Research Article
Preparation and Photocatalytic Performances of WO₃/TiO₂ Composite Nanofibers

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The use of sunlight for photocatalytic oxidation is an ideal strategy, but it is limited by factors such as insufficient light absorption intensity of the photocatalyst and easy recombination of photogenerated electron holes. TiO₂ is favored by researchers as an environment-friendly catalyst. In this paper, TiO₂ is combined with WO₃ to obtain a nanofiber with excellent catalytic performance under sunlight. The WO₃/TiO₂ composite nanofibers were synthesized by using the electrospinning method. The X-ray diffraction (XRD) analysis indicated that WO₃ was successfully integrated onto the surface of TiO₂. The photodegradation performance and photocurrent analysis of the prepared nanofibers showed that the addition of WO₃ really improved the photocatalytic performance of TiO₂ nanofibers, methylene blue (MB) degradation rate increased from 72% to 96%, and 5% was the optimal composite mole percentage of W to Ti. The scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), UV-Vis diffuse reflectance spectra (UV-Vis DRS), and Brunauer-Emmett-Teller (BET) analysis further characterized the properties of 5% WO₃/TiO₂ nanofibers. The H₂ generation rate of 5% WO₃/TiO₂ nanofibers was 107.15 μmol·g⁻¹·h⁻¹, in comparison with that of TiO₂ nanofibers (73.21 μmol·g⁻¹·h⁻¹) under the same condition. The 5% WO₃/TiO₂ produced ·OH under illumination, which played an important role in the MB degradation. Also, the enhanced photocatalytic mechanism was also proposed based on the detailed analysis of the band gap and the active species trapping experiment. The results indicated that the effective separation of Z-scheme photogenerated electron-hole pairs and transfer system constructed between TiO₂ and WO₃ endowed the excellent photocatalytic activity of 5% WO₃/TiO₂ nanofibers.

1. Introduction

Photocatalytic oxidation is a green, environmentally friendly, inexpensive, and efficient wastewater treatment technology. The efficient degradation of toxic and hazardous substances in wastewater is the goal that researchers have always sought and has achieved very good results. For example, Jiao and coworkers have prepared a series of environmentally friendly composite hydrogel photocatalysts, which can efficiently degrade the toxic and harmful substances nitrophenol and nitroaniline that are difficult to degrade in wastewater [1–3].

The core of photocatalytic oxidation technology is photocatalyst. Since Fujishima reported that TiO₂ would decompose water under ultraviolet light irradiation in 1972 [4], TiO₂ has attracted considerable attention in photocatalysis because of its superior photocatalytic activity, good chemical stability, nontoxicity, low cost, and no secondary pollution [5]. However, several disadvantages of TiO₂ photocatalyst severely blocked its practical application such as the limited visible light response, low specific surface area, and high recombination efficiency of charge carriers, which lead to the fact that the photocatalytic activity of TiO₂ was relatively unsatisfactory [6]. Numerous efforts such as morphology designing [7], noble metal [8, 9], or nonmetal doping [10], ion doping [11, 12], composite material forming [13, 14], and heterojunction fabricating [15] had been devoted to improving its photocatalytic performance.
the abovementioned methods, heterojunction fabricating had been considered as an efficient strategy for broadening spectrum response range and effectively improving the separation efficiency of photogenerated charge carriers. For instance, Li and coworkers [16] fabricated TiO2/MoS2 nanoheterojunctions by electrospinning and hydrothermal method and demonstrated that as-prepared samples exhibited super photocatalytic hydrogen evolution activity of 171.24 μmol·L⁻¹·h⁻¹. Chen et al. [17] also reported that coupling LaNiO3 with TiO2 would remarkably enhance the photocatalytic activity of TiO2 and explained that the heterojunction formed between them played an important role in improving the photocatalytic performance. Recently, TiO2-N,C,N4 [18], CdS/TiO2 [19], TiO2/NiO [20], and TiO2/Cu2O [21] had been reported and shown enhanced photocatalytic performance for organic pollutant degradation and H2 evaluation.

