Direct Bandgap Narrowing of TiO₂/MoO₃ Heterostructure Composites for Enhanced Solar-Driven Photocatalytic Activity

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Abstract: TiO₂ nanobelts/MoO₃ nanosheets (TM) heterostructure composites have been synthesized via an in-situ growth method in which the TiO₂-MoS₂ was used as precursor. The whole fabrication process involved the preparation of MoS₂ nanoparticles modified TiO₂ nanobelts (TiO₂ Nbs) and subsequently transformation of the MoS₂ to MoO₃ nanosheets. The properties of TM were characterized by XRD, FE-SEM, TEM, EDX, DRS, FT-IR, XPS and PL, respectively. The photocatalytic activity of TM was evaluated by photocatalytic degradation of Rhodamine B (Rh B) aqueous solution under simulated sunlight irradiation. And its photoabsorption energy (PE, the energy required to excite valence band electrons of TiO₂ nanobelts to conduction band states of MoO₃ nanosheets (MoO₃)) properties are related to the physical and chemical interaction between TiO₂ Nbs and MoO₃. The experimental results showed that TM exhibited a much better photocatalytic activity than that of pure TiO₂, and showed an excellent recyclability property for its photocatalytic applications.

Key words: Direct band narrowing; TiO₂/MoO₃; Heterostructure composites; Solar-driven photocatalytic activity

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1. Introduction

The new energy technologies are currently attracting academic and commercial interest due to the global energy crisis and environment protection [1, 2]. Since Fujishima and Honda firstly reported the photoelectrochemical water splitting on a TiO_2 electrode in 1972, researches on semiconductor oxides application for energy and environmental protection by using solar energy has been reported extensively [3, 4]. Among various semiconductor oxides, titanium dioxide (TiO_2), due to its unique prospects, such as nontoxicity, photo and chemical stability and low production cost, et al, attracts much interest in the field of dye-sensitized solar cells (DSSCs) [5], photocatalysis [6], and so on. However, application of the TiO_2 on the environmental protection procedures is largely limited because of its two inherent properties: on one hand, with a large bandgap about~3.2 eV, TiO_2 only can absorb UV photons, which represent only about 5% of the energy in the solar spectrum. On the other hand, TiO_2 has a low photocatalytic activity on account of the fast recombination of photogenerated electron and hole pairs [7-9]. Therefore, many strategies have been developed to enhance the photoabsorption of the TiO_2 -based materials under solar light irradiation and the separate efficiency of photogenerated carriers, such as doping with metal and nonmetal ions [10], modified with noble metals [11], coupling with other semiconductors (Bi_2WO_6 , ZnO , MoO_3 , and CdS , etc.) [12] and sensitizing with different solar light sensitive organic materials [13-15], etc. Among these techniques, coupling TiO_2 with other semiconductors to form a heterojunction structure has been deemed to be an effective approach to improve the photocatalytic activity of TiO_2 . It's because that it can transfer photoexcited electrons from valence band (VB) to the conduction band (CB) of the TiO_2 , and then to the CB of the other semiconductors, so that extend the lifetime of photoexcited electron-hole pairs.

MoO_3 , as one of the most important layered materials, it is a n-type semiconductor and it has attracted widely attention because of its unique properties in many fields such as photochromic and electrochromic devices, gas sensors, energy storage and catalysis [16]. In addition, selective oxidation ability of Mo species has

1 been extensively researched in photocatalytic oxidation reactions, such as
2 dehydrogenation, CH₃OH oxidation and oxidation of other organic pollutants [17-20].
3 Coupling TiO₂ with MoO₃, it can become true that the transformation of photoexcited
4 electrons from the VB of TiO₂ to the CB of MoO₃ directly through Ti-O-Mo bond, so
5 as to narrow the bandgap of TiO₂ and achieve the purpose of increasing the visible
6 light response and extending the lifetime of the photoexcited electron-hole pairs.

