Ex Situ Synthesis and Characterizations of MoS<sub>2</sub>/WO<sub>3</sub> Heterostructures for Efficient Photocatalytic Degradation of RhB

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Abstract: In this study, novel hydrothermal ex situ synthesis was adopted to synthesize MoS<sub>2</sub>/WO<sub>3</sub> heterostructures using two different molar ratios of 1:1 and 1:4. The “bottom-up” assembly was successfully developed to synthesize spherical and flaky-shaped heterostructures. Their structural, morphological, compositional, and bandgap characterizations were investigated through XRD, EDX, SEM, UV-Visible spectroscopy, and FTIR analysis. These analyses help to understand the agglomerated heterostructures of MoS<sub>2</sub>/WO<sub>3</sub> for their possible photocatalytic application. Therefore, prepared heterostructures were tested for RhB photodegradation using solar light irradiation. The % efficiency of MoS<sub>2</sub>/WO<sub>3</sub> composites for 30 min irradiation of 1:1 was 91.41% and for 1:4 was 98.16%. Similarly, the % efficiency of 1:1 MoS<sub>2</sub>/WO<sub>3</sub> heterostructures for 60 min exposure was 92.68%; for 1:4, it was observed as 98.56%; and for 90 min exposure, the % efficiency of 1:1 was 92.41%, and 98.48% was calculated for 1:4 composites. The photocatalytic efficiency was further verified by reusability experiments (three cycles), and the characterization results afterward indicated the ensemble of crystalline planes that were responsible for the high efficiency. Moreover, these heterostructures showed stability over three cycles, indicating their future applications for other photocatalytic applications.

Keywords: MoS<sub>2</sub>/WO<sub>3</sub>; heterostructures; solar light; photocatalysis; degradation

1. Introduction

The unprecedented growth of industrialization has led to organic contaminants in the environment. The degradation of pollutants by using semiconductor photocatalysis has been regarded as a promising technology [1,2]. Photocatalysis has gained increasing attention recently due to its potential to provide an ecologically friendly method for converting sunlight into chemical energy in mild reaction environments through photocatalytic processes and photochemical reactions. Several heterojunction photocatalysts have been developed and are being employed for water-splitting and the photocatalytic degradation of organic compounds. Among them, solar-responsive metallic oxides/sulfides have gained attention due to their effective redox processes [3,4].

For visible light photocatalysis, tungsten trioxide (WO<sub>3</sub>) is an excellent choice because of its nontoxicity and distinctive optical properties. In addition, it is inexpensive, easy to synthesize, has strong stability in both acidic and basic environments, and has high electron carrier efficiency [5]. Due to its limited light absorption range and the quick recombination of photo-generated electron-hole pairs, pure WO<sub>3</sub> photocatalytic activity is severely limited. To improve solar light absorption, impurities and higher conduction band
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semiconducting materials such as TiO$_2$ (−0.29 eV), Ag$_3$PO$_4$ (+0.3 eV), and BiVO$_4$ (0 eV) were used [6]. The addition of impurities by doping, on the other hand, reduces the thermal stability of the material and provides defect sites that act as additional recombination centers. A unique approach for separating photo-generated electron–hole pairs driven by a self-built electric field while also broadening the spectrum absorption range is currently being investigated [5].

Molybdenum disulfide (MoS$_2$) is a widely used photocatalyst due to its large specific surface area, abundant unsaturated active sites, and visible spectrum absorption. The photochemical performance of MoS$_2$ can be improved by coupling it with other semiconductors [6]. MoS$_2$ possesses a more powerful negative conduction band (−0.06 eV) than WO$_3$; the addition of MoS$_2$ might make it possible to overcome WO$_3$’s low conduction band position. Few studies have reported on the use of MoS$_2$ on WO$_3$ to increase photocatalytic performance because of the very small contact area between these two semiconductors [7,8].

