Mussel Shell-Supported Yttrium-doped Bi$_2$MoO$_6$ Composite with Superior Visible-Light Photocatalytic Performance

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Abstract: A series of Yttrium (Y)-doped Bi$_2$MoO$_6$ composites with calcined mussel shell powder (CMS) as supports were synthesized using a solvothermal method. The as-prepared samples were analyzed using multiple techniques to investigate their microscopic morphology, composition structure, and optical properties. The photocatalytic performance of the as-prepared samples was assessed via examining their capacity to degrade Rhodamine B (RhB) under visible-light irradiation. The photocatalytic data showed that the Y-doped Bi$_2$MoO$_6$/CMS composites exhibited better photocatalytic activity compared to pure Bi$_2$MoO$_6$ and undoped Bi$_2$MoO$_6$/CMS samples. Among the samples, the 0.5%Y-doped Bi$_2$MoO$_6$/CMS (0.5%Y-BC) showed the highest photocatalytic activity, achieving a maximum degradation rate of 99.7% within 60 min. This could be attributed to highly reactive sites due to Y doping, a narrower band gap, and a lower recombination rate of photoinduced electron–hole pairs. Additionally, the 0.5%Y-BC photocatalyst exhibited excellent stability and reusability properties even after four cycles, making it suitable for practical applications. The findings provided a feasible synthesis of nanocomposite photocatalysts with outstanding properties for organic pollutant removal from the solution system.

Keywords: Bi$_2$MoO$_6$; yttrium; mussel shell; visible-light photocatalysis; dye degradation

1. Introduction

Environmental pollution caused by organic dyes has been a longstanding and pressing concern, prompting researchers and scientists to seek effective wastewater treatment methods [1]. Among the various technologies available, photocatalytic technology has emerged as a promising method for pollution control due to its numerous advantages, including its ease in preparation, cost-effectiveness, minimal energy consumption, remarkable degradation efficiency, and outstanding safety and stability [2–7]. As a result, research on photocatalytic materials has become a central focus [8,9].

Bismuth molybdate (Bi$_2$MoO$_6$) has garnered significant attention as a photocatalyst due to its unique layered structure. The structure consists of [Bi$_2$O$_6$]$^{2+}$ slices and Mo$_6$ octahedra that share corner oxygen atoms [10]. The conduction band in Bi$_2$MoO$_6$ is primarily composed of Mo3d orbitals, while the valence band is formed via the hybridization of Bi 6s and O2p orbitals [11]. This special band structure results in Bi$_2$MoO$_6$ having a relatively narrow band gap ranging from 2.5 to 2.9 eV [12]. Additionally, Bi$_2$MoO$_6$ exhibits exceptional chemical stability, non-toxicity, and good corrosion resistance, making it a promising candidate in the field of photocatalysis [13,14]. However, its high recombination rate of photo-generated electron and hole pairs leads to poor catalytic performance, limiting its application [15]. To enhance the efficiency of Bi$_2$MoO$_6$ in photocatalytic reac-
tions, various modification techniques have been utilized, including morphological control, semiconductor combination, and element doping [16]. Among these approaches, element doping is a commonly used method to reduce the band gap energy and inhibit the recombination of photo-generated electrons and holes [17,18].

Rare earth ions possess a rich 4f electron configuration, and exhibit unique optical properties that have the potential to improve the photocatalytic activity of semiconductors [19,20]. Due to their similar ionic radii to bismuth ions, rare earth metal ions can be easily dispersed in Bi₂MoO₆, making them an effective approach to improve photocatalytic activity [21]. Several experiments have been carried out to evaluate the photocatalytic efficiency of Bi₂MoO₆ doped with rare earth metals such as Eu, Zr, Ce, Ho, Yb, Gd, Lu, Tb, Er, and Sm [22–25]. Among these metals, yttrium has gained attention due to its favorable characteristics, including increased photo absorption capacity and the ability to trap photo-excited electrons. These attributes can assist in reducing the rate of photogenerated electron–hole pair recombination in the photocatalyst [26,27]. For instance, in a study conducted by Vaddi et al., it was shown that doping ZnO nanorods with yttrium resulted in a significant reduction in their bandgap, which in turn led to an improvement in their photodegradation activity [28]. Similarly, Vaddi et al. used a solvothermal method to synthesize Yttrium-doped BiOF/RGO, and found that Y³⁺ ions had a synergistic effect in reducing the electron–hole recombination rate of BiOF with RGO [29]. However, to the best of our knowledge, no study has been carried out on Yttrium-doped Bi₂MoO₆.

