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ZnCuAl-LDH/Bi₂MoO₆ Nanocomposites with Improved Visible Light-Driven Photocatalytic Degradation

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Abstract: In this study, pure Bi₂MoO₆ was synthesized via a solvothermal method. A ZnCuAl-layered double hydroxide (LDH)/Bi₂MoO₆ (denoted as LDH/Bi₂MoO₆) nanocomposite was synthesized via a steady-state co-precipitation route using Bi₂MoO₆ as the matrix material. LDH was deposited on the surface of Bi₂MoO₆ with a close contact interface. The specific surface area of the resulting LDH/Bi₂MoO₆ composite increased up to 19.1 m²·g⁻¹ owing to the stacking arrangement between LDH and the Bi₂MoO₆ nanosheets, resulting in the generation

of a large number of reactive sites. In addition, the light absorption region of the LDH/Bi₂MoO₆ composite was larger than those of pure LDH and Bi₂MoO₆ because of the formation of a heterojunction structure and the possible quantum size effect. The photocatalytic performance of the as-prepared samples was evaluated by carrying out the degradation of rhodamine B (RhB) using them under visible light irradiation. Compared to pure LDH and Bi₂MoO₆, the LDH/Bi₂MoO₆ nanocomposite exhibited enhanced photocatalytic activity for the degradation of RhB. With an increase in the LDH content, the photocatalytic activity of the LDH/Bi₂MoO₆ composite first increased and then decreased. Although the addition of an optimum amount of LDH was beneficial for the generation of electron-hole pairs, excessive LDH on the surface of Bi₂MoO₆ decreased the visible light absorption ability of both the components, thus reducing photocatalytic activity of the composite. This indicates that an appropriate LDH:Bi₂MoO₆ molar ratio is necessary for obtaining LDH/Bi₂MoO₆ composites with excellent photocatalytic activity. Furthermore, the LDH/Bi₂MoO₆ composite showed high photocatalytic stability and reusability. The structure of the LDH/Bi₂MoO₆ composite remained almost unchanged even after four photodegradation cycles. The enhanced photocatalytic performance of the composite can be attributed to the combined effect of its heterojunction structure and high specific surface area, which are beneficial for effective separation of photogenerated charge carriers and the availability of a large number of active sites for photocatalysis. It was found that •OH and O₂^{•-} were the main reactive species, while e⁻ and h⁺ contributed little to the photodegradation process. The generation, transfer, and separation of photoinduced electrons and holes in the composites were investigated by transient photocurrent responses, electrochemical impedance spectroscopy Nyquist plots, and photoluminescence measurements. The results showed that the heterojunction structure of the composites played a key role in enhancing their photocatalytic activity. A possible photodegradation mechanism was proposed for the composite. This study will provide a facile approach for the preparation of LDH- and/or Bi₂MoO₆-based nanocomposites. The LDH/Bi₂MoO₆ nanocomposite prepared in this study showed huge potential to be used as a visible-light photocatalyst for degrading environmental pollutants.

Key Words: Layered double hydroxide; Bi₂MoO₆; Nanocomposite; Active site; Visible-light photodegradation; Heterojunction

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ZnCuAl-LDH/Bi₂MoO₆ 纳米复合材料的构建及其可见光催化降解性能

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摘要: 本工作采用稳态共沉淀法制备了 ZnCuAl-LDH/Bi₂MoO₆ (LDH/Bi₂MoO₆) 纳米复合材料, 并研究了所得材料在可见光下降解污染物罗丹明 B (RhB) 的光催化性能。结果表明, 所得 LDH/Bi₂MoO₆ 纳米复合材料比单纯的 ZnCuAl-LDH 和 Bi₂MoO₆ 具有显著提高的光催化活性和较好的稳定性。光催化性能的提高得益于异质结的形成以及高的比表面积, 从而有利于光生电子-空穴对的有效分离和更多光催化活性位点的暴露。研究发现, 在光降解过程中, 所产生的 $\cdot\text{OH}$ 和 $\text{O}_2^{\cdot-}$ 是主要的反应性物种, 而 e^- 和 h^+ 的贡献较少。基于实验结果, 提出了一种可能的光催化机制。本工作提供了一种制备基于 LDH 和(或)Bi₂MoO₆ 纳米复合材料的方法, 所得 LDH/Bi₂MoO₆ 纳米复合材料可望作为一种可见光光催化剂, 在净化环境和缓解资源短缺方面有潜在应用。

