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Effect of Mn^{2+} dopants on the photocatalytic efficiency of MoS_2

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ABSTRACT

The Mn-doped MoS_2 (Mn-MoS_2) material is fabricated by a facile one-step calcination method. The Mn^{2+} content introduced into MoS_2 is ranged from 1 wt% to 7 wt%. The X-ray diffraction (XRD) and scanning electron microscopy SEM results suggest that the doping of Mn^{2+} does not alter the crystal structure and the morphology of MoS_2. However, it helps the Mn-doped MoS_2 to exhibit stronger visible light absorption and higher magnetism. Especially, in the RhB degradation under visible light irradiation, better photocatalytic performance of the as-prepared Mn-doped MoS_2 is observed compared to that of pure MoS_2.

Introduction

MoS_2 is a two-dimensional (2D) layer transition metal that is currently attracting the interest of many scientists because of its wide applicability in the field of photocatalytic degradation of organic dyes [1], hydrogen evolution [2], and photoelectrochemical cell [3]. However, the band gap of MoS_2 sheets is small (about 1.3 eV in bulks) so photon-generated electron-hole pairs are rapidly recombined, leads to low photocatalytic efficiency. According to Sara et al [4] MB degradation efficiency over MoS_2 photocatalyst is only 20% with MoS_2 catalyst. Therefore, to improve the photocatalytic efficiency of materials, doping metal or nonmetal elements into MoS_2 2D crystals is currently being extensively studied [5]. Doping can improve the intrinsic properties of metals as well as nonmetals, increasing the properties of 2D materials. The presence of doping elements can increase the band gap of MoS_2, thus enhances the separation of photon-generated electron-hole pairs and improve the photocatalytic activity in degradation of organic compounds. Morever, magnetic properties are also improved, which increases the charge transfer capacity, thereby significantly improving the photocatalytic efficiency of the material [6].

There are many doping methods available, but the disadvantage is the complex of the process and high cost due to the use of precious metals [3, 7]. Therefore, this study aims to development of a simple method for synthesis MoS_2 material by one step. In this study, Mn was selected for doping into MoS_2 to increase the photocatalytic efficiency of the material due to its low cost and the ionic radius of 0.80 A° [8] similarity in compared to Mo^{4+} 0.79 A° of MoS_2. There are many elements used for the MoS_2 doping process, but no published work on the inclusion of Mn doped in MoS_2 network to improve the photocatalytic efficiency of the materials. The results of this study can open up new research directions in the application of other transition metals on semiconductors, to fully exploit the properties of materials in many different applications, especially, the process of degradation persistent organic substances pollutes the environment.

Experimental

Synthetic materials

Materials, chemicals: materials and chemicals used for this study include $(NH_4)_6Mo_7O_{24}.4H_2O$, thiourea, $Mn(CH_3COO)_2.4H_2O$, ethanol and rhodamine B (China).

The Mn-MoS_2 material is synthesized by a simple calcination method. In a typical experiment, $(NH_4)_6Mo_7O_{24}.4H_2O$, $(NH_2)_2CS$, as the precusors, were dissolved in a solvent of water : ethanol (1:1. v/v) under vigorously stirring at room temperature for 30 minutes. A proper amount of $Mn(CH_3COO)_2.4H_2O$ was added and continuously stirred for another 1h to obtain a homogeneous solution. The resulting solution was heated at 60°C under stirring to evaporate solvents, and then, a solid was obtained. This solid was well ground and calcinated at 650°C for 1 hour in N_2 gas. The obtained sample was labeled as Mn-MoS_2. For comparison, MoS_2 was also prepared in the same procedure without the addition of $Mn(CH_3COO)_2.4H_2O$.

Characterization of Materials

The synthetic material samples are analyzed to determine their structural characteristics by the methods such as: X-ray diffraction (XRD-Siemen D-500-Bruker), structural bonding by infrared spectrum (FT-IR– GX-PerkinElmer), Scanning electron microscope (SEM – SEM-JEOL-JSM 5410 LV), Energy-dispersive X-ray spectroscopy (EDX – Jeol 5419), Electron paramagnetic resonance (EPR - Bruker) and Visible ultraviolet diffuse reflection (UV-Vis DRS – Cary 5000, Varian).