In recent years, the utilization of waste biomass materials for the preparation of photocatalyst supports has become a central research topic due to their low cost, high efficiency, and renewability [30–34], such as egg shell [35], coconut shell [36], and mussel shell [37–39]. Among these, mussel shell, a major byproduct of the mussel aquaculture industry, is usually discarded, leading to environmental pollution. However, mussel shell is naturally biomineralized material, characterized by a substantial presence of calcium carbonate and a distinctive “brick-mud” structure [40,41]. Moreover, they contain various trace metal elements, rendering them well-suited for the development of high-value-added products [37,42]. Several studies have indicated that shells could serve as carriers for photocatalysts due to their special microstructure [37–39]. The trace metal elements in the shell can act as modifiers to enhance the catalyst’s performance [37]. Our previous study has demonstrated that the mussel shell can effectively disperse the photocatalyst and prevent its aggregation, to enhance electron transport and improve the photocatalytic activity [43]. We intended to further enhance the photocatalytic performance of the composite catalyst by doping rare earth elements.

In this study, we prepared a novel ternary Y-doped Bi₂MoO₆/CMS composite using the solvothermal method. We examined the effect of yttrium content on the chemical composition, morphology, and optical properties. Additionally, we evaluated the photocatalytic activities, stability, and reusability of samples via degrading RhB under visible light irradiation. Finally, we explored the photocatalytic degradation mechanism through active species trapping experiments.

2. Materials and Methods

2.1. Materials

The mussel shells were collected from Shengsi Shunda Seafood Co., Ltd. in Zhejiang Province, China. They were washed thoroughly with distilled water to remove any surface impurities.

Bismuth nitrate pentahydrate (Bi(NO₃)₃·5H₂O, 99%), sodium molybdate (Na₂MoO₄, 99%), Yttrium Nitrate Hexahydrate (Y(NO₃)₃·6H₂O, 99%), ethanol (>99.7%), glycol and hydrochloric acid were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Rhodamine B (RhB, C₂₈H₃₁N₂O₃Cl) was obtained from Beijing Chemical Reagent Co., Ltd. (Beijing, China). All chemicals were analytical grade and used without further purification.
2.2. Preparation of Y-Doped BiMoO₆/CMS Photocatalyst

Initially, the pretreated mussel shells were immersed with 0.1% HCl for 24 h, washed with distilled water until neutral, and dried at 80 °C in the oven for 4 h. The dried mussel shells were calcined at 900 °C for 3 h in a tube furnace with high-purity nitrogen (N₂, 99.99%) flowing into the furnace at a rate of 100 mL/min. The resulting calcined sample was cooled, ground into powder (100 mesh), and named CMS.

Next, 0.363 g Bi(NO₃)₃·5H₂O and 0.0907 g Na₂MoO₄·2H₂O were dissolved in a 7 mL ethylene glycol solution via sonication for 30 min. Different amounts of Y(NO₃)₃·6H₂O were dissolved in 10 mL absolute ethanol, and slowly added dropwise to the Bi-Mo solution to obtain a mixed solution I with a molar ratio of Y to Bi of 0.063%, 0.125%, 0.25%, 0.5%, and 1%, respectively. Simultaneously, 0.1306 g CMS powder was dispersed in 10 mL of absolute ethanol for 1 h using ultrasonic treatment. The prepared solution I was then slowly added to the CMS suspension under continuous stirring for 2 h to obtain a mixed solution II. The mixed solution II was transferred into a 50 mL Teflon-lined stainless-steel autoclave, heated at 160 °C for 12 h, and cooled to room temperature. Finally, the as-prepared sample was filtered, washed with absolute ethanol and deionized water several times. Then, the material was dried in an oven at 60 °C for 12 h, and further pyrolyzed at 400 °C for 120 min in a tube furnace under a nitrogen atmosphere, while the heating rate was set at 10 °C/min at a nitrogen flow rate of 100 mL/min to produce the Y-doped Bi:MoO₆/CMS composite. Different molar ratios of Y to Bi were prepared using a similar method and named 0.063%Y-BC, 0.125%Y-BC, 0.25%Y-BC, 0.5%Y-BC, and 0.1%Y-BC, accordingly. As a reference, pure Bi:MoO₆ was synthesized under a similar procedure without the addition of CMS and Y(NO₃)₃·6H₂O, and Bi:MoO₆/CMS was synthesized without the use of Y(NO₃)₃·6H₂O.

