Synthesis of nano-Bi$_2$MoO$_6$/calcined mussel shell composite with enhanced visible light photocatalytic activity

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Abstract. In this study, a new nano-Bi$_2$MoO$_6$/calcined mussel shell composite photocatalyst was successfully prepared via a facile solvothermal method. Scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), and UV-vis diffuse reflection spectroscopy (DRS) were employed to investigate the morphology, crystal structure, optical properties. It was shown that the nanometer-scaled Bi$_2$MoO$_6$ crystals was assembled with calcined mussel powder, and forming a similar spheroid structure. The obtained samples were displayed higher photocatalytic activities than pure Bi$_2$MoO$_6$ for the degradation of MB under visible-light irradiation. Among them, the Bi$_2$MoO$_6$/calcined mussel shell mass ratio of 0.7 exhibited the highest activity, and the MB degradation efficiency reached up to 62.46% within 60 min. As a photocatalytic reactor, its recycling performance showed a good stability and reusability. This new composite photocatalyst material holds great promise in the engineering field for the environmental remediation.

1. Introduction

Dyeing wastewater discharged from many industries such as textiles, leather, paper and plastics is a serious contamination for environment. Without proper treatment, the release of these colored wastewater will destroy the ecological balance and threaten human’s health$^{[1]}$.

Semiconductor photocatalysis, as a green and energy-saving technology applied in the treatment of dyeing wastewater, has drawn considerable attention$^{[2,3]}$. Recently, a variety of bismuth-based semiconductor photocatalysts with high activity have been developed, such as BiVO$_4$$^{[4,5]}$, Bi$_2$WO$_6$$^{[6,7]}$, Bi$_2$MoO$_6$$^{[8,9]}$, BiOX (X = Cl, Br, I)$^{[10,11,12]}$, BiO(OH)$^{[13]}$, etc. Among these photocatalysts, Bi$_2$MoO$_6$ which has flower-like microspheres and hollow spheres, exhibited superior photocatalytic activity. Moreover, the hierarchical nanostructures have apparent advantages of facilitating molecular diffusion with enhancing light harvest and supplying abundant reactive site, which are crucial for improving the...
photocatalytic performance\[8\]. However, the photocatalytic activity of pristine Bi$_2$MoO$_6$ is still hindered by some drawbacks, such as the photo-corrosion and high recombination rate of electron-hole pairs. A variety of research has focused on studying hierarchical porous materials to be carrier for Bi$_2$MoO$_6$\[14,15\]. However, these materials are not only high cost and difficult to prepare.

Shells have attract more and more attention, because of their hierarchically ordered structure at multiscale levels\[16,17\]. The shells consists of about 95 weight % (wt %) of CaCO$_3$ and 5 wt % of organic materials\[18\]. And the organic and inorganic layers have a “brick-and-mortar” microstructure\[19\]. In our previous work, after calcining under inert gas at temperatures above 600°C, the organic material of shells will escape, CaCO$_3$, part of carbon and microelement form a special kind of skeleton materials, which is an excellent mesoporous carrier.

In this work, we report the synthesis of nano-Bi$_2$MoO$_6$/calcined mussel shell composite by simply depositing nanometer-scaled Bi$_2$MoO$_6$ onto the surface of calcined mussel shell. The effect of nano-Bi$_2$MoO$_6$/calcined mussel shell composite on photocatalytic activity was investigated by degrading Methylene blue (MB) dye under visible-light irradiation. The role of calcined mussel shell in Bi$_2$MoO$_6$/calcined mussel shell composite was also evaluated and discussed in details. Materials and methods

2. Experimental details

2.1 Materials
Mussel shells were collected from Shengsi, Zhejiang, China. Bi(NO$_3$)$_3$•5H$_2$O, Na$_2$MoO$_4$•H$_2$O, glycol and ethanol ( > 99.7%) were purchased from Sinopharm Chemical Reagent Co., Ltd. China. All chemicals were analytical grade and used as received without further purification.

2.2 Preparation of calcined mussel shell
The mussel shells were repeatedly washed several times with distilled water and then were dried overnight in oven at 80°C. The shell were calcined in a tubular furnace under nitrogen flow (100 mL min$^{-1}$) up to 700 °C with a rate of 10 °C/min, and the final temperature was hold for 3h. The dried mussel shells were ground into powder and sieved (particle size < 250μm). The obtained mussel shell powder and KOH powder was mixed at a mass ratio 1:1. Then the mixture was calcined in a tubular furnace under nitrogen flow (100 mL min$^{-1}$) up to 800°C with a rate of 10°C/min, and final temperature was hold for 3h. After cooling down to the room temperature, the obtained materials was washed with distilled water three times and dried at 80°C in oven for 12 h.

