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Enhanced visible light photocatalytic degradation of Rhodamine B by Bi/Bi₂MoO₆ hollow microsphere composites†

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Bi/Bi₂MoO₆ hollow microsphere (BMO-HMS) composites were successfully synthesized *via* a microwaveassisted reaction of a Bi₂MoO₆ precursor in an ethylene glycol solution using a microwave synthesis system and subsequent annealing in a nitrogen atmosphere. The morphology, structure and photocatalytic performance of the composites in the degradation of Rhodamine B (RhB) were characterized by scanning electron microscopy, X-ray diffraction, electrochemical impedance spectra, UV-vis absorption spectroscopy, Raman spectroscopy and nitrogen adsorption–desorption, respectively. The results show that the BMO-HMS composites exhibit enhanced photocatalytic performance in the degradation of RhB with a maximum degradation rate of 91% under visible light irradiation compared with the pure Bi₂MoO₆. The improved photocatalytic performance is ascribed to the enhanced light absorption and the reduced electron–hole pair recombination with the presence of Bi in the composites.

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1. Introduction

Over the past few decades, environmental pollution and energy shortages have become the focus of world attention.^{1,2} As one of the most promising solutions for these issues, semiconductor photocatalysis has attracted much attention, because it is a green technology for the degradation of organic pollutants, reduction of heavy metal ions, air purification and hydrogen production.³⁻¹⁰ However, the traditional photocatalysts such as TiO₂ only exhibit high photocatalytic activity under ultraviolet light irradiation, which limits their practical applications.¹¹⁻¹³ To better utilize solar light which is composed of about 45% visible light, it is desirable to exploit novel visible light-sensitive semiconductor photocatalysts.

Bi₂MoO₆, as an aurivillius oxide semiconductor with a narrow band gap of 2.66 eV, has attracted considerable attention because of its non-toxicity and high quantum yield for photocatalysis under visible light irradiation.^{14–17} It is known that the photocatalytic performance depends on the morphology and microstructure of photocatalysts.^{18,19} Bi₂MoO₆ photocatalysts with various morphologies such as nanosheets,²⁰ nanoparticles,²¹ microboxes²² and microspheres²³ have been synthesized, which showed different photocatalytic performances in the degradation of organic pollutants under visible light irradiation. Among these structures, hollow microsphere (HMS) have attracted great interest due to its high surface area, low density and effective light-harvesting property for wide application in supercapacitors, lithium ion batteries and photocatalysis.24-28 Miao et al.29 synthesized Bi2MOO6 HMS by aerosol-spraying and found that it exhibited high photocatalytic activity in the degradation of Rhodamine B (RhB) under visible light irradiation. Tian et al.23 and Yin et al.³⁰ prepared Bi₂MoO₆ HMS using solvothermal and hard-template method, which showed much better photocatalytic performance in the degradation of RhB and phenol under visible light irradiation than solid Bi₂MoO₆. However, the quick recombination of photo-generated charge carriers still exists in Bi₂MoO₆ HMS, which decreases its photocatalytic performance.14

Bi, as a semi-metal with high carrier mobility, has attracted extensive interest as good thermoelectric material and catalyst.³¹⁻³⁴ Recently, many promising studies have been reported to combine Bi with Bi_2O_3 or TiO_2 for photocatalysis, and the incorporation of Bi was found to enhance the photocatalytic performance of Bi_2O_3 or TiO_2 obviously due to the enhanced light absorption and reduced recombination of photogenerated electron-hole pairs.^{32,35,36} Therefore, development of composite material based on Bi and Bi_2MOO_6 should be a promising method for more effective photocatalysis. Unfortunately, so far little attention has been focused on the application of Bi/Bi_2MOO_6 (BMO) composites in photocatalysis.

In this work, BMO-HMS composites were synthesized through microwave-assisted reaction of Bi₂MoO₆ precursor in an ethylene glycol (EG) solution and subsequent annealing in

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nitrogen atmosphere. The possible mechanism for the formation of BMO-HMS composites was discussed. Due to special HMS composite structure of the BMO-HMS composites exhibit excellent photocatalytic performance under visible light irradiation.