2.3. Characterization

The surface morphologies of the samples were examined using scanning electron microscopy (SEM, Hitachi S-4800, Tokyo, Japan). The specific surface areas and pore size distribution of the samples were analyzed using a Micromeritics ASAP 2010 instrument (Micromeritics Instrument Ltd., Atlanta, GA, USA) and calculated via the BET method. To characterize the functional groups and crystal structure of the samples, Perkin Elmer Fourier transform infrared spectrometer (FTIR, Thermo Scientific Nicolet IS 50, Waltham, MA, USA) and X-ray diffraction (XRD, Rigaku Ultima IV, Tokyo, Japan) with Cu Kα radiation (V = 30 kV, I = 25 mA) were employed, respectively. The X-ray photoelectron spectroscopy (XPS, ThermoScientific Escalab 250 Xi, Waltham, MA, USA) with Al Kα X-ray radiation was used to analyze the existence of elements and their chemical states on the surface of the sample. To monitor the recombination rate of electron–hole pairs, photoluminescence spectra (PL, FLS980 Series of Fluorescence Spectrometers, Edinburgh Instruments, UK) were recorded. Additionally, the optical properties of the samples were analyzed using a UV-vis spectrophotometer and its integral sphere accessories (UV, Shimadzu UV 2600, Kyoto, Japan).

2.4. Photocatalytic Activity Test

The photocatalytic activity of Y-doped Bi:MoO₆/CMS photocatalyst was tested by conducting the degradation of RhB in a photochemical reactor (PhchemIII, Beijing, China). A 300 W Xenon lamp, equipped with a 420 nm cut-off filter, was employed as the simulative visible light source, and the entire reaction device was maintained at room temperature using a cooling-water-cycle system. Briefly, 20 mg of the as-prepared photocatalyst was mixed with 40 mL of 6 mg/L RhB in a 50 mL glass beaker under magnetic stirring conditions. Before illuminating the visible light, the reaction system of photocatalyst and RhB was kept in the dark for 3 h to establish an adsorption–desorption equilibrium, and illuminated and kept for 1 h. We utilized UV-visible spectroscopy (UV, Shimadzu UV 2600, Kyoto, Japan) to measure the degradation rate of RhB by the photocatalysts, based
on the absorbance values of RhB at a wavelength of 554 nm. The degradation efficiency was calculated from Equation (1). The reaction rate was estimated using the Langmuir–Hinshelwood kinetic equation, as shown in Equation (2) [44].

\[
\text{Photocatalytic degradation} = \left[ \frac{[A_0 - A_t]}{A_0} \right] \times 100\% ,
\]

where \( A_0 \) is an initial photocatalytic degradation of RhB and \( A_t \) represents RhB adsorption measured at a definite time.

\[
\ln \left( \frac{C_0}{C_t} \right) = K t,
\]

\( C_0 \) represents the initial concentration of RhB, while \( C_t \) represents the concentration of RhB during the photocatalytic process at the time \( t \). Moreover, \( K \) is the reaction rate constant. The direct decomposition of RhB without any catalyst under visible irradiation was omitted.

2.5. Cycle Experiment

To evaluate the chemical stability and practical applicability of the as-prepared photocatalyst, we performed a four-cycle degradation of RhB using Y-doped Bi₂MoO₆/CMS. After each cycle of photocatalytic degradation, the catalyst was collected through centrifugation, washed with deionized water, and dried in an 80 °C oven. The collected photocatalysts were then reused for subsequent cycles of degradation under the same conditions.

2.6. Active Species Trapping Experiments

Briefly, 2 mL of isopropanol (IPA, 0.1 mol/L), sodium oxalate (Na₂C₂O₄, 0.1 mol/L) and \( p \)-benzoquinone (BQ, 0.1 mol/L) were prepared as scavengers for \( \cdot \text{OH} \), \( \text{h}^+ \), and \( \cdot \text{O}_2^- \) species. These scavengers were added to the reaction solution to be degraded before the illumination process, respectively. Through this setup, the active species participating in the photocatalytic reaction were analyzed.

