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## Facile synthesis of few-layer MoS<sub>2</sub> in MgAl-LDH layers for enhanced visible-light photocatalytic activity

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A new photocatalyst, few-layer MoS<sub>2</sub> grown in MgAl-LDH interlayers (MoS<sub>2</sub>/MgAl-LDH), was prepared by a facile two-step hydrothermal synthesis. The structural and photocatalytic properties of the obtained material were characterized by several techniques including powder X-ray diffraction (XRD), Raman spectroscopy, field emission scanning electron microscopy (FESEM), high-resolution transmission electron microscopy (HRTEM), Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), photoluminescence spectroscopy (PL) and UV-vis absorption spectroscopy. The MoS<sub>2</sub>/MgAl-LDH composite showed excellent photocatalytic performance for methyl orange (MO) degradation at low concentrations (50 mg L<sup>-1</sup> and 100 mg L<sup>-1</sup>). Furthermore, even for a MO solution concentration as high as 200 mg L<sup>-1</sup>, this composite also presented high degradation efficiency (>84%) and mineralization efficiency (>73%) at 120 min. The results show that the MoS<sub>2</sub>/MgAl-LDH composite has great potential for application in wastewater treatment.

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### 1. Introduction

Groundwater contamination due to dyes is still a serious environmental pollution problem, mainly because of the high toxicity and widespread use of dyes.<sup>1–4</sup> Semiconductor photocatalytic degradation of organic pollutants in wastewater using inexhaustible and environmentally friendly solar energy has attracted much attention.<sup>5,6</sup> TiO<sub>2</sub> is a commercially available semiconductor photocatalyst.<sup>21,24</sup> However, it shows poor utilization of sunlight, due to the wide band gap of 3.2 eV which only absorbs sunlight with a wavelength of less than 420 nm. Therefore, researchers have been looking for other semiconductor photocatalysts as replacements for TiO<sub>2</sub>.

As a typical graphene-like transition metal disulfide, MoS<sub>2</sub> is a potential photocatalyst.<sup>7–9,25</sup> Unlike other semiconductor materials, based on the quantum confinement effect, the band gap of MoS<sub>2</sub> increases with the number of layers. Moreover, bulk MoS<sub>2</sub> is an indirect bandgap semiconductor with a band gap of 1.2 eV, and single-layer MoS<sub>2</sub> is a direct bandgap semiconductor with a band gap of 1.9 eV.<sup>10</sup> It can be seen that single-

layer or few-layer MoS<sub>2</sub> is a potential photocatalytic semiconductor material. In addition, there are many unsaturated bonds and more active sites due to the complex edge structure of two-dimensional (2D) MoS<sub>2</sub>. Therefore, preparation of single-layer or few-layer MoS<sub>2</sub> is particularly important for application in photocatalysis. For example, like for the preparation of graphene, single and few-layer MoS<sub>2</sub> have been prepared using mechanical exfoliation, the so-called “Scotch Tape Method”.<sup>11</sup> Obviously, the “Scotch Tape Method” is not a scalable process. Recently the Coleman group prepared a single-layer of MoS<sub>2</sub> by a surfactant-assisted sonication pioneering method.<sup>12–15</sup> However, even if a single-layer of MoS<sub>2</sub> is prepared, the surface defects will lead to a high photoelectron–hole pair recombination efficiency, thus affecting the photocatalytic performance of MoS<sub>2</sub>. Therefore, how to prepare single or few-layers of MoS<sub>2</sub> and inhibit the recombination of photoelectron–hole pairs is a challenging subject.

Based on the above reasons, we designed a single or few-layer MoS<sub>2</sub>-intercalated layered double hydroxide (MoS<sub>2</sub>/MgAl-LDH) composite as a novel photocatalyst. Few-layer MoS<sub>2</sub> can be obtained by the “space-confining” effect of the LDH interlayer. On the one hand, 2D MoS<sub>2</sub> can contribute more active sites. On the other hand, LDHs have excellent performance as carriers for photocatalyst composites. For example, Šárka *et al.* prepared ZnCr–CO<sub>3</sub> LDHs and derived mixed oxides that exhibited excellent adsorption and photocatalytic properties for Orange II.<sup>35</sup> Wu *et al.* prepared Cu<sub>2</sub>O/ZnAl calcined layered double hydroxide (Cu<sub>2</sub>O/ZnAl-CLDH) photocatalysts with superior photocatalytic activity.<sup>33</sup> Here we prepared MoS<sub>2</sub>/MgAl-LDH

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composites by hydrothermal synthesis, evaluated the catalytic performance of the catalyst by degrading methyl orange organic dyes, and conducted in-depth research on the synergistic mechanism of MoS<sub>2</sub> and MgAl-LDH.

## 2. Experimental

### 2.1. Synthesis of various materials

All reagents were analytical grade and used without further purification. MoS<sub>2</sub>/MgAl-LDH was prepared by a simple two-step hydrothermal process. First, MgAl-LDH with MoO<sub>4</sub><sup>2-</sup> intercalated in the interlayer (MoO<sub>4</sub><sup>2-</sup>/MgAl-LDH) was prepared by a hydrothermal method. During the synthesis process, Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (4.615 g) and Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (3.376 g) with a M<sup>2+</sup>/M<sup>3+</sup> molar ratio of 2.0/1.0 were dissolved in 50 mL degassed distilled water to form solution A. Then, NaOH (2.516 g) was dissolved in 25 mL degassed distilled water to produce solution B. Na<sub>2</sub>MoO<sub>4</sub>·2H<sub>2</sub>O (7.561 g) was dissolved in 25 mL degassed distilled water to form solution C. Solutions A and B were added dropwise to a reaction vessel containing solution C with vigorous, constant stirring at a constant pH of 10 and at 60 °C. After the addition, the resultant slurry was cooled to room temperature and aged for 10 h at 140 °C. MoO<sub>4</sub><sup>2-</sup>/MgAl-LDH was washed several times with large amounts of deionized water and lyophilized in a vacuum freeze dryer.

Then, MoO<sub>4</sub><sup>2-</sup>/MgAl-LDH (0.5 g) and thiourea (0.38 g) were added to 60 mL degassed distilled water and stirred. After stirring, the resultant slurry was subsequently aged for 24 h at 205 °C. MoS<sub>2</sub>/MgAl-LDH was washed several times with a large amount of deionized water and lyophilized in a vacuum freeze drier.

For comparison, MgAl-LDH with CO<sub>3</sub><sup>2-</sup> intercalated in the interlayer (MgAl-LDH) was also fabricated by the same procedure except that solutions A and B were mixed dropwise in a reaction vessel without solution C. Pure MoS<sub>2</sub> was also prepared by hydrothermal processing. Na<sub>2</sub>MoO<sub>4</sub>·2H<sub>2</sub>O (0.3 g) and thiourea (0.8 g) were dissolved in 65 mL degassed distilled water. The clear solution was aged for 24 h at 205 °C. Then, MoS<sub>2</sub> was washed several times with deionized water and lyophilized.

### 2.2. Characterization

The samples were characterized using X-ray diffraction (XRD, X'Pert PRO MRD), Raman spectroscopy (DXR Raman microscope), field emission scanning electron microscopy (FESEM, S-4800), high-resolution transmission electron microscopy (HRTEM, JEM-2100F), FTIR spectroscopy (Thermo Nicolet NEXUS 670), nitrogen adsorption-desorption experiments for surface and porosity quantification (NOVA-1200e) and X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi). The photoluminescence spectra of the materials were obtained with a fluorescence spectrophotometer (FluoroMax-4). The electrical behavior test was carried out using a semiconductor characterization system (4200-SCS). The degradation efficiency was determined by the concentration of MO studied by the spectrophotometer (UV-3600, Shimadzu). The mineralization

efficiency was measured by a Total Organic Carbon analyzer (multi N/C 3100).

