal layer, and the narrow band gap has good complementary characteristics with TiO2. 

Tang et al. synthesized a series of anatase TiO2@MoS2 assisted by a porous material for the photocatalytic degradation of tannic acid. 

2. EXPERIMENTAL SECTION

2.1. Materials. Raw chemicals, molybdenum trioxide (MoO3, 99.9% Shanghai Aladdin Biochemical Technology Co., Ltd.), urea (CH4N2O, 99%, Shanghai Aladdin Biochemical Technology Co., Ltd.), thiourea (CH2CSNH2, 99%, Chengdu Cologne Chemical Co., Ltd.), and nano titanium dioxide (P25, 99.9% Shanghai King Chemical Co., Ltd.), were used without any further purification.

2.2. Synthesis of 1T-MoS2, 2H-MoS2, and MoS2@TiO2. 

Two-dimensional (2D) composite materials of 1T-MoS2@MIL-101(Cr) were prepared using a solvothermal method. For the preparation of 1T-MoS2@MIL-101(Cr), 96 mg of MoO3, 112 mg of thiourea, and 0.96 g of urea were dissolved in 58.8 mL of deionized water and then 5.3 g of TiO2 was added. After stirring for 2 h, the solution was transferred to a Teflon-lined autoclave reactor, which was kept in an oven at 200 °C for 12 h. Thereafter, it was cooled to room temperature and then the autoclave reactor was taken out. Finally, the as-prepared 1T-MoS2@TiO2 was collected and washed with distilled water and ethanol and then stored in deionized water before use. In theory, 2% 1T-MoS2@TiO2 was obtained based on the above statement. Composites with different compositions of MoS2 were prepared by changing the MoO3/urea ratio using the same procedure listed above.

2.3. Photocatalytic Degradation of Tannic Acid. 

The photocatalytic degradation of tannic acid was carried out in a reactor (model BL-GHX-V, Shanghai Bilang Instrument Co., Ltd.). Because the light source is a 1000 W mercury lamp, which has a high heat output, the equipment is equipped with a cold trap, and water is continuously supplied to protect the equipment during the reaction. The experiment was divided into the dark response stage and the light reaction stage. The dark reaction stage was to ensure that the material and the tannic acid in the solution reach a physical adsorption−desorption equilibrium within 120 min. After the material reached the physical adsorption−desorption equilibrium, the photocatalysis reaction was carried out (m/v = 1.8 mg/mL, CTA = 40 ppm, T = 300 K, UV intensity = 1000 W). During the photocatalytic reaction (dark reaction stage and light reaction stage), the tannic acid solution was sampled and
filtered every 20 min, and then the absorbance of tannic acid in the solution was tested with a UV2600 ultraviolet–visible spectrophotometer. Through the formula \( \frac{C}{C_0} = \frac{A}{A_0} \), the tannin concentration value was obtained.

2.4. Active Species Capture Experiment. The experiment was divided into four groups, and the amount of compound sample and tannic acid remained unchanged \((m/v = 1:8, 5 \text{ mg}; 40 \text{ mL}, C_{TA} = 40 \text{ ppm})\). Isopropyl alcohol (IPA) (2 mL), ethylenediaminetetraacetic acid (EDTA) (2 mg), and Na\(_2\)SO\(_4\) (2 mg) were added to the first three groups and the last group was a blank control. The experiment was divided into dark reaction and light reaction for 2 h each and the light source was a mercury lamp. The samples are taken for testing at the end of the dark reaction and light reaction.

2.5. Characterization. The morphology of MoS\(_2@\)TiO\(_2\) was investigated by scanning electron microscopy (SEM, Carl Zeiss, Ultra 55) and transmission electron microscopy (TEM, Carl Zeiss, Libra 200). The elemental mapping was recorded on a TEM equipped with an energy dispersive spectrometer. Powder X-ray diffraction (XRD) patterns were performed on a Cu K\(\alpha\) radiation PAN analytical X-ray diffractometer. A laser Raman spectrometer (inVia) was used to analyze the samples by Raman spectroscopy. X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific) was used to analyze the elemental composition and valence of the materials. The light absorption characteristics of the samples were carried out on a solid ultraviolet absorption spectrometer (UV–vis, Shimadzu Enterprise Management (China) Co., Ltd.) with the equipment model Solidspec-3700. UV–vis absorbance spectra were detected on a UV2600 UV–vis spectrophotometer (Unico Instruments Co., Ltd.). The Mott–Schottky curve (Mott–Schottky) and AC impedance (EIS) of the cell with the as-prepared sample as an electrolyte are examined on an electrochemical analyzer of CHI instruments (Shanghai Chenhua Instrument Company, CHI660C) and the details are shown in the Supporting information.