3. Results

3.1. Chemical Composition Analysis

The crystal composition and structure of the as-prepared samples were analyzed using XRD measurements. Figure 1a displays the XRD patterns of the pure Bi₂MoO₆, CMS Bi₂MoO₆/CMS, and Y-doped Bi₂MoO₆/CMS samples. In comparison to the XRD patterns of pure Bi₂MoO₆ and CMS, those of Bi₂MoO₆/CMS and Y-doped Bi₂MoO₆/CMS showed the diffraction peaks of the orthorhombic phase of Bi₂MoO₆ and the calcite phase of CaCO₃. The diffraction peaks at 28.1°, 32.3°, 46.7°, 55.3° and 58.2° were corresponded to the (131), (200), (062), (331), and (191) crystal planes of the orthorhombic phase Bi₂MoO₆ (JCPDS No. 76-2388). Similarly, the diffraction peaks at 29.4°, 35.9°, 43.1°, and 47.4° were attributed to the (104), (110), (202) and (024) planes of the calcite phase CaCO₃ (JCPDS 83-1762). The Y-doped Bi₂MoO₆/CMS did not show any evident XRD peak of yttrium compounds or other impurities. However, in further amplification of the spectrum (as shown in Figure 1b), a slight shift to lower 20 values was observed in the peak corresponding to the (131) crystal plane after Y doping. This shift indicated the substitution of some Bi³⁺ with Y³⁺ ions, which was an indication of the insertion and substitution of the Bi with rare earth ions in the lattice of Bi₂MoO₆ [45–47]. Furthermore, the crystallite size of different samples was calculated using the Scherrer equation [48], and the results are presented in Table 1. The crystalline size of Bi₂MoO₆ was reduced in comparison to undoped Bi₂MoO₆/CMS. This suggested that the introduction of Y³⁺ ions hinder the growth of Bi₂MoO₆ in the composite. This was because the insertion of Y in Bi₂MoO₆ created lattice defects, which further prevented the growth of Bi₂MoO₆ [49–51]. A suitable amount of
lattice defects can serve as efficient photo–electron–hole capture centers, thereby promoting the separation of photogenerated electron–hole pairs and enhancing the photocatalytic activity of the catalyst [52,53].

Figure 1. (a) X-ray diffraction patterns of Bi2MoO6/CMS and Y-doped Bi2MoO6/CMS; (b) magnified patterns with the 2θ between 27° and 30° X-ray diffraction patterns.

Table 1. Physico-chemical properties of the prepared photocatalysts.

<table>
<thead>
<tr>
<th>Photocatalysts</th>
<th>Average Crystallite Size (nm)</th>
<th>BET Surface Area (m²/g)</th>
<th>Average Pore Diameter (nm)</th>
<th>Pore Volume (cm³/g)</th>
<th>Band Gap Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi2MoO6/CMS</td>
<td>10.81</td>
<td>28.64</td>
<td>9.63</td>
<td>0.07</td>
<td>3.00</td>
</tr>
<tr>
<td>0.063%Y-BC</td>
<td>10.65</td>
<td>29.91</td>
<td>9.76</td>
<td>0.07</td>
<td>2.98</td>
</tr>
<tr>
<td>0.125%Y-BC</td>
<td>8.49</td>
<td>37.94</td>
<td>14.71</td>
<td>0.14</td>
<td>2.94</td>
</tr>
<tr>
<td>0.25%Y-BC</td>
<td>8.38</td>
<td>38.23</td>
<td>14.07</td>
<td>0.13</td>
<td>2.92</td>
</tr>
<tr>
<td>0.5%Y-BC</td>
<td>8.91</td>
<td>42.50</td>
<td>7.92</td>
<td>0.08</td>
<td>2.91</td>
</tr>
<tr>
<td>1%Y-BC</td>
<td>9.15</td>
<td>20.60</td>
<td>8.15</td>
<td>0.04</td>
<td>2.83</td>
</tr>
</tbody>
</table>