Research on RhB decomposition photocatalytic process

Photocatalytic activities were evaluated through the photodegradation of RhB in aqueous solution under the visible light irradition. For the typical experiment, 0.1g of the photocatalyst was dispersed into a 400 ml RhB solution with a concentration of 20 mg/L under stirring at room temperature. Before irradition, the suspension was stirred in the dark for 2 hours to reach the adsorption-desorption equilibrium of RhB molecules on the surface of the photocatalyst before being illuminated by the compact light (60W-220V). After every interval of 30 minutes, 4 mL solution was taken out and centrifuged to remove the photocatalyst. The residual concentration of RhB as a function of investigated time was determined by recording its absorbance at 553 nm using a UV-Vis spectrometer. On the basis of comparison with the initial RhB concentration, the RhB conversion and the activity of the material were determined.

Results and Discussion

Investigate the effect of the Mn content on the structure of MoS_2

The results of crystal and structure characteristics of MoS_2 and n% Mn-MoS_2 materials (with n = 1% Mn, 3% Mn, 5% Mn and 7% Mn) are shown on X-ray diffraction pattern in the Figure 1.

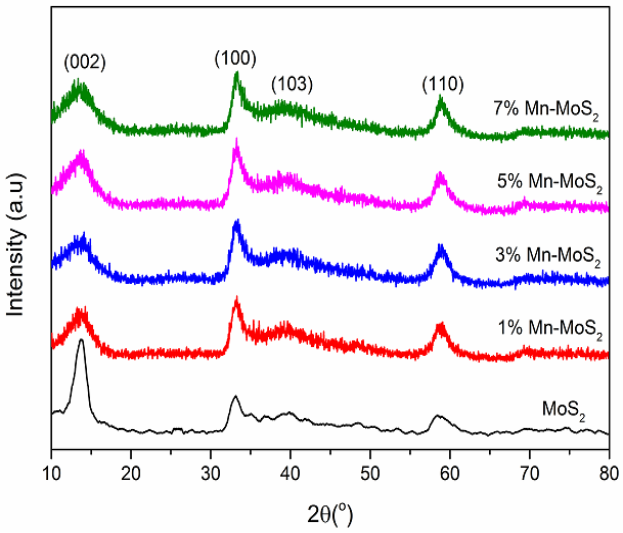

Fig 1: Effect of Mn content on crystal phase characteristics of Mn-doped samples (n% Mn-MoS_2, with n = 1% Mn, 3% Mn, 5% Mn and 7% Mn)

The results showed that in Mn-doped MoS_2 material samples, the presence of characteristic peaks of MoS_2 appeared at 2θ = 14.1; 33.6; 39.84 and 58.1°, respectively (002), (100), (103), and (110) are completely consistent with the 2H hexagonal phase of MoS_2 [9]. The peaks on the faces (100) and (110) were sharp, indicating very good crystallinity of the composites. Meanwhile, the peak in the face (002) of the n%Mn-MoS_2 samples flat and the intensity was much lower than that of the undoped MoS_2 sample, possibly due to the presence of Mn^{2+} ions in the MoS_2 network. Furthermore, with the addition of Mn, there are no remarkable changes in the XRD patterns and no addition peak indexed to MnS or to any other secondary phases can be identified, indicating that Mn^{2+} ions might be doped into the MoS_2 crystal or maybe the Mn^{2+} ions content used for the doping process are too low [10].

The chemical bonding characteristics in the structure of MoS_2 and n%Mn-MoS_2 materials were shown on the FTIR spectra(Figure 2).

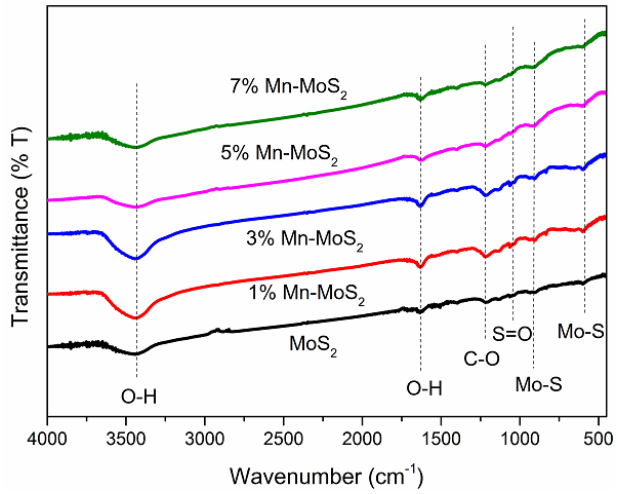

Fig 2: FT-IR spectra of MoS_2 and n%Mn-MoS_2

The results showed that the peaks around 528 cm^{-1}, 920 cm^{-1} corresponded to Mo-S stretching vibrations [11,12], while the peak at 1119 cm^{-1} was for S=O linkage [13] and the peak at 1250 cm^{-1} atributed to C-O vibration [14] the vibration bands around 1632 and 3200-3500 cm^{-1} could be ascribed to O-H streching of water adsorption on the surface of the material [15]. Because the amount of Mn doped is too small, the characteristic of the bonds are not shown in the Mn-MoS_2 samples (this was also shown in the XRD spectrum). To know the difference of Mn doped (Mn-MoS_2) and undoped (MoS_2) is clearly shown in EPR spectrum.