2.3 Preparation of Bi$_2$MoO$_6$/calcined mussel shell
The synthesis of Bi$_2$MoO$_6$/calcined mussel shell (B/C) adopt the solvothermal method\[20\]. 0.363 g Bi(NO$_3$)$_3$•5H$_2$O and 0.0907g Na$_2$MoO$_4$•2H$_2$O were dissolved in 7 ml ethylene glycol respectively. Then 0.098 g calcined mussel shell was dissolved in 20 ml ethanol. The three solutions were mixed together under magnetic stirring for 30 min. The solution was transfer into a Teflon-lined stainless steel autoclave, then heated to 160°C and maintained at this temperature for 12 h. After the autoclave cooling down to the room temperature, the obtained composite was washed with ethanol and distilled water three times, respectively. Finally the composite was dried at 60°C for 12 h in oven. The obtained product with the Bi$_2$MoO$_6$/calcined mussel shell mass ratio was 0.7/1 was denote B/C-70%. By adjusting the amount of calcined mussel shells, a series of Bi$_2$MoO$_6$/calcined mussel shell with different mass ratio (0:1, 0.6:1, 0.7:1, 0.8:1, 1:0 ) were obtained and denoted as calcined mussel shell, B/C-60%, B/C-70%, B/C-80%, and Bi$_2$MoO$_6$, respectively.

2.4 Characterization
The synthesized products were characterized with X-ray diffraction ( Ultima IV X-Ray Diffractometer, Rigaku Corporation, Japan), Fourier-transform infrared spectra(FTIR, Nicolet 6700, Thermo Fisher Scientific, USA), scanning electron microscopy (SEM, Hitachi S-4800, Hitachi, Japan) and UV-vis
diffuse reflectance spectra (DRS, UV 2600 spectrophotometer, Shimadzu, Japan).

2.5 Photocatalytic experiments
The photocatalytic activity of obtained samples were evaluated by degrading MB under 300W Xenon lamp light irradiation (Beijing NBeT Technology Co., Ltd). The temperature of the reaction system was kept constant by cycling cool water. Photocatalyst (15mg) was added into MB (50ml, 50mg/L) dye solution. Before light on, the suspension was stirred for 180min in the dark. During the photocatalytic test, 2mL suspension was collected at certain time and centrifuged for measure.

In the stability test, four cycles of MB degradation over B/C-70% were performed. After each cycle, the photocatalyst were washed with distilled water and dried at 60°C in an oven for 2 hour. After that, it was added into the fresh MB solution (50ml, 50mg/L) to initiate the reaction.

3. Results and Discussion

3.1 Structural and surface morphological studies
As it is shown in Fig 1, powder X-ray diffraction (XRD) pattern is employed to characterize the crystal structure and phase analysis of the as-prepared of five different samples. Diffraction peaks at about 29.405, 39.428, 43.200 and 47.46 could be perfectly indexed to the (104), (113), (202) and (018) crystal faces of CaCO3 (JCPDS Card No. 83-1762), respectively, which explains that shell powder may consists of calcium carbonate calcining 800°C. For pure Bi2MoO6, all the diffraction peaks in Fig. 1 could be indexed to the tetragonal phase of Bi2MoO6 (JCPDS no. 20-0102) [21]. Moreover, the characteristic peaks for mussel shell powder and Bi2MoO6 are all both observed, which indicates that Bi2MoO6 is successfully loaded on mussel shell powder.

![Figure 1. XRD patterns of Bi2MoO6, B/C-60%, B/C-70%, B/C-80%, and mussel shell powder.](image)

3.2 The FTIR spectra of samples
The FTIR spectra of as-prepared samples are presented in Fig. 2. The peaks on calcined mussel shell powder at 1424 cm⁻¹ and 872 cm⁻¹ attributed to characteristics absorption peaks of calcium carbonate. The fourier transform infrared (FTIR) spectrum of Bi2MoO6 sample contains a band at 736 cm⁻¹ is due to Mo(VI)-O tetrahedral stretching. A weak band appearing at 840 cm⁻¹ may be attributed to Mo = O
stretching vibration. The band appearing at 580 cm\(^{-1}\) may be ascribed to the bending mode of the MoO\(_6\)\(^{22,23}\). For the B/C sample (Fig. 2), characteristic peaks for calcined mussel shell powder and Bi\(_2\)MoO\(_6\) are all both observed, which indicates the successful formation of nano-Bi\(_2\)MoO\(_6\)/calcined mussel shell powder composite.