The XPS testing was used to investigate the surface chemical composition of Bi2MoO6/CMS and Y-doped Bi2MoO6/CMS samples, as shown in Figure 2. The results revealed that the Bi2MoO6/CMS and Y-doped Bi2MoO6/CMS samples were composed of Bi, Mo, O, Ca, and C. However, the Y XPS peaks were not detected in the survey spectra due to the low amount of doping and overlap with the Bi 4f peak [45]. The high-resolution XPS spectra of Bi 4f show two strong peaks at 164.0 eV and 158.6 eV (Figure 2b), assigned to Bi4f7/2 and Bi4f5/2, respectively, indicating the trivalent chemical state of Bi [54,55]. The Bi peak shifted towards higher binding energy with the increase in the Y doping ratio, suggesting changes in the Bi chemical environment due to Y doping into the Bi2MoO6 lattice and charge transfer between Bi and Y [56,57]. Y doping had no significant effect on the Mo element as seen from the Mo3d3/2 and Mo3d5/2 peaks. The fine spectrum of O1s in the XPS spectrum clearly revealed the different forms of O element. As shown in Figure 2, two strong peaks at 530.7 eV and 532.3 eV were attributed to the proximity of O vacancies and lattice O, respectively, and a weak peak at 529.2 eV represented the binding energy of adsorbed O [57,58]. The relative content of three forms of oxygen could be determined based on the proportion of peak area, while the oxygen vacancies in the samples showed a significant increasing trend with the increase in Y doping amount. Furthermore, Figure 2d revealed that the binding energies for Y3p1/2 and Y3p3/2 of Y in 0.5%Y-BC were around
301.1 eV and 310.6 eV, respectively, indicating Y\(^{3+}\) were successfully doped into Bi\(_2\)MoO\(_6\) [45].

The FTIR spectrum of samples were presented in Figure 3. The spectrum of Y-doped samples was similar to the undoped samples. The absorption bands at 841, 733, and 565 cm\(^{-1}\) correspond to the stretching vibration of Mo=O, tetrahedral stretching vibration of Mo-O, and bending vibration of MoO\(_6\) respectively [59]. The band at 450 cm\(^{-1}\) was assigned to the Bi-O stretching vibration [60]. Additionally, four peaks at 1794, 1420, 872, and 729 cm\(^{-1}\) were identified as the characteristic peaks of CaCO\(_3\) in CMS [61,62]. A broad peak in the 3200–3600 cm\(^{-1}\) could be assigned to the O-H stretching vibration, which is due to the water molecule’s adsorption on the surface area [27,63,64]. No obvious Y-O vibration peak was observed in the spectrum, likely due to the low doping amount of Y\(^{3+}\) in the samples.

Figure 2. XPS survey spectra (a) and high-resolution XPS spectra of Bi4f (b), Mo3d (c), Y3p (d) and O1s (e,f) of BiMoO\(_6\)/CMS and Y-doped BiMoO\(_6\)/CMS.
Figure 3. FT-IR spectra of CMS, pure Bi$_2$MoO$_6$, Bi$_2$MoO$_6$/CMS, and Y-doped Bi$_2$MoO$_6$/CMS.

3.2. Morphology and Texture Analysis

The morphologies of samples, including pure Bi$_2$MoO$_6$, CMS, Bi$_2$MoO$_6$/CMS, and Y-doped Bi$_2$MoO$_6$/CMS, were characterized using SEM, and the results are presented in Figure 4. Pure Bi$_2$MoO$_6$ exhibited a hollow spherical structure assembled from nanosheets (Figure 4a). The CMS had an irregular block-like structure, with many nanorods on its surface (Figure 4b). Bi$_2$MoO$_6$/CMS exhibited a morphology composed of stacked lamellar nanosheets, primarily supported by CMS (Figure 4c). The morphologies of 0.063% Y-BC and Bi$_2$MoO$_6$/CMS were similar (Figure 4d), indicating that the trace amount of yttrium did not significantly alter the host materials. However, as the doping amount increased, the size of Bi$_2$MoO$_6$ nanosheets decreased. When the doping amount reached 0.5%, the sample displayed a homogeneous sheet-like structure that tended to aggregate into clusters (Figure 4g). Furthermore, at a Y doping concentration of 1%, the particles exhibited an increase in size and thickness, accompanied by a smooth surface (Figure 4h). As shown in Figure 5i, the TEM image of 0.5% Y-BC demonstrated that the Bi$_2$MoO$_6$ nanosheets were attached to the surface of the nanorods of CMS and formed a clustered structure, confirming with the SEM images.
Figure 4. SEM image of Bi₂MoO₆ (a), CMS (b), Bi₂MoO₆/CMS (c), 0.063%Y-BC (d), 0.125%Y-BC (e), 0.25%Y-BC (f), 0.5%Y-BC (g), 1%Y-BC (h); TEM image of 0.5%Y-BC (i).