Contrary to the single-component system, heterojunction photocatalysts have become a more feasible option for the breakdown of toxic contaminants. Here, the ex situ approach was used to synthesize binary composites of MoS$_2$/WO$_3$ in various weight ratios [9]. Combining two catalysts with similar band gaps increases photocatalytic activity by creating a heterojunction, which increases the promotion of photo-generated charges and decreases the recombination rate. Therefore, a heterojunction can be formed using several semiconducting materials, such as WO$_3$/MoS$_2$, WO$_3$/CuBi$_2$O$_4$, and WO$_3$/CdS, which would improve the catalyst effectiveness and ability to absorb light. Given that MoS$_2$ has a sizable surface area and strong electrical mobility, the MoS$_2$/WO$_3$ (MSW) pair is an excellent choice for creating the heterojunction [10].

We have successfully synthesized WO$_3$, MoS$_2$, and MoS$_2$/WO$_3$ composites and evaluated photocatalytic degradation of Rhodamine (RhB) dye under solar light. A significant increase in the rate of photodegradation of RhB in the presence of heterojunction photocatalysts has been observed. To investigate the photocatalytic effectiveness of ex situ hydrothermally synthesized MoS$_2$/WO$_3$ nanocomposites of varied weight ratios, RhB photodegradation studies were carried out in this study. Several investigations, including pH, concentration, and reusability assays, were conducted to evaluate the effectiveness and performance of the catalyst prepared. To demonstrate the photocatalyst’s superiority, its degrading effectiveness was also compared to that of the literature.

Additionally, the mechanism of the composite-enhanced photocatalytic activity was investigated, which could be useful for understanding the hydrogen evolution process for future applications.

2. Materials and Methods

All the chemicals used were of analytical grade, purchased from Sigma-Aldrich, (St. Louis, MO, USA), and were used without further purification.

2.1. Synthesis of MoS$_2$

MoS$_2$ was produced utilizing a two-step hydrothermal technique under acidic circumstances, employing MoO$_3$ and Ammonium Thiocyanate (NH$_4$SCN) as starting materials. A total of 1.5 mmol MoO$_3$ (0.22 g) was dissolved in 40 mL of deionized water and sonicated for 30 min, after which the pH value of the solution was adjusted to 1 by stirring for 30 min with a 1 mol/L HCl solution. These samples were then transferred to a 50 mL Teflon-lined stainless steel autoclave for hydrothermal treatment at 180 °C for 12 h, which was cooled down at room temperature, yielding a black powder of MoS$_2$ by centrifugation for 10–15 min, washed multiple times with ethanol and deionized water, and dried for 12 h in an oven at 80 °C.

2.2. Synthesis of WO$_3$

The sodium tungstate dehydrates (Na$_2$WO$_4$) (0.1 M) were dissolved in distilled water (10 mL) to maintain a pH value of ~8. Then, hydrochloric acid (HCl) (0.5 M) was added
dropwise at 50 °C to form a homogeneous solution. After continuous stirring for 15 min, the pH of the resulting solution was set to ~1. The resulting solution was then shifted to a 50 mL Teflon-lined Stainless-Steel Autoclave and placed in the oven at 180 °C for 6 h for hydrothermal treatment. After naturally cooling down, blue precipitates were separated, centrifuged, and washed several times simultaneously with deionized water and absolute ethanol, then dried in an oven at 80 °C for 12 h. The resultant powder was obtained after annealing at 400 °C for 2 h in a muffle furnace.

2.3. Synthesis of MoS2/WO3

Already-prepared MoS2 and WO3 samples were used for this process. MoS2/WO3 (1:1) and MoS2/WO3 (1:4) nanocomposites were prepared by using an ex situ synthesis in which the first MoS2 solution was prepared with 10 mL of ethanol, and the second WO3 solution was prepared with 10 mL of ethanol. Following that, WO3 solution was added dropwise to the MoS2 solution while continuous stirring was maintained for the next 30 min. The resulting solution was then centrifuged and washed simultaneously with deionized water and ethanol. The resultant dark greyish powder was obtained after drying in an oven at 80 °C for 12 h. After drying, the agglomerated material was ground in mortar and pestle to a fine powder of MoS2/WO3 (1:1) and MoS2/WO3 (1:4).