![Figure 2 FTIR spectra of Bi\(_2\)MoO\(_6\), B/C-60%, B/C-70%, B/C-80%, and calcined mussel shell.](image)

3.3 SEM of the as-prepared samples
The morphology of the obtained samples were illustrate by SEM (Fig. 3). The calcined mussel shell has some holes on the surface (Fig. 3-a). The pure Bi\(_2\)MoO\(_6\) consist of Hollow microspheres, average size around 1 to 2 \(\mu\)m (Fig. 3-b). In Fig. 3-5, they were illustrated that the nanoplates is assembled with calcined mussel powder, and forming a similar spheroid structure. As the increase of calcined mussel shell mass ratio, the spheroid structure will collapse.

![Figure 3 SEM images of calcined mussel shell (a), Bi\(_2\)MoO\(_6\)(b), B/C-60% (c), B/C-70% (d), and B/C-80% (e).](image)
3.4 UV-vis diffuse reflectance spectra

Fig. 4 shows the different photocatalytic performance of samples. It can be seen that the absorption edge of Bi$_2$MoO$_6$ could extend to 478 nm, which is corresponding to a band gap energy $E_g$ of about 2.59 eV. Moreover, the light absorption abilities of the B/C composites are different with different mussel shell powder contents, and the absorption edges of B/C-70% composites could reach the most severely red shifted among them, indicating that it may be an excellent photocatalyst in the photocatalytic degradation of organic pollutants.

![Figure 4. UV-vis DRS spectra of Bi$_2$MoO$_6$, B/C-60%, B/C-70%, B/C-80%, and mussel shell powder.](image)

3.5 Photocatalytic activity

The photocatalytic activity of the above samples are investigated by photocatalytic dye degradation under visible light irradiation. As it is shown in Fig. 5, there are evident differences of optical performance among different sample. Significantly, the highest photocatalytic activity is obtained by B/C-70%, which is appreciably higher than that of pure Bi$_2$MoO$_6$ and mussel shell powder.
Figure 5 Degradation efficiency of MB for Bi$_2$MoO$_6$, B/C-60%, B/C-70%, B/C-80%, and mussel shell powder.

What’s more, the actual photocatalytic process of MB for as-prepared samples fits well with the pseudo first-order kinetic model (Fig. 5), which is denoted as follows Eq.

$$\ln \left( \frac{C_t}{C_0} \right) = -kt$$

Where $C_0$ and $C_t$ are the MB concentrations in solution at times 0 and t, respectively, and k is the apparent first-order rate constant.

Concretely, B/C-70% shows higher photocatalytic activity than pure Bi$_2$MoO$_6$ and mussel shell powder with the maximum value of k, while the k is 0.017 min$^{-1}$. Based on the results, the formation of the heterojunction between Bi$_2$MoO$_6$ and mussel shell powder may increases the transfer and separation of electron–hole pairs, which could improve photocatalytic performance of sample.
3.6 Recyclability studies

The recyclability experiments of the photocatalyst are implemented to evaluate the photocatalytic efficiency of the B/C-70%. As shown in Fig 7, the photocatalytic performance of B/C-70% shows no distinct decline after four continuous experiments. The photocatalytic degradation of MB for B/C-70% could still reach at 60.12%, indicating that B/C-70% has stability and efficiency to be used as a good photocatalyst.

Figure 6. Kinetic process of MB degradation for Bi$_2$MoO$_6$, B/C-60%, B/C-70%, B/C-80%, and mussel shell powder.

Figure 7. Photodegradation of MB solution with a composite photocatalyst B/C-70% in different testing cycles.
4. Conclusion
In summary we have fabricated Bi$_2$MoO$_6$/calcined mussel shell by a facile method. As shown in our study, the nanometer-scaled Bi$_2$MoO$_6$ crystals was assembled with calcined mussel powder, and forming a similar spheroid structure. Among all the samples, the Bi$_2$MoO$_6$/calcined mussel shell composite mass ratio of 0.7/1 achieved the best photocatalytic activity, and the MB degradation efficiency reached up to 62.46% within 60 min. The excellent photocatalytic property could be ascribed to the synergistic effect of Bi$_2$MoO$_6$ and calcined mussel shell powder. As a photocatalytic reactor, its recycling performance showed a good stability and reusability. This new composite photocatalyst has great potential in the engineering field for the environmental remediation.

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