WO3 as an n-type semiconductor with an energy band gap of 2.7 eV has also been considered as an efficient candidate for the formation of heterojunction with other photocatalysts due to its excellent physiochemical stability and strong visible light response [22, 23]. Thus, fabricating WO3 with TiO2 to form heterojunction might be an effective strategy to enhance the photocatalytic performance of TiO2. For example, Pan et al. prepared WO3-coated TiO2 catalysts via alcohothermal synthesis; thus, the WO3-coated TiO2 heterostructure exhibited excellent photocatalytic performance compared with anatase TiO2 [24]. Hunge et al. synthesized WO3/TiO2 thin films by the two-step spray pyrolysis method, and because a junction is formed between the WO3 and TiO2, their photoelectrocatalytic activity was enhanced [25]. Khan et al. fabricated hybrid TiO2/WO3 samples, and TiO2 and WO3 act in synergy effectively separated holes and electrons and improved photocatalytic performance [26].

The photocatalytic performance of the catalyst was closely related to its micromorphology and porous structure. The fibrous photocatalyst had a large specific surface area and more exposed active sites, which ensured its higher adsorption capacity and better photocatalytic activity [27]. Moreover, the special fibrous structure was beneficial to transfer photogenerated electrons and holes from the bulk phase to the catalyst surface and inhibited the recombination of electron-hole pairs. Therefore, fibrous photocatalysts could generate higher photocatalytic performance in comparison with traditional materials [28, 29]. Hu et al. synthesized TiO2/WO3 nanofibers by electrospinning technique and clarified that the heterojunction formed after the addition of WO3 in TiO2 fibers increased H2 production rate [30]. Gao et al. prepared TiO2/WO3 nanofibers where the hydrogen production rate was 27.73 μmol·h⁻¹ and clarified the formation of band bending and artificial Z-scheme when there is a WO3 contact with TiO2 [31]. Soares and Alves synthesized TiO2/WO3 fibers by electrospinning which increased the photocatalytic performance due to the addition of H2WO4 and degraded 51% of the dye in 135 min [32].

In this work, the fibers TiO2 and WO3/TiO2 fibers were successfully synthesized through a one-step electrospinning process and were characterized by using XRD, SEM, XPS, UV-Vis DRS, and BET techniques. The photocatalytic performance and stability of as-prepared samples were estimated by photocatalytic degradation of MB and hydrogen evolution under UV-Vis light irradiation. Finally, the possible enhanced photocatalytic mechanism of WO3/TiO2 heterojunction nanofibers was proposed.

2. Experimental

2.1. Synthesis by Electrospinning. The nanofibers of TiO2 were obtained from the precursor solution made by mixing 2.50 g of tetrabutyl titanate, 9.0 mL of glacial acetic acid, 1.10 g of polyvinylpyrrolidone (PVP), and 10 mL of ethanol solution containing N,N-dimethylformamide (v : v = 1:1) as the solvent. The WO3/TiO2 precursor solution was prepared by mixing the abovementioned reactants plus different amounts of (NH4)2WO4. These solutions were continuous stirring for 12 h and then transferred into an electrospinning device. The electrospinning parameters were optimized such as flow rate for solution 2.7 mL/h, an applied voltage of 14 kV, and the tip to collector distance of 11 cm. The samples collected on aluminum-foil collectors were designated as precursors.

Finally, the precursors prepared were heated up to 520°C at a heating rate of 1°C/min for four hours in a tube furnace, and the nanofibers of TiO2 and WO3/TiO2 were obtained. We prepared a set of WO3/TiO2 nanofibers by varying (NH4)2WO4 molar percent at 1%, 5%, and 10% where all other parameters remained unchanged.

