Synthesis, characterization and photocatalytic performance of chemically exfoliated MoS$_2$

S V Prabhakar Vattikuti$^1$ and Jaesool Shim$^1$

$^1$School of Mechanical Engineering, Yeungnam University, Gyeongsan, South Korea, 712-749

Abstract. Two-dimensional (2D) layered structure transition metal dichalcogenides (TMDs) has gained huge attention and importance for photocatalytic energy conversion because of their unique properties. Molybdenum disulfide (MoS$_2$) nanosheets were synthesized via one-pot method and exfoliated in (dimethylformamide) DMF solution. Subsequent exfoliated MoS$_2$ nanosheets (e-MoS$_2$) were used as photocatalysts for degradation of Rhodamine B (RhB) pollutant under solar light irradiation. The e-MoS$_2$ nanosheets exhibited excellent photocatalytic activity than that of pristine MoS$_2$, owing to high specific surface area with enormous active sites and light absorption capacity. In addition, e-MoS$_2$ demonstrated remarkable photocatalytic stability.

1. Introduction

Photocatalysis process can convert solar energy into chemical energy for wide range of applications in environmental control technologies. The development of visible-driven photocatalysts has received significant attention in recent years [1]. Generally, traditional photocatalysts for example TiO$_2$ have an inherent drawback in that they only active under UV-light irradiation [1, 2]. Therefore, the design of efficient visible light driven photocatalysts is highly desirable.

Molybdenum disulfide (MoS$_2$) has been reported as a distinguished precious metal free photocatalysts for degradation of organic pollutants based on its unique layered features, cost effectiveness and solar energy utilization [3]. In a previous study, we successfully synthesized layered MoS$_2$ and discovered that this precious metal free photocatalyst demonstrated efficient photocatalytic activity for the removal of organic pollutants from aqueous solution under visible light irradiation [3]. Unfortunately, MoS$_2$ alone does not show excellent photocatalytic performance due to recombination of charge carriers. Recently, E. Parzinger et al. [4] developed few layered MoS$_2$ via micromechanical exfoliation from bulk crystal and used as photocatalyst for photocatalytic hydrogen (H$_2$) evolution. B. Han et al. [5] reported intercalated exfoliated MoS$_2$ is used as co-catalyst for photocatalytic hydrogen evolution from water splitting. Bai et al. [6] demonstrated chemically exfoliated metallic MoS$_2$ nanosheets as cocatalyst for improved the photocatalytic activity of commercial TiO$_2$ nanocrystals. However, these synthetic procedure comprising of various sequence of steps and complexity to synthesis.

Therefore, it is necessary to fabricate a new facile method for exfoliation of MoS$_2$ that could be produce an ultra-thin 2D nanosheets at the large scale and low cost for its potential application in various fields.

In this work, we developed a simple and facile chemical route to exfoliate the bulk layered MoS$_2$ materials into few layered e-MoS$_2$ nanosheets. These e-MoS$_2$ can scale-up with ease. The e-MoS$_2$ nanosheets were employed as photocatalyst for degradation of RhB pollutant. The e-MoS$_2$ nanosheets exhibited excellent photocatalytic performance compared to as-synthesizes MoS$_2$ ones. Moreover, the
used photocatalyst is successfully recovered and reused three times and observed no loss of photocatalytic activity.

2. Experimental details

2.1. Synthesis of MoS$_2$ and e-MoS$_2$ nanosheets

In a typical synthesis procedure, 1.5 mol of ammonium hepta molybdate tetrahydrate and 60 mmol of C$_2$H$_5$NS were dissolved in 50 mL of ethanol and 25 mL deionized water under constant stirring. Then, 5 mol/L HCl was used to adjust the pH of the mixed solution to 2–2.8 and the solution was stirred for 30 min at room temperature. Then the above solution was transferred into a 100-mL Teflon-lined stainless steel autoclave, sealed, and maintained at 180°C for 24 h. After being cooled, the product was obtained by centrifuging, washed repeatedly with deionized water and ethanol three times, and dried in a vacuum oven at 120°C for 4h. To prepare few-layer e-MoS$_2$, a sonication method was employed. Typically, 50 mg of the as-synthesized MoS$_2$ and 100 mL dimethylformamide were added to a beaker, which was submerged in a 200-W ultra-sonication machine for 1 h. Then, final precipitates were collected by centrifugation (6000 rpm) and washed with ethanol and dried at 70°C in vacuum oven.