7 Herein, a simple and effective approach through a two-step hydrothermal
8 procedure was developed to prepare TM by using TiO₂-MoS₂ as a precursor. This
9 method can ensure the good contact of the two different phases at utmost and avoid
10 the phase splitting in the application process. The structure and its solar-driven
11 photocatalytic property of as-prepared TM were also investigated.

12 **2. Experimental**

13 **2.1. Synthesis of TiO₂ nanobelts (TiO₂ Nbs)**

14 TiO₂ Nbs were prepared via a typical hydrothermal method. A similar process
15 had been described in our previous work [21]. In detail, 0.4 g TiO₂ powder (P25) was
16 dissolved into 70 mL of 10 M NaOH aqueous solution under the continuous stirring
17 for 30 min. Then, the obtained mixture solution was transferred into a Teflon-lined
18 autoclave with 100 mL capacity. The autoclave was maintained at 180°C for 24 h and
19 then cooled to room temperature naturally. The obtained powder were washed with
20 0.2 M HCl aqueous solution to pH=7, Then washed with deionized water and absolute
21 ethanol several times and then dried at 80 °C for 12 h. Finally, the TiO₂ Nbs were
22 obtained.

23 **2.2. Synthesis of TM heterostructure composites**

24 The fabrication process of TM heterostructure composites was described as
25 follows. Typically, 0.04 g of TiO₂ Nbs was mixed with 0.06g of Na₂MoO₄·H₂O and
26 0.12 g of thiourea in 70 mL of deionized water [22]. Then, the suspension was
27 transferred into a Teflon-lined autoclave and held at 180 °C for 24 h. The as-prepared
28 products were collected by centrifugation, washed with distilled water and ethanol
29 several times, and then dried in an oven at 80 °C for 6 h. Finally, the TM

heterostructures were obtained through an annealing process at 450 °C for 1 h. For comparison, the pure MoO₃ were synthesized without presence of the TiO₂ Nbs matrix under the same experimental conditions.

2.3. Characterization

The products were analyzed by X-ray diffraction (XRD, D/max-2200) using Cu K α radiation (λ =0.154 nm). The microstructural and morphological details of the products were performed with a Hitachi S-4800 field emission scanning electron microscopy (FE-SEM) and a Tecnai G2 transmission electron microscope (TEM) images at an acceleration voltage of 200 kV. UV-visible absorbance spectra were obtained for the dry-pressed disk samples with a UV-visible spectrophotometer (Lambda-950, Perkin Elmer, and USA). BaSO₄ was used as a reflectance standard in a UV-visible diffuse reflectance experiment. IR spectra were recorded using a FT-IR spectrophotometer (VECTOR-22, Bruker, Germany) at room temperature with KBr pellets in the range 4000-400 cm⁻¹. X-ray photoelectron spectroscopy (XPS) was performed using an ESCALAB 250Xi. Photoluminescence (PL) spectra were measured at room temperature on a Fluorescence Spectrophotometer (F-7000, Hitachi, Japan). The excitation wavelength was 325 nm, the scanning speed was 240 nm/min. Photocurrent was measured on an electrochemical workstation (CH1660D Instruments, shanghai)) in a standard three-electrode system using the prepared samples as the working electrodes, a Pt wire as the auxiliary electrode, and a silver chloride electrode (Ag/AgCl) as a reference electrode.

2.4. Photocatalytic activity

The photocatalytic tests of TiO₂ Nbs and the TM were carried out by the degradation of Rhodamine B (Rh B) under simulated sunlight irradiation. In a typical experiment, 70 mL Rh B solution (10 mg/L) was equally transferred into seven quartz beakers, and 70 mg of the sample was equally dispersed in every quartz beaker. The suspension was allowed to reach an adsorption-desorption equilibrium among the photocatalyst, Rh B and water before light irradiation. A 500 W Xe lamp was used as a simulated sunlight source to trigger the photocatalytic reaction. During illumination, a circulation of water through an external cooling coil was conducted to maintain the

1 temperature of suspension at about 25 °C. After irradiation for an appropriate interval,
2 the reaction solution was filtrated and concentration of RhB was determined by an
3 UV-vis spectrophotometer (Lambda-950, Perkin Elmer, and USA). For the study of
4 the recyclability of the TiO₂ Nbs and the TM, the photocatalysts were separated from
5 solution after the photodegradation process via simple filtering, rinsed with ethanol to
6 fully remove the residual organic species and reused for the next time.