Meanwhile, the light absorption of the samples MoS_2 and n%Mn-MoS_2 changed depending on the presence of Mn as observed in the Figure 3.

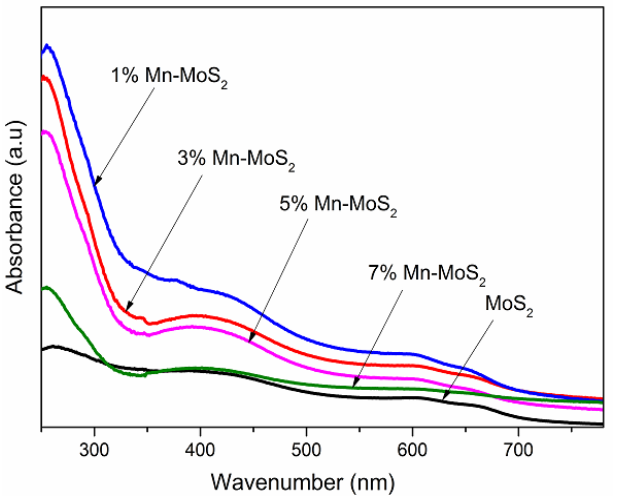

Fig 3: UV-Vis DRS spectra of MoS_2 and n%Mn-MoS_2

The results showed that the adsorption edges of MoS_2 and n%Mn-MoS_2 extended to 800 nm, suggesting that those materials could be photocatalytic active in the visible light region. The light absorption intensity of the n%Mn-MoS_2 samples was much stronger than that of the undoped MoS_2 samples. This indicated that the doping of Mn^{2+} ions into MoS_2 networks might improve the photocatalytic activity of the material during RhB dye degradation under the visible light irradition.

The structural morphology of MoS_2 and 3%Mn-MoS_2 samples was described by SEM and EDX images as presented in Figure 4.

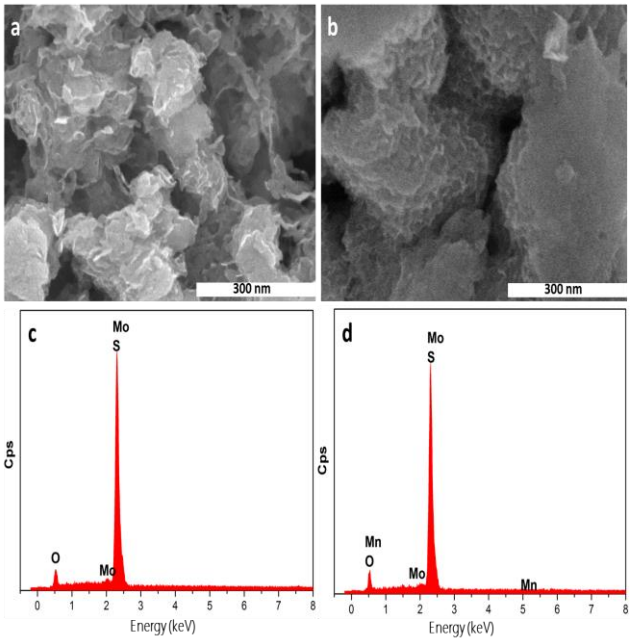

Fig 4: SEM images of MoS_2 (a) and 3%Mn-MoS_2 (b); EDX spectra of MoS_2 (c) and 3%Mn-MoS_2 (d)

The SEM image of MoS_2 depicted typical wrinkled sheet. After doping Mn into MoS_2, the structure of the wrinkled was remained. This might be due to the Mn^{2+} ions amount use for doping too small, leading to no structural change of the material could be observed. In addition, EDX results also showed the presence of Mo and S elements at the ratio of 1: 2 suitable for the MoS_2 linkage in the material (Figure 4c) and Mn, Mo and S elements in Mn-MoS_2 sample (Figure 4d). This again confirmed that we have successfully synthesized the Mn-MoS_2 material.