### 2.3. Photocatalytic activity

The photocatalytic efficiency was measured by the degradation of methyl orange (MO) as a model contaminant. In general, 50 mg catalyst (1 g L<sup>-1</sup>) was added to a 50 mL MO solution with a certain initial concentration (50, 100, 150 or 200 mg L<sup>-1</sup>), and the pH of the solution was adjusted by 0.1 mol L<sup>-1</sup> HNO<sub>3</sub> or 1 mol L<sup>-1</sup> NaOH (pH = 3, 5, 7, 9 and 11). The mixture was stirred in the dark for 30 min to achieve adsorption/desorption equilibrium of MO with the catalyst. Then, the reaction system was exposed to light irradiation from a 500 W xenon lamp ( $\lambda > 420$  nm) using a photochemical reaction apparatus (BL-GHX-V). During irradiation, 3 mL of the reaction solution was removed with a pipette at specific time intervals. The photocatalyst was removed from the solution *via* centrifugation. The MO concentration was measured by an ultraviolet-visible spectrophotometer at  $\lambda = 464$  nm.

The degradation efficiency was calculated by the following formula:

$$\text{Degradation efficiency (\%)} = 100 \times (C_0 - C)/C_0 \quad (1)$$

where  $C_0$  is the initial concentration of MO (mg L<sup>-1</sup>) and  $C$  is the concentration of MO at another given irradiation time (mg L<sup>-1</sup>). The mineralization efficiency was calculated by the following formula:

$$\text{Mineralization efficiency (\%)} = 100 \times (\text{TOC}_0 - \text{TOC})/\text{TOC}_0 \quad (2)$$

where TOC<sub>0</sub> is the initial total organic carbon of MO (mg L<sup>-1</sup>) and TOC is the total organic carbon of MO at another given irradiation time (mg L<sup>-1</sup>).

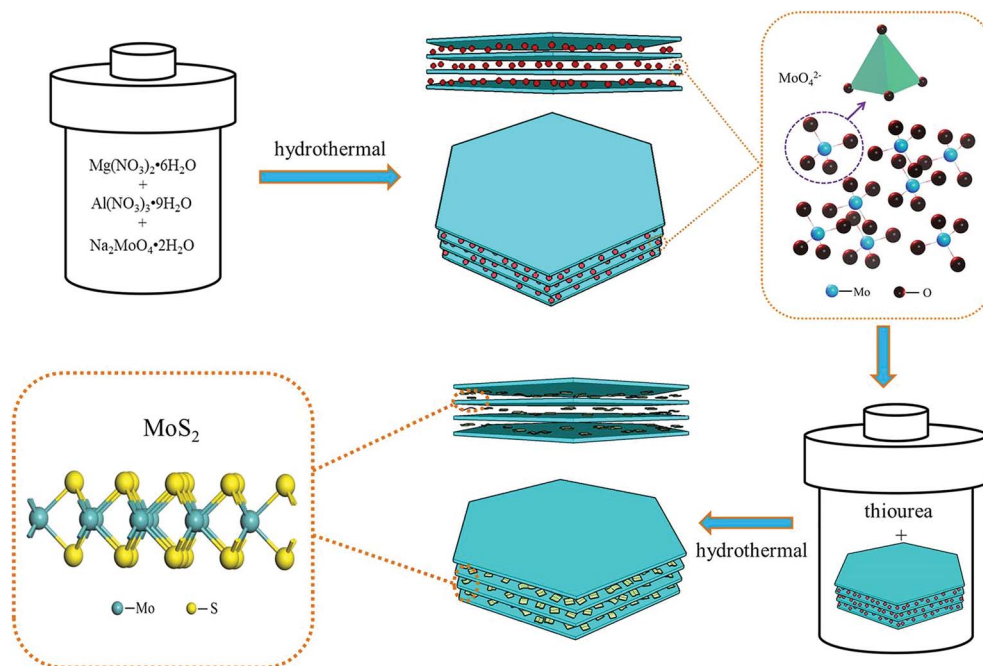
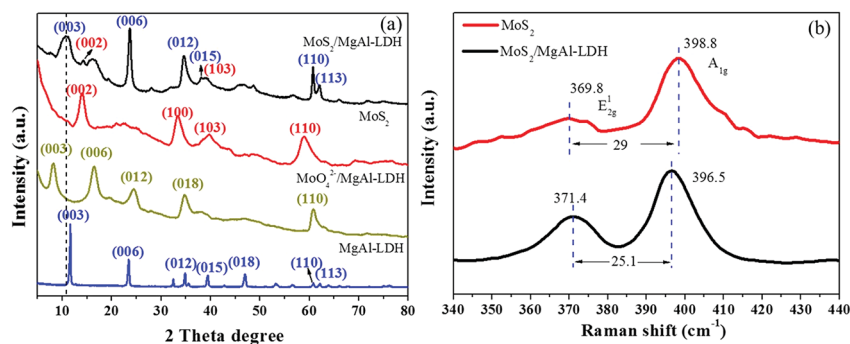
## 3. Results and discussion

### 3.1. Structural design of the composite

The design of the MoS<sub>2</sub>/MgAl-LDH composite is shown in Scheme 1. First, MoO<sub>4</sub><sup>2-</sup> ions were added to the precursor solution of MgAl hydrotalcite. Due to the exchangeability of anions in the MgAl-LDH layers, MoO<sub>4</sub><sup>2-</sup>/MgAl-LDH was prepared by a hydrothermal method. Subsequently, MoO<sub>4</sub><sup>2-</sup>/MgAl-LDH was vulcanized in a hydrothermal process in a mild liquid phase environment. In this process, thiourea not only acts as a source of sulfur, but also releases H<sub>2</sub>S as a protective atmosphere. In addition, in the liquid phase, it can improve the uniformity of the reaction sites of MoO<sub>4</sub><sup>2-</sup> as well as acting as a sulfur source, which is beneficial to form few-layer MoS<sub>2</sub> in the MgAl-LDH layers.

### 3.2. Structural characterization of the composite

Fig. 1a shows the XRD patterns of MgAl-LDH, MoO<sub>4</sub><sup>2-</sup>/MgAl-LDH, MoS<sub>2</sub> and MoS<sub>2</sub>/MgAl-LDH. The XRD pattern of MgAl-LDH has four diffraction peaks at 11.7°, 23.4°, 34.9° and 60.8°, which correspond to the (003), (006), (012) and (110) planes, respectively, of MgAl-LDH with the general formula

Scheme 1 Design of the MoS<sub>2</sub>/MgAl-LDH growth process.Fig. 1 XRD patterns of MgAl-LDH, MoO<sub>4</sub><sup>2-</sup>/MgAl-LDH, MoS<sub>2</sub> and MoS<sub>2</sub>/MgAl-LDH (a), and Raman spectra of MoS<sub>2</sub> and MoS<sub>2</sub>/MgAl-LDH (b).