Figure 5 displays the N₂ adsorption and desorption isotherms, as well as the corresponding pore size distribution curves for Bi₂MoO₆/CMS and Y-doped Bi₂MoO₆/CMS samples. The N₂ adsorption and desorption isotherms showed that all the samples exhibited type IV isotherms with an obvious H3-type hysteresis loop in the high relative pressure range of 0.9–1.0 (P/P₀), indicating the presence of mesopores [65,66]. The pore size distribution curve measured via the BJH method revealed that the pore width was mainly distributed in the 2–30 nm range. The specific surface areas of Bi₂MoO₆/CMS, 0.063%Y-BC, 0.125%Y-BC, 0.25%Y-BC, 0.5%Y-BC, and 1%Y-BC were measured to be 28.64, 29.91, 37.94, 38.23, 42.50, and 20.60 m²/g (Table 1), respectively, and showed a gradual increase with increasing the doping amount of Y element. The sample with 0.5% doping exhibited the highest specific surface area among all the samples. However, with a further increase in the doping amount, the specific surface area decreases due to the excess Y potentially causing the aggregation of Bi₂MoO₆ nanosheets or blocking of pre-existing pores. The increase in specific surfaces could enhance the adsorption and degradation of organic pollutants. It also provided more active sites for the photogenerated electrons and holes, leading to an improved photocatalytic performance [24,67].
3.3. Optical Properties

The optical properties of the as-prepared samples were measured using UV–vis diffuse reflectance spectroscopy, as shown in Figure 6. All samples exhibited significant absorbance in the visible-light region. Compared to Bi₂MoO₆/CMS, the Y-doped Bi₂MoO₆/CMS samples showed a red shift of the absorption edges. The band gap value was calculated using the Kubelka–Munk equation, as follows.

\[(\alpha hv)^2 = A(hv - E_g)\]  \( (3) \)

where \( \alpha \), \( hv \), \( A \), and \( E_g \) are the absorption coefficient, photonic energy, Planck constant, and band gap, respectively [68].

Using Equation 3, the curves of these samples were fitted, and the results are presented in the inset of Figure 6. The estimated band gaps of pure Bi₂MoO₆, Bi₂MoO₆/CMS, 0.063%Y-BC, 0.125%Y-BC, 0.25%Y-BC, 0.5%Y-BC, and 1%Y-BC were approximately 2.65, 3.00, 2.98, 2.94, 2.92, 2.91 and 2.83 eV, respectively. Notably, the band gap of Y-doped Bi₂MoO₆/CMS had slightly decreased compared to Bi₂MoO₆/CMS. This decrease could be due to the charge transfer transition occurring between 4f or 5d electrons of Y elements and the conduction or valence band of Bi₂MoO₆ [19,69]. These findings indicated that Y-doping effectively broadened the light absorption range of the catalyst [45]. Consequently, this was considered beneficial for improving the utilization of light photons.

**Figure 5.** Nitrogen adsorption–desorption isotherms and pore size distributions of Bi₂MoO₆/CMS and Y-doped Bi₂MoO₆/CMS.

**Figure 6.** UV–vis DRS spectra of Bi₂MoO₆, Bi₂MoO₆/CMS, and Y-doped Bi₂MoO₆/CMS. The inset is the plot of \( (\alpha hv)^2 \) versus hv for Bi₂MoO₆, Bi₂MoO₆/CMS, and Y-doped Bi₂MoO₆/CMS.
The efficiency of the photocatalytic material in dye degradation relies on the effective separation of the photogenerated charge carriers, which could be determined through analysis of the photocatalysts’ photoluminescence spectra (PL) [47,70]. A lower PL intensity indicated a lower recombination rate of electron–hole pairs, resulting in improved photocatalytic performance [71,72]. In Figure 7, the PL spectra of Bi2MoO6/CMS and 0.5%Y-BC were depicted, showing a strong peak at 467 nm due to photoinduced electron transfer transitions between O 2p (VB) and empty Mo 5d orbital (CB) [18]. Notably, the peak intensity of 0.5%Y-BC was lower than that of Bi2MoO6/CMS, indicating that the recombination rate of photogenerated electrons and holes in 0.5%Y-BC was lower than that of undoped Bi2MoO6/CMS.