3. RESULTS AND DISCUSSION

3.1. Composite Materials Characterization Results. Figure 2a,b shows the scanning electron microscopy images of IT-MoS\(_2@\)TiO\(_2\) and 2H-MoS\(_2@\)TiO\(_2\), respectively. It can be seen that (1T/2H) MoS\(_2\) and TiO\(_2\) grow together to present a sheet-like package structure, connecting into one piece and piling up. It can be seen from Figure S1a,b in the Supporting Information that 1T-MoS\(_2\) and 2H-MoS\(_2\) have similar particle sizes and morphology. Figure 2c,d shows the transmission microscope images of IT-MoS\(_2@\)TiO\(_2\). It can be seen that the gray part is TiO\(_2\) nanoparticles, and the black banded part is IT-MoS\(_2\) distributed uniformly on the TiO\(_2\) surface. The images in Figure S2a,b in the Supporting Material further
prove the uniformity of MoS₂ distributed on the TiO₂ surface. The inset in the upper right corner shows that 1T-MoS₂ has a lattice spacing of 0.89 nm corresponding to its (002) plane, and TiO₂ has a lattice spacing of 0.30 nm corresponding to its (101) plane. Figure 2e shows a high-resolution TEM image of 2H-MoS₂@TiO₂. It can be seen that the black band-like 2H-MoS₂ is also supported on the surface of TiO₂. The upper right part of Figure 2e shows that the lattice spacing of 2H-MoS₂ is 0.61 nm corresponding to its (002) plane. The lattice spacing of TiO₂ is 0.30 nm corresponding to its (101) plane. Figure 2f shows the energy-dispersive spectrometry (EDS) energy spectrum analysis of the four elements Mo, S, Ti, and O in the composite material, which indicates that MoS₂ is distributed evenly on the surface of TiO₂. The EDS results show that Mo and S are distributed in the same area. SEM and TEM analyses have proved that two components (MoS₂ and TiO₂) form a heterojunction material.

Figure 3a shows the XRD patterns of anatase TiO₂, 2H-MoS₂, 1T-MoS₂, and composite materials 1T-MoS₂@TiO₂ and 2H-MoS₂@TiO₂. The diffraction peaks of TiO₂ at 25.27, 37.77, and 47.99° correspond to (101), (004), (200) of anatase TiO₂. The peaks of 53.88, 55.05, 62.83, 70.26, and 75.04° correspond to (211), (105), (204), (116), (220), and (215) crystal planes. These results indicate that the anatase phase of TiO₂ is obtained in the current catalysts. The (002) crystal face of 2H-MoS₂ is detected at 14.37° in 2H-MoS₂@TiO₂, and the (002) crystal face unique to 1T-MoS₂ is detected at 9.12° in 1T-MoS₂@TiO₂. However, the remaining crystal planes of 2H-MoS₂ and 1T-MoS₂ are not detected, which might be due to the small proportions of these two materials in the composite samples. The XRD results indicate that the TiO₂ is distributed evenly in the composite materials. Due to the difference in the structure, their Raman characteristics are also different. Figure 3b shows the Raman spectra of the two composite materials. It can be seen that 1T-MoS₂@TiO₂ has a stronger Raman spectrum at 146 cm⁻¹ than 2H-MoS₂@TiO₂, which is attributed to 1T-Mo—Mo stretching vibration in MoS₂. The Raman shift (326, 512 cm⁻¹) is related...
to the phonon mode in 1T-MoS₂. 2H-MoS₂ exhibits typical Raman shifts of ∼378 and 404 cm⁻¹ for E₂g₁ and A₁g, respectively, which are substantially different from those of 1T-MoS₂.

Figure 4 shows the UV-vis diffuse reflectance spectra of TiO₂, 2H-MoS₂, 1T-MoS₂, and their composite materials 1T-MoS₂@TiO₂ and 1T-MoS₂@TiO₂. The adsorption band below 400 nm is the intrinsic band gap of TiO₂, which is in the ultraviolet light range. 2H-MoS₂ and 1T-MoS₂ present total absorption in the tested wavelength, with an apparent absorption in the visible light range. The spectra of 1T/2H-MoS₂@TiO₂ display combined features of MoS₂ and TiO₂, having the absorption wavelength range of 200-400 nm.