Besides, EPR spectroscopy was used to measure the effect of doped Mn on magnetic properties of MoS_2 materials. The results of EPR spectroscopy analysis on MoS_2 and 3%Mn-MoS_2 samples are shown in the Figure 5.

Figure 5 showed that the peak of undoped MoS_2 sample was low, while it was much stronger the Mn^{2+} doped MoS_2, demonstrate that the material is magnetic. Moreover, EPR spectra of Mn-MoS_2 sample showed characteristic hyperfine lines of Mn^{2+} (I = 5/2), showing that Mn^{2+} ion was actually doped into MoS_2 network. On the other hand, based on EPR spectroscopy, the type of defects shown in the sample's nanoparticles can be determined by the coefficient g, calculated by the formula: g = hν/BH [16]. The value of the coefficient g of the sample Mn-MoS_2 (g = 2.00) is lower than that of the simple MoS_2 sample (g = 2.003), indicating the presence of Mn^{2+} ions in the MoS_2 crystal lattice.

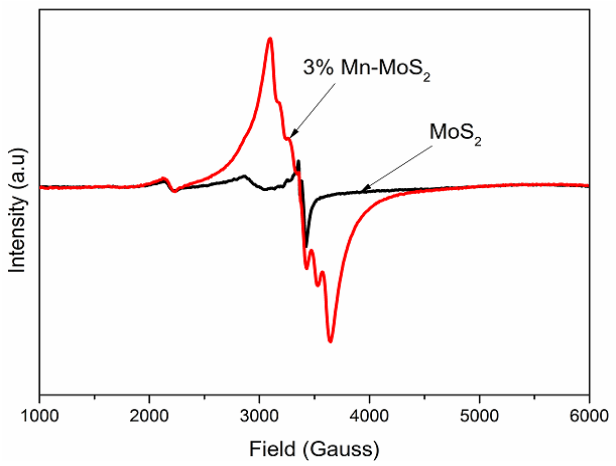

Fig 5: EPR spectroscopy of MoS_2 and 3%Mn-MoS_2

Investigation of the photocatalytic activity of the material

Before investigating the catalytic activity, MoS_2 and Mn-MoS_2 materials were tested for determination of RhB adsorption equilibrium. The dependence of the adsorption capacity of MoS_2 and Mn-MoS_2 materials for RhB on time are shown in Figure 6.

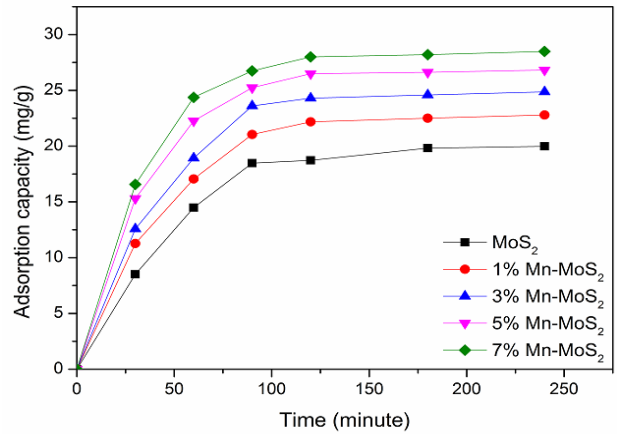

Fig 6: RhB adsorption capacity of MoS_2 and n%Mn-MoS_2 samples

From the Figure 6, it can be seen that the time needed for reach adsorption equilibrium is 2 hours for all tested materials. The n%Mn-MoS_2 samples had better adsorption capacity than the undoped MoS_2 sample.

Thus, the catalytic investigation of the material will be conducted in visible light after 2 hours of adsorption in the dark. Research results of changing RhB concentration according to illumination time are presented in Figure 7.

