MoSe₂/Montmorillonite Composite Nanosheets: Hydrothermal Synthesis, Structural Characteristics, and Enhanced Photocatalytic Activity

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Received: 7 May 2018; Accepted: 15 June 2018; Published: 21 June 2018

Abstract: MoSe₂/montmorillonite composite nanosheets were successfully synthesized by a facile hydrothermal method, and the photocatalytic activities of the samples were evaluated by the decoloration of Rhodamine B. The structural characterizations indicate that the MoSe₂ nanosheets grow uniformly on the surface of montmorillonite with interface interaction, and the active sites on the nanosheet edges are exposed. Montmorillonite can inhibit the agglomeration of MoSe₂ nanosheets, improve the hydrophilicity and dispersibility of composites, and provides a larger surface area and more reactive sites for photocatalytic reaction. MoSe₂/montmorillonite possesses the highest adsorption properties and photocatalytic abilities, and the overall decoloration rate is up to 98.2% after visible light irradiation for 45 min. The assembly of montmorillonite could enhance the photocatalytic ability of MoSe₂, and the possible photocatalytic reaction mechanism of MoSe₂/montmorillonite for Rhodamine B was explored. MoSe₂/montmorillonite has potential applications in the photodegradation of organic dyes in the wastewater.

Keywords: montmorillonite; MoSe₂; catalytic activity; composite nanosheets; hydrothermal synthesis

1. Introduction

Since one-atom-thick graphene was exfoliated, two-dimensional (2D) nanomaterials have been receiving great attention in new material areas. 2D nanomaterials have found broad applications in many fields [1], including energy storage and conversion, electronics, catalysis, and environmental remediation due to their special structure and distinctive physicochemical properties. Besides graphene, various 2D nanomaterials have been developed over the past decade, such as transition metal oxide nanosheets [2], transition metal dichalcogenides [3], black phosphorus [4], layered double hydroxides [5], and MXenes [6]. Multiple 2D composite nanosheets with novel structures and exceptional properties have also been explored and prepared for high technology application.

Transition metal dichalcogenides are a category of narrow-band-gap semiconductors with a lamellar crystal structure [7,8]. Their band gaps usually range from 1.0 to 2.0 eV, which are appropriate for visible light catalysis. As it is one of the transition metal dichalcogenides, MoSe₂, with its structural unit of a Se-Mo-Se sandwich layer, possesses a band gap of 1.4 eV, which matches the solar spectrum very well [9]. MoSe₂ is a promising photocatalytic material with high anti-photocorrosion stability, and its catalytic active sites are located at the edges [10]. MoSe₂ nanosheets possess a larger specific surface area, more active sites, and a higher catalytic activity than the bulk material [11]. Various physical and chemical methods have been used to obtain the MoSe₂ nanosheets, such as hydrothermal synthesis [12,13], chemical vapor deposition [14], electrodeposition, and sonochemical
synthesis. However, MoSe₂ nanosheets are usually easy to agglomerate together during the aqueous phase due to the high surface energy and hydrophobicity. The assembly of MoSe₂ nanosheets on the supporting materials is one of the most simple and effective solutions. The common supporting materials include graphene [15], metal [16], titanium dioxide [17], and porous materials [18].

Natural clay is one of the most abundant minerals on earth and is the most widely used material [19]. Montmorillonite (MMT) is typical hydrophilic clay with a two-dimensional nanosheet-like morphology. The structural unit layer of MMT is composed of two silicon-oxygen tetrahedral sheets and a central aluminum-oxygen octahedral sheet. Due to its large specific surface area, abundant surface hydroxyl groups, high adsorptive property, and hydrophilicity [20], MMT demonstrates great potential in the fields of wastewater treatment [21,22], pollutant adsorption [23], catalyst supports [24,25], energy storage matrix [26,27], and drug delivery systems [28]. The supporting of MoSe₂ on MMT might inhibit the agglomeration of nanosheets and improve the hydrophilicity and dispersibility of composites, which could provide a larger surface area and more reactive sites, as well as enhance the photocatalytic activity.