2.2. Characterization

Powder X-ray diffraction (XRD) patterns of the as-prepared photocatalysts were obtained using a Shimadzu LabX X-ray diffractometer (XRD 6100 model) using Cu Kα radiation (λ= 0.154 nm) at 40 kV and 30 mA. X-ray photoelectron spectroscopy (XPS) analysis was conducted using a Thermo Scientific instrument and K-alpha surface analysis. N$_2$ adsorption-desorption isotherms were recorded using a Micromeritics ASAP 2420 surface area analyser at the temperature of liquid N$_2$. Before gas adsorption, all photocatalysts were degassed for 2 h at 180°C. To determine the surface morphology transmission electron microscopy (TEM) at an accelerating voltage of 300 kV. High-resolution TEM (HRTEM) studies were performed using a Hitachi H-7000 and a Tecnai G2 F 20 s-twin TEM.

2.3. Photocatalytic activity test

Typically, the photocatalytic activity of the samples was tested at the natural pH of an RhB organic dye solution (10 ppm in concentration). The test was performed under visible-light irradiation with a MAX-300 Xe lamp (λ> 400 nm). In a typical run, a mixture comprising 50 mg of various photocatalysts was suspended in 100 ml of RhB aqueous solution and stirred for 30 min in order to achieve an adsorption-desorption equilibrium mixture. During light irradiation, 5 ml of the reaction mixture was sampled at 5-min intervals with a syringe. The collected samples were examined with a UV-Vis-NIR Cary 500 spectrophotometer. The photocatalysts were then separated from the degraded solution by centrifuging (5000 rpm), washed with ethanol to fully take away the residual dye moieties then again washed with water and reused for consequent runs.

3. Results and discussion

The powder XRD patterns of the e-MoS$_2$ nanosheets is shown in figure 1a. The diffraction peaks of e-MoS$_2$ is matched with JCPDS card: 751539, with 2θ =14.12°, 28.42°, 32.91°,39.53°, 49.41°, 55.44°, 58.62°, and 69.47 corresponding to (002), (004), (100), (103), (105), (106), (110), and (200) planes of hexagonal MoS$_2$ materials and were confirmed by previous reports [3]. The XRD results represented that the obtained materials have pure phase, and no characteristic peaks were observed from impurities. To investigate the chemical compositions and nature of chemical bonding of constituent elements are presented in e-MoS$_2$. X-ray photoelectron spectroscopy (XPS) was carried out, resulted are shown in figure 1b-d. The existence of core levels of Mo and S elements confirms by survey, results reflecting the high purity of e-MoS$_2$ as shown in figure 1b. XPS pattern of Mo 3d with characteristic peaks at binding energies of 229.34 and 232.85 eV, which are ascribed to the spin orbit of Mo 3d$_{3/2}$ and Mo 3d$_{5/2}$ of the Mo$^{2+}$ chemical state, respectively (figure 1c). The two peaks at binding energies of 161.18 and 162.34 eV are ascribed to the S 2p$_{3/2}$ and S 2p$_{1/2}$ of the S$^{2-}$ chemical state [3], respectively (figure 1d).
Figure 2 shows the morphology of e-MoS\textsubscript{2} nanosheets was investigated by scanning electron microscopy (SEM) and high resolution transition electron microscopy (HRTEM). Figure 2a shows exfoliated MoS\textsubscript{2} are distributed randomly. To further confirm the purity of e-MoS\textsubscript{2}, SEM EDX study was carried out. It is obvious from figure 2b, that the entire sample comprising of Mo and S elements, no other impurities were detected. Figure 2c shows HRTEM image of the pristine MoS\textsubscript{2}. From the HRTEM images (figure 2c-e), it is clear that e-MoS\textsubscript{2} grew in sheet like morphology having very dense and uniform structure with an average length in few nanometers to submicron. SAED pattern of e-MoS\textsubscript{2} represents the existing of pure phase grew along with diffraction planes of (100), (103), (105), and (110).

![Figure 1.](image)

**Figure 1.** (a) XRD pattern of e-MoS\textsubscript{2}, (b) survey spectra of e-MoS\textsubscript{2}, (c) XPS spectra of Mo 3d and (d) XPS spectra of S 2p element.

