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Preparation of Bi$_2$MoO$_6$@Diatomite composite and its visible light driven reduction of Cr(VI) and removal of tetracycline hydrochloride

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Abstract

The use of cheap and porous substrates to support visible light photocatalyst is an effective solution to avoid the agglomeration of catalyst. Herein, the Bi$_2$MoO$_6$@Diatomite composite has been prepared through hydrothermal reaction with Bi(NO$_3$)$_3$ and Na$_2$MoO$_4$ as precursors and diatomite as substrate. XRD, SEM, TEM, XPS, and DRS are applied to characterize these composite photocatalysts. The photocatalytic performance of the obtained composites were studied through the Cr(VI) reduction and tetracycline hydrochloride (TC) degradation under visible light irradiation ($\lambda > 400 \text{ nm}$). The photocatalytic experimental results display that the sample with 6% diatomite mass fraction (Bi$_2$MoO$_6$@6%DE) has the highest catalytic performance in all materials. In the Cr(VI) solution, the Bi$_2$MoO$_6$@6%DE can reduce 90.1% of Cr(VI) in 60 min, while Bi$_2$MoO$_6$ can only reduce 71.7% of pollutants in the same time. In the TC solution, the Bi$_2$MoO$_6$@6%DE can reduce 74.7% of TC in 120 min, while Bi$_2$MoO$_6$ can only reduce 30.5% of pollutants in the same time. The photocatalytic mechanism was further investigated through the test of active radical capture. The main active radicals in the reduction of Cr(VI) is photogenerated electrons. The -HO$^-$, -O$_2^-$ and holes (h$^+$) are active free radicals in the removal process of TC, and photogenerated holes (h$^+$) have the greatest influence. This composite has good photocatalytic activity and recyclability, so it has great application potential in waste water treatment.

1. Introduction

Industrial and agricultural production process produces a large number of water pollutants, for example, heavy metals, organic dyes and antibiotics are harmful to human health. How to effectively remove the pollution in waste water has become a hot topic [1–3]. The common methods to remove water pollutants mainly include physical adsorption [4–6], electrochemical methods [7] and photocatalytic technology [8–11]. Semiconductor photocatalysis technology, which can be effective utilizing solar energy, is a promising method for water pollution treatment. Titanium dioxide-based photocatalyst is the most commonly used material in waste water treatment [8–11]. However, TiO$_2$ has the problem of low utilization of solar energy because it can only utilize ultraviolet light (about 4% of sunlight) [12, 13]. Thus, the development of high activity visible light photocatalyst has far-reaching significance for waste water treatment [14–16].

Recently, bismuth-based (Bi-based) materials have been discovered to show superior visible-light-driven photocatalytic performance due to their relatively narrowband-gap and high photocatalytic stability [17–22]. Among these Bi-based photocatalysts, Bi$_2$MoO$_6$ has showed excellent visible light photocatalytic activity due to its narrow band gap of 2.7 eV, and shows great potential for degrading heavy metals and organic pollutants under visible light [23–25]. However, Bi$_2$MoO$_6$ nanosheets are prone to agglomeration during photocatalysis, which will result in the reduction of photocatalytic activity. Recent studies have shown that the use of substrates
such as graphene [26], g-C3N4 [27], CNTs [28], MOFs [29] to support Bi2MoO6 is an effective solution to this problem. Among these substrates, diatomite attracts wide attention due to its special characterization, for example, easy availability, inexpensive, non-toxicity, superior stability, and so on. In addition, diatomite has been widely used as a carrier to support TiO2, Cu2O, ZnO, BiOI, BiOCl and other catalysts [30–33]. Therefore, diatomite should be an ideal carrier for supporting Bi2MoO6.

Herein, Bi2MoO6@Diatomite (Bi2MoO6@DE for short) composites were prepared through hydrothermal reaction with Bi(NO3)3 and Na2MoO4 as precursors and diatomite as substrate. The prepared composites show excellent activities in the visible-light-driven reduction of Cr(VI) and TC degradation, and the sample with 6% diatomite mass faction (Bi2MoO6@6%DE) has the highest catalytic performance in all materials. The possible photocatalytic mechanism was proposed through the test of active radical capture.

2. Experiment sections

2.1. Materials

All chemicals used were analytic grade reagents without further purification. Ultra-pure water was used throughout this study.