2.4. Photocatalytic Activity

The RhB dye was used to investigate photocatalytic activity. The research was carried out under the presence of a solar simulator, namely, the "Abet Technologies Sunlight TM Solar Simulator." The catalysts (MoS2/WO3) were washed by a series of centrifugation and washing steps before being reused for the subsequent degradation. Three cycles were performed to test the catalysts’ reusability and stability. The dye solution catalytic decolorization is a pseudo-first-order reaction, and the degradation rate was estimated using Equation (1) [11]:

\[
\text{Degradation (\%) } = \left( 1 - \frac{C_t}{C_0} \right) \times 100\%
\]

where \( C_t \) and \( C_0 \) are the dye’s concentration at time \( t \) and initial concentration, respectively. The degradation of 100 mL of aqueous RhB dye (10 ppm) was examined at dark, 30 min, 60 min, and 90 min. All the tests were carried out with 0.1 mg of the catalyst at its natural pH. During the photocatalytic degradation process, the distinctive absorption peak of RhB at 554 nm was set. In the absence of a catalyst, there was essentially no degradation, or at the very least, the rate of degradation was minimal. The catalytic activity of MoS2/WO3 was also tested in the dark for one hour.

3. Results and Discussion

3.1. Structural Analysis

Structural properties of MoS2/WO3 heterostructures were examined out using XRD analysis, as shown in Figure 1. The XRD was performed through Analytical X’Pert emitting CuK (Alpha) X-rays at the scanning range of 10–70°. All the diffracted peaks for MoS2/WO3(1:1) and MoS2/WO3(1:4) prepared heterostructures were matched with JCPDS 73-1508 for MoS2 and JCPDS 89-4480 for WO3, confirming the successful synthesis of heterostructures. The corresponding hkl parameters are marked in Figure 1. The observed pattern shows the increase in the WO3 ratio, and the intensity of WO3 peaks is also increased compared to MoS2 peaks. Moreover, the composition of the MoS2/WO3 heterostructures was also confirmed by using the EDX spectra, as shown in Figure S1.
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![XRD patterns of MoS$_2$/WO$_3$ heterostructures](image)

**Figure 1.** XRD patterns of MoS$_2$/WO$_3$ heterostructures; blue represents the molar ratio (1:1), while red shows (1:4).

3.2. Morphological Analysis

SEM analysis of MoS$_2$/WO$_3$ heterostructures (SEM) is shown in Figure 2a–d. Figure 2a,b are SEM images of MoS$_2$/WO$_3$ (1:4) heterostructures, where the prepared nanostructures have a relatively small size in comparison to Figure 2c,d for MoS$_2$/WO$_3$ (1:1). Figure 2b spherical agglomerates are smaller than Figure 2d agglomerates due to changed concentration, which may result in a decrease in crystalline size and an increase in the surface area [12]. SEM images of MoS$_2$ and WO$_3$ has been provided in Figure S2.

![SEM images of MoS$_2$/WO$_3$](image)

**Figure 2.** SEM Analysis of MoS$_2$/WO$_3$ with (a) molar ratio 1:4 at 5 µm, (b) molar ratio 1:4 at 1 µm, (c) molar ratio 1:1 at 5 µm, and (d) molar ratio 1:1 at 1 µm.

3.3. FTIR Analysis

For WO$_3$ (in Figure 3), a very weak shoulder peak observed at 930 cm$^{-1}$ was attributed to the W=O stretching vibration. As strong absorption peaks of W-O vibrational frequency near 1100 cm$^{-1}$ in MoS$_2$/WO$_3$ 1:1 and 1:4 heterostructures, this peak was slightly shifted to 1100 cm$^{-1}$ [12], and it overlaps with W-O at 1100 cm$^{-1}$ in MoS$_2$/WO$_3$ (1:1) and MoS$_2$/WO$_3$ (1:4) heterostructure peaks. Due to the overlap of S-O and W-O peaks, the intense sharp peaks of both heterostructures appear as stronger peaks than the parent WO$_3$ and MoS$_2$ molecules. Another peak at 1365 cm$^{-1}$ was absent in WO$_3$ but appeared as a prominent peak in MoS$_2$/WO$_3$ 1:1 and 1:4 heterostructures corresponding to W-OH vibrational frequency in the form of a bending peak, but slight and broad and intensely sharp peaks were observed at 3450 cm$^{-1}$ and 1612 cm$^{-1}$ corresponding to OH stretching and bending peaks due to water molecules present in the WO$_3$ crystal, respectively. Both became broader, more intense, and sharper in MoS$_2$/WO$_3$ 1:1 and 1:4, which shows the presence of strong H-bonding. A sharp peak of Mo-O H vibration was observed for both heterostructures spectra, but it was absent in the WO$_3$ spectrum and appeared as a slight impression in the MoS$_2$ spectrum. It is inferred that both heterostructures were prepared by strong forces, which help composite molecules bind firmly together, and H-bonding due to water crystallization plays a vital role in this regard [12,13].
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3.4. UV-Visible Spectroscopy Analysis