2. Experimental

2.1 Synthesis of BMO-HMS

All the reagents were analytical grade and used without further purification. 0.121 g Na₂MoO₄·2H₂O was dissolved in 10 mL EG to obtain solution A. A certain amount of glucose and 0.485 g Bi(NO₃)₃·5H₂O were dissolved in 10 mL EG to obtain solution B. Then solution A was added into solution B under vigorous stirring and stirred for 30 min to produce a uniform transparent mixture solution. Subsequently, the mixture solution was placed in a 35 mL microwave tube and then put into an automated focused microwave system (Explorer-48, CEM Co.) and treated at 160 °C with a microwave irradiation power of 150 W for 10 min. The samples synthesized using 0, 0.02, 0.1, 0.2 and 0.4 mmol glucose, named as Bi₂MoO₆, BMO-1, BMO-2, BMO-3 and BMO-4 were isolated by washing three times with distilled water, dried in a vacuum oven at 80 °C for 24 h, and then annealed at 450 °C in nitrogen atmosphere for 120 min. For the electrochemical impedance spectra (EIS) testing, the as-synthesized composites with 5 wt% cellulose binder were homogenously mixed in terpineol to form a slurry. Then, the resultant slurries were coated on the FTO using a screen-printing approach. Finally, these prepared electrodes were dried at 100 °C for 30 min.

2.2 Characterization

The surface morphology, structure and composition of the samples were characterized by field-emission scanning electron microscopy (FESEM, Hitachi S-4800), X-ray diffraction (XRD, Holland Panalytical PRO PW3040/60) with Cu-Ka radiation (V = 30 kV, I = 25 mA), and energy dispersive X-ray spectroscopy (EDS, JEM-2100), and Raman spectroscopy (Renishaw inVia), respectively. The Brunauer-Emmett-Teller (BET) specific surface areas (S_{BET}) of the samples were evaluated on the basis of nitrogen adsorption isotherms measured at 77 K using a BELSORP-max nitrogen adsorption apparatus (Micrometitics, Norcross, GA). The diffuse absorption spectra of the samples were recorded on a UV-vis spectrophotometer (Hitachi U-3900) equipped with an integrated sphere attachment. EIS measurement was carried out on an electrochemical workstation (AUTOLAB PGSTAT302N) under dark condition using a three electrode configuration with the as-prepared films as working electrodes, a Pt foil as counter electrode and a standard calomel electrode as reference electrode. The electrolyte was 10 mg L⁻¹ RhB aqueous solution. EIS were recorded in the frequency range of 0.1 Hz-1 MHz, and the applied bias voltage and ac amplitude were set at open-circuit voltage and 10 mV.

2.3 Photocatalytic experiments

The photocatalytic performance of the samples was evaluated through a photochemical reactor (Bilon Co., Ltd). The distance between metal halogen lamp and quartz tube is 60 mm, and the filter size ($\lambda > 400$ nm) is 30 mm \times 100 mm. The samples (80 mg) were dispersed in 80 mL RhB aqueous solutions (10 mg L^{-1}). The mixed suspensions were first magnetically stirred in the dark for 30 min to reach the adsorption-desorption equilibrium. Under ambient conditions and stirring, the mixed suspension was exposed to the visible irradiation produced by a 400 W metal halogen lamp ($\lambda > 400$ nm) and the UV irradiation produced by a 500 W high pressure Hg lamp with the main wave crest at 365 nm (no filter), respectively. At certain time intervals, 2 mL of the mixed suspensions were extracted and centrifuged to remove the photocatalysts. The filtrates were analysed by recording the UV-vis spectra of RhB using Hitachi U-3900 UV-vis spectrophotometer.