7 **3. Results and discussion**

8 A systematic XRD study was carried out to study the crystal structure of the
9 as-prepared samples and the results are shown in Fig. 1. The diffraction peaks of the
10 pure TiO₂ Nbs match well with the standard peaks of the anatase phase TiO₂ material
11 (JCPDS card No.21-1272) [23], a major peak centered at 25.28° can be ascribed to the
12 (101) facet of anatase TiO₂, which is corresponding to the interlayer space of 0.35 nm
13 [24]. Moreover, there are some miscellaneous peaks (Ti₆O₁₁) in TiO₂ Nbs, which may
14 be caused by the introduced oxygen vacancies defects during the calcination process.
15 As for the pure MoO₃, the XRD peaks shown at 2θ=12.8°, 23.3°, 25.8°, 27.3°, 33.7°,
16 35.2°, 38.9°, 46.1°, 49.3°, 59.6° and 64.8° correspond to the (020), (110), (040), (021),
17 (130), (111), (060), (061), (002), (081) and (062) planes of orthorhombic structure
18 MoO₃ (JCPDS card No. 35-0609) [25], and the lattice constants a=0.3963 nm,
19 b=1.3855 nm, and c=0.3696 nm [26]. The strong and sharp peaks suggest that the
20 as-prepared materials are crystalline. It can be clearly seen from TM curve, all the
21 diffraction peaks can be well indexed either TiO₂ Nbs or MoO₃, which indicate that
22 TM is prepared successfully through this process, and the result is well consistent
23 with the following EDX analysis.

24 Fig. 2 presents the corresponding FESEM images of the TiO₂ Nbs, TiO₂/MoS₂
25 precursor, TM and the pure MoO₃ in low and high magnifications. As shown in Fig. 2
26 (a), the TiO₂ Nbs are with a uniform morphology and a well dispersion, and its
27 surface is very smooth. Furthermore, they are of up to hundreds of micrometers in
28 length and 50-250 nm in width. Fig. 2 (b) presents the morphology of TiO₂/MoS₂
29 precursor, it can be seen that the MoS₂ nanoparticles are clearly observed on TiO₂ Nbs,

1 which have a good monodispersity. Fig. 2 (c) is the low magnification SEM image of
2 TM, the results indicates that the TM heterostructure composites are prepared
3 successfully after annealing process. Compared with the $\text{TiO}_2/\text{MoS}_2$ precursor, the
4 morphology of TM has great changes, the surface of TiO_2 Nbs turn from
5 nanoparticles to nanosheets after annealing process. In addition, taking into account
6 the light absorption, reflection, and scattering within such a unique nanosheets
7 structure, the effective light-activated surface area can be significantly enhanced,
8 which would improve the photoabsorption efficiency of the TM catalyst. And the high
9 magnification SEM image of TM is shown in Fig. 2 (d). It can be seen that the MoO_3
10 nanosheets are connected well with TiO_2 nanobelts. Fig. 2 (e) and (f) show the pure
11 MoO_3 nanosheets in low and high magnification, it can be seen that pure MoO_3 is
12 clutter stacked in the form of nanosheets, and the MoO_3 nanosheets are about 500 nm
13 in length and with a thickness of 50 nm.