The UV-Vis spectroscopy model Shimadzu UV-1800 (Kyoto, Japan) was used to record absorption. Furthermore, by using Tauc’s plot, the optical bandgaps of prepared heterostructures of MoS$_2$/WO$_3$ were calculated by using Equation (2) [14].

$$\alpha h\nu = A (h\nu - E_g)^n,$$

where $n$ depends on electron transitions, and $n = 1/2$ corresponds to indirect electron transitions with an indirect optical bandgap, and where $h\nu$ is the photon energy, $\alpha$ is a constant, and $E_g$ is the optical bandgap energy. MoS$_2$/WO$_3$ (1:1) exhibited a bandgap of 2.06 eV in Figure 4a, while MoS$_2$/WO$_3$ (1:4) exhibited a narrow bandgap of 1.59 eV in Figure 4b. Their absorption spectra have been provided in Figure S3.
3.5. RhB Photodegradation

Photocatalytic activity of the prepared MoS2/WO3 heterostructures at 1:1 was performed by studying the degradation of RhB under solar light irradiation. The absorption intensity peak of RhB was centered at 554 nm and gradually decreased with an increase in the irradiation time, as shown in Figure 5a. Figure 5b represents the absorption and photodegradation curves of an aqueous solution of RhB photodegraded by a photocatalyst at a concentration of 0.1 gm over time. Photodegradation of MoS2/WO3 heterostructures with 1:4 under dark conditions was also observed, and the characteristic peak was taken as 554 nm of RhB dye used as a standard parameter during the photocatalytic degradation process. It was also observed that the concentration of RhB decreased with time, which was attributed to its degradation by a catalyst [14].

![Figure 4. Optical bandgap of (a) MoS2/WO3 (1:1) and (b) MoS2/WO3 (1:4).](image)

![Figure 5. Graphs between wavelength vs. absorbance for MoS2/WO3 under dark conditions and at varying times of 30, 60, and 90 min for molar ratios: (a) (1:1) and (b) (1:4).](image)

The photocatalytic activity was observed under solar light irradiation for 30 min, 60 min, and 90 min in Figure 6a, showing the relationship between % efficiency and irradiation time for MoS2/WO3 (1:1) and (1:4) heterostructures. Efficiencies of 91.41%, 92.41%, and 92.68% were observed for MoS2/WO3 (1:1), and efficiencies of 98.16%, 98.48%, and 98.56% were observed for MoS2/WO3 (1:4).
Figure 6. Graphs of: (a) % efficiency and time; (b) irradiation time vs. degradation \( \frac{C}{C_0} \); (c) irradiation times versus \( \ln\left(\frac{C}{C_0}\right) \) and % efficiency; (d) cycles vs. % efficiency for MoS\(_2\)/WO\(_3\) prepared heterostructures.

Figure 6b shows the degradation rate \( \frac{C}{C_0} \) versus time (minutes), i.e., under dark, it was 0.0448, while for 30 min of solar light irradiation, it was 0.0858; for 60 min, it was 0.7314, and for 90 min it was 0.0758 for MoS\(_2\)/WO\(_3\) (1:1). Likewise, the degradation rate \( \frac{C}{C_0} \) under dark for MoS\(_2\)/WO\(_3\) (1:4) was observed as 1, for 30 min under solar light irradiation it was 0.018, for 60 min it was 0.014, and for 90 min it was 0.015.