2.2. Characterization of As-Prepared Samples. XRD patterns of samples were collected in the range of 10–80° using a 6100 X-ray diffract meter with Cu Kα radiation. The morphologies of photocatalysts were characterized by VTGAS 3BH scanning electron microscopy. XPS analysis was performed using a K-alpha photoelectron spectroscopy. UV-Vis DRS of photocatalysts were analyzed by UV-2102, UV-Vis spectrophotometers with BaSO4 as the internal reflectance standard. The BET surface area of samples was carried out using the JUK-1212 W apparatus. The photocurrent was measured using a CHI-660b electrochemical analyzer.

2.3. Evaluation of Photocatalytic Activity

2.3.1. Photocatalytic Degradation of MB. The photocatalytic performance was estimated by the degradation of MB and was performed. In a typical process, 50 mg of as-prepared samples was dispersed in 50 mL 20 mg·L⁻¹ MB and stirred in the dark for 30 min before irradiation to reach the adsorption/desorption equilibrium. Then, the solution was illuminated with a 250 W Xenon lamp. 5 mL of the sample was collected sequentially at every 20 min and then centrifuged, and the supernatant dye solution was analyzed by TU-1901 spectrophotometer at 664 nm. The degradation efficiency was calculated according to the equation of D = (A0 − Ar)/A0 × 100%. A0 and Ar were the were the absorbance of MB at an initial time and time t, respectively.
2.3.2. Photocatalytic Hydrogen Evolution. The photocatalytic hydrogen evolution experiments were carried out by a DS-GHX-V system with a 100 W Mercury lamp as the light source. In short, 30 mg of as-prepared photocatalysts was added to a sealed 100 mL quartz tube containing a mixture of 60 mL of 0.25 mol·L⁻¹ Na₂S and 0.35 mol·L⁻¹ Na₂SO₃ aqueous solution as a sacrificial agent. Before irradiation, the reaction solution was purged with N₂ for 30 min to exhaust the air in the quartz tube. The quartz tube was kept in a circulating cooling water system to maintain the temperature at 25°C and stirred continuously to make an even dispersed solution. A Thermo Trace 1300 gas chromatograph equipped was adopted to determine the amount of hydrogen production on an 80/100 PORAPAK N molecule column. The temperature of the thermal conductivity detector, column box, and filament was assigned at 200, 150°C, and 300°C, respectively, and the gas flow rate is 10 mL/min in the constant pressure mode. The holding pressure is 60.0 kPa and the ion mode is in negative ion mode. After preheating the gas chromatography, 300 μL of air for zero adjustments was injected. After each irradiation for one hour, 300 μL of gas was taken out to analyze the quantity of hydrogen according to the peak areas with the retention time around 0.625–0.630 min through the external standard method.

3. Results and Discussion

3.1. XRD Analysis. XRD was employed to investigate the crystal phase structures of the samples as shown in Figure 1, and the characteristic peaks of pure TiO₂ corresponding to both anatase and rutile were observed. The peaks at 2θ of 25.3°, 37.9°, 48.2°, and 62.7° were indexed to (101), (004), (200), and (204) planes of anatase TiO₂ (PDF NO. 21–1272), and those at 2θ of 27.4°, 36.1°, 41.2°, and 54.3° corresponded to (110), (101), (111), and (211) planes of rutile TiO₂ (PDF NO. 21–1276), respectively [33]. For WO₃/TiO₂ nanofibers, the diffraction peaks of were similar to those of TiO₂ and the characteristic peaksof pure TiO₂ corresponding to both anatase and rutile were observed. In addition, no diffraction peaks related to WO₃ were detected which might be due to its high dispersion or low content [34].