14 The TEM images of the TM in low magnification are illustrated in Fig. 3 (a). As
15 shown in the image, the surface of the TiO_2 Nbs is uniformly modified by MoO_3
16 nanosheets. Fig. 3 (b) is the HRTEM images of the TM. It shows that the lattice
17 fringes of the MoO_3 and the TiO_2 Nbs can be clearly observed, suggesting the
18 well-defined crystal structure. And their interlayer spaces are 0.326 nm and 0.35 nm,
19 corresponding to the (021) plane of orthorhombic MoO_3 and the (101) plane of
20 anatase TiO_2 , respectively. What's more, there are some cross lattice fringes in Fig. 3
21 (b), seen the area of red dotted line, it can be seen that the TiO_2 Nbs combine with
22 MoO_3 very well, and form a unique heterojunction structure, which may provide the
23 possibility for photogenerated electrons to transfer from the VB of the TiO_2 to the CB
24 of the MoO_3 directly through Ti-O-Mo bond formed between TiO_2 Nbs and MoO_3
25 interface, and this is beneficial to the photocatalytic activity [27]. A typical selected
26 area electron diffraction (SAED) taken from the interface between TiO_2 Nbs and
27 MoO_3 is also depicted in Fig. 3 (c). These diffraction spots imply preferential growth
28 along (101) and (021) plane, respectively. In addition, the EDX analysis of the TM
29 was carried out to verify the elements composition, and the results are given in the Fig.
30 3 (d). It can be clearly seen that the Ti, Mo and O atoms present in the selected area,

1 and the weight percentages of each component are 46.84% (O), 36.49% (Mo) and
2 14.68% (Ti), respectively.

3 UV-visible absorption spectra of pure TiO₂ Nbs, MoO₃ and TM are shown in Fig.
4 4 (a). It can be seen that the spectrum of the pure TiO₂ Nbs shows a significant
5 absorption edge at wavelength shorter than 400 nm, which can be assigned to its
6 intrinsic bandgap absorption. For MoO₃, its absorption in the visible region is slightly
7 larger than that of TiO₂ Nbs. Compared with the TiO₂ Nbs and MoO₃, the TM shows
8 a better absorption property in visible light region, and the absorption edge of TM
9 appear an obvious red shifted, this may be attributed to the formation of chemical
10 bonding between TiO₂ and MoO₃. Fig. 4 (b) shows the plots of $(Ah\nu)^{1/2}$ versus $(h\nu)$, It
11 is immediately evident in Fig. 4 (b) that the PE increasingly shifts to lower energy
12 (longer wavelength) in TM, and these energies are red shifted relative to TiO₂ Nbs
13 ($E_g=3.2$ eV) and MoO₃ ($E_g=2.9$ eV). In addition, the unique heterojunction structure
14 of TM would improve the light harvest, which is also beneficial to their photocatalytic
15 performance [28].

16 To further confirm the formation of the heterojunction structure of TM
17 composites and existing of Ti-O-Mo bond between their interfaces, the FT-IR spectra
18 of TiO₂ Nbs, MoO₃ and TM were performed and the results are shown in Fig. 5. In
19 the spectrum of TiO₂ Nbs, the bands at 774 and 975 cm⁻¹ are related to the vibration of
20 Ti-O bond and the rotation of Ti-O-Ti bond, respectively [29, 30]. The broad bands
21 from 500 to 650 cm⁻¹ in the spectrum of MoO₃ is a typical vibration of the Mo₂O₂
22 entity formed by the edge shared MoO₆ polyhedra that form the orthorhombic
23 α -MoO₃ structure, and the band at 870 cm⁻¹ is associated with the vibration of
24 Mo-O-Mo bridging bonds, while the band at 990 cm⁻¹ is characteristic of the vibration
25 of the Mo=O terminal bond [31]. Compared with that of the two pure components, it
26 can be seen that a new band appears at 948 cm⁻¹ in the spectrum of TM, which is
27 attributed to the vibration of the Ti-O-Mo species. It indicates that in the formation
28 process of the heterostructure composites, Ti-O-Mo bond is generated at the interface
29 between the MoO₃ and TiO₂ Nbs and narrow the bandgap of TM, so that the electrons
30 transfer become possible from the TiO₂ Nbs to MoO₃ under simulated sunlight

1 irradiation [32, 33].