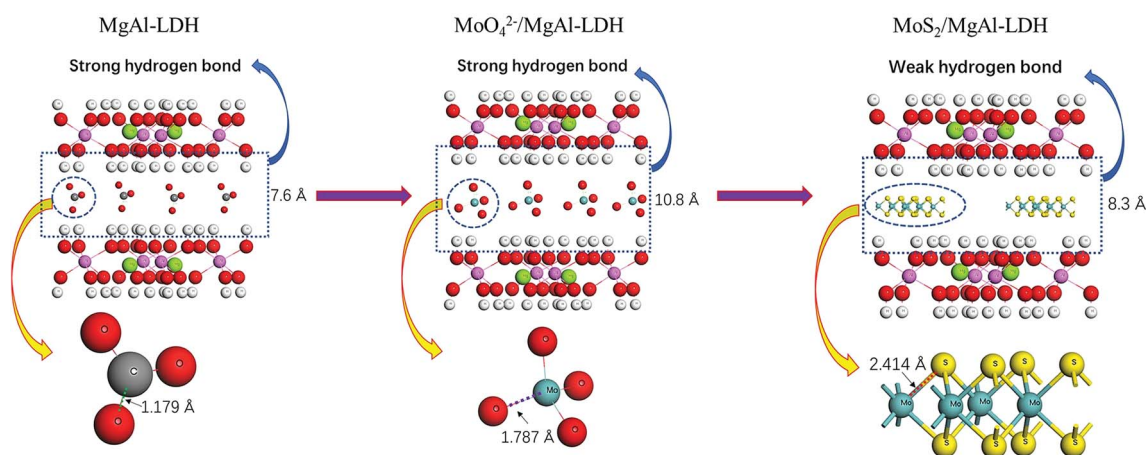
(Mg<sub>0.667</sub>Al<sub>0.333</sub>)(OH)<sub>2</sub>(CO<sub>3</sub>)<sub>0.167</sub>(H<sub>2</sub>O)<sub>0.5</sub> (JPCDS no. 89-0460). The pristine MgAl-LDH pattern shows typical Bragg reflections of hexagonal LDH phases with interlayer carbonate anions. The MoO<sub>4</sub><sup>2-</sup>/MgAl-LDH composite has major diffraction peaks at 8.2°, 16.5°, 24.7° and 60.8°, which correspond to the (003), (006), (012) and (110) planes, respectively, of MgAl-LDH. The MoS<sub>2</sub>/MgAl-LDH composite not only has major diffraction peaks at 10.65°, 23.4°, 34.9° and 60.8°, corresponding to the (003), (006), (012) and (110) planes of MgAl-LDH, but also has major diffraction peaks at 14.1° and 39.5°, which can be attributed to the (002) and (103) planes of MoS<sub>2</sub>, respectively. In addition, the “*a*” value of the unit cell parameter did not change (as shown in Table 1). The unit cell parameters of LDHs correspond to the cation–cation distance in the brucite layer, which can be calculated by  $a = 2 \times d(110)$ . When MoO<sub>4</sub><sup>2-</sup> and MoS<sub>2</sub> were inserted into MgAl-LDH, the substrate spacing increased from 7.6 Å to 10.8 Å and 8.3 Å, respectively. As shown in Scheme 2, the

length of the C–O bond in the CO<sub>3</sub><sup>2-</sup> anion is 1.179 Å in MgAl-LDH. When MoO<sub>4</sub><sup>2-</sup> replaced the CO<sub>3</sub><sup>2-</sup> anion in the MgAl-LDH layer, the spacing of the (003) plane increased from 7.6 Å to 10.8 Å. This is because the length of the Mo–O bond in the MoO<sub>4</sub><sup>2-</sup> anion is 1.787 Å, which is larger than that of the C–O bond in the CO<sub>3</sub><sup>2-</sup> ion. When MoS<sub>2</sub> was inserted into the LDH interlayer, the spacing of the (003) plane decreased to 8.3 Å, even though the length of the Mo–S bond was 2.414 Å. This is attributed to the weakening of the hydrogen bonding force between the MoS<sub>2</sub> compounds and the LDH layer. Fig. 1b shows the Raman spectra, which further reveal the microstructure of MoS<sub>2</sub> and MoS<sub>2</sub>/MgAl-LDH. For MoS<sub>2</sub>, two different Raman peaks at 369.8 and 398.8 cm<sup>-1</sup> are attributed to the typical E<sub>2g</sub><sup>1</sup> and A<sub>1g</sub> modes of hexagonal MoS<sub>2</sub> crystals, respectively. In the case of MoS<sub>2</sub>/MgAl-LDH, the two MoS<sub>2</sub> peaks are shifted to 371.4 and 396.5 cm<sup>-1</sup>. Obviously, the frequency difference between the E<sub>2g</sub><sup>1</sup> and A<sub>1g</sub> modes belonging to MoS<sub>2</sub> was 29 cm<sup>-1</sup>, while for

Table 1 Structural characteristics of the samples obtained by hydrothermal synthesis<sup>a</sup>

	MgAl-LDH	MoO <sub>4</sub> <sup>2-</sup> /MgAl-LDH	MoS <sub>2</sub> /MgAl-LDH	MoS <sub>2</sub>
<i>a</i> (Å)	3.05	3.05	3.05	—
<i>c</i> (Å)	22.8	32.4	24.9	—
<i>c'</i> (Å)	7.6	10.8	8.3	—
The thickness of the interlayer gallery <sup>b</sup> (Å)	2.8	6.0	3.5	—
Band gap (eV)	—	—	1.82	1.61

<sup>a</sup>  $a = 2d_{110}$ ,  $c = 3d_{003}$  and  $c = 3c'$ . <sup>b</sup> The difference between  $c'$  and 4.8 Å (the thickness of the brucite-like sheet).<sup>16</sup>



Scheme 2 Schematic of the spacing change of the (003) plane.

MoS<sub>2</sub>/MgAl-LDH this was reduced to 25.1 cm<sup>-1</sup>. This confirms that the thickness of the MoS<sub>2</sub> nanosheets has been significantly reduced.<sup>36</sup>

Fig. 2 shows the FTIR spectra of the various materials. As shown in Fig. 2a, strong and broad absorption bands at 3449, 3455 and 3449 cm<sup>-1</sup> are observed for MgAl-LDH, MoO<sub>4</sub><sup>2-</sup>/MgAl-LDH and MoS<sub>2</sub>/MgAl-LDH, respectively. These can be attributed to the stretching vibration of the OH groups in the brucite-type layers and water molecules in the interlayer. The bands at 1618, 1635 and 1616 cm<sup>-1</sup> can be attributed to the bending vibration of interlayer water. The absorption bands at 3422 and 1624 cm<sup>-1</sup> for MoS<sub>2</sub> can be assigned to the stretching vibration

of the OH groups and the bending vibrations of water molecules adsorbed on the MoS<sub>2</sub> surface, respectively. Between 1000 and 400 cm<sup>-1</sup>, the bands can be assigned to metal–oxygen (M–O) and metal–hydroxyl (M–OH) vibrations.<sup>17,18</sup> The intense band characteristic of the  $\nu_3$  vibrations (antisymmetric stretching) of CO<sub>3</sub><sup>2-</sup> ions located in the interlayer region can be observed at approximately 1360 cm<sup>-1</sup>. The CO<sub>3</sub><sup>2-</sup> peak intensities of MoS<sub>2</sub>/MgAl-LDH and MoO<sub>4</sub><sup>2-</sup>/MgAl-LDH are much weaker than those of MgAl-LDH in the FTIR spectra. For MoO<sub>4</sub><sup>2-</sup>/MgAl-LDH, the antisymmetric stretching vibration band of Mo–O–Mo is observed at 820 cm<sup>-1</sup>. The bands in the range of 400–1200 cm<sup>-1</sup> for MoS<sub>2</sub> and MoS<sub>2</sub>/MgAl-LDH are shown in Fig. 2b. In the

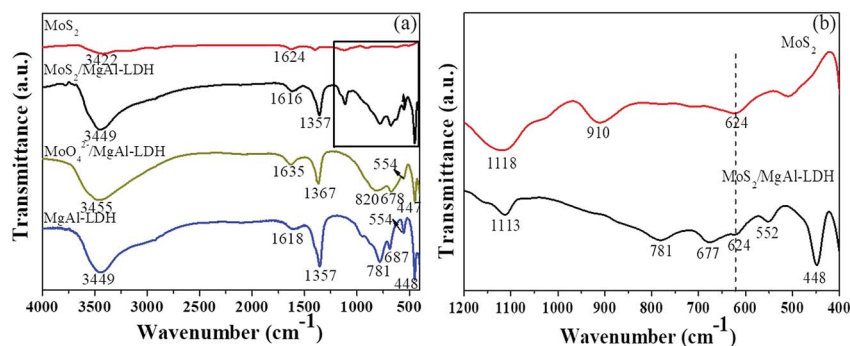


Fig. 2 FTIR spectra (a) of MgAl-LDH, MoS<sub>2</sub>/MgAl-LDH and MoS<sub>2</sub> in the range of 400–4000 cm<sup>-1</sup>; and (b) of MoS<sub>2</sub>/MgAl-LDH and MoS<sub>2</sub> in the range of 400–1200 cm<sup>-1</sup>.