3.2. Photocatalytic Degradation Performance. The photocatalytic performance of TiO₂ and WO₃/TiO₂ nanofibers was assessed by degrading MB under Xenon lamp illumination. The experimental results are displayed in Figure 2(a). Apparently, as shown in Figure 2(a), 5% WO₃/TiO₂ exhibited the highest photocatalytic activity with the elimination rate of 96.2% for MB within 150 min, in comparison with that of TiO₂ nanofibers (72.0%), 1% WO₃/TiO₂ (91.5%) nanofibers, and 10% WO₃/TiO₂ nanofibers (79.0%) under the same condition. This result indicates that the content of WO₃ in WO₃/TiO₂ composites had a significant effect on the degradation efficiency of MB. The reasons could be attributed to the following: the lower the amount of WO₃ is, the less the electron transfer center can be formed, leading to the low photocatalytic activity; on the contrary, too much amount of WO₃ might change the electron transfer centers to the electron-hole recombination centers; in addition, the W⁶⁺ could scramble electrons from TiO₂; all of these lead to the low photocatalytic activity. In terms of the charge layer thickness, excessive doping of WO₃ can make the depth of incident light less than the surface charge layer thickness, decreased potential difference, and reduced the electron-hole migration force. Thus, the recombination of photogenerated electrons and holes becomes more easily. Moreover, the larger specific surface area of 5% WO₃/TiO₂ nanofibers could supply more magnificent active sites, resulting in the promoted photocatalytic performance.

The photocatalytic activity of 5% WO₃/TiO₂ nanofibers is shown in Figure 2(b). With the photocatalytic degradation, the absorption peak at 664 nm blueshifts and turns broadened at the same time, which may be caused by the gradual deethylation of MB [35]. The strong chromophore and conjugated structure of MB were destroyed during degradation [36]. Those characteristic peaks disappeared after 150 min irradiation, indicating that the aromatic rings and the conjugated π bond in the MB molecules were completely broken [34]. Obviously, 5% WO₃/TiO₂ nanofibers could degrade MB completely under illumination.

The significant stability of the photocatalyst was very substantial for its practical applications. To confirm the stability of 5% WO₃/TiO₂ nanofibers, recycling degradation tests were conducted by successive batches degradation of MB as shown in Figure 3. It was clear that at the end of the 5th cycle, 5% WO₃/TiO₂ nanofibers could still degrade 93% MB within 140 min (shown in Figure 3(a)) under Xenon lamp illumination, indicating the high stability of 5% WO₃/TiO₂ nanofibers. The crystal structure of used 5% WO₃/TiO₂ nanofibers was also determined to be stable as shown in Figure 3(b). In summary, 5% WO₃/TiO₂ nanofibers showed
high photocatalytic activity and stability in the catalytic process.

3.3. Photocurrent Analysis. The photocurrent test is one of the important means to characterize the response intensity of carriers to illumination and the difficulty of carrier separation. A common method for detecting photocurrent is to use a photocatalyst as a working electrode and a saturated calomel electrode as a reference electrode. When light is irradiated, due to the photoelectric effect, the movement of the electrons emitted by the electrode will form a photocurrent. The intensity of the generated photocurrent is closely related to the nature of the photocatalyst, and the intensity of the photocurrent is directly proportional to the separation efficiency of photogenerated carriers.

The TiO₂ and WO₃/TiO₂ nanofibers were coated on the glass plate as the working electrode (coating amount is 3 mg), and the working electrode was irradiated by the 125 W Mercury lamp every 10 s, and the cycle was repeated. The results are shown in Figure 4. It can be seen from Figure 4 that the photocurrent response intensity of WO₃/TiO₂ nanofibers is significantly higher than that of TiO₂. The photocurrent intensity of 1% WO₃-TiO₂, 5% WO₃-TiO₂, and 10% WO₃-TiO₂ nanofibers after five cycles is 96.2%, 95.9%, and 94.4%, respectively. The XRD patterns of the catalysts before and after photocatalysis are shown in Figure 3(b). The XRD patterns confirm the presence of both anatase and rutile phases in the catalysts. The JCPDS numbers for anatase and rutile are 21-1272 and 21-1276, respectively.
TiO\textsubscript{2} nanofibers is higher than that of TiO\textsubscript{2} nanofibers (0.7 \times 10^{-6} A/cm\textsuperscript{2}), which indicates that the doping of WO\textsubscript{3} improves the separation efficiency of photogenerated carriers. 5\% WO\textsubscript{3}/TiO\textsubscript{2} nanofibers have the highest photocurrent response intensity, reaching 3.0 \times 10^{-6} A/cm\textsuperscript{2}, indicating that the light-induced electron-hole pairs are effectively separated in the 5\% WO\textsubscript{3}/TiO\textsubscript{2} nanofiber system, and the recombination trend is lower.