关键词: 层状双氢氧化物; Bi₂MoO₆; 纳米复合材料; 活性位点; 可见光降解; 异质结
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1 Introduction

In recent years, the large amount of toxic waste water was discharged into the environment due to the great development of industrialization, which has a serious impact on water resources. In addition, the increasing demand of water and the declining of available fresh water were more serious problems in water resources. The purification and recycling of industrial waste water has become an important research field^{1,2}. Therefore, there is an urgent issue to develop an environmental, efficient and stable visible-light-response semiconductor photocatalyst to deal with industrial wastewater^{3,4}.

Bismuth molybdate is a direct transition n-type semiconductor material with a narrow forbidden band width ($E_g < 3.2$ eV) and thus a potential visible light absorption capacity⁵. Bismuth molybdate has three typical crystal structures, *i.e.* α -Bi₂Mo₃O₁₂, β -Bi₂Mo₂O₉ and γ -Bi₂MoO₆⁶. Among these three crystal structures, γ -Bi₂MoO₆ is the only layered Aurivillius structure with a structural stability at low temperatures⁷. However, the photocatalytic effect of the single Bi₂MoO₆ was not ideal, because of the low visible light absorption efficiency and the high recombination rate of electron holes^{8,9}. The hetero-junction semiconductor photocatalysis tends to have beneficial photocatalytic activity¹⁰. Hence, the researchers have attempted to prepare many high-performance photocatalyst materials by combining bismuth molybdate with other semiconductor materials, such as BiOI/Bi₂MoO₆¹¹, Bi₂O₂CO₃/Bi₂MoO₆¹², MoS₂/Bi₂MoO₆¹³ and CdS/Bi₂MoO₆¹⁴.

Layered composite hydroxides (LDHs), with a brucite regular octahedral structure, consist of a positively charged host laminate and interlayered anions as a guest. The general formula is $[\text{M}_1^{2+}_x\text{M}_2^{3+}_y(\text{OH})_z]^{n+}(\text{A}^{n-})_{x/n}\cdot y\text{H}_2\text{O}$, where M^{2+} represents a divalent cation, M^{3+} a trivalent cation, and A^{n-} interlayered anion, respectively^{15,16}. Because LDHs have large specific

surface area, positively charged host layers, host-guest interactions and tunable interlayer space^{17,18}, they showed a great advantage in the field of adsorption^{19,20}, bio/medical fields^{21,22} and environmental friendly functional additives^{23,24}. At present, some reports about hydrotalcite-based semiconductor photocatalysts have been widely studied, such as ZnCr-LDH²⁵, ZnFe-LDH²⁶, g-C₃N₄/NiFe-LDH²⁷, BiOI/NiFe-LDH²⁸ and BiVO₄/LDH²⁹. However, there are few discussions about new composites of hydrotalcite and bismuth molybdate, and the visible-light-driven photocatalytic performance of LDH-based catalysts is still not satisfactory for practical applications.

In this work, we have synthesized LDH/Bi₂MoO₆ nanocomposite by using a steady state co-precipitation method. The photocatalytic performance of the obtained sample was investigated in detail through the degradation of RhB solution under visible light irradiation. Subsequently, the active species and the corresponding photocatalytic mechanism were explored.

2 Experimental

2.1 Materials

Aluminum nitrate nonahydrate (Al(NO₃)₃·9H₂O, AR, 99.0%), zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O, AR, 98.0%) and copper nitrate hexahydrate (Cu(NO₃)₂·6H₂O, AR, 99.0%) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. Bismuth nitrate pentahydrate (Bi(NO₃)₃·5H₂O, AR, 99.0%), sodium molybdate dehydrate (Na₂MoO₄·2H₂O, AR, 99.0%), sodium hydroxide (NaOH, AR), ethylene glycol ((CH₂OH)₂, AR, 99.7%) and absolute ethanol (CH₃CH₂OH, AR, 99.7%) were purchased from Shanghai Sinopharm Chemical Reagent Co., Ltd. All chemicals were directly used without further purification.