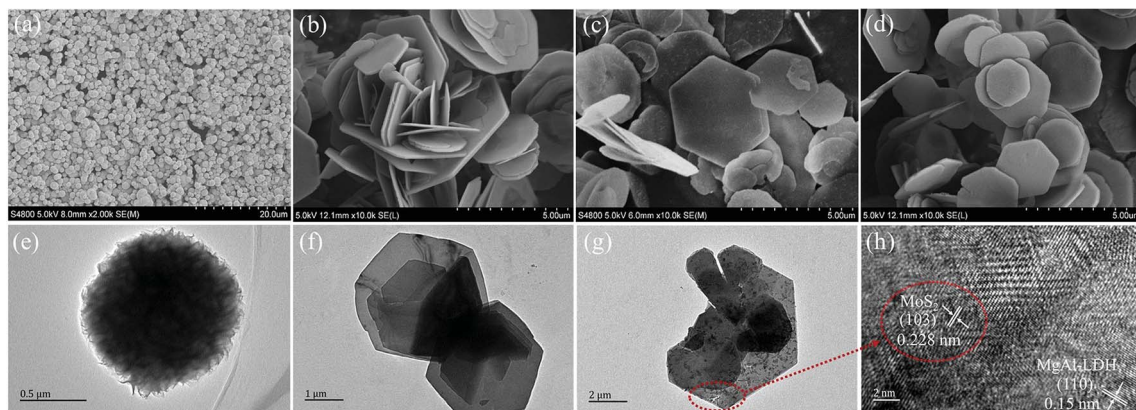


Fig. 3 FESEM images of MoS<sub>2</sub> (a), MgAl-LDH (b), MoO<sub>4</sub><sup>2-</sup>/MgAl-LDH (c), and MoS<sub>2</sub>/MgAl-LDH (d). TEM images of MoS<sub>2</sub> (e), MgAl-LDH (f), and MoS<sub>2</sub>/MgAl-LDH (g) and HRTEM image of MgAl-LDH (h).

spectrum of MoS<sub>2</sub>, the peak at 910 cm<sup>-1</sup> can be attributed to the Mo=O stretching vibration, which may be caused by the formation of a small amount of oxide on the MoS<sub>2</sub> surface. The peaks at 1113 and 1118 cm<sup>-1</sup> for MoS<sub>2</sub>/MgAl-LDH and MoS<sub>2</sub>, respectively, can be attributed to the S=O asymmetric stretching vibration. In the spectra of MoS<sub>2</sub>/MgAl-LDH and MoS<sub>2</sub>, the peak at 624 cm<sup>-1</sup> can be assigned to the Mo-S stretching vibration.

Typical FESEM images of the samples are shown in Fig. 3a–d. As shown in Fig. 3a, the morphology of pure MoS<sub>2</sub> is flower-like. Moreover, each MoS<sub>2</sub> microsphere has an average diameter of approximately 1 μm. Fig. 3b–d show the morphology of MgAl-LDH, MoO<sub>4</sub><sup>2-</sup>/MgAl-LDH and MoS<sub>2</sub>/MgAl-LDH, respectively. It can be observed that all the samples maintain a hexagonal-like sheet structure. As shown in Fig. 3d, we didn't find any particles with a similar morphology to pure MoS<sub>2</sub> in the MoS<sub>2</sub>/MgAl-LDH composite. This indicates that the morphology of MgAl-LDH has not changed after ion exchange and vulcanization. The microstructures of the samples were investigated through TEM (Fig. 3e–g) and HRTEM (Fig. 3h). Fig. 3e shows MoS<sub>2</sub> samples displaying flower-like spherical structures with diameters of 1–1.2 μm and Fig. 3f shows that MgAl-LDH is a highly dispersed flake. Interestingly, as shown in Fig. 3g, it is clearly shown that the MoS<sub>2</sub> nanosheet exhibits an irregular sheet-like structure in the layers of MgAl-LDH, and MgAl-LDH is decorated by MoS<sub>2</sub> and serves as a carrier. Moreover, the HRTEM image of MoS<sub>2</sub>/MgAl-LDH is shown in Fig. 3h. The interplanar spacings of 0.228 and 0.15 nm can be attributed to the (103) and (110) planes of MoS<sub>2</sub> and MgAl-LDH, respectively. This also indicates that MoS<sub>2</sub> was successfully grown between the MgAl-LDH layers.

To verify the interfacial nature of MoS<sub>2</sub> and MgAl-LDH in the MoS<sub>2</sub>/MgAl-LDH sample, XPS measurements were carried out. As shown in Fig. 4a, the XPS spectra of MoS<sub>2</sub>/MgAl-LDH show Al 2p, S 2p, Mo 3d, C 1s, O 1s and Mg 1s binding energy peaks at 73.8 eV, 160.2 eV, 227.2 eV, 284.6 eV, 531.4 eV and 1303.7 eV, respectively. As shown in Fig. 4b, two peaks were observed at 228.3 and 231.6 eV, which could be attributed to Mo 3d<sub>5/2</sub> and Mo 3d<sub>3/2</sub> binding energies, respectively,<sup>19,20</sup> and are the characteristic peaks of Mo<sup>4+</sup> in MoS<sub>2</sub>. Two peaks at 232.5 and

235.7 eV are related to the Mo 3d<sub>5/2</sub> and 3d<sub>3/2</sub> binding energies of Mo<sup>6+</sup>, respectively.<sup>16</sup> The small peak at 225.6 eV corresponds to the S 2s binding energy of MoS<sub>2</sub>.<sup>16</sup> The S spectrum is shown in Fig. 4c. Two main peaks at 160.2 and 161.3 eV can be assigned to the S 2p<sub>3/2</sub> and S 2p<sub>1/2</sub> lines of MoS<sub>2</sub>, respectively. The small peak at 167.5 eV suggests the existence of bridging disulfides S<sup>4+</sup>.<sup>22</sup> As illustrated in Fig. 4d, the C 1s spectrum can be decomposed into a dominant peak at 284.6 eV for C=C/C-C<sup>23</sup> and a weak peak at 288.5 eV for C=O in oxygen-containing functional groups. The XPS results show that there is no chemical bond between MoS<sub>2</sub> and MgAl-LDH in the MoS<sub>2</sub>/MgAl-LDH catalyst.

The XRD, FTIR, FESEM, HRTEM and XPS analysis showed that few-layer MoS<sub>2</sub> was successfully prepared in the MgAl-LDH layers by the hydrothermal method, which takes advantage of the “space-confining” effect of MgAl-LDH. Therefore, the synthetic design was reasonable *via* Scheme 1.