With the development of society's economy and industrialization, environmental pollution problems are attracting more and more attention [29–32]. A large amount of organic dye waste waters are discharged annually from the paper, textile, printing, and photographic industries which severely threatens the health of humans and animals. Rhodamine B (RhB) is a type of industrial dye that is used in fluorescent material which can cause irritation to the skin, eyes, and respiratory tract, as well as affect reproduction, neural toxicity and carcinogenicity. Photocatalytic degradation is one of the most promising methods to treat the organic dye containing wastewater [33,34], and the development of high-efficiency and low-cost photocatalyst is one of the key techniques [35,36].

MoSe₂ is an efficient photocatalyst for the degradation of the organic dye, however its poor dispersion during the aqueous phase and the tendency of the nanosheet to agglomerate restrict its further application. MMT is one of the natural hydrophilic clays, which has advantages including its low cost and high adsorption of the organic dye. The construction of MoSe₂/montmorillonite (MoSe₂/MMT) composite nanosheets might be an effective strategy to obtain high-efficiency and low-cost photocatalysts, through MMT inhibiting the agglomeration and improving the dispersibility of MoSe₂. In this study, MoSe₂/MMT composite nanosheets were first designed and prepared via in-situ hydrothermal growth MoSe₂ nanosheets on the surface of MMT from Na₂MoO₄·2H₂O and Se. The photocatalytic activities of the samples were evaluated by the decoloration of Rhodamine B, and the effects of the different MoSe₂ amounts on the photocatalytic performances were also studied. The microstructure and the morphology of MoSe₂/MMT were characterized, and the synergistic effects of MoSe₂ and MMT for enhancing the photocatalytic activity were investigated. The possible photocatalytic reaction mechanism of MoSe₂/MMT for RhB was explored and illustrated.

2. Materials and Methods

2.1. Materials

The montmorillonite (MMT) that was used was raw Na-montmorillonite (>97%) from Shaoxing, China. Sodium molybdate (Na₂MoO₄·2H₂O), selenium powder (Se), sodium borohydride (NaBH₄), and Rhodamine B (C₂₈H₃₁ClN₂O₃) were purchased from Sinopharm Chemical Reagent Co. Ltd. (Beijing, China). All of the reagents were analytical grade and were used without further purification.

2.2. Preparation

The MoSe₂/montmorillonite (MoSe₂/MMT) composite nanosheets were successfully synthesized by a facile hydrothermal method [12]. In a typical synthesis, Na₂MoO₄·2H₂O (0.005 mol), Se (0.010 mol), and NaBH₄ (0.010 mol) were added to 60 mL of deionized water by sonication for 30 min to yield a homogeneous solution. Then, 1.000 g of MMT was added into the above solution, and the suspension was stirred for 30 min at room temperature. The suspension was transferred to a 100 mL Teflon-lined
stainless-steel autoclave and was treated at 200 °C for 24 h. After cooling to room temperature naturally, the precipitates were collected by filtration and were subsequently washed three times with deionized water. The final products were dried at 80 °C for 24 h to obtain the MoSe₂/MMT composite nanosheets. For comparison, a pure MoSe₂ sample was synthesized using a similar process without MMT.

2.3. Characterization

X-ray powder diffraction (XRD) patterns of the samples were examined by a RIGAKU D/max-2550 PC X-ray diffractometer (Cu Kα, λ = 0.15406 nm) (Rigaku Corporation, Tokyo, Japan) with a scan rate of 0.02°/s. The morphologies of the samples were examined using scanning electron microscopy (SEM, JEOL JSM-6360LV, JEOL Ltd., Tokyo, Japan) that were equipped with an energy dispersive spectroscopic (EDS) detector. The sample for SEM was sprayed with gold to enhance the surface conductivity. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) were performed on a JEOL JEM-2100F transmission electron microscope (JEOL Ltd., Tokyo, Japan) with an acceleration voltage of 200 kV. Fourier transform infrared (FTIR) spectra were conducted on a Nicolet Nexus 670 FTIR spectrophotometer (Nicolet iS10, Thermo Nicolet Corporation, Madison, WI, USA) using KBr pellets, and the data were recorded between 4000 and 400 cm⁻¹ with a resolution of 2 cm⁻¹. The photoluminescence (PL) spectra were obtained by a Hitachi F-4500 fluorescence spectrometer (Triad scientific, Manasquan, NJ, USA) with an excitation wavelength of 254 nm. X-ray photoelectron spectroscopy (XPS) spectra were collected by a Thermo Scientific ESCA Lab 250 spectrometer (Thermo Fisher Scientific, Waltham, MA, USA).