Based on the above analysis results, we believe that 5\% WO\textsubscript{3}/TiO\textsubscript{2} nanofibers are the best composite percentage samples, and their comprehensive performance is the best. Therefore, 5\% WO\textsubscript{3}/TiO\textsubscript{2} nanofibers were further characterized and their hydrogen production performance was studied.

### 3.4. SEM and EDS Analysis

The SEM images of TiO\textsubscript{2} and 5\% WO\textsubscript{3}/TiO\textsubscript{2} nanofibers are displayed in Figure 5. From Figures 5(a) and 5(c), it was clear that the TiO\textsubscript{2} precursor and 5\% WO\textsubscript{3}/TiO\textsubscript{2} precursor were composed of smooth fibers with about 200 nm in diameter and 20–30 \mu m in length. After calcination, these smooth fibers fractured to short fibers with several hundred nanometers in length and the surface became rough as shown in Figures 5(b) and 5(d), which might be resulting from the oxidative decomposition of precursor fibers. As we all know, a rough surface possessed a larger surface area and is conducive to the adsorption reaction, which is helpful to improve the photocatalytic activity [37].

To further identify the chemical composition of both TiO\textsubscript{2} nanofibers and 5\% WO\textsubscript{3}/TiO\textsubscript{2} nanofibers, EDS analysis was conducted, and the results are illustrated in Figure 6. As expected, TiO\textsubscript{2} nanofibers were composed of Ti, O elements as shown in Figure 6(a). Three Ti, O, and W elements were detected in 5\% WO\textsubscript{3}/TiO\textsubscript{2} nanofibers as shown in Figure 6(b), implying the successful incorporation of WO\textsubscript{3} into TiO\textsubscript{2} nanofibers. Table 1 shows the element contents of TiO\textsubscript{2} and 5\% WO\textsubscript{3}/TiO\textsubscript{2} samples, which were basically consistent with the raw material ratio in the precursor.

### 3.5. XPS Analysis

The surface chemical status and elemental composition of the as-prepared 5\% WO\textsubscript{3}/TiO\textsubscript{2} nanofibers were analyzed by XPS. Figure 7(a) demonstrates the survey XPS spectra of sample, which indicated that 5\% WO\textsubscript{3}/TiO\textsubscript{2} nanofibers consisted of Ti, W, and O elements, in consistent with EDS results (Figure 6(b)). As indicated in Figure 7(b), the typical peak at 285.49 eV could be ascribed to the carbon contamination in the XPS measurements [38] or organic residues from raw material PVP while calcination [23]. Figure 7(c) displays the high-resolution XPS spectra of O1s with the binding energy at 530.69 eV, which could be attributed to O atom in Ti-O bond and W-O; they share the orbital O1s [26, 39]. The binding energies of Ti 2p\textsubscript{3/2} and Ti 2p\textsubscript{1/2} at 459.3 and 464.8 eV in Figure 7(d) confirmed the existence of Ti\textsuperscript{4+} in 5\% WO\textsubscript{3}/TiO\textsubscript{2} [40]. The peaks centered at 37.52 and 35.78 eV in Figure 7(e) were attributed to W 4f\textsubscript{5/2} and W 4f\textsubscript{7/2}, which fitted well with the characteristic peaks of W\textsuperscript{6+} [30].