### 3.3. Photocatalytic performance

To better understand the photocatalytic performance of the MoS<sub>2</sub>/MgAl-LDH composite, different solution pH values were used for the photodegradation of MO, as shown in Fig. 5a. The degradation rate of MoS<sub>2</sub>/MgAl-LDH was the lowest at pH = 11, with only 19.23% of the MO degraded after 120 min. The photocatalytic ability of the sample increased as the pH decreased, and the degradation rate reached its highest at pH = 3, implying that the optimal photocatalytic capacity of MoS<sub>2</sub>/MgAl-LDH occurred under acidic conditions. Fig. 5b compares the degradation rate and mineralization rate of MO under different pH values under visible light irradiation for 2 h. The degradation efficiency and mineralization efficiency of MO without the catalyst were only 0.48% and 0.09% respectively, which indicates that the MO molecule and intermediate products were difficult to self-degrade. When the MO solution pH = 3, the degradation efficiency and mineralization efficiency achieved 84.88% and 73.25%, respectively. Therefore, the optimal condition in this study was pH = 3.

The degradation rate using MoS<sub>2</sub>/MgAl-LDH for different concentrations of MO is shown in Fig. 5c. The MO solution

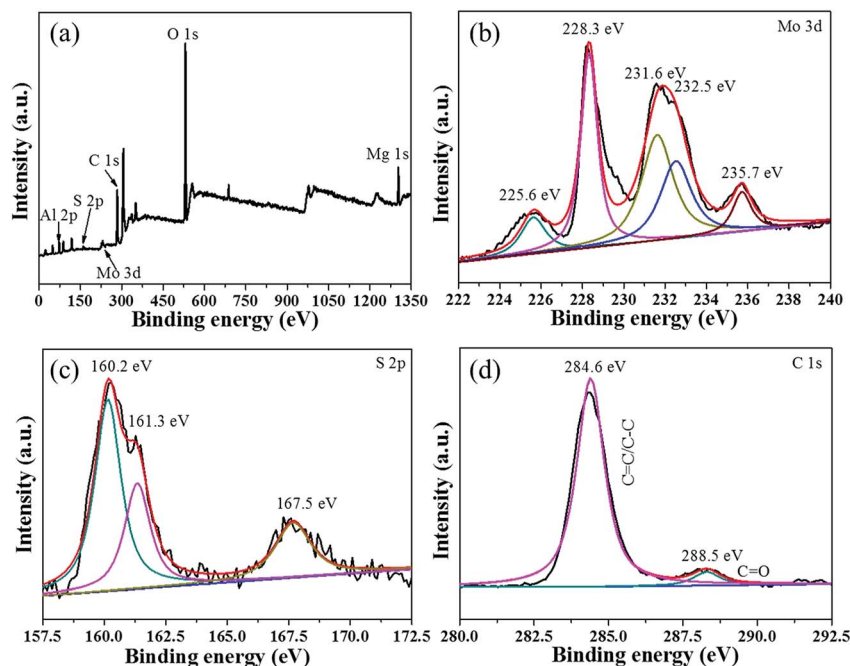


Fig. 4 XPS spectra of the MoS<sub>2</sub>/MgAl-LDH sample (a) and high-resolution XPS spectra of Mo 3d (b), S 2p (c), and C 1s (d).

concentrations were 50, 100, 150 and 200 mg L<sup>-1</sup>. As shown in Fig. 5c, the MO solutions with initial concentrations of 50 mg L<sup>-1</sup> and 100 mg L<sup>-1</sup> were completely degraded after reacting for 45 min and 105 min, respectively. In addition, the degradation efficiency was over 84% after 120 min when the initial concentrations of MO were 150 mg L<sup>-1</sup> and 200 mg L<sup>-1</sup>. In addition, the mineralization efficiency of MO (Fig. 5d) at initial concentrations of 50 mg L<sup>-1</sup>, 100 mg L<sup>-1</sup>, 150 mg L<sup>-1</sup> and 200 mg L<sup>-1</sup> achieved 97.25%, 96.74%, 79.56% and 73.25%, respectively. Compared with other catalysts (in Table 2), MoS<sub>2</sub>/MgAl-LDH exhibited excellent catalytic performance at high concentrations of MO. To better verify the catalytic effect of the catalyst, a methyl orange concentration of 200 mg L<sup>-1</sup> was selected for subsequent tests.

For comparison, pure MoS<sub>2</sub> and MgAl-LDH were also tested under the same conditions. The photocatalytic performances of the samples under visible-light irradiation are shown in Fig. 5e and f. The degradation efficiency and mineralization efficiency were 38.66% and 10.25% for MoS<sub>2</sub>, 16.57% and 2.73% for MgAl-LDH, respectively. These are lower than the values (84.88% and 73.25%) for MoS<sub>2</sub>/MgAl-LDH, indicating that the synergistic effect between MoS<sub>2</sub> and MgAl-LDH enhanced the catalytic activity.

Fig. 5g shows the MO kinetic analysis with MoS<sub>2</sub>, MgAl-LDH and MoS<sub>2</sub>/MgAl-LDH. The kinetics of photocatalytic reactions of organic pollutants are usually described by the Langmuir-Hinshelwood model. The photocatalytic process of MO can be expressed by the following pseudo first-order kinetic equation:<sup>26</sup>

$$-\ln\left(\frac{C_t}{C_0}\right) = K_{app}t \quad (3)$$

$$t_{1/2} = \frac{\ln 2}{K_{app}} \quad (4)$$

where  $C_0$  and  $C_t$  are the initial MO concentration and the concentration at time  $t$ , respectively, and  $K_{app}$  is the photocatalytic reaction rate constant (min<sup>-1</sup>). The  $K_{app}$ , linearization coefficient ( $R^2$ ) and half-life ( $t_{1/2}$ ) are given in Table 3. The high value of the linear regression coefficient ( $R^2$ ) indicates that the photocatalytic reaction is well matched to the pseudo first-order kinetic model. MoS<sub>2</sub>/MgAl-LDH showed the best photocatalytic performance, which was indicated by the largest value of  $K_{app}$ . The catalytic cycling performance of MoS<sub>2</sub>/MgAl-LDH was investigated by reusing it four consecutive times as shown in Fig. 5h, and the degradation rate of MO was still above 80% after four cycles. This shows that the MoS<sub>2</sub>/MgAl-LDH catalyst has excellent catalytic performance and reusability, even with a MO concentration as high as 200 mg L<sup>-1</sup>. Fig. 5i shows the FTIR spectra of MoS<sub>2</sub>/MgAl-LDH before and after photocatalysis. After photocatalysis, no characteristic peak of MO appeared in the FTIR spectra, proving that MoS<sub>2</sub>/MgAl-LDH acts on MO *via* photocatalysis instead of adsorption.