2.2 Preparation of photocatalysts

Pure Bi₂MoO₆ was synthesized by a solvothermal method³⁰. In a typical synthetic process, a desired amount of

$\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (1 mmol) and $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ (0.5 mmol) were respectively added into the mixed solution of ethylene glycol (20 mL) and absolute ethanol (40 mL) under the vigorous stirring to form a clear solution. Then, NaOH ($2 \text{ mol} \cdot \text{L}^{-1}$) solution was dropwise added into the above solution to adjust pH value to 5. The resulted mixture was heated at 160°C for 12 h using a stainless steel Teflon-lined autoclave. The target precipitate was washed by distilled water and absolute ethanol, and then dried at 60°C overnight.

The synthetic process of LDH/ Bi_2MoO_6 nanocomposite is shown in Scheme 1. 1 mmol of Bi_2MoO_6 was well dispersed in distilled water (40 mL) with a ultrasonic treatment for 1 h, and then 1 mmol of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 0.5 mmol of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and 0.5 mmol $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were added into the above suspension, respectively. The pH value of the precursor solution was also adjusted to 9 using NaOH ($2 \text{ mol} \cdot \text{L}^{-1}$) solution with a continuous stirring. After 10 h, the resultant LDH/ Bi_2MoO_6 nanocomposite (denoted as LDH/ Bi_2MoO_6) was collected, washed and dried at 60°C for 12 h. Other LDH/ Bi_2MoO_6 - x photocatalysts were also prepared by the same procedure, where x represented the molar ratio (1 : 2, 1 : 3, 2 : 1 and 3 : 1) between LDH and Bi_2MoO_6 . For comparison, ZnCuAl -LDH (denoted as LDH) was also prepared by a similar process without the addition of Bi_2MoO_6 .

2.3 Characterization

The X-ray powder diffraction (XRD) patterns of the prepared materials were obtained on a Shimadzu XRD-6000 diffractometer using $\text{Cu } K_\alpha$ radiation. The FT-IR spectra were recorded on a NICOLET IS-10 spectrometer. The morphology was observed through scanning electron microscopy (FEI QUANTA 200) and transmission electron microscopy (TEM) (JEM-2100, an acceleration voltage of 200 kV). The Brunauer Emmett Teller (BET) specific surface areas were measured with N_2 adsorption/desorption isotherms recorded on a Beckman Coulter SA 3100 instrument at 77 K. X-ray photoelectron spectra (XPS) was performed on a photoelectron spectrometer (ThermoFisher Inc., ESCALAB 250Xi) using $\text{Al } K_\alpha$ radiation. The UV-Vis-Visible diffuse reflectance spectra were measured by a Shimadzu UV-3600 spectrophotometer using BaSO_4 as a reference. The photoluminescence (PL) spectra were detected by a JASCO FP 6500 fluorescence spectrometer at an excitation wavelength of 325 nm.

The electrochemical measurements were carried out on an electrochemical workstation (CHI-660D, Shanghai Chenhua) with a standard three electrode cell. The photocurrent was measured under a visible light irradiation at a bias voltage of 0.5 V using a $0.5 \text{ mol} \cdot \text{L}^{-1}$ Na_2SO_4 electrolyte solution. The electrochemical impedance spectroscopy (EIS) was performed at an open circuit potential of 5 mV in the frequency range of 0.01 Hz–1000 kHz using a mixed solution of KCl ($0.1 \text{ mol} \cdot \text{L}^{-1}$), $\text{K}_3[\text{Fe}(\text{CN})_6]$ ($5 \text{ mmol} \cdot \text{L}^{-1}$), and $\text{K}_4[\text{Fe}(\text{CN})_6]$ ($5 \text{ mmol} \cdot \text{L}^{-1}$) as an electrolyte solution.

2.4 Photocatalytic evaluation

For each photocatalytic experiment, 0.1 g of photocatalyst was dispersed into RhB solution ($5 \text{ mg} \cdot \text{L}^{-1}$, 200 mL) with a stirring for 30 min in dark. Then, the above mixed suspension solution was irradiated under visible light (300 W Xenon lamp, $\lambda \geq 420 \text{ nm}$). During the irradiation, the certain volume of solution ($\sim 5 \text{ mL}$) was taken out for the further analysis by a UV-Vis spectrophotometer at 554 nm.