2.2. Purification of diatomite

Diatomite is produced from low-grade diatomite of grade 2 and 3 in baishan city, Jilin Province. The original diatomite was ground for 15 min (300 r min−1) and then calcined in air at 600 °C for 2 h to remove impurities. The calcined diatomite is further immersed in dilute H2SO4 to remove the transition metal.

2.3. Synthesis of Bi2MoO6 and Bi2MoO6@Diatomite composites

The Bi2MoO6@Diatomite composites were prepared through a facile in situ hydrothermal process. The preparation of the Bi2MoO6@Diatomites is shown in figure 1. In a typical procedure, different amounts of diatomite (3% = 0.0183 g, 6% = 0.0360 g, 9% = 0.0507 g) were dispersed in 20 ml nitric acid solution (2 M) containing 2 mmol Bi(NO3)3·5H2O, respectively. Then 10 ml Na2MoO4 solution with a concentration of 0.1 M was added to the above solution under constant intense magnetic stirring, leading to the immediate formation of an amorphous white precipitate. After that, the pH value of the solution was adjusted to 5 with concentrated ammonia under stirring. After violently stirring 30 min, the light yellow suspension was transferred into a 50 ml capacity Teflon-lined stainless steel autoclave, then heated to 180 °C and kept for 24 h. After cooling the reactor in the air to room temperature, the precipitates obtained by centrifugation were washed with ultra-pure water and anhydrous ethanol for several times and dried at 80 °C for 12 h. A series of Bi2MoO6@Diatomite composites were prepared and named as pure Bi2MoO6, 3%DE-Bi2MoO6, 6%DE-Bi2MoO6 and 9%DE-Bi2MoO6, respectively (3%–9% indicates the mass of diatomite added).

2.4. Characterization

The x-ray diffraction (XRD) patterns of the synthesized catalysts were performed using a PANalytical X’Pert [3] Powder x-ray diffractometer at 45 kV and 40 mA with Cu Kα radiation (λ = 1.54056 Å). The morphology and micro area composition of the products were examined by field emission scanning electron microscopy (TESCAN MIRA3 LMH FESEM) and energy dispersive spectrometer (OXFORD X-MAXN 50). High-resolution transmission electron microscopy (HRTEM) observation was carried out on an FEI TECNAI G2 F20 instrument operated at an accelerating voltage of 200 kV. The UV–vis diffuse reflectance spectra (DRS) were collected on a Dual-beam UV–vis spectrophotometer (TU-1901) using BaSO4 as a reference to determine their band gaps.
X-ray photoelectron spectroscopy (XPS) analysis (Thermo Scientific Escalab 250) was used to identify the elemental composition and the chemical state of Samples.

2.5. Tests of photocatalytic activity
The photocatalytic activities of samples were systematically investigated by the photocatalytic reduction of Cr(VI) (60 mg l\(^{-1}\), which was based on a dilute K\(_2\)Cr\(_2\)O\(_7\) solution) and photocatalytic oxidation of TC (50 mg l\(^{-1}\)) under visible-light irradiation. The 300 W Xe lamp is used as the visible source, with a 400 nm cut-off filter to remove light of \(\lambda < 400 \) nm. The amount of photocatalyst used was 1 g l\(^{-1}\), before irradiation, 50 mg DE-Bi\(_2\)MoO\(_6\) composites were evenly dispersed in Cr(VI) (25 ml Cr(VI) and 25 ml IPA) solutions or TC solutions (50 ml) and stirred in darkness for 30 min. After the adsorption-desorption equilibrium, turn on the Xe lamp and take out 3 ml suspension at the same time interval. After centrifugation, the filtrate was analyzed by Dual-beam UV-vis spectrophotometer (TU-1901).

The photo-reduction efficiency of Cr(VI) and the photooxidation efficiency of TC were calculated from the following expression:

\[
\eta = \frac{C_0 - C_t}{C_0} \times 100\%
\]

Where \(\eta\) is the photocatalytic efficiency; \(C_0\) is the initial concentration of reactant; \(C_t\) is the concentration of reactant after illumination time \(t\).

2.6. Active free radicals trapping
It is universally acknowledged that \((h^+)\), \(\cdot\)OH and \(\cdot\)O\(_2^−\) are the major active factors in the photocatalytic system. To further evaluate the photocatalytic mechanism of the DE-Bi\(_2\)MoO\(_6\) composites, we also added some trapping agents (triethanolamine (TEOA), isopropanol (IPA), benzoquinone (BQ)) to detect the main active species during the photocatalytic process. TEOA is an effective scavenger of holes, IPA can effectively eliminate \(\cdot\)OH, BQ has the ability to trap \(\cdot\)O\(_2^−\) by a simple electron transfer mechanism.