### 3.6. UV-Vis DRS Analysis

The optical absorption property of TiO\textsubscript{2} and 5\% WO\textsubscript{3}/TiO\textsubscript{2} nanofibers was characterized by UV-Vis diffuse reflectance technique. Figure 8(a) indicated that the light absorption ability of 5\% WO\textsubscript{3}/TiO\textsubscript{2} nanofibers was slightly enhanced compared with TiO\textsubscript{2} nanofibers. The band gaps of TiO\textsubscript{2} and 5\% WO\textsubscript{3}/TiO\textsubscript{2} nanofibers were evaluated according to the equation [41] \((ah\nu)^2 = A(\nu - E_g)\), where \(A\) is a constant, \(h\) is Planck’s constant, \(\nu\) is the photon frequency, \(a\) is the absorption coefficient (replaced with absorbance in the calculation), and \(E_g\) is the band gap energy. Figure 8(b) displays the plots of \((ah\nu)^2\) versus \((h\nu)\) and the band gap energy of TiO\textsubscript{2} and 5\% WO\textsubscript{3}/TiO\textsubscript{2} nanofibers was estimated to be 3.23 eV and 3.16 eV, respectively, by extrapolating the linear portion of the graphs to energy axis.

### 3.7. BET Analysis

N\textsubscript{2} adsorption-desorption measurements were conducted to characterize the specific surface areas and pore size distributions of TiO\textsubscript{2} and 5\% WO\textsubscript{3}/TiO\textsubscript{2} nanofibers. According to the International Union of Pure and Applied Chemistry (IUPAC) classification, the N\textsubscript{2} adsorption-desorption isotherms of both TiO\textsubscript{2} and 5\% WO\textsubscript{3}/TiO\textsubscript{2} nanofibers in Figure 9(a) all corresponded to type IV with the obvious H3-type hysteresis loops, indicating the existence of large mesopores. Figure 9(b) shows the Barret-Joyner-Halenda (BJH) pore size distribution curves of TiO\textsubscript{2} and 5\% WO\textsubscript{3}/TiO\textsubscript{2} nanofibers. The pore size of TiO\textsubscript{2} and 5\% WO\textsubscript{3}/TiO\textsubscript{2} nanofibers was mainly distributed in the range of 2–10 nm, further confirming the existence of mesopores. In addition, the BET specific surface areas and detailed BJH pore size of TiO\textsubscript{2} and 5\% WO\textsubscript{3}/TiO\textsubscript{2} nanofibers are listed in Table 2. The 5\% WO\textsubscript{3}/TiO\textsubscript{2} nanofibers had a larger surface area (51.457 m\textsuperscript{2}/g) than that of TiO\textsubscript{2} (45.067 m\textsuperscript{2}/g), implying that the coupling of WO\textsubscript{3} with TiO\textsubscript{2} boosts the specific surface areas and provided abundant active sites for absorption of water molecules.
Figure 5: SEM patterns of TiO$_2$ precursor (a), TiO$_2$ nanofibers (b), 5% WO$_3$/TiO$_2$ precursor (c), and 5% WO$_3$/TiO$_2$ nanofibers (d).

Figure 6: EDS of TiO$_2$ (a) and 5% WO$_3$/TiO$_2$ (b) nanofibers.

Table 1: Elemental composition and content of TiO$_2$ and 5% WO$_3$/TiO$_2$ nanofibers.

| Sample         | Element | Weight percentage | Atomic percentage |
|----------------|---------|-------------------|-------------------|
| TiO$_2$        | O       | 39.89             | 66.02             |
|                | Ti      | 60.11             | 32.89             |
| 5% WO$_3$/TiO$_2$ | O     | 37.21             | 67.18             |
|                | Ti      | 51.87             | 31.17             |
|                | W       | 10.52             | 1.64              |
adsorption and surface reactions, which could be attributed to their rough surface as shown in Figure 5(d).