Figure 4b shows that the curve of (ahν)⁻¹/2 changes with the photon energy. The tangent intercept is the band gap value of the material, where the band gap value of TiO₂ and 2H-MoS₂ is 3.2 and 1.9 eV, respectively. Because MoS₂ has a narrow band gap value, it can change its band gap value when combined with TiO₂. The absorption wavelength range of the two composite materials, 2H-MoS₂@TiO₂ and 1T-MoS₂@TiO₂, is between 200 and 400 nm, which is in the ultraviolet wavelength range.

XPS is used to analyze the chemical composition of the product (Figure S3 in the Supporting Material). The XPS spectra show the existence of Mo, S, Ti, and O, and the consistency of the valence state with pure MoS₂ and TiO₂. The Mo 3d spectrum of the 1T-MoS₂@TiO₂ material has characteristic peak positions at around 231.18 and 227.98 eV, which means that the Mo⁴⁺ of the composite material shifts to the direction of lower binding energy. XPS is used to analyze the chemical composition of the product (Figure S3 in the Supporting Material). The XPS spectra show the existence of Mo, S, Ti, and O, and the consistency of the valence state with pure MoS₂ and TiO₂. The Mo 3d spectrum of the 1T-MoS₂@TiO₂ material has characteristic peak positions at around 231.18 and 227.98 eV, which means that the Mo⁴⁺ of the composite material shifts to the direction of lower binding energy. Similarly, the weaker peaks produced by pure 1T-MoS₂ at 229.38 and 233.28 eV also move to the lower binding energy direction, which decreased to 229.05 and 232.72 eV, respectively. Therefore, it is proved that composite materials are more conducive to the transfer of electrons. Figure Sb shows the location of the characteristic peaks of the
S 2p_{1/2} and S 2p_{3/2} orbitals of pure 1T-MoS_2 at around 162.68 and 161.68 eV. The locations of the characteristic peaks of the S 2p_{1/2} and S 2p_{3/2} orbitals in the 1T-MoS_2@TiO_2 material are around 161.98 and 160.98 eV, demonstrating that S^{2−} in the 1T-MoS_2@TiO_2 material also shifts to the low binding energy.

Figure 5c,f shows the comparison spectra of Ti 2p and O 1s of 1T-MoS_2@TiO_2 and pure TiO_2, respectively. The characteristic peaks of pure TiO_2 are at around 464.38 and 458.68 eV, which correspond to Ti^{4+} by Ti 2p_{1/2} and Ti 2p_{3/2} orbitals, respectively. The position of the characteristic peaks generated by the Ti 2p_{1/2} and Ti 2p_{3/2} orbitals of 1T-MoS_2@TiO_2 is around 464.68 and 458.88 eV, the position of the characteristic peaks generated by the O 1s orbital of pure TiO_2 is about 529.98 eV, and the O 1s orbital of 1T-MoS_2@TiO_2 is at around 530.08 eV. These results show that the characteristic peaks of Ti^{4+} and O^{2−} in 1T-MoS_2@TiO_2 are shifted to the high binding energy, while the characteristic peaks of Mo^{4+} and S^{2−} are shifted to the low binding energy. This shifting demonstrates electron transfer from TiO_2 to MoS_2 and improved the successful recombination of MoS_2 and TiO_2.

In Figure 5d, it can be seen that the characteristic peaks of the Mo 3d_{3/2} and Mo 3d_{5/2} orbitals of pure 2H-MoS_2 are at around 232.18 and 228.78 eV, and the Mo 3d_{3/2} and Mo 3d_{5/2} characteristic peaks of the 2H-MoS_2@TiO_2 material are located near 231.28 and 227.98 eV, so they are also shifted to the direction of low binding energy. The weaker peaks of pure 2H-MoS_2 at 229.48 and 232.98 eV also shift to the low binding energy direction, shifting to 229.35 and 232.48 eV, respectively. The shift peaks show that composite materials can accelerate electron transfer. It can be found in Figure 5e that the characteristic peaks of the S 2p_{1/2} and S 2p_{3/2} orbitals of pure 2H-MoS_2 are around 162.88 and 161.78 eV, and the characteristic peaks of the S 2p_{1/2} and S 2p_{3/2} orbitals of the 2H-MoS_2@TiO_2 material are located at the position of around 161.98 and 160.98 eV. According to the spectrum analysis, it can be seen that the comparison spectrum of Ti 2p and O 1s of 2H-MoS_2@TiO_2 and pure TiO_2 also displays the shift of the characteristic peaks of Ti^{4+} and O^{2−} of the 2H-MoS_2@TiO_2 to the direction of high binding energy (Figure S4 in the Supporting Material).