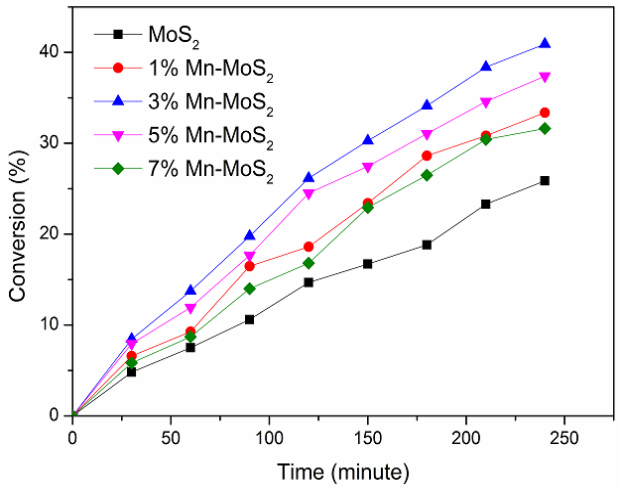

Fig 7: Photocatalytic efficiency MoS_2 and n%Mn-MoS_2 samples in RhB degradation

From the Figure 7, it could be observed that, after 240 minutes of photodegradation, the concentration of RhB decreased by about 25,9% in the presence of MoS_2; significantly reduced by n%Mn-MoS_2 corresponding to n = 1; 3; 5 and 7% is 33.3; 40.9; 37.4 and 31.6%, respectively.

Thus, the single MoS_2 showed the lowest activity with RhB conversion reaching 25.9% after 4 hours. This is completely consistent with the disadvantage of MoS_2 that it has small band gap energy, so recombination of the rapid photo-generated electron-hole pairs leads to a decrease in photocatalytic activity. Meanwhile, the 3%Mn-MoS_2 doped sample showed the highest photocatalytic decomposition results with an efficiency of 40.9% after 4 hours of illumination. This result is consistent with observations from sample characteristics and the role of Mn metal when dope in the sample increases the charge transfer capacity as shown in the EPR spectrum (Figure 5). This increases the catalytic sites which should lead to improved photocatalytic efficiency of the material. However, photocatalytic activity decrease when n at higher values of 5 and 7%. The reason may due to that the more modified dosage of Mn could cause trapping centers in the material structure, which increases the

recombination photon-generated electron - hole pairs [17].

The photocatalytic kinetics and the rate constant of the reaction are one of the important parameters to evaluate the RhB photodegradation process. The Langmuir - Hinshelwood model was applied to study the process dynamics and the results showed in Figure 8 and Table 1.

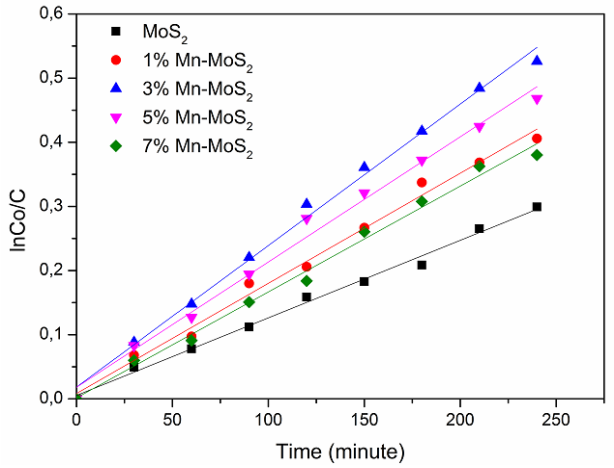

Fig 8: Kinetic model Langmuir - Hinshelwood applied to MoS_2 and n%Mn-MoS_2

Table 1: Data on the Langmuir – Hinshelwood kinetic model applied to MoS_2 and n%Mn-MoS_2

Samples	The rate constant k (in unit of min^{-1})	Correlation coefficients R^2
MoS_2	0.00121	0.994
1%Mn-MoS_2	0.00172	0.991
3%Mn-MoS_2	**0.00221**	**0.994**
5%Mn-MoS_2	0.00195	0.990
7%Mn-MoS_2	0.00165	0.991

From the results in Figure 8 and Table 1 showed that the Langmuir - Hinshelwood kinetic model is suitable for RhB photodegradation catalytic samples with correlation coefficient $R^2 \geq 0.99$. Calculation of the rate constant showing 3%Mn-MoS_2 material gives the fastest degradation rate with the rate constant k = 0.00221.

Conclusions

Successfully synthesized Mn-MoS_2 material by simple calcination method. With the amount of Mn doped into MoS_2 makes the material magnetic, increasing the charge transfer capacity, leading to improved photocatalytic activity of the material. In which, 3% Mn-MoS_2 sample had the highest efficiency of 40.9% during RhB degradation after 4 hours of illumination under visible light irradition. However, the photocatalytic improvement efficiency of Mn-MoS_2 material is not high. Therefore, the next research direction will incorporate a 2D material with a large specific surface area (reduced graphene oxide - rGO) in the composite form to significantly improve the photocatalytic efficiency of the material for the RhB degradation process in wastewater.

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