#### 3.4. The mechanism of the improvement in photocatalytic performance for MoS<sub>2</sub>/MgAl-LDH

Fig. 6a and b show the nitrogen adsorption-desorption isotherms and corresponding BJH pore size distributions, respectively, of MoS<sub>2</sub>, MgAl-LDH and MoS<sub>2</sub>/MgAl-LDH. The isotherms are IV isotherms with H3 hysteresis loops, indicating porous flat agglomerates or lamellar particles.<sup>37</sup> The calculated BET surface area was 14.06 m<sup>2</sup> g<sup>-1</sup> for MgAl-LDH, 13.18 m<sup>2</sup> g<sup>-1</sup> for MoS<sub>2</sub>, and 9.83 m<sup>2</sup> g<sup>-1</sup> for MoS<sub>2</sub>/MgAl-LDH. The results demonstrate that the excellent photocatalytic performance of

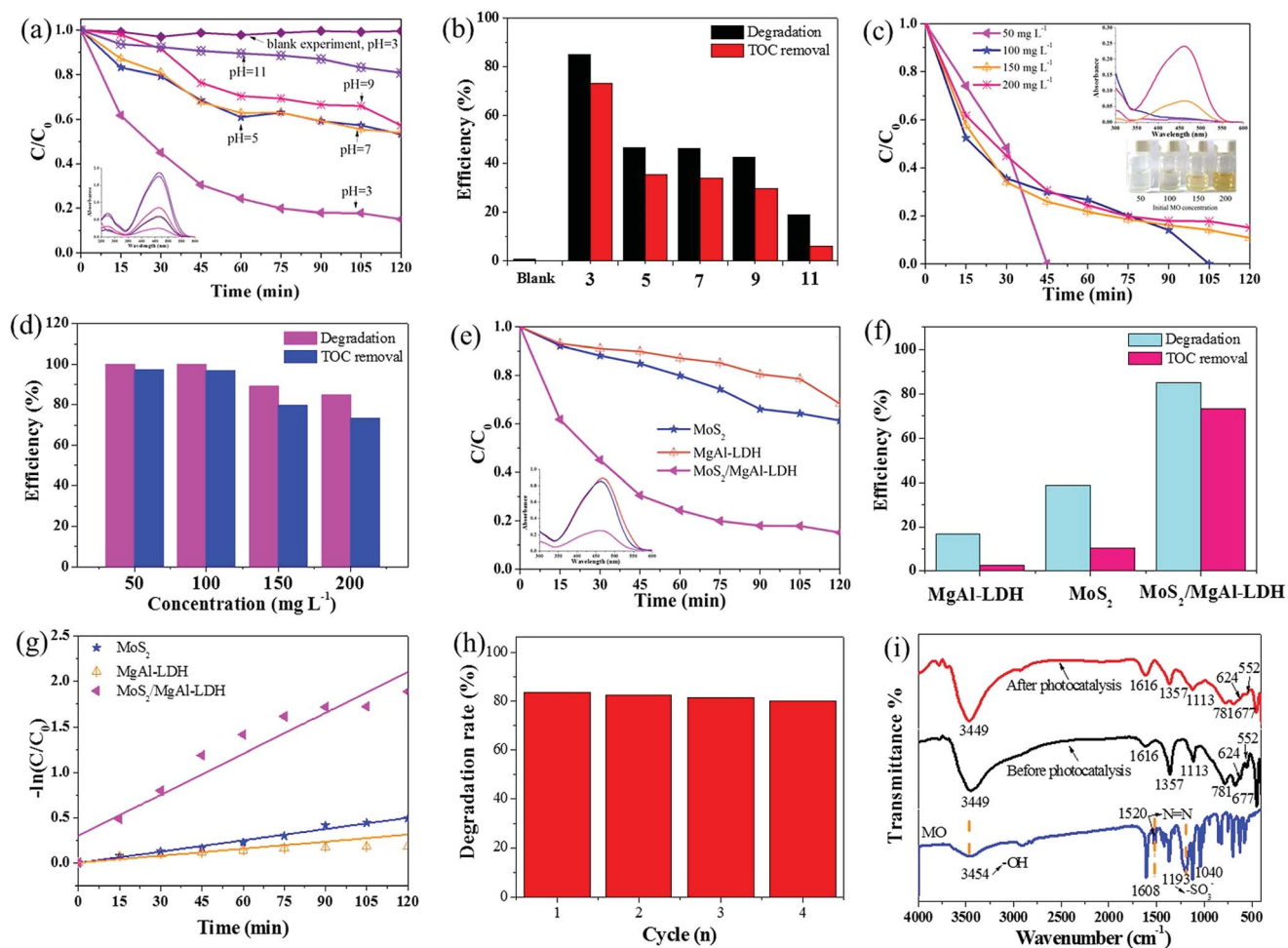


Fig. 5 Effect of initial solution pH values on the photodegradation (a) and mineralization (b) of MO (conditions: initial MO concentration  $200 \text{ mg L}^{-1}$ , photocatalyst dosage  $1 \text{ g L}^{-1}$ ). Inset: UV-vis spectra of catalyzed solutions. Effect of initial MO concentration on the photodegradation (c) and mineralization (d) of MO (conditions: initial solution pH = 3, adsorbent dosage  $1 \text{ g L}^{-1}$ ). Inset: the UV-vis spectra of catalyzed solutions (top) and optical photographs of supernatants obtained by centrifugation (bottom). Photocatalytic degradation curves (e) and mineralization efficiency (f) of the samples. Inset: the UV-vis spectra of catalyzed solutions. The kinetic analysis of the samples (g). Cycles of photocatalytic degradation of MO using  $\text{MoS}_2/\text{MgAl-LDH}$  (h) and FTIR spectra of  $\text{MoS}_2/\text{MgAl-LDH}$  before and after photocatalysis (i).

$\text{MoS}_2/\text{MgAl-LDH}$  does not depend on the specific surface area. As shown in Fig. 6c, compared with that of pure  $\text{MoS}_2$  and  $\text{MgAl-LDH}$ , the absorbance of  $\text{MoS}_2/\text{MgAl-LDH}$  in the visible region is enhanced. The enhanced absorption of  $\text{MoS}_2/\text{MgAl-LDH}$  will yield more photons to produce more photogenerated carriers, which could enhance the photocatalytic activity. The optical

band gaps of the prepared photocatalysts were determined by the following equation ( $\alpha = A(h\nu - E_g)^{n/2}/h\nu$ ).<sup>38</sup> As shown in Fig. 6d and e, the bandgap of  $\text{MoS}_2$  increases from 1.62 to 1.78 eV, which is due to the decreasing domain size of  $\text{MoS}_2$  grown in the  $\text{MgAl-LDH}$  layers. The recombination distance of electron-hole pairs is increased with the increased band gap of  $\text{MoS}_2$ .

Table 2 The photocatalytic activity of several photocatalysts for MO

Photocatalyst	MO concentration	Photocatalyst dosage	Results	References
$\text{TiO}_2/\text{MoS}_2@zeolite$	$20 \text{ mg L}^{-1}$	$0.5 \text{ g L}^{-1}$	Removal of 100% in 60 min	30
$\text{Ag}/\text{TiO}_2$	$5 \times 10^{-5} \text{ M}$ ( $16.3 \text{ mg L}^{-1}$ )	$1 \text{ g L}^{-1}$	Removal of 100% in 80 min	31
$\text{MoS}_2/\text{YVO}_4$	$10 \text{ mg L}^{-1}$	$1 \text{ g L}^{-1}$	Removal of 100% in 30 min	32
$\text{Cu}_2\text{O}/\text{ZnAl-CLDH}$	$20 \text{ mg L}^{-1}$	$1 \text{ g L}^{-1}$	Removal of approximately 90% in 420 min	33
$\text{TiO}_2/\text{biochar}$	$20 \text{ mg L}^{-1}$	$0.25 \text{ g L}^{-1}$	Removal of 100% in 150 min	34
<b><math>\text{MoS}_2/\text{MgAl-LDH}</math></b>	<b><math>50 \text{ mg L}^{-1}</math></b>	<b><math>1 \text{ g L}^{-1}</math></b>	<b>Removal of 100% in 45 min</b>	<b>This work</b>
	<b><math>100 \text{ mg L}^{-1}</math></b>	<b><math>1 \text{ g L}^{-1}</math></b>	<b>Removal of 100% in 105 min</b>	
	<b><math>200 \text{ mg L}^{-1}</math></b>	<b><math>1 \text{ g L}^{-1}</math></b>	<b>Removal of approximately 84% in 120 min</b>	