2.5 Active species trapping

To identify the role of the active species, $10 \text{ mmol} \cdot \text{L}^{-1}$ of different scavengers, including isopropanol (IPA), benzoquinone (BQ), sodium oxalate ($\text{Na}_2\text{C}_2\text{O}_4$) and potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$), were added into the RhB aqueous solution, respectively. These scavengers are related to $\cdot\text{OH}$, $\cdot\text{O}^{2-}$, h^+ and e^- , respectively^{3,31}. Then, the remaining testing process was the same to the above photocatalytic processes.

3 Results and discussion

The crystal structures of LDH, Bi_2MoO_6 and LDH/ Bi_2MoO_6 were measured by means of XRD patterns. As shown in Fig. 1a, some characteristic peaks at 10.60° , 21.11° , and 34.14° can be respectively indexed to (003), (006) and (101/012) planes of the regular layered structure of LDH, indicating the formation of the octahedron phase of LDH. For pure Bi_2MoO_6 , some diffraction peaks at 10.81° , 28.29° , 32.58° and 33.19° are related to (020), (131), (200/002) and (060) planes, respectively. After combining LDH with Bi_2MoO_6 , the characteristic peaks of Bi_2MoO_6 are maintained in LDH/ Bi_2MoO_6 composite although their intensities become weak to a certain extent, indicating that the introduction of LDH does not affect the layered structure of Bi_2MoO_6 . Additionally, the characteristic peaks of LDH are not visible in LDH/ Bi_2MoO_6 composite owing to the formation of

Scheme 1 A schematic illustration for preparing LDH/ Bi_2MoO_6 nanocomposite.

Fig. 1 (a) XRD patterns, (b) FT-IR spectra, (c) N₂ adsorption-desorption isotherms, and (d) UV-visible DRS spectra of LDH, Bi₂MoO₆ and LDH/Bi₂MoO₆ (Inset is the $(ah\nu)^{1/2}$ versus photo energy ($h\nu$) of the as-prepared samples.).

an overlapping peak and/or a relatively low mass ratio of LDH.

The local structures of the as-prepared samples were measured using FT-IR spectra (Fig. 1b). The bulk LDH shows the absorption bands at 1381, 1636 and 3528 cm⁻¹, attributed to the NO₃⁻ stretching vibration, the deformation vibration of H—O—H, and tensile vibration of —OH, respectively^{32,33}. For pure Bi₂MoO₆, the absorption peaks at 1000–400 cm⁻¹ are assigned to lattice vibrations of M—O^{34,35}, and peaks at 3524 and 1637 are corresponded to —OH vibration. The peak at 1380 cm⁻¹ is assigned to NO₃⁻ stretching vibration, which is caused by nitrates from raw materials. Peak around 1050 cm⁻¹ is associated with the adsorbed CO₂ on Bi₂MoO₆. After combining LDH with Bi₂MoO₆, the obtained LDH/Bi₂MoO₆ shows three characteristic absorption peaks (842, 797 and 737 cm⁻¹) owing to the stretching vibration of Mo—O bond, and other peaks (575 and 448 cm⁻¹) due to the telescopic vibration of Bi—O bond^{36–38}. Compared with pure Bi₂MoO₆ and LDH, the absorption characteristic peaks of LDH/Bi₂MoO₆ show a slight shift due to the interaction between LDH and Bi₂MoO₆.

Fig. 1c shows nitrogen adsorption-desorption isotherms of LDH, Bi₂MoO₆ and LDH/Bi₂MoO₆. Pure LDH shows typical IV isotherms related to capillary condensation in mesoporous region³⁹, and hysteresis loop at low relative pressure due to the formation of slit-shaped pores. Both Bi₂MoO₆ and LDH/Bi₂MoO₆ show typical II isotherms⁴⁰. In addition, the specific surface areas of LDH and Bi₂MoO₆ are calculated to be 5.5 and 15.0 m²·g⁻¹, respectively. After combining LDH with Bi₂MoO₆, the specific surface area of the resulted LDH/Bi₂MoO₆ is increased to 19.1 m²·g⁻¹, which is attributed to

the stacking arrangement between LDH and Bi₂MoO₆ nanosheets. The larger specific surface area means more reactive sites exposed to enhance the visible-light-driven photocatalysis.