3. Results and discussions
The synthesis processes of Bi\(_2\)MoO\(_6@DE\) are displayed in figure 1 and experimental section (supporting information). Firstly, in order to remove impurities, the original DE powder (figure S1 available online at stacks.iop.org/MRX/7/105909/mmedia) was calcinated in natural air atmosphere at 600 °C for 2 h, then the calcined DE is immersed in 12% H\(_2\)SO\(_4\) solution and stirred at 80 °C for 4 h to remove metal impurities. Finally, the cleaned DE was washed to neutral with ultra-pure water and dried for later use. The Bi\(_2\)MoO\(_6@DE\) composites were prepared through hydrothermal method with diatomite, Bi\((\text{NO}_3)_3\), Na\(_2\)MoO\(_4\), HNO\(_3\) and NH\(_3\)·(H\(_2\)O) as raw materials at 180 °C. This can realize the in situ growth of Bi\(_2\)MoO\(_6\) nanosheets on the surface of DE.

Figure 2 shows the XRD patterns of pure Bi\(_2\)MoO\(_6\), Bi\(_2\)MoO\(_6@3%\)DE, Bi\(_2\)MoO\(_6@6%\)DE, Bi\(_2\)MoO\(_6@9%\)DE and purified DE. According to the XRD results of this reference [34], the diffraction peak of various mineral, including montmorillonite, feldspar, quartz and muscovite phase can be observed in the figure S2, which is consistent with that reported in the literature. The diffraction peaks at 2θ = 10.3°, 28.3°, 32.6°, 33.2°, 35.9°, 46.7°, 55.6°, 56.1° and 58.4° correspond to (020), (131), (002), (060), (151), (202), (331), (133) and (191) crystal planes of Bi\(_2\)MoO\(_6\) (JCPDS:76-2388), respectively. The diffraction peaks of Bi\(_2\)MoO\(_6\) are found in XRD patterns of all composite samples. However, it is hard to observe the diffraction peaks of diatomite in composite samples because of its weak crystalline and low content.

The morphologies of purified DE and Bi\(_2\)MoO\(_6@DE\) were characterized by SEM and TEM. As shown in figure 3(a), the purified DE has a smooth disc-like porous structure, and it is available to supporting semiconductor catalyst. The SEM and local enlargement picture of Bi\(_2\)MoO\(_6@DE\) are shown in figures 3(b) and (c). Bi\(_2\)MoO\(_6\) nanosheets are evenly distributed on DE, formed a good composite photocatalyst. The EDS result proves the existence of Bi, Mo, O and Si in composites (figure 3(d)). The TEM pictures of Bi\(_2\)MoO\(_6@DE\) are displayed in figures 3(e) to (f). Figure 3(e) shows that Bi\(_2\)MoO\(_6\) nanosheets are uniformly deposited on the diatomite disc without completely covering the pores of diatomite, forming an advanced structure, which can facilitate the adsorption and photocatalytic degradation of pollutants. Figure 3(f) revealed that the size of Bi\(_2\)MoO\(_6\) nanosheets is about 50 nm, and these nanosheets exhibit an irregular layered structure. Figure 3(g) displays the HRTEM picture of the Bi\(_2\)MoO\(_6\), and the lattice spacing is 0.315 nm, corresponding to the 131 crystal plane of Bi\(_2\)MoO\(_6\). The SEM elemental mapping pictures of Bi\(_2\)MoO\(_6@6%\)DE are displayed in figures 3(h)–(l). The Bi and Mo elements are dispersed on the right side, and the Si and O elements are homogeneously dispersed.
The element chemical states in the Bi$_2$MoO$_6$@DE composite are studied by XPS test. The full scan XPS spectrum of Bi$_2$MoO$_6$@DE composite is shown in figure S3. The peaks of Bi 4f$_{7/2}$ at 159.3 eV and Bi 4f$_{5/2}$ at 164.6 eV can be assigned to Bi$^{3+}$ in the Bi$_2$MoO$_6$@DE composite (figure 4(a)) [35, 36]. The HR-XPS of Mo 3d
reveals the signals at 232.56 eV and 235.7 eV, which can be related to Mo 3d\textsubscript{5}/2 and Mo 3d\textsubscript{3}/2 (figure 4(b)) [37–39]. The peak of Si 2p at 103.8 eV should be attributed to diatomite (figure 4(c)) [30]. Based on Gaussian curve fitting, the HR-XPS curve of O 1s is split into two peaks, the binding energies at 530.3 eV and 532.5 eV can be attributed to Mo–O and O–H, respectively (figure 4(d)).