The photocatalytic activity of the pristine MoS\textsubscript{2} and e-MoS\textsubscript{2} were studied with RhB degradation under simulated solar light illumination. Figure 3a displays the sequential changes of the UV–vis absorption spectra of RhB solution treated with simulated solar light as a function of time, which were obtained in the presence of e-MoS\textsubscript{2}. There is a strong adsorption peak at 554 nm that decreases gradually with as the irradiation time increases from initial to clear ones at 60 min, which reflects the pink color of the initial RhB solutions gradually faded during the process of photodegradation.
Figure 2. (a) SEM image of e-MoS$_2$, (b) SEM-EDX mapping, HRTEM image of (c) pristine MoS$_2$, and (d, e) e-MoS$_2$, and SAED pattern of e-MoS$_2$.

Figure 3b shows the photodegrading efficiency expressed as changes in the RhB organic dye relative concentration ($C/C_0$, $C$-final concentration, $C_0$-initial concentration), which was obtained as a function of irradiation time with various catalyst under simulated solar light irradiation. A blank experiment was carried out in the absence of photocatalyst and demonstrated no change in the RhB concentration within 60 min of reaction under simulated solar light irradiation. The e-MoS$_2$ can greatly enhance the photocatalytic activity under simulated solar light irradiation. Under simulated solar light irradiation, both photocatalysts exhibited remarkable photodegradation performance. The highest photocatalytic activity was obtained over e-MoS$_2$, with which more than 99.94% of the RhB was degraded within 60 min, owing to more active sites for RhB adsorption and degradation and enhance the photodegradation [3]. These results designate that the e-MoS$_2$ play an important role in the adsorption and photocatalytic degradation process of RhB. Figure 3c displays the kinetic plot of ln ($C/C_0$) with respect to time, which followed the first-order kinetics. To examine the photostability and reusability of the photocatalyst, three successive recycling tests were accomplished for the degradation of RhB under simulated solar light irradiation, as shown in figure 3d. After three cycles, the e-MoS$_2$ demonstrated no significant loss in activity and the decomposition efficiency was consistent. Thus, the e-MoS$_2$ are very stable with prolonged irradiation time and significantly enhanced the visible light photocatalytic activity. This result denotes that e-MoS$_2$ photocatalyst have high stability and can be reusable.
Figure 3. (a) UV-Vis absorption spectra changes of RhB aqueous solution in the presence of e-MoS$_2$, (b) Photocatalytic activities, and (c) Kinetic linear simulation of RhB photocatalytic degradation of pristine MoS$_2$ and e-MoS$_2$ photocatalysts, and (d) Recycling test results of the e-MoS$_2$ photocatalyst for the degradation of RhB under simulated solar light irradiation.

4. Conclusions

MoS$_2$ nanosheets were synthesized via a hydrothermal method and then, chemically exfoliated MoS$_2$ into few layered nanosheets in presence of DMF. The comparative photocatalytic studies were performed over pristine MoS$_2$ and exfoliated MoS$_2$ (e-MoS$_2$) for photodegradation of RhB pollutant under simulated solar light irradiation. The e-MoS$_2$ nanosheets showed greater photocatalytic degradation of RhB under simulated solar light irradiation compared to pristine one. In addition, the photocatalyst activity demonstrated good stability during the photoreactions with no significant deactivation observed after three test runs with the recycled catalyst. The simplicity this entire synthetic process could facilitate numerous significant applications for exfoliation of other inorganic materials.

References

[1] Martin D J, Liu G, Moniz S J A, Bi Y, Beale A M, Ye J and Tang J 2015 Chem. Soc. Rev. 44 7808.
[2] Dong H, Zeng G, Tang L, Fan C Z, Zhang C, He X and He Y 2015 Water Research 79 128.
[3] Vattikuti S V P, Byon C and Reddy C V 2015 Superlattice. Microstruct. 85 124.
[4] Parzinger E, Miller B, Blaschke B, Garrido J A, Ager J W, Holleitner A and Wurstbauer U 2015 ACS nano, 9 (11) 11302
[5] Han B and Hu Y H 2016 Energy Sci. Eng. 4(5) 285.
[6] Bai S, Xiaoyi L W, Junteng C and Xiong D Y 2015 Nano Res. 8(1) 175.