3.2. Photocatalytic Degradation of Tannic Acid. The photocatalytic activities of 1T-MoS_2@TiO_2 and 2H-MoS_2@TiO_2 were evaluated by testing the degradation rate of tannic acid (TA) in water with a concentration of 40 mg/L under ultraviolet light. The data in Figure 6a shows the photocatalytic degradation capacity of tannic acid over blank sample, TiO_2, 1T-MoS_2, and composite materials of x% 1T-MoS_2@TiO_2 (x = 2, 6, 10, 16, 20). The data in Figure 6a shows that the composite materials are far more active than the blank, TiO_2, and 1T-MoS_2 materials with an order of x% 1T-MoS_2@TiO_2 > 1T-MoS_2 > TiO_2 > blank.

The adsorption capability of pure TiO_2 is stronger than that of the composite 1T-MoS_2@TiO_2 and 2H-MoS_2@TiO_2 materials. We can see significant desorption in the beginning of the photoreaction stage for the pure TiO_2. That is, the plot of the photodegradation of tannic acid in the first 40 min (Figure 6a,b,d,e) of the reaction has a slight increasing trend, which is due to the remarkable desorption of tannic acid adsorbed by the material in the dark reaction stage. As the photocatalytic reaction progresses, the amount of photocatalytic degradation gradually increases and then exceeds the analytical amount, so the graph shows a downward trend.

Figure 6b shows the degradation plot of tannic acid regarding the typical amount of 1T-MoS_2. Significant enhancement in the degradation of 63% is achieved with 2% 1T-MoS_2 in 1 h as compared to that of 31% using the TiO_2 sample without MoS_2. A further degradation improvement is found when 1T-MoS_2 increases to 6 and 10%. The optimal amount of 1T-MoS_2 is found to be 16% with 98% degradation. The degradation efficiency is not improved by increasing the 1T-MoS_2 content to 20% or more (Figure S5).

We guess that there may be two reasons for this phenomenon. First, MoS_2 is combined with TiO_2 to form a heterojunction material, and photogenerated electrons and holes are separated on the surface of MoS_2 and TiO_2, respectively. A commercial TiO_2 was used for comparison. Second, as the load of 1T-MoS_2 increases, the overall color of the composite material becomes darker. After adding the tannic acid solution, the whole solution becomes more turbid. During the photoreaction, part of the light source cannot reach the surface of the catalyst. Therefore, the photogenerated excitons cannot diffuse on the surface of MoS_2 and TiO_2 and form photogenerated electrons and holes. The materials cannot undergo redox reactions with tannic acid, thereby reducing the photocatalytic degradation efficiency.
rate of commercial TiO$_2$ is 38%. The as-prepared MoS$_2@$TiO$_2$ in this study shows much better photocatalytic activity than nano-TiO$_2$-coated tiles with 76% tannic acid degraded in 6 h.\textsuperscript{53}

This heterojunction material also has a comparable ability on the degradation of tannic acid using titanium oxide-coated magnetic activated carbon ($m/v = 2.1$, $C_{TA} = 100$ ppm) or Fe–N codoped SiO$_2$@TiO$_2$ ($m/v = 1.1$ mg/mL, $C_{TA} = 30$ ppm) with 98% degradation rate in 150 min and 99% degradation rate in 80 min.\textsuperscript{52,54} It is interesting that we use less catalysts ($m/v = 1:8$, $C_{TA} = 40$ ppm) and achieve a similar performance. The significantly improved photocatalytic activity might be contributed to the large surface area, excellent electron transfer ability, and enhanced active sites of the 1T-MoS$_2@$TiO$_2$ heterojunction material. Therefore, we can see that our results are promising in terms of materials selection and degradation activity toward tannic acid.

