Application of MoS2/reduced graphene oxide for photocatalytic degradation of rhodamine B in water environment

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Abstract. In this study, MoS2 was composited with RGO (the reduced form of graphene oxide) for enhancing the photocatalytic degradation of RhB in aqueous solution by applying visible light irradiation. A new approach to synthesize graphene was applied by reduction of graphene oxide using ascorbic acid. Factors affecting the photocatalytic degradation including pH, initial rhodamine B concentration, light source intensity and quencher existence were investigated. The results showed that MoS2/RGO composite exhibited better photocatalytic activity in the degradation of RhB (with a conversion of 80 %) compared to pure MoS2 (with a conversion of 30.8 %) under visible light irradiation. The higher photocatalytic performance of MoS2/RGO was found in slight acidic environment. Among the tested free radical killers, ammonium oxalate revealed the most significant effect on the photocatalytic degradation of RhB. This research also indicated that MoS2/RGO composite can be considered as a potential catalyst for the degradation of persistent organic dyes in wastewater.

Keywords: Rhodamine B, photocatalyst, MoS2/RGO composite, graphene

1. Introduction

Environmental pollution is becoming serious, especially organic materials and dyes in wastewater originated from industrial plants. One of the methods currently being the interest of the scientists—thanks to its cost effectiveness, proficiency and practical perspective—is the photocatalytic treatment. The advantage of this method is that it makes use of the sun light to decompose the organic pollutants in the wastewaters. Various kinds of semiconductors such as TiO2, ZnO, SnO2 have been widely used as catalysts for photocatalytic water treatment processes, but they only show their high photocatalytic activity under the ultraviolet light due to large band gap [1]. Among semiconductors with low band gap, molybdenum disulphide (MoS2) is rather new one. This semiconductor has narrow band gap of \( \approx 1.6 \) eV, implying a high working efficiency in sunlight. However, the disadvantage of narrowing the band gap of semiconductors is the rapid recombination of the photo-generated electron-hole pairs, resulting in low photocatalytic activity. Therefore, finding solutions for preventing this phenomenon is of high interest [2].

Combining a semiconductor with other materials to form composites has been conducted as one of solutions for an improvement of its photocatalytic activity. Different kinds of materials have been used
for making composite such as g-C3N4, carbon nanotube (CNT), graphene to increase the ability of electronic transmission of the original semiconductors. As the results, their photocatalytic activities have been much improved as noted by Li et al. during the degradation of methylene blue over TiO2/graphene porous composites [3]. Among these materials, graphene and its derivatives are being emerged because of their excellent properties, such as high crystal quality, large surface area (2600 m²/g), good conductivity, high optical transmission speed [4]. Especially, when performing the oxidation of graphene to form graphene oxide (GO), its surface holds many functional groups containing oxygen making it hydrophilic. Then, further reduction to from reduced graphene oxide (RGO) is often applied to generate a high affinity towards organic compounds [5].

Therefore, in this research, graphene will be selected for making composite MoS2/RGO and tested for its ability in improving the photocatalytic activity of MoS2 in the degradation of rhodamine B under visible light.

2. Materials and method

2.1. Materials
Graphite powder (Merck, Germany), ascorbic acid (India), KMnO4, NaNO3, H2SO4, HCl, H2O2, C2H5OH, (NH4)6Mo7O24·4H2O, thiourea, rhodamine B (China) were used as origin without further purification.

2.2. Preparation of samples
GO was synthesized from graphite powder via the Hummers method [5, 6]. For the synthesis of RGO, GO powder was dispersed into 100 mL of water by ultrasonification for 1 h to achieve a homogeneous dispersion, followed by the addition of 1 g ascorbic acid and heated at 70 °C and stirred for 8 h. This solid was cleansed with water and ethanol three times and dried at 80 °C for 12 h [7]. MoS2 was prepared via calcination of the mixture of hexaammonium heptamolybdate tetrahydrate ([NH4]6Mo7O24·4H2O) and thiourea. For the preparation of the MoS2/RGO composite, hydrothermal synthesis at 180 °C for 10 h was applied. After being cooled down to room temperature, the mixture in the vessel was centrifuged at 2000 rpm for 15 min to separate black solid from solution. This solid was then cleansed with water and ethanol three times before being dried at 80 °C for 10 h to obtain the MoS2/RGO composite.