2.4. Catalytic-Activity Evaluation

The photocatalytic activities of the samples were determined by the photodegradation of Rhodamine B (RhB). A 300 W xenon lamp that was equipped with a 420 nm cutoff optical filter was used as a visible light source. Typically, 0.100 g of the catalyst was dispersed in 100 mL of RhB aqueous solution (0.02 mmol/L), and the suspension was stirred in the dark for 15 min to analyze the adsorption ability. Then, 1 mL of 3% H₂O₂ was added as an oxidant to initiate the reaction under visible light irradiation. About 3 mL of suspension was withdrawn from the reaction system every 5 min, and the catalyst was removed by centrifugation. The clarified solution was analyzed with a UV-visible spectrophotometer (UV-2450, Shimadzu, Tokyo, Japan), and the characteristic absorbance (A) at 554 nm was measured to monitor the degradation process. The decoloration rate (%) was expressed by the formula: decoloration rate (%) = (A₀ − A)/A₀ × 100%, where A₀ was the initial absorbance, and A was the absorbance at homologous times.

3. Results and Discussion

The general morphologies of MMT and MoSe₂/MMT were inspected by SEM observation. As shown in Figure 1a, MMT presents a lamellar morphology, which could be conducive to the assembly of the MoSe₂. From the SEM image of MoSe₂/MMT (Figure 1b), MoSe₂ nanosheets are dispersed on the surface of MMT, which could inhibit the agglomeration of MoSe₂ and could expose more catalytic active sites. The EDS spectrum reveals that MoSe₂/MMT was mainly comprised of Se (24.76 wt %), Mo (15.13 wt %), Si (28.51 wt %), Al (8.43 wt %), Mg (1.49 wt %), Na (1.53 wt %), and O (20.15 wt %).

The further microstructure and morphology of the samples were identified by TEM and HRTEM. Figure 2a shows the TEM image of MMT, and the two-dimensional laminar nanosheets with smooth surfaces are observed clearly. The TEM images of MoSe₂/MMT reveal that the MoSe₂ nanosheets grow on the surface of MMT (the triangular matrix) uniformly (Figure 2b). In the HRTEM image of MoSe₂/MMT (Figure 2c), the active sites of the MoSe₂ nanosheet edges are exposed. As shown in Figure 2d, we can see the layer structure of MoSe₂ with a spacing of 0.65 nm, corresponding to the (002) lattice plane.
The crystallographic structures and the phase compositions of the samples were determined by XRD, and the patterns of MMT and MoSe$_2$/MMT are shown in Figure 3a. In the XRD pattern of MMT, the diffraction peaks corresponding to the (001), (100), and (110) planes of Na-montmorillonite could be detected at 7.2°, 19.7°, and 34.7° ($2\theta$). As shown in the XRD pattern of MoSe$_2$/MMT, the diffraction peaks at 13.7° are attributed to the (002) plane of hexagonal MoSe$_2$, indicating the $d$ spacing of 0.65 nm, which is consistent with the result of TEM.

The specific surface area of MMT and MoSe$_2$/MMT were investigated by N$_2$ adsorption-desorption isotherms, as shown in Figure 3b. The N$_2$ adsorption/desorption isotherm curves of
the samples exhibit type IV adsorption branch with a H3 hysteresis loop, which is characteristic of the mesoporous structure. The Brunauer-Emmett-Teller (BET) specific surface area of MMT and MoSe₂/MMT are calculated to be 38 and 47 m²·g⁻¹, respectively. The larger specific surface area of MoSe₂/MMT could be attributed to the uniform distribution of MoSe₂ nanosheets on the surface of MMT [8], which could supply more adsorption and reactive sites for photocatalytic reactions.