To evaluate the optical behavior of composite samples, we characterized them by UV–vis DRS (figure 5(a)). The visible absorption range of pure Bi\textsubscript{2}MoO\textsubscript{6} is between 400 and 500 nm. Moreover, the absorption intensity decreases slightly as the amount of diatomite increases in the composites. It indicates that as a support material,
Diatomite has no ability to absorb visible light. Based on the Kubelka-Munk function, the calculated band gaps of Bi$_2$MoO$_6$, Bi$_2$MoO$_6$@6%DE are 2.72 eV and 2.75 eV (figure 5(b)).

The visible-light-driven photocatalytic activities of pure Bi$_2$MoO$_6$ and Bi$_2$MoO$_6$@DE were investigated by Cr(VI) reduction and TC degradation. Figure 6 shows the photoreduction results of Cr(VI). As showed in figure 6(a), by using pure Bi$_2$MoO$_6$, the reduced efficiency of Cr(VI) can approach 71.7% after 60 min reaction. Comparing with pure Bi$_2$MoO$_6$, the photo reduction efficiency increases gradually with the content of diatomite increases in the composites. When the diatomite mass percentage reaches 6%, the composite photocatalysts (namely, Bi$_2$MoO$_6$@6%DE) has the highest activity, the maximum photo reduction efficiency reaches about 90.1% within 60 min. This should be related to diatomite provided more photocatalytic activities due to its unique porous structure. Yet, with the content of diatomite increased to 9%, the photo reduction rate decreased to 85.5%. This should be related to the visible light absorption capacity of Bi$_2$MoO$_6$@9%DE is lower than that of diatomite.

Figure 6. (a) Photocatalytic degradation curves of Cr(VI) over DE, pure Bi$_2$MoO$_6$ and Bi$_2$MoO$_6$@DE composites under the irradiation of Visible light ($\lambda > 400$ nm), (b) Time-dependent UV–vis absorption spectra recorded during the reduction Cr(VI) catalyzed by Bi$_2$MoO$_6$@6%DE, (c) and (d) The rate of degradation and Kinetic study of degradation of Cr(VI) by DE, pure Bi$_2$MoO$_6$ and Bi$_2$MoO$_6$@DE composites. (e) Five-cycles of the photocatalytic reduction of Cr(VI) using Bi$_2$MoO$_6$@6%DE as the photocatalyst under Visible-light irradiation for 60 min, (f) Photocatalytic degradation of Cr(VI) over Bi$_2$MoO$_6$@6%DE photocatalysts alone and with the addition of TEOA or IPA.
Bi$_2$MoO$_6$@6%DE (Figure 5(a)). Figure 6(b) shows the temporal evolution of absorption spectra of pollutants Cr(VI) by Bi$_2$MoO$_6$@6%DE composite photocatalysts. The peak intensity of Cr(VI) decreases gradually, which indicates the Cr(VI) is degraded. Figures 6(c) and (d) show the calculated reaction rate constant $k$ [$\ln(C_0/C_t) = kt$] of catalysts. The reaction rate constant increase gradually with the content of diatomite from 0 to 6%, and the $k_{app}$ value of the Bi$_2$MoO$_6$@6%DE reaches the maximum about 0.04358 min$^{-1}$. However, in comparison with Bi$_2$MoO$_6$@6%DE, the $k_{app}$ value for Bi$_2$MoO$_6$@9%DE decreases to 0.03222 min$^{-1}$, which coincides with the photo reduction efficiency result of Cr(VI). As a photocatalyst, the samples recycling performance has been evaluated, and the result shown in figures 6(e) and S4. After five cyclic tests, the reduction rate decreased from 93.1% to 92.5%. This slight decrease was negligible and proved the stability of the catalyst. To investigate the photodegradation mechanism of Bi$_2$MoO$_6$@DE composite photocatalyst to reduce Cr(VI), triethanolamine (TEOA) and isopropanol (IPA) were added into solution before photocatalytic experiment, as
scavengers of photogenerated holes (h\(^+\)) and ·OH\(^-\), respectively. The Bi\(_2\)MoO\(_6@6\)%DE was selected for the testing experiments, and the testing results are displayed in figure 6(f). The reduction rate of Cr(VI) solution was almost the same as Bi\(_2\)MoO\(_6@6\)%DE after adding IPA and TEOA. These results indicate that the photocatalytic process is less affected by holes (h\(^+\)) and ·HO\(^-\). Therefore, the main active radicals in the reduction of Cr(VI) should be photogenerated electrons [40].