3.8. Photocatalytic Hydrogen Production Performance. Hydrogen production performance of 5% WO$_3$/TiO$_2$ nanofibers by water splitting was evaluated under 100 W Mercury lamp irradiation. O$_2$ and Na$_2$SO$_3$ solution were added to splitting water to capture photogenerated holes and accelerate the outward migration of photogenerated electrons, which is conducive to H$_2$ generation. Figure 10(a) shows the photocatalytic H$_2$ evolution capabilities of WO$_3$, TiO$_2$, and 5% WO$_3$/TiO$_2$ nanofibers. It was obvious that WO$_3$ exhibits no H$_2$ generation activity, perhaps due to the higher positive CB potential (0.79 eV) [42] than H$^+$/H$_2$O (−0.33 eV), while TiO$_2$ nanofibers display a relatively low photocatalytic H$_2$ production activity with 73.32 μmol·g$^{-1}$·h$^{-1}$, due to the rapid
recombination of electrons in CB and holes in VB. For the 5% WO3/TiO2 nanofibers, the H2 yield rate was 107.15 μmol·g−1·h−1, which was approximately 1.5 times that of TiO2 nanofibers. This result can be attributed to the formation of WO3/TiO2 Z-scheme heterostructure, which can effectively separate useful electrons and holes, and the relatively useless electrons and holes are compounded nearby. In other words, the photoinduced electrons were injected onto the CB of TiO2, while the holes were migrated onto the VB of WO3. Thus the recombination of photogenerated charge carries was effectively inhibited. As a result, the reduction of H+ to H2 could easily be achieved on 5%
WO₃/TiO₂ nanofibers system by electrons, while the holes were reacted with S²⁻ and SO₃²⁻.

Some photocatalytic materials can only oxidize (electron acceptor) or reduce (electron donor) water to generate oxygen or hydrogen with the participation of sacrificial agents (including electron acceptor and electron donor). Therefore, sacrificial agents are widely used to verify the photocatalytic properties of the materials. Therefore, the selection of the sacrificial agent has a great influence on hydrogen production. In this experiment, Na₂S/Na₂SO₃, triethanolamine, and ethanol were selected as electron donors, which are combined with photogenerated holes to promote hydrogen production and prevent photocorrosion. From Figure 10(b), it was apparent that the mixture of Na₂S/Na₂SO₃ was the best sacrificial agents for hydrogen evolution over 5% WO₃/TiO₂ photocatalyst.

Therefore, the reason why 5% WO₃/TiO₂ nanofibers have high hydrogen production activity may be that, on the one hand, the structure of the catalyst is Z-scheme heterojunction, which reduces the recombination probability of photogenerated electrons and holes; on the other hand, the addition of Na₂S and Na₂SO₃ hole trapping agents further inhibits the recombination of photogenerated electrons and holes.

3.9. Photocatalytic Mechanism Analysis. The band edge positions of 5% WO₃/TiO₂ nanofibers were theoretically calculated by the following empirical equation [43]:

\[
\begin{align*}
E_{\text{CB}} &= E_{\text{VB}} - E_g, \\
E_{\text{VB}} &= X - E_e + 0.5E_g,
\end{align*}
\]

where \(X\) is the electronegativity of the semiconductor (\(X_{\text{TiO}_2} = 5.81\) eV and \(X_{\text{WO}_3} = 6.59\) eV [44]), \(E_e\) is the energy of free electrons on the hydrogen scale (≈4.5 eV), and \(E_g\) is the band gap energy of the semiconductor (\(E_g\)WO₃ = 2.6 eV). According to this empirical expression, the calculated CB (\(E_{\text{CB}}\)) and VB (\(E_{\text{VB}}\)) edge positions for WO₃ and TiO₂ are displayed in Figure 11(a). The CB potential of WO₃ (+0.79 eV) is more negative than the VB of TiO₂ (−0.31 eV) but more positive than the CB of TiO₂ (+2.93 eV); therefore, a Z-scheme charges transportation system is formed between WO₃ and TiO₂. The photoinduced electrons on the CB of TiO₂ can efficiently inject onto the CB of WO₃ and the holes on VB of WO₃ can transfer onto the VB of TiO₂. As a result, the highly effective separation and migration system are generated for boosting the photocatalytic performance of 5% WO₃/TiO₂ composite nanofibers.