3. Results and discussion

The XRD patterns of Bi₂MoO₆, BMO-1, BMO-2 and BMO-3 are shown in Fig. 1. Bi₂MoO₆ exhibits several diffraction peaks at 10.9°, 23.5°, 28.3°, 32.7°, 33.2°, 36.1°, 46.7°, 47.2°, 55.5°, 56.3° and 58.5°, indexed to (020), (111), (131), (200), (060), (151), (202), (062), (133), (191) and (262) crystal planes of Bi_2MoO_6 (JCPDS 21-0102).37,38 Compared with Bi2MoO6, the new diffraction peaks at 27.8° , 38.0° and 39.6° , corresponding to the (012), (104) and (110) planes of Bi (JPCDS 44-1246), appear in XRD patterns of BMO-1, BMO-2, BMO-3 and BMO-4, which confirms the existence of Bi in the BMO composites. It should be noticed that the diffraction peaks of Bi enhance with the increase of glucose in precursor solution, which indicates that more Bi was reduced. Similar result is also reported by others.^{31,32} Moreover, the XRD pattern of BMO-2 before annealing is also provided in Fig. 1 for comparison. It is observed that there is no diffraction peak of Bi in BMO-2 before annealing, indicating that the Bi was generated after annealing.

Fig. 2(a)–(e) show FESEM images of Bi_2MOO_6 , BMO-1, BMO-2, BMO-3 and BMO-4. Bi_2MOO_6 nanosheets show a self-assembly



Fig. 1 XRD patterns of (a) Bi_2MoO_{6} , (b) BMO-1, (c) BMO-2 (annealed and unannealed), (d) BMO-3 and (e) BMO-4.



Fig. 2 FESEM images of (a) $Bi_2MoO_{6^r}$ (b) BMO-1, (c) BMO-2, (d) BMO-3 and (e) BMO-4, (f) EDS spectrum of BMO-2.

coralline structure. It can be observed from the Fig. 2(b)–(e) that the BMO samples are entirely composed of spheres with an average diameter of about 500 nm. The BMO spheres display hollow structure with cage-like pores on the outer shell. The walls of BMO-HMS consist of nanoparticles with size of approximately 50 nm. The result indicates that the glucose plays a key role in determining the morphology of BMO samples. Meanwhile, the shell thickness was reported to increase with the increase of glucose content in precursor solution because of the enhanced density of condensed glucose and bimetallic complexes.²⁹ The BMO-2 sample was identified by EDS linked to FESEM, as shown in Fig. 2(f). The peaks of Bi, Mo and O in EDS spectrum prove the existence of Bi₂MOO₆. The atom ratio of Bi and Mo is 2.2, indicating the presence of excessive Bi in the BMO-2 sample, which is in agreement with the XRD result.

To well understand the formation mechanism of BMO-HMS, the sample synthesized using 0.1 mmol glucose at different microwave reaction times were examined by SEM. Fig. 3(a) and



Fig. 3 FESEM images of the samples obtained at different microwave treatment times: (a) 1 min, (b) 10 min.

(b) show the FESEM images of the samples prepared *via* microwave treatment for 1 min and 10 min, respectively. It can be found that the morphology is dependent on the microwave reaction time. After microwave treatment for 1 min, microspheres with a smooth surface and a diameter of about 300 nm were obtained, as shown in Fig. 3(a). When the microwave reaction time was prolonged to 10 min, hierarchical flower-like BMO-HMS was obtained, as shown in Fig. 3(b). The flower-like BMO-HMS would further crystallize in annealing process. Finally, the BMO-HMS with cage-like pores on the outer shell consisting of nanoparticles was formed after annealing in nitrogen (Fig. 2(c)).

The possible growth mechanism of BMO-HMS is proposed in Scheme 1. The Mo^{6^+} and Bi^{3^+} were co-coordinated to be complex compounds with the EG.^{23,29} At the initial reaction stage (1 min), the Bi_2MoO_6 nanoparticles tended to assemble into spherical agglomerates driven by reducing the surface energy of nanoparticles. With increased reaction time (10 min), the formed microspheres dissolved and recrystallized, and the hierarchical flower-like BMO-HMS was formed through the mass diffusion and Ostwald ripening process.³⁹ Moreover, the chelation occurred between glucose and Bi^{3^+} ions, which led to a stable five-membered ring coordinated cation.³² During the following process of calcination, the five-membered ring coordinated cation could be decomposed and the Bi^{3^+} was reduced to Bi, leading to the formation of BMO-HMS with cage-like pores on the outer shell.²⁹



Scheme 1 The formation mechanism of BMO-HMS composite.