2.3. Characterization
Powder X-ray diffraction (XRD) was registered on a Siemen D-500 (Germany) diffractometer operated at 30 kV and 10 mA with Cu-Kα radiation. The surface morphology and structure of the samples were determined using a SEM-JEOL-JSM 5410 LV (Japan) and JEOL TEM–2100F microscope. Fourier transform infrared spectra (FTIR) were analyzed on a GX–Perkin Elmer spectrometer. The UV-Vis absorption spectra were registered with a GBC Instrument–2885 spectrophotometer. The XPS spectrum was obtained using ESCALab220i-XL electron.

2.4. Photocatalytic degradation
The MoS2/RGO composite photocatalytic activity was evaluated on degradation of RhB in aqueous solution under visible light irradiation. For a specific test, 20 mg of the photocatalyst was dispersed in 80 mL RhB solution at the concentration of 20 mg/L. Before lighting, the suspension was stirred in the dark for 2–3 h to get the adsorption-desorption equilibrium between the catalyst and RhB solution. Then, the solution was illuminated by the incandescent light of 60 W and stirred constantly. Every 1 h, an aliquot of solution was taken out and centrifuged to remove the catalyst and analyzed using a UV-Vis (CE-2011) spectrophotometer for determination of the remained RhB concentration.
3. Results and discussion

3.1. Structure of MoS2 and MoS2/RGO

The XRD patterns of MoS2 and MoS2/RGO composite are shown in figure 1. In both XRD patterns, three main peaks at $2\theta = 14.1^\circ$, $33.6^\circ$ and $58.1^\circ$, respectively for (002), (100) and (110) crystal facets of MoS2 and representative for the hexagonal 2H phase of MoS2 [8, 9] can be observed. In the XRD pattern of the composite, apart from the representative peaks for MoS2, the peak characterized for RGO is also recorded at $2\theta = 26^\circ$. However, the diffraction peaks of the composite are lower and larger than those of the pristine MoS2 due to coverage RGO layers over MoS2 crystals in the composite. This result confirms the success of synthesis of MoS2/RGO composite by combination of calcination and hydrothermal methods.

3.2. Morphology analysis

The morphology of the as-prepared MoS2 and MoS2/RGO composites are presented in figure 2. MoS2 shows scaled sheets which are stacked together (figure 2a). The morphology of MoS2/RGO composite (figure 2b) is clearly observed with curled RGO nanosheets contacted with MoS2 well, which is an advantage for the photo-generated carriers separation. The presence of MoS2 in the composite has been confirmed by EDX (figure 3), and the ratio of Mo:S atoms is 1:2.3, which is almost similar to

![Figure 1. XRD patterns of pure MoS2 and MoS2/RGO composite.](image)

![Figure 2. (a) SEM images of MoS2 and (b) MoS2/RGO.](image)
the theoretical proportion of MoS$_2$ (table 1) [1]. Moreover, the morphology of MoS$_2$/RGO composite was elucidated by TEM as shown in figure 4.

As being seen, the composite material was formed with layers structure. The MoS$_2$ was appeared in between of wrinkled RGO layers, proving the formation of composite between MoS$_2$ and RGO [9, 10].

3.3. X-ray photoelectron spectroscopy of MoS$_2$/RGO composite

XPS spectra are used to affirm the structure and composition of MoS$_2$/RGO composite with the results shown in figure 5.

![EDX spectra of MoS$_2$/RGO.](image)

**Figure 3.** EDX spectra of MoS$_2$/RGO.

| Element | Mo  | S   | C   | O   | Mo  | S   | C   | O   |
|---------|-----|-----|-----|-----|-----|-----|-----|-----|
| Weight (%) | 5.94| 7.51| 74.43| 12.12 | 2.57 | 1.08 | 85.85 | 10.50 |
| Atomic (%) | Mo | S | C | O | Mo | S | C | O |

**Table 1.** Element composition of the MoS$_2$/RGO composite.

![TEM image of MoS$_2$/RGO composite.](image)