![Figure 3](image.png)

**Figure 3.** (a) X-ray powder diffraction (XRD) patterns of MMT and MoSe₂/MMT; (b) N₂ adsorption/desorption isotherm curves of MMT and MoSe₂/MMT.

The vibrational bands of MMT and MoSe₂/MMT were investigated by FTIR, as shown in Figure 4a. For MMT, the bands corresponding to the stretching vibration of O–Si–O and the bending vibration of Si–O from the silicon-oxygen tetrahedron of MMT are observed at 1021 and 472 cm⁻¹, respectively. The obvious band at 3620 cm⁻¹ is attributed to the hydroxy stretching vibration from the Al–OH group on the surface of MMT. The bands at 3453 and 1637 cm⁻¹ are due to the H–O–H stretching vibration and the –OH bending vibration of the hydrogen bond water, respectively. The band at 1441 cm⁻¹ is probably due to the stretching vibration of carbonate from the impurity mineral [37]. In the FTIR spectrum of MoSe₂/MMT, the band at 461 cm⁻¹ could be attributed to the stretching vibration of Mo–Se and MoSe₂. The bands of the hydroxy group obviously decrease, and the band corresponding to the O–Si–O stretching vibration shifts to 1039 cm⁻¹ from 1021 cm⁻¹, suggesting the existence of interaction between MoSe₂ and MMT.

Figure 4b shows the PL spectra of MMT and MoSe₂/MMT, with an excitation wavelength of 254 nm. For MMT, the peaks corresponding to the intrinsic defects of the surface surplus oxygen and the diamagnetic defect center could be observed at 354 and 398 nm, and the peaks around 470 nm are attributed to the neutral oxygen vacancy [38]. The other weaker peaks around 450–500 nm are probably due to the hydroxyl radicals on the surface of MMT. In the PL spectrum of MoSe₂/MMT, the peak intensity is lower than that of MMT, indicating the lower recombination rate of the photogenerated electron hole pair.
The surface elemental composition and the chemical status of MMT and MoSe$_2$/MMT were characterized by XPS. In the XPS survey spectrum of the samples (Figure 5a), the peaks of the Si and Al elements in MMT and the peaks of the Mo, Se, Si, and Al elements in MoSe$_2$/MMT could be observed. As shown in the high-resolution scans for Mo 3d and Se 3d electrons of MoSe$_2$/MMT (Figure 5b,c), the binding energies of Mo3d$_{3/2}$, Mo3d$_{5/2}$, Se3d$_{3/2}$, and Se3d$_{5/2}$ peaks are located at 232.9, 229.5, 56.4, and 55.5 eV, respectively, indicating that the chemical statuses of Mo$^{4+}$ and Se$^{2-}$ dominate in MoSe$_2$/MMT. The high-resolution spectrum of O 1s (Figure 5d) could be deconvolved into two peaks of the hydroxyl oxygen and the lattice oxygen. The hydroxyl oxygen of MoSe$_2$/MMT decreases with the MoSe$_2$ decoration, which is consistent with the FTIR result.

The decoloration of the organic dyes’ RhB was chosen to assess the adsorption properties and the photocatalytic abilities of the samples. Figure 6a shows the variation in the decoloration rates for
MMT, MoSe$_2$, and MoSe$_2$/MMT. The RhB solution hardly discolors without a catalyst over 60 min, indicating that RhB could not self-degrade under visible light irradiation. The adsorption properties of the samples for RhB were measured in the dark for 15 min. The adsorption rate of MMT for RhB was higher than that of MoSe$_2$, due to the abundant surface hydroxyl of MMT. MoSe$_2$/MMT possesses the highest adsorption rate for RhB up to 22.9%, which could be attributed to the cooperative adsorption of MMT and MoSe$_2$. The decoloration rate of MMT for RhB had no obvious change under the visible light irradiation, indicating that MMT has no photocatalytic activity. MoSe$_2$/MMT exhibits the highest photocatalytic ability for RhB, and the overall decoloration rate was up to 98.2% after the visible light irradiation for 45 min. This might because MMT restrains the agglomeration of the MoSe$_2$ nanosheets and improves the hydrophilicity and dispersibility of the composites in the RhB solution, which could provide a larger surface area and more reactive sites for photocatalytic reactions. MoSe$_2$/MMT has potential applications in the photodegradation of organic dyes in the wastewater.