The UV-visible diffuse reflectance spectra (DRS) of the as-prepared samples are shown in Fig. 1d. The absorption edges of LDH, Bi₂MoO₆ and LDH/Bi₂MoO₆ can be estimated to be 425, 475 and 520 nm, respectively⁴¹, showing that LDH/Bi₂MoO₆ can be excited to produce more charge carriers than pure Bi₂MoO₆ and LDH. The absorption band between 600 and 1000 nm in LDH is attributed to Cu²⁺ ²E_g → ²T_{2g}(D) *d-d* transitions of Cu²⁺, which is a distorted six-fold coordination with octahedral arrangement of Cu²⁺ due to Jahn-Teller effect occurring in LDH framework^{42,43}. Furthermore, the absorption edge of LDH/Bi₂MoO₆ nanocomposite exhibits an obvious red-shift to a longer wavelength (520 nm), which is attributed to the synergistic effect between LDH and Bi₂MoO₆.

The band gap value can be calculated based on the following equation: $ah\nu = A(h\nu - E_g)^{n/2}$, where a , h , ν , E_g , are the absorption coefficient, Planck's constant, optical frequency and band gap, respectively^{44–46}. The inset of Fig 1d shows the plots of $(ah\nu)^{2/n}$ vs $h\nu$ for LDH, Bi₂MoO₆ and LDH/Bi₂MoO₆. For direct transition semiconductors of LDH and Bi₂MoO₆, n equals 1. The band gap energy ($E_g = 2.40$ eV) of LDH/Bi₂MoO₆ is smaller than that of Bi₂MoO₆ ($E_g = 2.70$ eV) and LDH ($E_g = 2.95$ eV), indicating that LDH adjusts the forbidden band structure of Bi₂MoO₆, leading to the enhanced light absorption ability of the resulted nanocomposite. In addition, the calculated bandgap value of LDH/Bi₂MoO₆ is smaller than that of pure LDH and Bi₂MoO₆ due to the formation of heterojunction structure (see

below) and the possible quantum size effect^{47,48}. The LDH/Bi₂MoO₆ composite with a larger optical-response range is expected to exhibit a better photocatalytic activity than its pure counterparts.

The morphology and microstructure of Bi₂MoO₆, LDH/Bi₂MoO₆ and LDH were investigated by SEM images. It can be clearly observed that bulk Bi₂MoO₆ (Fig. 2a, b) shows a sheet-like structure with a thickness of 30–40 nm. As shown in Fig. 2c, d, pure LDH is consisted of many regularly stacked nanosheets with a thickness of 10–15 nm. After combining LDH with Bi₂MoO₆, the resulted sample of LDH/Bi₂MoO₆ composite (Fig. 2e, f) exhibits an agglomeration, which is mainly due to the deposition of LDH on the surface of Bi₂MoO₆ by a self-assembly process through the electrostatic interaction.

As LDH and Bi₂MoO₆ both have a layered structure, such a 2D-2D close contact may lead to the formation of heterojunction between two components. The formed heterojunction between LDH and Bi₂MoO₆ is beneficial for the effective separation of

photo-excited electron/holes pairs, leading to the improved photocatalytic activity.

To further reveal the morphology and microstructure in the resulted LDH/Bi₂MoO₆ nanocomposite, TEM images were taken and are displayed in Fig. 3. The overlapping layers can be clearly observed with the dark black-like rectangular areas for Bi₂MoO₆ and greyish areas for LDH (Fig. 3a, b). The enlarged HRTEM images of LDH/Bi₂MoO₆ are shown in Fig. 3c, d. Three sets of inter-planar spacing values of 0.26, 0.35 and 0.38 nm can be observed due to the (101) plane of LDH, and (121) and (111) planes of Bi₂MoO₆, respectively. It further confirms the formation of a heterojunction structure between LDH and Bi₂MoO₆. The SAED image of LDH/Bi₂MoO₆ (Fig. 3e) also provide a direct evidence for the presence of both LDH ((101) plane) and Bi₂MoO₆ ((131), (040) and (021) planes). As shown in Fig. 3f, EDS spectrum of LDH/Bi₂MoO₆ nanocomposite consists of Bi, Mo, O, Zn, Cu and Al elements, indirectly illustrating the coexistence of both LDH and Bi₂MoO₆.