**Figure 4.** TEM image of MoS$_2$/RGO composite.
As being observed in figure 5a, peaks at 226.41 eV, 229.16 eV, 232.43 eV and 235.5 eV correspond to the S 2s, Mo 4+ 3d5/2, Mo 4+ 3d3/2 and Mo 6+ [11]. Among them, peaks of Mo 4+ 3d5/2 and Mo 4+ 3d3/2 are representative for MoS2 and S 2s for MoS2. Peak at 235.5 eV of MoO3 or MoO42- (Mo6+) is a proof of oxidizing Mo4+ to Mo6+ in the MoS2 pattern due to the fact that oxygen has entered during the calcination. Besides, peaks appeared at 162.3 eV and 163.3 eV (figure 5b) are found to be corresponded to the S2p3/2 and S2p1/2 in the composite [12]. Peaks observed at 284.78 eV, 286.8 eV and 288.7 eV (figure 5c) may be attributed to the C-C or C=C, C-O and O=C-O bonds of functional groups in the RGO or the C-S bond [12, 13]. This completely confirms the presentation of S2- ion in MoS2 sample. Moreover, the O1s (figure 5d) is separated into two peaks at 530.5 eV and 532.1 eV, indicating the presence of lattice oxygen and adsorbed oxygen [13]. As a result, XPS spectra affirm that the composite material has been successfully synthesized by the combination of calcination and hydrothermal methods.

3.4. Specific surface area of composite

Figure 6 presents the N2 adsorption-desorption isotherms of MoS2 and MoS2/RGO composite. The N2-BET specific surface areas of MoS2 and MoS2/RGO composite calculated from the isotherms are 14.7 m2/g and 88.15 m2/g, respectively. Higher specific surface area of MoS2/RGO composite compared to pure MoS2 demonstrates that RGO could play an effective role in improving the specific surface area of MoS2/RGO composite, generating in high adsorption capacity of this material.

Figure 5. XPS spectra of MoS2/RGO composite.
3.5. **UV-Vis spectroscopy**

For the determination of the light absorption and band gaps energy of the samples, the UV-Vis diffuse reflectance spectra of MoS$_2$ and MoS$_2$/RGO composites were taken and presented in figure 7. The results indicate that the absorption edges of MoS$_2$ and MoS$_2$/RGO composites extend to 700 nm, expanding the light absorbability of the photocatalyst towards the visible light region, and as a result increasing its photocatalytic applications in the reality. Besides, the presence of RGO can also increase the band-gap energy of MoS$_2$-based catalyst, up to 2.16 eV, decreasing the photogenerated electron–hole recombination, thus improving the photocatalytic activity of the composite [12].

3.6. **Photocatalytic degradation of RhB**

The results of degradation of RhB with the existence of MoS$_2$ and MoS$_2$/RGO composite under visible light is described in the figure 8.

![Figure 6](image1.png)

**Figure 6.** (a) N$_2$ adsorption-desorption isotherms of MoS$_2$ and (b) MoS$_2$/RGO composite.

![Figure 7](image2.png)

**Figure 7.** (a) UV-Vis spectra of MoS$_2$ and MoS$_2$/RGO composite and (b) corresponding plot of the transformed Kubelka-Munk function versus the energy of the light of sample MoS$_2$/RGO.
The results show that the photocatalytic activity of pure MoS$_2$ is much lower than the one of MoS$_2$/RGO composite with 30.8% and 80% RhB degraded, respectively. These results prove that RGO plays a significant part for the enhancement of photocatalytic efficiency of MoS$_2$/RGO composites. By increasing the MoS$_2$ dispersion over RGO, the recombination of the photo-generated electron-hole pairs will be reduced. In addition, when MoS$_2$ is combined with RGO, the adsorption capacity of the material increases, improving the photocatalytic activity of MoS$_2$/RGO in the visible light.

3.7. Factors affecting the photocatalytic degradation of rhodamine B

3.7.1. Effect of pH and initial rhodamine B concentration. The results of analyzing the influence of pH and initial RhB concentration on the photocatalytic efficiency of RhB degradation are presented in figure 9.

At low concentrations, due to the strong adsorption capacity of the material, the photocatalytic role is not significant (figure 9a). As the RhB concentration increases from 20 mg/L to 100 mg/L, the efficiency of the photocatalytic degradation decreases from 80% to 14% after 7 h of lighting.