To determine the active species involved in the degradation of tannic acid, Figure 7 shows the effect of photocatalytic degradation of tannic acid by the two composite materials after adding different quenchers. The quencher for *OH is IPA, the quencher for holes ($h^+$) is EDTA, and the quencher for e$^-$ is Na$_2$SO$_4$. It can be seen from Figure 7a,b that in the dark reaction stage, the effect of the quencher on its adsorption performance is almost negligible. For the two materials in the light reaction stage, the inhibitory effect after adding IPA is significantly higher than EDTA and Na$_2$SO$_4$. That is, *OH suppression has the most significant impact on the photocatalytic performance of this material. The photogenerated

![Figure 7. Degradation efficiency of the composite materials under different quenchers. (a) 1T-MoS$_2@$TiO$_2$. (b) 2H-MoS$_2@$TiO$_2$.](image)

![Figure 8. (a) Electrochemical impedance diagram. (b) Mott–Schottky curve of TiO$_2$. (c) Mott–Schottky curve of 1T-MoS$_2$. (d) Mott–Schottky curve of 2H-MoS$_2$.](image)
From the Nyquist diagram, it can be seen that the arc radius shows the electrochemical impedance of several materials. TiO₂, we tested the energy band position by the Mott–Schottky (MS) method and observed from the MS curve that the Fermi level of 1T-MoS₂ is less than that of 2H-MoS₂. The high-frequency response of the Nyquist diagram is characteristic of the charge transfer process, and the arc radius of the AC impedance spectrum curve represents the resistance between the surface of the electrode material and the interface layer. The smaller the arc radius, the faster the charge transfer speed. Therefore, the surface charge transfer resistance of 1T-MoS₂@TiO₂ is less than that of 2H-MoS₂@TiO₂, which is more conducive to the separation of electrons and holes to improve the efficiency of the photocatalytic reaction. Compared with TiO₂ alone, the composite materials of 1T-MoS₂@TiO₂ and 2H-MoS₂@TiO₂ are significantly more effective in photocatalytic degradation of tannic acid. To study the conductivity and valence state of (1T/2H)-MoS₂ and TiO₂, we tested the energy band position by the Mott–Schottky (MS) method and observed from the MS curve that TiO₂ is an n-type semiconductor body. To clarify the energy band position of the material, the Mott–Schottky curves of TiO₂, 1T-MoS₂, and 2H-MoS₂ are shown in Figure 8b–d, respectively. Figure 8c shows that the 1T-MoS₂ Fermi level of the metal phase is −0.02 eV. The Eᵥ values of TiO₂ and 2H-MoS₂ are −0.07 and −0.11 V, respectively.

### 3.4. Photocatalytic Degradation Mechanism

Here, we try to explain the charge transfer mechanism of the two heterojunction materials. For 1T-MoS₂@TiO₂, when light is irradiated on the surface of the composite material, the MoS₂ and TiO₂ surfaces form a tight surface because 1T-MoS₂ belongs to the metal phase conductor. The large heterojunction interface can accelerate the transfer of electrons generated on the surface of TiO₂, greatly improving the efficiency of photocatalytic degradation. For 2H-MoS₂@TiO₂, when light hits the surface of the material, the photogenerated excitons diffuse rapidly on the surface of the material and dissociate into free electrons and holes at the conduction and valence bands of 2H-MoS₂ and TiO₂ respectively. The photogenerated electrons rapidly transfer from the conduction band of TiO₂ to the conduction band of MoS₂. An electron accumulation layer is formed in the conduction band of molybdenum sulfide, and a hole accumulation layer is formed in the valence band of titanium dioxide. The heterojunction enables the spatial separation of the electron–hole pairs to reduce the recombination rate effectively. The presence of MoS₂ in the two composite materials relatively shortens the original band gap value of TiO₂, enabling rapid electron migration, accelerates the separation of electron and hole pairs, and improves the efficiency of the photocatalytic reaction. Figure 9 schematically depicts the two possible reaction mechanisms behind the enhanced photocatalytic performance of these materials.

### 4. CONCLUSIONS

In summary, the composite materials 1T-MoS₂@TiO₂ and 2H-MoS₂@TiO₂ have been successfully synthesized. The results of the photocatalytic degradation of tannic acid show that these materials have significant effects on photocatalytic activity to degrade tannic acid. Loading 16% 1T-MoS₂ and 13% 2H-MoS₂ in the composite exhibits high photocatalytic degradation capacity of 98 and 75% in 60 min, much higher than that obtained by a commercial TiO₂. The degradation speed of 16% 1T-MoS₂@TiO₂ is much higher than that of 13% 2H-MoS₂@TiO₂. We believe that the tight interface between MoS₂/TiO₂ can effectively promote the transfer of light-induced electrons and provide many active sites for photocatalytic reactions. These features are key to the high-efficiency photocatalytic activity of MoS₂@TiO₂ photocatalysts. This study demonstrates the importance of MoS₂@TiO₂, a two-dimensional material, in improving the efficiency of photocatalytic activity. It provides a new idea for photocatalytic degradation of organic acids similar to tannic acid.

### ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c02500.
Additional FTO electrode preparation and cell configuration, SEM images and high-resolution TEM images of MoS2@TiO2, and XPS spectra of the as-prepared materials (PDF)

■ AUTHENTIC INFORMATION

Corresponding Authors
Cairong Jiang — School of Materials Science and Engineering, Sichuan University of Science and Engineering, Zigong 643000, P. R. China; orcid.org/0000-0001-8499-4062; Email: crjiang@suse.edu.cn

Tao Duan — National Co-Innovation Center for Nuclear Waste Disposal and Environmental Safety, Southwest University of Science and Technology, Mianyang 621010, P. R. China; State Key Laboratory of Energy Materials, Southwest University of Science and Technology, Mianyang 621010, P. R. China; orcid.org/0000-0002-0944-6995; Email: duant@ustc.edu.cn

Authors
Ruixi Liu — School of Materials Science and Engineering, Sichuan University of Science and Engineering, Zigong 643000, P. R. China; National Co-Innovation Center for Nuclear Waste Disposal and Environmental Safety, Southwest University of Science and Technology, Mianyang 621010, P. R. China; State Key Laboratory of Energy Materials, Southwest University of Science and Technology, Mianyang 621010, P. R. China

Linzhen Wu — National Co-Innovation Center for Nuclear Waste Disposal and Environmental Safety, Southwest University of Science and Technology, Mianyang 621010, P. R. China; State Key Laboratory of Energy Materials, Southwest University of Science and Technology, Mianyang 621010, P. R. China

Hao Liu — National Co-Innovation Center for Nuclear Waste Disposal and Environmental Safety, Southwest University of Science and Technology, Mianyang 621010, P. R. China; State Key Laboratory of Energy Materials, Southwest University of Science and Technology, Mianyang 621010, P. R. China

Youkui Zhang — National Co-Innovation Center for Nuclear Waste Disposal and Environmental Safety, Southwest University of Science and Technology, Mianyang 621010, P. R. China; State Key Laboratory of Energy Materials, Southwest University of Science and Technology, Mianyang 621010, P. R. China

Jianjun Ma — School of Materials Science and Engineering, Sichuan University of Science and Engineering, Zigong 643000, P. R. China; orcid.org/0000-0002-0016-6313

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.1c02500

Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was funded by the National Natural Science Foundation of China (21976148), the China Basic Research Project (JCKY2018404C008), and the Sichuan Science and Technology Program (grant numbers 2019YFH0177 and 2021YFH0092).

■ REFERENCES

(1) Rahimi-Nasrabadi, M.; Ghaderi, A.; Banafshe, H. R.; Eghbali-Arani, M.; Akbari, M.; Ahmad, F.; Pourmasoud, S.; Sobhani-Nasab, A. Preparation of Co2TiO4/CoTiO3/Polyaniline ternary nano-hybrids for enhanced destruction of agriculture poison and organic dyes under visible-light irradiation. J. Mater. Sci.: Mater. Electron. 2019, 30, 15854–15868.

(2) Kooshki, H.; Sobhani-Nasab, A.; Eghbali-Arani, M.; Ahmad, F.; Ameri, V.; Rahimi-Nasrabadi, M. Eco-friendly synthesis of PbTiO3 nanoparticles and PbTiO3/carbon quantum dots binary nano-hybrids for enhanced photocatalytic performance under visible light. Sep. Purif. Technol. 2019, 211, 873–881.

(3) Han, D.; Currell, M. J.; Cao, G. Deep challenges for China’s war on water pollution. Environ. Pollut. 2016, 218, 1222–1233.

(4) Benitez-Navarro, J.; Salgado-Mojena, M. In Compaction of Solid Wastes in Countries Without Disposal Facility: A Prelude of Future Troubles, Etewede, 2002; pp 160–163.

(5) Rahman, R. O. A.; Ibrahim, H. A.; Hung, Y.-T. Liquid radioactive wastes treatment: a review. Water 2011, 3, 551–565.

(6) Ha, S. H.; Menchavez, R. N.; Koo, Y.-M. Reprocessing of spent nuclear waste using ionic liquids. Korean J. Chem. Eng. 2010, 27, 1360–1365.

(7) Ma, X.; Xiang, Q.; Liao, Y.; Wen, T.; Zhang, H. Visible-light-driven CdSe quantum dots/graphene/TiO2 nanosheets composite with excellent photocatalytic activity for E. coli disinfection and organic pollutant degradation. Appl. Surf. Sci. 2018, 457, 846–855.