As shown in Figure 6b, the samples were added in the aqueous phase, and the dispersibilities were observed. MoSe$_2$/MMT exhibits favorable dispersibility in the aqueous phase, which conduces to enhance the photocatalytic ability of the composites. MoSe$_2$ could not disperse in the aqueous phase and floated in the water. The contact angles of the water droplets that were collected on the surface of the samples are shown in Figure 6c. The contact angles of MMT, MoSe$_2$, and MoSe$_2$/MMT are 18.7, 50.3, and 35.6$^\circ$, respectively. Through the support of MMT, the MoSe$_2$/MMT composite nanosheets have better hydrophilicity than MoSe$_2$.

Figure 6. (a) The decoloration of Rhodamine B (RhB) with MMT, MoSe$_2$, and MoSe$_2$/MMT; (b) a digital photograph of the samples dispersed in water; (c) the contact angles of the water droplets that were collected on the surface of MMT, MoSe$_2$, and MoSe$_2$/MMT.

The possible photocatalytic reaction mechanism of MoSe$_2$/MMT for RhB is schematically illustrated in Figure 7. Under the visible light irradiation, the photogenerated electron and hole pairs are yielded in the conduction band (CB) and the valence band (VB) of MoSe$_2$ [9]. The surface hydroxyl groups of MMT could trap the photogenerated holes (h$^+$) to produce hydroxyl radicals (OH) [24], and the oxygen molecules (O$_2$) in the solution could react with photogenerated electrons (e$^-$) to produce superoxide radical anions (O$_2^-$). These help to reduce the recombination of the electron and hole pairs and strengthens the photocatalytic ability. The large surface area and the charge separation could improve the photocatalytic activity in the MoSe$_2$/MMT composite together. Finally, the RhB was degraded to nontoxic, small molecules by H$^+$, OH$^-$ and O$_2^-$. The high adsorption property and the hydrophilicity of the composites could increase the apparent concentration of RhB around the surface, and could further enhance the photocatalytic ability synergistically.
4. Conclusions

In summary, MoSe$_2$/montmorillonite composite nanosheets have been successfully synthesized by a facile hydrothermal method with enhanced photocatalytic activity. The MoSe$_2$ nanosheets uniformly grow on the surface of MMT, and the active sites on the nanosheet edges are exposed. The interface interaction exists between MoSe$_2$ and MMT, and the chemical statuses of Mo$^{4+}$ and Se$^{2-}$ dominate in MoSe$_2$/MMT. MoSe$_2$/MMT possesses the highest adsorption properties and photocatalytic abilities due to the synergy of MoSe$_2$ and MMT, and the overall decoloration rate is up to 98.2% after visible light irradiation for 45 min. MMT could inhibit the agglomeration of MoSe$_2$ nanosheets and could improve the hydrophilicity and dispersibility of composites in the RhB solution, which could provide a larger surface area and more reactive sites for photocatalytic reactions. MoSe$_2$/MMT has potential applications in the photodegradation of organic dyes in the wastewater.

Author Contributions: K.P. and X.L. (conceiving the project), X.L. (writing initial drafts of the work), K.P. (writing the final paper), X.L. (designing and performing the experiments and characterizing the samples). All of the authors discussed the results and commented on the manuscript.

Funding: This research was supported by the National Natural Science Foundation of China (51704030), the China Postdoctoral Science Foundation (2017M610617, 2017M623182, and 2018T111054), Shaanxi Postdoctoral Science Foundation (2017BSHEDZZ10), and the Special Fund for Basic Science Research of Central Colleges of Chang’an University (310831171002, 300102318402).

Acknowledgments: This work was supported by the National Natural Science Foundation of China (51704030), the China Postdoctoral Science Foundation (2017M610617, 2017M623182, and 2018T111054), Shaanxi Postdoctoral Science Foundation (2017BSHEDZZ10), and the Special Fund for Basic Science Research of Central Colleges of Chang’an University (310831171002, 300102318402).

Conflicts of Interest: The authors declare no conflict of interest.

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