**Table 3** Parameters of the pseudo first-order kinetic model for photocatalytic degradation

Photocatalysts	$K_{app}$ ( $\text{min}^{-1}$ )	$R^2$	$t_{1/2}$ (min)
MoS <sub>2</sub>	0.00416	0.9832	166.59
MgAl-LDH	0.00259	0.89659	267.62
MoS <sub>2</sub> /MgAl-LDH	0.01505	0.90051	46.06

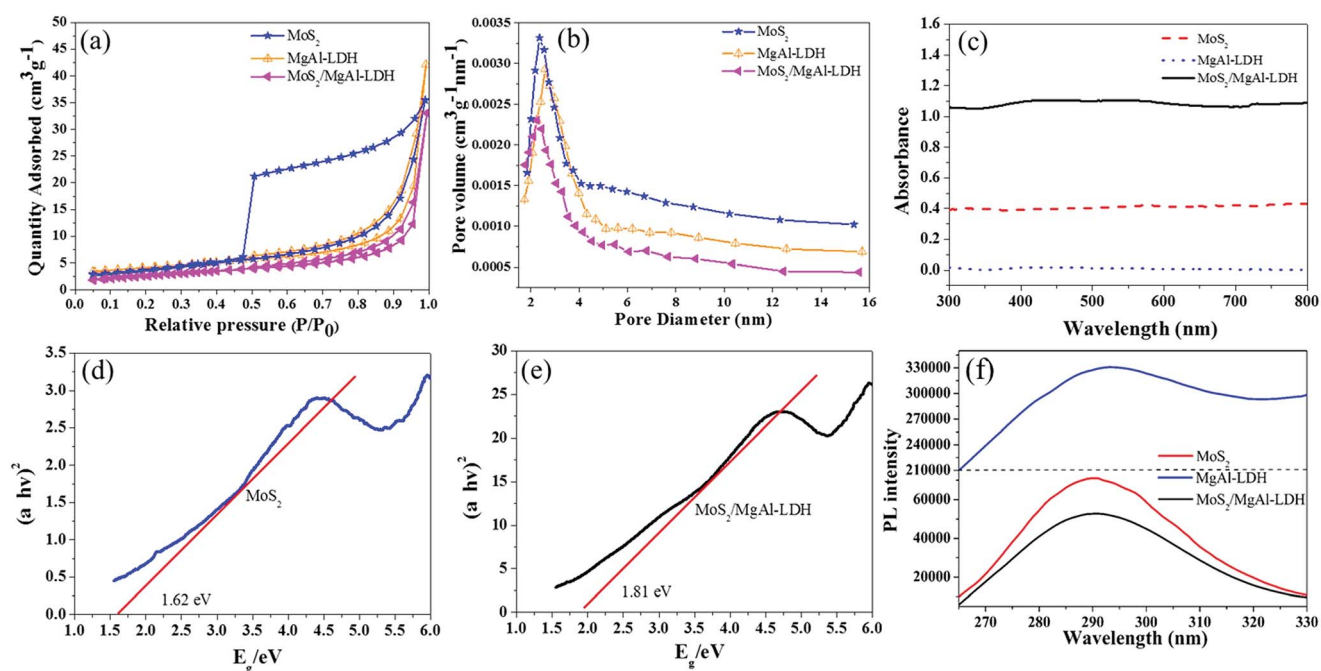
To verify the synergistic mechanism between MoS<sub>2</sub> and MgAl-LDH in MoS<sub>2</sub>/MgAl-LDH, photoluminescence (PL) measurements of the samples were also carried out. The PL spectra of the samples in the range  $\lambda = 265\text{--}330$  nm with an excitation wavelength of 250 nm are shown in Fig. 6f. These materials exhibited a strong PL emission peak at  $\lambda \approx 290$  nm due to charge carrier capture on the surface.<sup>27</sup> Compared with that of pure MoS<sub>2</sub> and MgAl-LDH, the PL signal of MoS<sub>2</sub>/MgAl-LDH was the weakest, which indicated the sample had the lowest photogenerated electron–hole pair recombination rate<sup>28</sup> and the highest electron–hole pair separation efficiency. Obviously, the recombination efficiency of electron–hole pairs was inhibited in MgAl-LDH when MoS<sub>2</sub> grew in the MgAl-LDH layers.

Usually, nano-sized noble metals are used to modify the surfaces of semiconductors to form metal–semiconductor junctions to enhance electron–hole separation.<sup>39</sup> However, there is no metal–semiconductor junction found in MoS<sub>2</sub>/MgAl-LDH composites, which can be confirmed by the above XPS results. Semiconductor testing is used to investigate the electrical behavior of the sample, as shown in Fig. 7. The samples

were prepared into wafers 10 mm in diameter and 0.2 mm in thickness. Fig. 7a–c show the resistance tests of MgAl-LDH (Fig. 7a), MoS<sub>2</sub> (Fig. 7b) and MoS<sub>2</sub>/MgAl-LDH (Fig. 7c), respectively. It can be clearly observed that the resistance meter of MgAl-LDH showed “O.L”, indicating that the sample was nonconducting. Interestingly, the resistance of MoS<sub>2</sub> varied from 1.52 to “O.L”, and the resistance of MoS<sub>2</sub>/MgAl-LDH varied from 8.74 to “O.L”. To better analyze the semiconductor characteristics of MoS<sub>2</sub> and MoS<sub>2</sub>/MgAl-LDH, the samples were tested using a semiconductor characteristic system. Fig. 7d and e showed obvious semiconductor characteristic curves, indicating similar semiconductor properties between MoS<sub>2</sub>/MgAl-LDH and MoS<sub>2</sub>. It was likely that MgAl-LDH played the role of conductive layer in MoS<sub>2</sub>/MgAl-LDH.

In addition, the effect of different capture agents on the photocatalytic activity of MoS<sub>2</sub>/MgAl-LDH is shown in Fig. 8. The scavengers of O<sub>2</sub><sup>•−</sup>, h<sup>+</sup> and OH<sup>•</sup> were benzoquinone (BQ), ethylenediaminetetraacetic acid (Na<sub>2</sub>-EDTA) and isopropanol (IPA), respectively. It is shown that adding IPA significantly inhibited MO degradation, indicating that OH<sup>•</sup> was one of the important active species in the photodegradation process. Likewise, the degradation ability of the composite is inhibited with the addition of Na<sub>2</sub>-EDTA and BQ. Therefore, h<sup>+</sup> and O<sub>2</sub><sup>•−</sup> are also major active species. In summary, OH<sup>•</sup>, h<sup>+</sup> and O<sub>2</sub><sup>•−</sup> are the major active species for catalyzing MO in MoS<sub>2</sub>/MgAl-LDH.

Based on the above discussion, the mechanism of the improvement in photocatalytic performance of MoS<sub>2</sub>/MgAl-LDH is revealed in Scheme 3. On the one hand, few-layer MoS<sub>2</sub> nanosheets were prepared by the “space-confining” effect of MgAl-LDH. The bandgap of MoS<sub>2</sub> is increased from



**Fig. 6** N<sub>2</sub> adsorption–desorption isotherm curves (a) and pore size distribution curves (b) of the samples. UV-vis spectra of MgAl-LDH, MoS<sub>2</sub> and MoS<sub>2</sub>/MgAl-LDH (c) and the bandgap curves of MoS<sub>2</sub> (d) and MoS<sub>2</sub>/MgAl-LDH (e). Fluorescence spectra of MgAl-LDH, MoS<sub>2</sub> and MoS<sub>2</sub>/MgAl-LDH (f).