(8) Xiang, Q.; Yu, J.; Jaroniec, M. Graphene-based semiconductor photocatalysts. Chem. Soc. Rev. 2012, 41, 782–796.

(9) Li, Q.; Li, X.; Wageh, S.; Al-Ghamdi, A.-A.; Yu, J. CdS/graphene nanocomposite photocatalysts. Adv. Energy Mater. 2015, 5, No. 1500010.

(10) Deng, D.; Novoselov, K.; Fu, Q.; Zheng, N.; Tian, Z.; Bao, X. Catalysis with two-dimensional materials and their heterostructures. Nat. Nanotechnol. 2016, 11, 218–230.

(11) Chen, B.; Bi, H.; Ma; Q.; Tan, C.; Cheng, H.; Chen, Y.; He, X.; Sun, L.; Lim, T.-T.; Huang, L. Preparation of graphene-MoS2 hybrid aerogels as multifunctional sorbents for water remediation. Science China. Materials 2017, 60, 1102–1108.

(12) Liu, X.; Ma, R.; Wang, X.; Ma, Y.; Wang, X.; et al. Graphene oxide-based materials for efficient removal of heavy metal ions from aqueous solution: A review. Environ. Pollut. 2019, 252, 62–73.

(13) Chen, B.; Meng, Y.; Sha, J.; Zhong, C.; Hu, W.; Zhao, N. Preparation of MoS2/TiO2 based nanocomposites for photocatalysis and rechargeable batteries: progress, challenges, and perspective. Nanoscale 2018, 10, 34–68.

(14) Eda, G.; Yamaguchi, H.; Voiy, D.; Fujita, T.; Chen, M.; Chhowalla, M. Photoluminescence from chemically exfoliated MoS2. Nano Lett. 2011, 11, 5111–5116.

(15) Huang, H.; Cui, Y.; Li, Q.; Dun, C.; Zhou, W.; Huang, W.; Chen, L.; Hewitt, C. A.; Carroll, D. L. Metallic 1T phase MoS2 nanosheets for high-performance thermoelectric energy harvesting. Nano Energy 2016, 26, 172–179.

(16) Voiy, D.; Salehi, M.; Silva, R.; Fujita, T.; Chen, M.; Asea, T.; Shenoy, V. B.; Eda, G.; Chhowalla, M. Conducting MoS2 nanosheets as catalysts for hydrogen evolution reaction. Nano Lett. 2013, 13, 6222–6227.

(17) Wang, J.; Jia, H.; Guo, Y.; Zhang, Y.; Xie, Q.; Zhu, H.; Sun, J.; Shi, F.; Liu, Z.-H.; Jiang, R. (TiO2 (B) Nanosheet) (Metallic Phase MoS2) Hybrid Nanostructures: An Efficient Catalyst for Photocatalytic Hydrogen Evolution. Solar RRL 2019, 3, No. 1900323.

(18) Shi, S.; Sun, Z.; Hu, Y. H. Synthesis, stabilization and applications of 2-dimensional 1T metallic MoS2. J. Mater. Chem. A. 2018, 6, 23932–23977.

(19) Zhang, L.; Wu, L.; Feng, Z.; Meng, Q.; Li, Y.; Duan, T. Adopting sulfur-atom sharing strategy to construct Co3S2/MoS2 heterostructure on three-dimensional nitrogen-doped graphene aerogels: A novel photocatalyst for wastewater treatment. J. Environ. Chem. Eng. 2020, 9, No. 104771.
(20) Schneider, J.; Matsuoka, M.; Takeuchi, M.; Zhang, J.; Horiiuchi, Y.; Anpo, M.; Bahnmann, D. W. Understanding TiO2 photocatalysis: mechanisms and materials. Chem. Rev. 2014, 114, 9919−9986.

(21) Asahi, R.; Morikawa, T.; Irie, H.; Ohwaki, T. Nitrogen-doped titanium dioxide as visible-light-sensitive photocatalyst: designs, developments, and prospects. Chem. Rev. 2014, 114, 9824−9852.

(22) Liang, Y.; Wang, H.; Casalongue, H. S.; Chen, Z.; Dai, H. TiO2 nanocrystals grown on graphene as advanced photocatalytic hybrid materials. Nano Res. 2010, 3, 701−705.

(23) Tang, X.; Chu, W.; Qian, J.; Lin, J.; Cao, G. Low Temperature Synthesis of Large-Size Anatase TiO2 Nanosheets with Enhanced photocatalytic Activities. Small 2017, 13, No. 1701964.