2 In order to further prove the existence of Ti-O-Mo bond in the nanocomposites, a
3 XPS study was carried out and the results are shown in Fig. 6. As shown in Fig. 6 (a),
4 the wide scan XPS spectrum reveals that the predominant elements are Ti, O, Mo and
5 C. Among these elements, Ti, O and Mo elements are from the prepared samples and
6 the C element is from the XPS instrument itself, and no other elements are detected.
7 Fig. 6 (b) is the high-resolution XPS spectrum of O 1s, and the binding energy is
8 located at 530.6 eV. In Fig. 6 (c) and (d), for TiO₂ Nbs, it can be clearly seen that the
9 binding energies of Ti 2p_{1/2}, Ti 2p_{3/2} peaks are located at 464.4 eV, 458.6 eV, and the
10 binding energies of Mo 3d_{3/2} and Mo 3d_{5/2} peaks are located at 236.7 eV and 233.5 eV,
11 respectively. However, for the TM, it suggest that the binding energies of Ti 2p_{1/2}, Ti
12 2p_{3/2} peaks are located at 464.8 eV, 459.1 eV, and the binding energies of Mo 3d_{3/2}
13 and Mo 3d_{5/2} peaks are located at 236.2 eV and 233.2 eV, respectively. It can be seen
14 that the binding energies of Ti 2p increased while that of Mo 3d decreased with the
15 formation of TM heterostructures. Therefore, it implies existence of a strong
16 interaction between the MoO₃ and TiO₂ Nbs, and Ti-O-Mo bond is generated in the
17 interface [34].

18 PL spectra have been carried out to evaluate the photogenerated charges
19 recombination performance. Fig. 7 shows the PL spectra of TiO₂ Nbs, MoO₃ and TM
20 at the excitation wavelength of 325 nm. As for TiO₂ Nbs and MoO₃, the strong peak
21 located at 468 nm and 470 nm can be attributed to the recombination of an electron
22 trapped in an oxygen vacancy with a hole in the valance band both of TiO₂ Nbs and
23 MoO₃. As for the PL spectrum of TM, the peak located at 470 nm decreased clearly
24 compared with that of TiO₂ Nbs and MoO₃, which is attributed to its unique
25 heterujunction structure. For TM, direct electron transfer from the VB of photoexcited
26 TiO₂ Nbs to the CB of MoO₃ is energetically favorable, so that suppressed
27 photogenerated charges recombination. In addition, it also implies that TM has the
28 lowest charge carriers recombination rate, inferring that the charge carriers have
29 longer lifetime and might form larger amount of active ·OH radicals in the
30 photocatalytic reaction.

The transient photocurrent responses of TiO₂ Nbs, MoO₃ and TM electrodes under intermittent illumination are shown in Fig. 8. The test was performed in 0.1 M L⁻¹ Na₂SO₄ aqueous solution. The photocurrent response is reversible as the illumination was turned on and off [35]. As for the TiO₂ Nbs and MoO₃, they show very low photocurrent density, which can be attributed to the fast recombination of photogenerated electrons and holes [36]. The photocurrent density (1.75 μA/cm²) of TM reach to the highest value rapidly under stimulated solar light illumination compared with that of the pure TiO₂ Nbs and MoO₃, which probably can be attribute to the formation of heterojunction structures between TiO₂ Nbs and MoO₃ resulting in the most effective separation of photogenerated electron-hole pairs. In addition, the trend of I-t curves also confirms the photocatalytic mechanism of TM in Fig. 11. Under the stimulated solar light irradiation, due to the Ti-O-Mo bond formed in the cross region between the TiO₂ Nbs and MoO₃ nanosheets, it makes the photogenerated electrons transmitted from the VB of the TiO₂ Nbs to the CB of the MoO₃ directly, and then transferred to the FTO glasses; when illumination disappeared, electrons stored in the MoO₃ can also transfer to the FTO glasses. At the same time, the results of I-t curves of TiO₂ Nbs, MoO₃ and TM are very consistent with the results of the PL spectra. The weakened PL intensity and enhanced photocurrent in TM both confirmed the high efficiency of TM heterojunction structure on suppression of photogenerated electron-hole pair recombination and promotion of electron transportation in the photocatalytic reactions.