Fig. 2 SEM images of (a, b) Bi₂MoO₆, (c, d) LDH, and (e, f) LDH/Bi₂MoO₆ at different resolutions.

Fig. 3 (a, b) TEM images, (c, d) HRTEM images, (e) SAED image and (f) EDS spectrum of LDH/Bi₂MoO₆.

Furthermore, STEM-EDS elemental mapping images of LDH/Bi₂MoO₆ are shown in Fig. 4. It is clearly visible that Bi₂MoO₆ is combined with LDH nanosheets, leading to the formation of heterojunction structure.

The positions of valence band and chemical states in LDH, Bi₂MoO₆ and LDH/Bi₂MoO₆ were studied by XPS technique. Fig. 5a shows two Zn 2p XPS peaks at 1022.2 eV (Zn 2p_{3/2}) and 1045.1 eV (Zn 2p_{1/2}) for pure LDH. By comparison, these two peaks at 1022.7 and 1045.7 eV can be also observed for LDH/Bi₂MoO₆, with a slight position change due to the interaction between LDH and Bi₂MoO₆. The introduction of Bi₂MoO₆ may greatly affect the chemical environment of Zn²⁺, leading to the disappearance of Zn²⁺ satellite peak in LDH/Bi₂MoO₆. The Cu 2p spectrum of pure LDH (Fig. 5b) shows four signals at approximate 935.1 eV (Cu 2p_{3/2}), 943.4 eV (Cu 2p_{3/2}), 954.8 eV (Cu 2p_{1/2}), and 962.8 eV (Cu 2p_{1/2})⁴⁹. As shown in Fig. 5c, two signals at 74.2 and 77.1 eV are attributed

to the Al 2p_{3/2} orbitals and 2p_{3/2} satellite peak of Al³⁺ in LDH³⁴. After combining with Bi₂MoO₆, Cu 2p and Al 2p spectra of LDH/Bi₂MoO₆ are almost the same as that of LDH.

As shown in Fig. 5d, three peaks at 529.9, 531.9 and 534.5 eV are related to M—O, —OH and H₂O in O 1s spectrum of LDH. The pure Bi₂MoO₆ shows two peaks at binding energies of 530.2 and 531.0 eV due to Bi—O and Mo—O, respectively³¹. For LDH/Bi₂MoO₆, peaks at 529.9, 530.7, 531.7 and 533.0 eV are clearly visible, corresponding to Bi—O, Mo—O, —OH and H₂O, respectively. The O 1s XPS spectrum of LDH/Bi₂MoO₆ is shifted positively, revealing the electron transfer between LDH and Bi₂MoO₆. In Fig. 5e, the Bi 4f spectrum of Bi₂MoO₆ shows two peaks of Bi³⁺ at binding energies of 159.3 and 164.6 eV, being slightly higher than those of LDH/Bi₂MoO₆. As shown in Fig. 5f, Mo 3d spectrum of Bi₂MoO₆ shows two signals at 232.6 eV (Mo 3d_{5/2}) and 235.8 eV (Mo 3d_{3/2}) due to the presence of Mo⁶⁺ in MoO₆^{8,50}. For LDH/Bi₂MoO₆, additionally, two new

Fig. 4 HRTEM image, STEM-EDS elemental mapping spectra, and the distribution of Zn, Cu, Al, Bi, Mo and O elements on LDH/Bi₂MoO₆.

Fig. 5 XPS spectra of (a) Zn 2p, (b) Cu 2p, (c) Al 2p, (d) O 1s, (e) Bi 4f and (f) Mo 3d of the as-prepared samples.

satellite peaks at 231.9 and 235.0 eV are visible, further confirming the presence of interaction between LDH and Bi_2MoO_6 .