As showed in figure 7(a), by using pure Bi\(_2\)MoO\(_6\), the degradation rate of TC can only be achieved 30.5% after 120 min reaction. Comparing with pure Bi\(_2\)MoO\(_6\), the photodegradation efficiency increases gradually with the content of diatomite increases in the composites. And the composite photocatalysts achieved the highest activity (nearly 74.7% within 120 min) when the mass percentage of diatomite is 6% (Bi\(_2\)MoO\(_6@6\)%DE). Yet, the degradation rate of TC decrease to 61.4% with the content of diatomite increased to 9%. Figure 7(b) shows the temporal evolution of absorption spectra of pollutants TC by Bi\(_2\)MoO\(_6@6\)%DE composite photocatalysts. The peak intensity of TC decreases gradually, which indicates the TC is degraded. Figures 7(c) and (d) show the calculated reaction rate constant \(k [\ln(C_0/C_t) = kt]\) of catalysts. The reaction rate constant increase gradually with the content of diatomite from 0 to 6%, and the \(k_{app}\) value of the Bi\(_2\)MoO\(_6@6\)%DE reaches the maximum about 0.01098 min\(^{-1}\). However, in comparison with Bi\(_2\)MoO\(_6@6\)%DE, the \(k_{app}\) value for Bi\(_2\)MoO\(_6@9\)%DE decreases to 0.00761 min\(^{-1}\), which coincides with the photodegradation efficiency result of TC. As a photocatalyst, the samples recycling performance has been evaluated, and the result shown in figures 7(e) and S5. After five cyclic tests, the reduction rate decreased from 74.7% to 73.1%, which shows super high stability of Bi\(_2\)MoO\(_6@6\)%DE. To investigate the photodegradation mechanism of Bi\(_2\)MoO\(_6@DE\) composite photocatalyst to degrade TC, TEOA, IPA and benzoquinone (BQ) were introduced into the TC solution before visible light irradiation, as scavengers of holes (h\(^+\)), ·OH\(^-\) and O\(_2\), respectively. The Bi\(_2\)MoO\(_6@6\)%DE was selected for the testing experiments, and the testing result is shown in figure 7(f). The degradation rate of TC solution decreased to 65.4%, 38.8% and 16.7% after adding IPA, BQ and TEOA. These results indicate that ·HO\(^-\), O\(_2\) and holes (h\(^+\)) are the mainly reactive radicals in TC solution, and photogenerated holes (h\(^+\)) have the greatest influence on the removal process of TC.

Based on free radical trapping tests results and related literature [41–44], a possible reaction mechanism is proposed. As showed in figure 8, upon visible light irradiation, the photogenerated electrons (e\(^-\)) on the valence band (VB) of Bi\(_2\)MoO\(_6\) can easily move to the conduction band (CB), whereas photogenerated holes (h\(^+\)) remain in the VB. The photoexcited electrons move to the surface of diatomite via the interface between diatomite and Bi\(_2\)MoO\(_6\). The absorbed K\(_2\)Cr\(_2\)O\(_7\) was reduced to Cr(III) by e\(^-\) on the surface of diatomite. The photoexcited electrons can be captured by oxygen molecules to produce O\(_2\), the O\(_2\) and ·HO\(^-\), holes (h\(^+\)) together promote the degradation of TC. It should be noted in particular that holes (h\(^+\)) are the mainly reactive radicals in TC solution.

### 4. Conclusion

In summary, the obtained Bi\(_2\)MoO\(_6@DE\) performed excellent visible light photocatalytic activities toward Cr(VI) reduction and TC degradation. The high photocatalytic performance of this material can be related to the following reasons. Bi\(_2\)MoO\(_6\) with proper band gap can effectively absorb visible light. Diatomite can effectively avoid the agglomeration of Bi\(_2\)MoO\(_6\) nanosheets, which is conducive to promoting the exposure of more active sites and the enlarge of specific surface area and result in high degradation efficient of Cr(VI) and TC. Based on the test of active radical capture, the photocatalytic degradation pathway of Cr(VI) and TC were put forward. The recycling test shows that Bi\(_2\)MoO\(_6@DE\) composite photocatalyst has super high stability. This non-toxic,
harmless cheap and easily available composite photocatalyst has wide application prospects for environmental treatment.

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