The electrochemical impedance spectra (EIS) are used to further investigate the charge transfer resistance and the separation efficiency of photo-generated charge carriers [37]. Fig. 9 shows Nyquist plots of the EIS spectra measured in 0.1 M Na₂SO₄ aqueous solution under Xenon lamp irradiation for TiO₂ Nbs, MoO₃ and TM, respectively. It can be clearly seen that the arc radius on EIS Nyquist plot of the TM sample is smaller than that of TiO₂ Nbs and MoO₃ samples. The EIS result implies that TM possesses higher separation efficiency and faster transfer rate of photogenerated electrons and holes. This could be attributed to the formation of the unique heterojunction structure and Ti-O-Mo bond. This result is in agreement with

1 previous analyses. In a word, the TM heterojunction structure is a very potential
2 photocatalyst with satisfying efficiency.

3 The photocatalytic performance of different photocatalysts was evaluated by
4 degradation of Rh B. As shown in Fig. 10 (a), it provided the concentration changes
5 of Rh B (C/C_0) as a function of irradiation time, where C_0 and C are its initial
6 concentration and the concentration after light irradiation, respectively. It can be seen
7 that the degradation rates of Rh B for P25, TiO₂ Nbs, MoO₃ and TM under simulated
8 sunlight irradiation about 150 min are 14.03%, 41.54%, 53.93% and 91.49%,
9 respectively. The experimental results indicated that the TM heterojunction structures
10 have an enhanced the photocatalytic activity. This could be mainly attributed to the
11 introduction of MoO₃. The formation of chemical bonds between MoO₃ and TiO₂ Nbs
12 can effectively suppress the charges recombination between photoinduced electrons
13 and holes. On the other hand, the enhanced photocatalytic activity of TM may be
14 corresponded to its unique heterujunction structure. This unique heterojunction
15 structure can make more use of light energy, thus enhance its photocatalytic activity.
16 Furthermore, it is worth noting that the TM exhibits a better absorption performance
17 for organic pollutants than that of P25, TiO₂ Nbs and MoO₃ in the photocalytic
18 reaction process. The strong absorption of TM photocatalyst could also be attributed
19 to the introduction of MoO₃ and its unique heterojunction structure. The MoO₃
20 nanosheets with a large surface area and the heterojunction structure both could
21 effectively increase the absorption ability of TM photocatalyst for organic pollutants.
22 This excellent absorption performance can promote the enrichment of the pollutants
23 in the surface of the photocatalyst and increase the probability of contact between
24 photocatalyst and pollutants, both of those properties are benefit to the enhancement
25 of photocatalytic activity of photocatalysts.

26 In addition, the photocatalytic degradation of Rh B is a pseudo-first-order
27 reaction and its kinetics can be expressed as: $\ln (C_0/C) = k \times t$, where k is the
28 photocatalytic reaction rate constant [38, 39]. The k value can be calculated from the
29 plots of $\ln (C_0/C)$ vs t , and the results are given in Fig. 10 (b). It can be seen that the k

values of P25, TiO₂ Nbs, MoO₃ and TM are $4.45 \times 10^{-4} \text{ min}^{-1}$, $3.83 \times 10^{-3} \text{ min}^{-1}$, $2.71 \times 10^{-3} \text{ min}^{-1}$ and $1.18 \times 10^{-2} \text{ min}^{-1}$, respectively. The k value of TM is the highest, it is because that introduction of MoO₃ can form heterojunction structures with TiO₂ Nbs, which can promote the separation of photogenerated electrons and holes.

The schematic diagram illustrating the energy band structure and occurrence of electrons and holes transfer in the TM are shown in Fig. 11. The band gap of TiO₂ Nbs and MoO₃ is closely 3.2 eV and 2.9 eV, respectively [40, 41]. As we all know, both TiO₂ and MoO₃ are wide bandgap semiconductors, and they can only be excited by ultraviolet light. However, the band gap (2.61 eV) between the VB of TiO₂ and CB of MoO₃ located in the visible region [27]. Under the stimulated solar light irradiation, due to the Ti-O-Mo bond formed in the cross region (interface) between the TiO₂ Nbs and MoO₃, the photogenerated electrons transmitted from the VB of the TiO₂ to CB of the MoO₃ directly through Ti-O-Mo bond become possible, and leaving behind holes in the VB of the TiO₂. The Ti-O-Mo bond promotes the transmission from the TiO₂ Nbs to the MoO₃, so as to narrow the bandgap of the TiO₂ and realize the solar light-driven photocatalytic reaction. And the photogenerated electrons and holes can be separated effectively and improve the photocatalytic activity of TM by this way.