![Figure 8. Photocatalytic degradation RhB of MoS$_2$ and MoS$_2$/RGO composites.](image)

![Figure 9. (a) Effect of initial RhB and (b) pH concentration in photocatalytic degradation RhB on MoS$_2$/RGO catalyst.](image)
Due to the increase of initial RhB concentration, the adsorption of dye molecules on the catalytic sites increases, reducing the generation of radical. In addition, an increase in the concentration of RhB leads to an increase in the density of RhB molecules, lowering the ability of MoS2 to contact light photons [14]. In acidic region, photocatalytic efficiency of the composite elevates from 57 % to 84 % as the pH increases from 2.03 to 4.05. However, as the pH reaches 6.04, the photocatalytic efficiency slightly decreases to 80 % and lowers to 32 % as the environment is completely in the alkaline environment (pH = 10.02) (figure 9b). This effect of pH is similar to the findings reported in other research [15].

3.7.2. Effect of light source intensity and quencher. The results of investigation on the effect of light source intensity and quencher on the photocatalytic efficiency of RhB degradation are presented in figure 10.

The results in figure 10a show that as the lamp intensity increases from 40 W to 100 W, the decomposition efficiency of RhB dyes also increases from 68 % to 84 %. This can be explained that as the intensity of the light increases, more energy is provided for the electrons excitation from the valence band to the conduction band, facilitating the process of photogenerated electron-hole separation, then improving the photocatalytic degradation efficiency [16].

Besides, the presence of quencher reduces the efficiency of the RhB degradation. Among the tested quenchers, DMSO (electron) and TB (‘OH) are less influential than AO (hole) and BQ (O2) (figure 10b). This proves that the superoxide radical anion (O2−) and photogenerated holes are both active particles that have a certain contribution to the optical degradation of RhB and can be explained based on the role of photogenerated holes in direct oxidation of organic compounds [2].

The photocatalytic degradation of RhB over MoS2/RGO can be illustrated by the graphical diagram in figure 11 [2, 14].

This mechanism is described in details as the following [14].

\[
\begin{align*}
\text{RhB + hv} & \rightarrow \text{RhB} \left( e_{CB}^- + h_{VB}^+ \right) \\
\text{MoS2/RGO + hv} & \rightarrow \text{MoS2/RGO} \left( e_{CB}^- + h_{VB}^+ \right) \\
\text{Adsorbed RhB} \left( e_{CB}^- + h_{VB}^+ \right) + \text{MoS2/RGO} & \rightarrow \text{MoS2/RGO} \left( e_{CB}^- \right) + \text{RhB} \left( h_{VB}^+ \right) \\
\text{MoS2/RGO} \left( e_{CB}^- \right) + \text{adsorbed O2 (or surface O2)} & \rightarrow \text{O2}^- + \text{MoS2/RGO} \\
\text{H}_2\text{O} & \rightarrow \text{H}^+ + \text{OH}^- \\
\text{O2}^- + \text{H}^+ & \rightarrow \text{HO}^- \\
\text{H}_2\text{O} + \text{MoS2/RGO} \left( h_{VB}^+ \right) & \rightarrow \text{H}^+ + \text{HO}^- \\
\text{Active species + RhB} & \rightarrow \text{intermediates} \rightarrow \text{CO2 + H2O}
\end{align*}
\]

**Figure 10.** (a) Effect of light source intensity and (b) quencher in photocatalytic degradation RhB on MoS2/RGO catalyst.
Figure 11. Suggested mechanism for the photocatalytic degradation RhB by MoS$_2$/RGO composites [2].

To confirm this mechanism, the intermediates and final products of RhB photocatalytic degradation are under analysis and will be published in the next article.

4. Conclusion
In this work, the MoS$_2$/RGO composite has been successfully synthesized via hydrothermal methods and its photocatalytic activity is much improved compared to the single MoS$_2$ with 84% RhB degraded at pH = 4.05 after 7 h lighting with a 60 W–220 V incandescent lamp. Among tested quenchers, DMSO and TB have a less effect on photocatalytic degradation of RhB compared to AO and BQ. With these results, the MoS$_2$/RGO composite material reveals a high potential in practical application for degradation of organic compounds in the water under solar condition.

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