To further elucidate the photocatalytic mechanism and identify the main reactive species in the MB degradation process, the active species trapping experiment was conducted. The detailed free radical capture experiment processes were similar to the photocatalytic activity experiments. The reactive free species in MB photocatalytic process over 5% WO₃/TiO₂ nanofibers were identified by using isopropanol (IPA), benzoquinone (BQ), sodium ethylenediaminetetraacetic acid (Na₂EDTA), and potassium bromate (KBrO₃) as scavengers of \(\cdot\text{OH}, \cdot\text{O}_2^-\), \(h^+\), and \(e^-\), respectively. As indicated in Figure 11(b), with the addition of IPA, BQ, and Na₂EDTA, the degradation efficiency of MB declined to 60.3%, 42.3%, and 60.5%, indicating that H₂O and/or OH⁻ trap \(h^+\) and turn into \(\cdot\text{OH}\) in the system. The addition of BQ did not show a significant impact on the photocatalytic activity, indicating that no \(\cdot\text{O}_2^-\) radicals involved in the process. The comparison results confirmed that \(\cdot\text{OH}, h^+,\) and \(e^-\) are the dominant reactive radicals in the MB photodegradation process. \(\cdot\text{OH}\) with strong oxidation ability (the standard redox potential is +2.8 eV) can oxidize most organic dyes. Due to the formation of Z-scheme heterojunction, the photogenerated electrons and holes were transferred onto the CB of TiO₂ and VB of WO₃, respectively. As the CB level of TiO₂ (−0.31 eV) is close to the potential value of \(\cdot\text{O}_2^-/\text{O}_2\) (−0.33 eV) [45], \(\cdot\text{O}_2^-\) could not be
formed on TiO₂. Since holes are accumulated on VB of WO₃ with more positive potential (+3.39 eV) than the redox potential of \( \cdot \text{OH}/\text{OH}^- \) (+2.27 eV) [45], therefore, large amounts of \( \cdot \text{OH} \) are generated in 5% WO₃/TiO₂ composite nanofibers.

The highest photocurrent response intensity of 5% WO₃/TiO₂ nanofibers further confirmed that intimate contact between TiO₂ and WO₃ could efficiently separate the photogenerated charge carriers and accelerate efficient charge transfer [34, 46].

4. Conclusions

In this paper, highly efficient WO₃/TiO₂ nanofibers were prepared by the electrospinning method. The mole percentage of W and Ti in the composite fibers has an important influence on their performance. The optimized 5% WO₃/TiO₂ nanofibers exhibited tremendous enhanced photocatalytic degradation capability for MB solution with a 96.2% removal rate under the Xenon lamp irradiation. In addition, under the irradiation of Mercury lamp, the photocatalytic H₂ production rate over 5% WO₃/TiO₂ nanofibers is 107.15 \( \mu \text{mol} \cdot \text{g}^{-1} \cdot \text{h}^{-1} \), which is about 1.5 times of TiO₂ nanofibers. The enhanced activity may be due to the formation of Z-scheme heterojunction, which is conducive to the effective separation and transfer of photoinduced carriers. It could be seen from the experimental results of free radical trapping that \( \cdot \text{OH} \) was the main oxidant for MB degradation. Our work provides a useful reference for the preparation of other TiO₂-based photocatalysts towards both solar energy conversion and wastewater recovery.

Data Availability

All the data generated or analyzed during this study are included within the article.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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