Fig. 4 Raman spectrum of BMO-2.

Fig. 4 shows the Raman spectrum of BMO-2. The A_{1g} peak at 802 cm⁻¹ is assigned to the symmetric stretch of a MoO₆ octahedron. The A_{1g} mode at 845 cm⁻¹ shows a characteristic of orthorhombic distortion of MoO₆ octahedron in Bi₂MoO₆ with aurivillius structure of layered slabs (Bi₂O₂²⁺) connected through the corner sharing of distorted MoO₆ octahedra.⁴⁰ The peaks at 145, 283, 354 cm⁻¹ are attributed to the bending modes of MoO₆ octahedral unit.⁴⁰ The weaker peak located at about 184 cm⁻¹ corresponds to second-order Raman scattering peaks of Bi.⁴¹ No characteristic peak of carbon is found in the Raman spectrum, indicating that carbon impurity was not generated after washing and annealing.

Nitrogen adsorption-desorption isotherms and pore size distribution curves (inset) of Bi_2MoO_6 and BMO-2 are displayed in Fig. 5, and the ones of other samples are shown in Fig. S1 ESI.[†] All of the samples show type IV isotherms with H₃ hysteresis loops.^{42,43} This behavior may be caused by the existence of non-rigid aggregates.⁴⁴ The specific surface areas of Bi_2MoO_6 , BMO-1, BMO-2, BMO-3 and BMO-4 are 9.85, 19.6, 17.8, 13.2 and 9.16 m² g⁻¹, respectively, which means that the glucose is helpful to increase the specific surface area of BMO-HMS. However, excessive glucose can decrease the specific surface area of BMO-HMS. The reason may be that the excessive glucose could reduce more Bi^{3+} to be Bi, which changes the porous structure of BMO-HMS.³⁵ The broad pore size distribution, as shown in the insets of Fig. 5 and S1,[†] indicates the existence of mesopores and macropores in these samples.

The UV-vis diffuse absorption spectra of Bi_2MoO_6 , BMO-1, BMO-2, BMO-3 and BMO-4 were measured using a UV-vis spectrophotometer with an integrating sphere (Hitachi U-3900), as shown in Fig. 6. The hollow structure is beneficial to the absorbance of BMO due to the multiple reflections, as shown in the inset of Fig. 6.⁴⁵ Therefore, the BMO-HMS composites exhibit higher absorbance than Bi_2MOO_6 . Furthermore, the absorbance of the BMO-HMS composites increases especially in visible light region with the increase of glucose content in precursor solution, possibly due to more Bi reduced in the BMO-HMS composites.³¹ Such an enhancement in the visible light absorbance of BMO-HMS is beneficial to the increase of photo-generated electrons and holes.¹²



Fig. 6 UV-vis diffuse absorption spectra of (a) Bi_2MOO_{6} , (b) BMO-1, (c) BMO-2, (d) BMO-3 and (e) BMO-4. Inset shows a schematic illustration of multiple reflections within the hollow structure.

The charge transfer and recombination behaviors of the samples were studied by analysing the EIS spectra under dark condition. Fig. 7 shows the typical Nyquist plots of Bi₂MoO₆, BMO-1, BMO-2, BMO-3 and BMO-4. The semicircle in the EIS spectra is ascribed to the contribution from the charge transfer resistance (R_{ct}) and constant phase element (CPE) at the photocatalyst/electrolyte interface.46 The inclined line, resulting from the Warburg impedance (Z_W) , corresponds to the ion diffusion process in the electrolyte. The corresponding equivalent circuit is shown in the inset of Fig. 7. It is clearly observed that the $R_{\rm ct}$ decreases with the increase of glucose content in precursor solution, possibly because more Bi in the BMO-HMS composite with the increase of the glucose content favors the electron transfer and suppresses the charge recombination.³⁵ Such an effect can be explained from the view of stepwise structure of energy levels constructed in BMO-HMS composites, as shown in Fig. 8. The conduction band (CB) and valence band (VB) of Bi₂MoO₆ is -0.32 V and 2.34 V (vs. NHE), respectively.^{16,17} The work function of Bi is -0.28 V (*vs.* NHE).⁴⁷ Such energy levels are beneficial for photo-induced electrons to transfer from the Bi₂MoO₆ CB to the Bi, which could efficiently separate the photoinduced electrons and hinder the charge recombination in electron-transfer processes, thus enhance the photocatalytic