Therefore, the changes in binding energies for Zn 2p, Cu 2p, Al 2p, Bi 4f, Mo 3d and O 1s XPS spectra are closely related to the space structure, valence and the surrounding chemical environment. Meanwhile, it indicates that there is a strong interfacial chemical interaction between Bi_2MoO_6 and LDH, which further confirms the formation of heterojunction between two components.

The photocatalytic performance was evaluated using RhB aqueous solution as an organic contamination under visible light. As displayed in Fig. 6a, no obvious degradation is observed for RhB aqueous solution in the blank test. Only 2.5% of the RhB concentration was reduced within 60 min for pure LDH due to the surfaced adsorption effect, while 30% for pure Bi_2MoO_6 . After combining LDH with Bi_2MoO_6 , the resulted LDH/ Bi_2MoO_6 nanocomposites presents a greatly increased photocatalytic activity with 80% RhB degraded within 60 min. As shown in Fig. S1 (see Supporting Information), as the added amount of LDH is increased, the photocatalytic activity of LDH/ Bi_2MoO_6 composites is firstly increased with a highest value for LDH/ Bi_2MoO_6 and then decreased. Although the proper amount of LDH is beneficial for the generation of electron-hole pairs, an excessive amount of LDH on the surface of Bi_2MoO_6 will cause the decreased visible light absorption ability for both components and then reduced photocatalytic activity. It indicates that an appropriate mole ratio between LDH and Bi_2MoO_6 is necessary for achieving an excellent

photocatalytic activity.

As shown in Fig. 6b, isopropanol ($\cdot\text{OH}$ scavenger), benzoquinone ($\text{O}_2^{\cdot-}$ scavenger), sodium oxalate (h^+ scavenger) and potassium dichromate (e^- scavenger) were employed to investigate the role of the active species. The residual amounts of RhB are 75%, 85%, 40%, and 45%, respectively, indicating that $\cdot\text{OH}$ and $\text{O}_2^{\cdot-}$ are the main reactive species, while e^- and h^+ contribute a little in the degradation process.

In view of the practical application of the photocatalyst, the photocatalytic stability of LDH/ Bi_2MoO_6 was also studied by recycling experiment (Fig. 6c). After photocatalytic degradation of RhB, the sample was re-used for the cycling experiment. After recycling for four times, there was no significant decrease of the photocatalytic activity and the slightly reduced activity is mainly owing to the mass loss of photocatalyst during the centrifugation to collect the used catalyst for the next use. In addition, the XRD pattern of LDH/ Bi_2MoO_6 (Fig. 6d) is almost unchanged before and after photocatalysis. These results indicate that LDH/ Bi_2MoO_6 nanocomposite has a good structural stability and recycling performance.

The electrochemical testing was employed to deeply explore the reasons for the enhanced photocatalytic activity. The transient photocurrent responses of LDH, Bi_2MoO_6 and LDH/ Bi_2MoO_6 under visible light are shown in Fig. 7a. The higher photocurrent density, the higher effective charge separation ability of photo-generated electron-hole pairs⁵¹. The pure Bi_2MoO_6 exhibits the lower photocurrent intensity. After combination with LDH, the photocurrent of LDH/ Bi_2MoO_6 is almost twice that of pure Bi_2MoO_6 , indicating that the

Fig. 6 (a) Visible light photocatalytic degradation rate of RhB solution over different samples, (b) effects of different scavengers on the degradation efficiency of RhB over LDH/ Bi_2MoO_6 , (c) photodegradation of RhB over LDH/ Bi_2MoO_6 for four successive cycles and (d) XRD patterns of LDH/ Bi_2MoO_6 before and after photodegradation of RhB.

Fig. 7 (a) Transient photocurrent response, (b) Nyquist plots of EIS for LDH, Bi₂MoO₆ and LDH/Bi₂MoO₆ thin film electrodes. (c) Photoluminescence (PL) spectra with an excitation wavelength of 325 nm for Bi₂MoO₆ and LDH/Bi₂MoO₆.

construction of hetero-junction between LDH and Bi₂MoO₆ can promote the effective separation of photo-generated electron-hole pairs and accelerates the interfacial charge transfer. This is the main reason for the excellent photocatalytic performance of LDH/Bi₂MoO₆.