The stability and recyclability property of the catalyst is crucial for its practical application. In order to evaluate the photostability of samples, we carried out experiments five times to test the recycle use of the photocatalysts by adding fresh Rh B solution (with same initial concentration). The photocatalysts were separated and washed with deionized water and dried to remove the ions absorbing on its surface after every 150 min cycle. The experiment results shown in Fig. 12 indicates that the degradation efficiency of TM almost did not change, the photocatalytic efficiency decreased only 4.7% after five cycling runs and exhibits an excellent recyclability property. The reasons for this decrease may be some catalysts washout during the repetitive steps. The excellent stability of TM catalyst suggests that the MoO₃ nanosheets are firmly connected to TiO₂ Nbs, and the introduction of MoO₃ into the TiO₂ Nbs enhances the solar-driven region photocatalytic activity of TiO₂ Nbs.

4. Conclusion

In summary, the TiO₂ nanobelts/MoO₃ nanosheets heterostructure composites (TM) have been obtained through a two-step hydrothermal method, in which the TiO₂-MoS₂ was used as the precursor. The as-synthesized TM showed a uniform heterogeneous structure in which the MoO₃ nanosheets grew along the surface of TiO₂ Nbs and intersected to form a 3D heterojunction structure. Due to the enhanced light absorption ability and higher separation efficiency of photo-generated electron-hole pairs caused by the unique heterogeneous structure, especially the unique direct transform of excited electrons from the VB of the TiO₂ to CB of the MoO₃ through the Ti-O-Mo bond form in the interface of the TiO₂/MoO₃ heterostructure composites, the TM showed a higher photocatalytic performance over the degradation of Rh B than that of the pure TiO₂ Nbs and MoO₃. Considering the extensive potential applications of the TiO₂-based heterojunction structure materials, the approach developed in this study may lead to new possibilities for the fabrication of TiO₂-based heterojunction structures endowed with multiple functionalities.

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Figure Captions

Fig. 1 XRD pattern of TiO_2 Nbs, MoO_3 and TM.

Fig. 2 FESEM images of pure TiO₂ Nbs (a); TiO₂/MoS₂ (b); TM in low and high magnification (c, d); pure MoO₃ in low and high magnification (e, f).

Fig. 3 TEM images of TM in low and high magnification (a, b); selected area electron diffraction pattern of TM (c); the EDX spectrum of as prepared TM (d).

Fig. 4 UV-visible absorption spectra (a) and plots of $(Ah\nu)^{1/2}$ versus $(h\nu)$ (b) of TiO₂ Nbs, MoO₃ and TM.

Fig. 5 FT-IR spectra of TiO₂ Nbs (a), MoO₃ (b) and TM (c).

Fig. 6 The XPS spectra: (a) The wide scan XPS spectrum of the TM; (b) O 1s of the TM; (c) Ti 2p of TiO₂ Nbs and TM; (d) Mo 3d of MoO₃ and TM.

Fig. 7 The PL spectra recorded at room temperature with an excitation wavelength of 325 nm of TiO₂ Nbs, MoO₃ and TM.

Fig. 8 The transient photocurrent responses of TiO_2 Nbs, MoO_3 and TM.

Fig. 9 EIS Nyquist plots of TiO₂ Nbs, MoO₃ and TM.

Fig. 10 The degradation rate of Rh B, (C/C_0) as the function of irradiation time (a) and (b) the plots of $\ln(C_0/C)$ vs t of P25, TiO_2 Nbs, MoO_3 and TM.

Fig. 11 The schematic diagram illustrating the energy band structure and occurrence of vectorial electrons and holes transfer in the TM

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2 **Fig. 12** Recycled photodegradation of Rh B under solar-driven irradiation of TM.