Figure 6c shows the graph between \( \ln\left(\frac{C}{C_0}\right) \) vs. time in minutes and vs. % efficiency. The values of \( \ln\left(\frac{C}{C_0}\right) \) for MoS\(_2\)/WO\(_3\) (1:1), for 30, 60, and 90 min are 2.454, 2.615, and 2.579, respectively. Meanwhile, MoS\(_2\)/WO\(_3\) (1:4) \( \ln\left(\frac{C}{C_0}\right) \) values for 30, 60, and 90 min are 3.996, 4.244, and 4.189, respectively. The rate constant \( k/h \) for MoS\(_2\)/WO\(_3\) (1:1) is calculated as 0.0278 and 0.0425 MoS\(_2\)/WO\(_3\) (1:4), indicating first-order kinetics with excellent photocatalytic activity. The stability of MoS\(_2\)/WO\(_3\) prepared heterostructures was tested for up to three cycles, as shown in Figure 6d. After 90 min of solar irradiation, prepared heterostructures showed excellent degradation and stability.

3.6. Proposed Photocatalytic Mechanism

The MoS\(_2\)/WO\(_3\) heterostructure demonstrated enhanced photocatalytic potential in two ways: (i) generation of p-n heterojunction by band alignment through the close contact interface and (ii) efficiency as a co-catalyst. Both mechanisms reduce incoming light by
forming electron–hole pairs. Under thermodynamic conditions, electrons in the MoS$_2$ conduction band (CB) migrate to WO$_3$ due to its bigger negative Fermi level, leaving holes in MoS$_2$. Electrons in MoS$_2$ CB can partially react with O$_2$ to generate •O$_2$, and holes in WO$_3$’s VB can partially react with H$_2$O to form •OH. Due to MoS$_2$ having slightly higher CB potential than O$_2$/•O$_2$, the electron’s reduction ability was so feeble that the production rate of •O$_2$ was substantially slower. The VB potential of WO$_3$ was larger than that of H$_2$O/•OH; therefore, enough •OH could be formed. The active species, •O$_2$ and OH, interacted with organic molecules, causing them to oxidize and produce CO$_2$ and H$_2$O as by-products. In addition, the holes acted as active specie directs, oxidizing the RhB to the final product. Figure 7 depicts the photocatalytic mechanism of MoS$_2$/WO$_3$ [15,16].

Figure 7. Schematic of photodegradation for MoS$_2$/WO$_3$.

4. Conclusions

A heterostructure binary nanocomposite, MoS$_2$/WO$_3$, at 1:1 and 1:4 ratios, was successfully prepared via ex situ synthesis. These prepared heterostructures were characterized, and the formation of heterojunctions was confirmed through XRD analysis. The optical bandgap energies for the MoS$_2$/WO$_3$ heterostructure were calculated as 2.06 eV and 1.59 eV for 1:1 and 1:4, respectively. An efficient RhB photodegradation was observed under solar light irradiation for prepared heterostructures. Among the already reported photocatalysts, MoS$_2$/WO$_3$ prepared heterostructures showed enhanced photocatalytic activity. The maximum photodegradation efficiency for MoS$_2$/WO$_3$ (1:4) was observed as 98.5%, indicating it is a suitable material for efficient photocatalytic degradation. The value of the K/h rate constant was observed as 0.0425, indicating the best photocatalytic activity was found when using RhB dye at 1:4. The relation between irradiation time to the rate constant Ln(C/C$_0$) for MoS$_2$/WO$_3$ heterostructures was observed as 0.0278 for MoS$_2$/WO$_3$ at 1:1. MoS$_2$/WO$_3$ showed a quick and overall degradation ability for RhB in just 30 min with good reusability behavior and photostability. With suitable bandgap engineering, the current heterostructure could be used for molecular hydrogen production. All of the mentioned findings indicate that the MoS$_2$/WO$_3$ composites made would have a wide range of potential applications for eliminating organic dyes from wastewater.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/nano12172974/s1, Figure S1: EDX spectra of MoS$_2$/WO$_3$ heterostructures; Figure S2: SEM image of (a,b) MoS$_2$ and (c) WO$_3$; Figure S3: Absorption Spectra of MoS$_2$/WO$_3$ (1:1) and MoS$_2$/WO$_3$ (1:4).

Author Contributions: W.S. designed and performed the experiments and wrote the manuscript. F.I. proposed, designed, and supervised all of the research work; M.U.T. helped with writing and
graphing; S.S. and M.A.I. helped in reviewing the manuscript; and J.R.C. helped with the final revision. All authors have read and agreed to the published version of the manuscript.

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