Fig. 5 Nitrogen adsorption–desorption isotherms and corresponding pore size distribution curves (inset) of (a) Bi_2MoO_6 and (b) BMO-2.



Fig. 7 Nyquist plots of (a) Bi_2MoO_6 , (b) BMO-1, (c) BMO-2, (d) BMO-3 and (e) BMO-4. Inset is the corresponding equivalent circuit model.



Fig. 8 Schematic diagram of energy levels of Bi₂MoO₆ and Bi.

performance.^{48–50} However, when the glucose content in precursor solution is further increased (BMO-3 and BMO-4), the $R_{\rm ct}$ increases, which is possibly because excessive Bi in the composite acts as recombination centre and promotes the recombination of photo-generated electron–hole pairs in Bi.³²

Photocatalytic degradation of RhB by Bi2MoO6, BMO-1, BMO-2, BMO-3, BMO-4 and commercial TiO₂ (P25, Degussa) were performed under visible light irradiation, as shown in Fig. 9. Photocatalytic degradation of RhB by BMO-2 was also performed under UV light irradiation for comparison. The normalized temporal concentration changes (C/C_0) of RhB during the photocatalytic process are proportional to the normalized maximum absorbance (A/A_0) , which can be derived from the change in the RhB absorption profile at a given time interval. The results of corresponding adsorption experiments before photocatalysis were shown in Fig. S2 ESI,† in which no significant difference between adsorption capacities of the Bi₂MoO₆ and BMO-HMS composites was observed. In Fig. 9, it can be seen that the concentration of RhB is hardly reduced under visible light irradiation in the absence of the photocatalysts and BMO-HMS composites exhibit better photocatalytic performance than Bi₂MoO₆ and P25. The photocatalytic performance of BMO-HMS composites depends on the glucose



Fig. 9 Photocatalytic degradation of RhB by (a) Bi_2MOO_6 , (b) BMO-1, (c) BMO-2, (d) BMO-3, (e) BMO-4, (f) P25 and (g) without photocatalysts under visible light irradiation, (h) photocatalytic degradation of RhB by BMO-2 under UV light irradiation.

content in precursor solution. The degradation rate of RhB for Bi_2MoO_6 is 66%. When the glucose is introduced into Bi_2MoO_6 precursor solution, the degradation rate of the sample (BMO-1) is increased to 73%, and reaches a maximum value of 91% for BMO-2. The enhancement of the photocatalytic performance should be mainly ascribed to the reduction in electron-hole pair recombination due to the stepwise energy level structure in the BMO-HMS composites and the increase in the light absorption with the presence of Bi, which have been confirmed by the EIS measurement and UV-vis absorption spectra.32,35 However, when the glucose content in precursor solution is further increased, the degradation rate is decreased to 79% and 53% for BMO-3 and BMO-4, which may be due to its increased recombination of photo-generated electron-hole pairs in Bi. Furthermore, the high degradation rate of RhB for BMO-2 under UV light irradiation indicates that BMO-2 is also an excellent UV light photocatalyst.

4. Conclusions

BMO-HMS composites were successfully synthesized *via* microwave-assisted method and subsequent annealing in nitrogen atmosphere, and their photocatalytic performances were investigated. The results show that (i) BMO-HMS composites exhibit better photocatalytic performance than Bi₂MoO₆, and their photocatalytic performances are related to the glucose content in precursor solution; (ii) BMO-2 achieves a highest RhB degradation rate of 91% at 120 min; (iii) the enhanced photocatalytic performance is ascribed to the increased light adsorption and reduced electron–hole pair recombination with the presence of Bi in the composites.

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