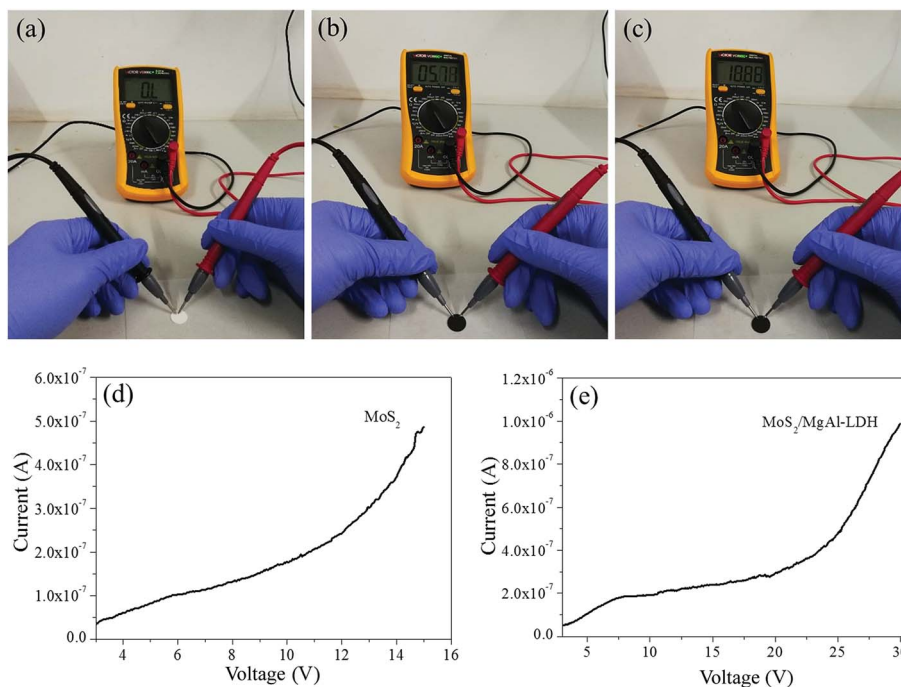


Fig. 7 Electrical characteristics of MgAl-LDH (a), MoS<sub>2</sub> (b), and MoS<sub>2</sub>/MgAl-LDH (c). Semiconductor characteristic curves of MoS<sub>2</sub> (d), and MoS<sub>2</sub>/MgAl-LDH (e).

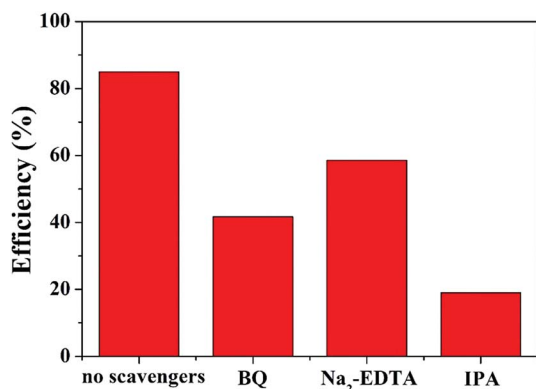
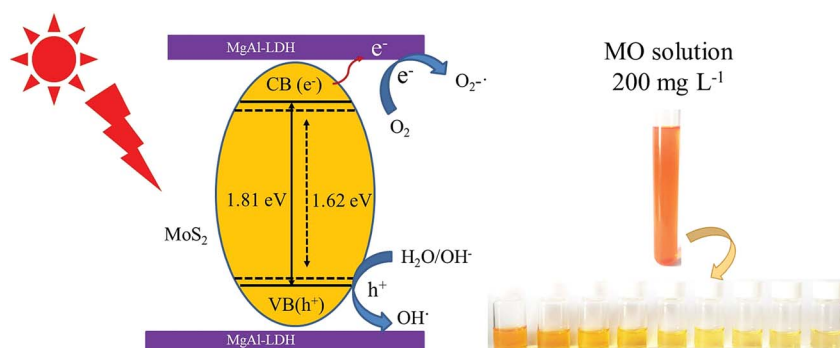


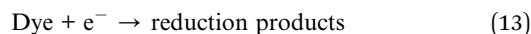
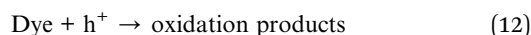
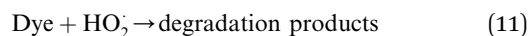
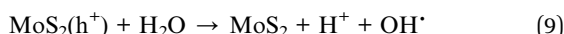
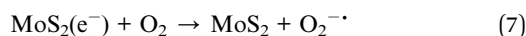
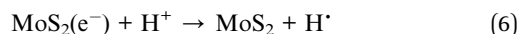
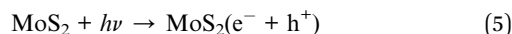
Fig. 8 Photocatalysis tests with different quenchers over MoS<sub>2</sub>/MgAl-LDH.

1.62 to 1.81 eV due to the quantum limitation effect, leading the photogenerated electron-hole pairs having a stronger redox ability. On the other hand, the MgAl-LDH layer acts as an inorganic conductive layer, which could rapidly transfer photogenerated electrons from MoS<sub>2</sub>, thus inhibiting the recombination of photogenerated electron-hole pairs. Moreover, a possible photocatalytic degradation mechanism can be proposed. First, the MO molecules are adsorbed in a layer on MoS<sub>2</sub>/MgAl-LDH due to the charge on the surface of MgAl-LDH. Meanwhile, under visible light, photoelectrons and holes are generated in the conduction and valence bands, respectively, of MoS<sub>2</sub>. Then, the photogenerated electrons transferred to the MgAl-LDH layer react with oxygen adsorbed on the surface or dissolved in water to produce superoxide. The excess holes on the valence band remain in MoS<sub>2</sub> and react with H<sub>2</sub>O and OH<sup>-</sup>



Scheme 3 Photocatalytic mechanism schematic of MO degradation by MoS<sub>2</sub>/MgAl-LDH.

to form active substances such as  $\text{OH}^\cdot$ .<sup>29</sup> Then, photocatalysis proceeds by a known mechanism of visible-light-driven electron emission from the valence band to the conduction band, and the formation of oxidative intermediate species,  $\text{O}_2^{\cdot-}$  and  $\cdot\text{OH}$ , results in the degradation of MO.



## 4. Conclusions

In summary, few-layer  $\text{MoS}_2$  was successfully grown in MgAl-LDH layers. By decreasing the domain size of  $\text{MoS}_2$ , the bandgap of  $\text{MoS}_2$  was increased from 1.62 eV (flower-like  $\text{MoS}_2$ ) to 1.81 eV ( $\text{MoS}_2/\text{MgAl-LDH}$ ), and the  $\text{MoS}_2/\text{MgAl-LDH}$  composite exhibits a significantly enhanced full-spectrum response in the wavelength range of 300–800 nm. More importantly, the MgAl-LDH layer acts as an inorganic conductive layer to transport photogenerated electrons efficiently. As a result, there is a lower recombination efficiency of photo-generated electron-hole pairs in the  $\text{MoS}_2/\text{MgAl-LDH}$  composite. Therefore, the  $\text{MoS}_2/\text{MgAl-LDH}$  composite exhibited an outstanding catalytic capacity and a superior cycle performance. The composite completely degraded the MO in  $50 \text{ mg L}^{-1}$  and  $100 \text{ mg L}^{-1}$  MO solutions in 45 min and 105 min, respectively. Furthermore, the composite also shows a degradation rate over 84% in 120 min even for a MO solution concentration as high as  $200 \text{ mg L}^{-1}$ , and retained 80% of the initial degradation rate after four cycles. The  $\text{MoS}_2/\text{MgAl-LDH}$  composite can be considered as a promising photocatalyst for waste water treatment.

## Conflicts of interest

There are no conflicts to declare.

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