(24) Sun, C.; Xu, Q.; Xie, Y.; Ling, Y.; Hou, Y. Designed synthesis of anatase–TiO2(B) biphase nanowire/ZnO nanoparticle heterojunction for enhanced photocatalysis. J. Mater. Chem. A 2018, 6, 8289−8298.

(25) Setyin, M.; Shi, X.; Huvala, J.; Simschitz, T.; Parkinson, G. S.; Schmid, M.; Di Valentin, C.; Selleni, A.; Diebold, U. Methanol on Anatase TiO2(101): Mechanistic Insights into Photocatalysis. ACS Catal. 2017, 7, 7081−7091.

(26) Wu, L.; Fu, C.; Huang, W. Surface chemistry of TiO2 connecting thermal catalysis and photocatalysis. Phys. Chem. Chem. Phys. 2020, 22, 9875−9909.

(27) Li, G.; Ciston, S.; Saponjic, Z. V.; Chen, L.; Dimitrijevic, N. M.; Rajh, T.; Gray, K. A. Synthesizing mixed-phase TiO2 nanocomposites using a hydrothermal method for photo-oxidation and photoreduction applications. J. Catal. 2008, 253, 105−110.

(28) Nekooie, R.; Shamspur, T.; Mostafavi, A. Novel CuO/TiO2/PANI nanocomposite: Preparation and photocatalytic investigation for chlorpyrifos degradation in water under visible light irradiation. J. Photochem. Photobiol., A 2021, 407, No. 113038.

(29) Liu, X.; Wang, Y.; Zhang, T. C.; Xiang, G.; Wang, X.; Yuan, S. One-Pot Synthesis of a Magnetic TiO2/PTHγ-Fe2O3 Heterojunction Nanocomposite for Removing Trace Arsenite via Simultaneous Photocatalytic Oxidation and Adsorption. Ind. Eng. Chem. Res. 2021, 60, 526−540.

(30) Wang, D.; Kanhere, P.; Li, M.; Tay, Q.; Tang, Y.; Huang, Y.; Sun, T. C.; Mathews, N.; Sritharan, T.; Chen, Z. Improving photocatalytic H2 evolution of TiO2 via formation of [010]−[010] quasi-heterojunctions. J. Phys. Chem. C 2013, 117, 22894−22902.

(31) Banerjee, B.; Amoli, V.; Maurya, A.; Sinha, A. K.; Bhaumik, A. Green synthesis of Pt-doped TiO2 nanocrystals with exposed (001) facets and mesoporous void space for photo-splitting of water under solar irradiation. Nanoscale 2015, 7, 10504−10512.

(32) Xing, M.-Y.; Yang, B.-X.; Yu, H.; Tian, B.-Z.; Bagwasi, S.; Zhang, J.-L.; Gong, X.-Q. Enhanced photocatalytic decomposition by Au nanoparticle loading on TiO2 single-crystal (001) and (110) facets. J. Phys. Chem. Lett. 2014, 5, 3910−3917.

(33) Han, X.; Kuang, Q.; Jin, M.; Xie, Z.; Zheng, L. Synthesis of titania nanosheets with a high percentage of exposed (001) facets and related photocatalytic properties. J. Am. Chem. Soc. 2009, 131, 3152−3153.

(34) Tang, Q.; Jiang, D.-e. Mechanism of Hydrogen Evolution Reaction on 1T-MoS2 from First Principles. ACS Catal. 2016, 6, 4953−4961.

(35) Kibombo, H. S.; Peng, R.; Rasalingam, S.; Koodali, R. T. Versatility of heterogeneous photocatalysis: synthetic methodologies epitomizing the role of silica support in TiO2 based mixed oxides. Catal. Sci. Technol. 2012, 2, 1737−1766.

(36) Tang, J.; Cowan, A. J.; Durrant, J. R.; Klug, D. R. Mechanism of O2 production from water splitting: nature of charge carriers in nitrogen doped nanocrystalline TiO2 films and factors limiting O2 production. J. Phys. Chem. C 2011, 115, 3143−3150.

(37) Khan, G.; Kim, Y. K.; Choi, S. K.; Han, D. S.; Abdel-Wahab, A.; Park, H. Evaluating the catalytic effects of carbon materials on the photocatalytic reduction and oxidation reactions of TiO2. Bull. Korean Chem. Soc. 2013, 34, 1137−1144.