Fig. 7b shows EIS Nyquist plots of the as-prepared samples to reveal the charge transfer process⁵². The resistance value (corresponding to the ordinate of the highest point of the arcs) of LDH, Bi₂MoO₆ and LDH/Bi₂MoO₆ is 550, 180 and 280 Ω, respectively. The magnitude of the resistance reflects a fairly reliable result. It intuitively reflects the fast electron transfer process of composite. Moreover, the arc radius of LDH/Bi₂MoO₆ is slightly larger than that of Bi₂MoO₆, indicating that the magnitude of the electron transport resistance is not a determinant of the photocatalytic performance.

The PL spectra of LDH/Bi₂MoO₆ and Bi₂MoO₆ are shown in Fig. 7c. The PL intensity was positively related to the recombination rate of the photo-generated electron-hole pairs⁵³. The lower peak intensity indicates the lower recombination rate of the electron-holes pairs⁵⁴. The emission intensity of LDH/Bi₂MoO₆ is obviously lower than that of Bi₂MoO₆, indicating that LDH/Bi₂MoO₆ can effectively accelerate the transfer of photo-generated electron-hole pairs. Hence, it also indicates that the formed heterojunction can significantly reduce the recombination of electron-hole pairs.

In order to further clarify the reason for the enhancement of photocatalytic activity, the CB and VB values of LDH and Bi₂MoO₆ were obtained according to the following formula^{55,56}:

$$E_{VB} = \chi - E_e + 0.5E_g$$

$$E_{CB} = E_{VB} - E_g$$

where χ , E_e and E_g are the absolute electronegativity, the energy of free electrons on the hydrogen scale (~4.5 eV), and the band gap energy of the semiconductor, respectively. The χ values of LDH and Bi₂MoO₆ are 5.25 and 5.54 eV⁸, respectively. Thus, the potentials of samples were calculated to be -0.68 eV (E_{CB}) and +2.27 eV (E_{VB}) for LDH, as well as -0.31 eV (E_{CB}) and +2.39 eV (E_{VB}) for Bi₂MoO₆. It can be seen that the forbidden band structure of LDH and Bi₂MoO₆ can meet the requirements for forming the hetero-junctions. As the $E_{VB} = +2.39$ eV of Bi₂MoO₆ is more positive than $E(\bullet\text{OH}/\text{OH}^-) = +1.99$ eV vs

Scheme 2 A schematic illustration for the proposed charge separation and transfer pathways in LDH/Bi₂MoO₆ nanocomposite under visible-light irradiation.

NHE)⁵⁷, the formed holes can directly react with OH⁻ to produce •OH radicals. The $E_{CB} = -0.68$ eV of LDH is more negative than $E(\text{O}_2/\text{O}_2^{\bullet-}) = +0.13$ eV vs NHE), the CB electrons allows the reduction of the dissolved O₂ into O₂^{•-} radicals⁵. The proposed charge separation and transfer pathways under visible-light irradiation in LDH/Bi₂MoO₆ nanocomposite are shown in Scheme 2.

4 Conclusions

In summary, we have successfully synthesized LDH/Bi₂MoO₆ nanocomposites by a steady-state co-precipitation route at room temperature, in which a 2D-2D close contact was achieved and hence a heterojunction structure was formed between two layered components. Compared with its pure constituents, the resulted LDH/Bi₂MoO₆ nanocomposite exhibited a greatly increased visible-light driven photocatalytic activity in the degradation of RhB as well as a good stability. The combined effects of the heterojunction structure and the high specific surface area are respectively beneficial for the effective separation of photogenerated charge carriers and exposure of more active sites for photocatalysis, leading to the enhanced photocatalytic performance. The produced •OH and O₂^{•-} are the main reactive species while e⁻ and h⁺ contribute a little in the photodegradation process. A possible mechanism for photocatalytic degradation

was proposed based on the experimental results. This work provides a simple way for the preparation of LDH- and/or Bi₂MoO₆-based nanocomposites and the obtained LDH/Bi₂MoO₆ nanocomposite might find potential application as visible light photocatalysts in purifying the environment and alleviating resource shortages.

Supporting Information: available free of charge via the internet at <http://www.whxb.pku.edu.cn>.

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