![Figure 7. PL spectra of Bi2MoO6/CMS and 0.5%Y-BC.](image)

3.4. Photocatalytic Degradation of RhB

The photocatalytic activity of pure Bi2MoO6, Bi2MoO6/CMS, and Y-doped Bi2MoO6/CMS photocatalysts were investigated by testing the degradation of RhB solution under visible-light irradiation. In Figure 8a, we observed that RhB had not degraded in the absence of a photocatalyst, indicating its high structural stability. All Y-doped Bi2MoO6/CMS samples exhibited a more efficient photodegradation rate than the undoped Bi2MoO6/CMS and pure Bi2MoO6. The 0.5%Y-BC exhibited the highest photocatalytic performance, achieving a remarkable degradation rate of 99.7% after 60 min of irradiation.

Kinetic studies were conducted using the pseudo-first-order model. Figure 8b shows that 0.5% Y-BC exhibited the highest rate constant, which was three times higher than Bi2MoO6/CMS and ten times higher than pure Bi2MoO6. This is because 0.5%Y-BC has a lower recombination efficiency of photogenerated electrons and holes, higher specific surface area, and lower band gaps. However, the increase in the yttrium content to 1% would result in a lower K value. The former BET surface area analysis shows that Y doping at a high concentration could decrease the surface area. Moreover, the excess Y3+ ions in 1%Y-BC may act as a recombination center for the photogenerated charges, decreasing the photocatalytic activity [73]. Thus, it is important to carefully control the Y3+ concentration to avoid decreasing the photocatalytic efficiency caused by the recombination of electron–hole pairs. Furthermore, a comparison of the photodegradation performance of 0.5% Y-BC with other photocatalysts reported in the literature is presented in Table 2. Although the initial concentration of pollutants in this study was slightly lower than the concentrations reported in the literature, while the K value of the 0.5% Y-BC was significantly higher than that of other catalysts, indicating its superior photocatalytic performance.
Figure 8. The photocatalytic degradation curves (a) and kinetics curves (b) of RhB over Bi2MoO6, Bi2MoO6/CMS, and Y-doped Bi2MoO6/CMS.

Table 2. Comparison of the photodegradation performance of Y-doped Bi2MoO6/CMS with other photocatalysts reported in the literature.

<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>Catalyst Dosage</th>
<th>Light Source</th>
<th>Irradiation Time</th>
<th>Pollutants</th>
<th>Efficiency</th>
<th>K (min⁻¹)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5%Y-BC</td>
<td>20 mg</td>
<td>300W Xe lamp</td>
<td>60 min</td>
<td>RhB, 6 mg/L, 40mL</td>
<td>99.7%</td>
<td>0.1022</td>
<td>This work</td>
</tr>
<tr>
<td>Bi2WO6/Calcined mussel Shell</td>
<td>20 mg</td>
<td>300W Xe lamp</td>
<td>150 min</td>
<td>RhB, 10.0 mg/L, 100mL</td>
<td>98.4%</td>
<td>0.0248</td>
<td>[36]</td>
</tr>
<tr>
<td>TiO2/Seashell</td>
<td>100 mg</td>
<td>Xe lamp</td>
<td>140 min</td>
<td>MB, 10 mg/L, 100mL</td>
<td>96%</td>
<td>/</td>
<td>[35]</td>
</tr>
<tr>
<td>TiO2/Calcined Mussel Shell</td>
<td>40 mg</td>
<td>UV light</td>
<td>300 min</td>
<td>MB, 10 mg/L, 20mL</td>
<td>97%</td>
<td>/</td>
<td>[39]</td>
</tr>
<tr>
<td>Co/N-graphitic carbon@Bi2MoO6</td>
<td>10 mg</td>
<td>300W Xe lamp</td>
<td>75 min</td>
<td>RhB/MO, 10 mg/L, 200mL</td>
<td>99.54%</td>
<td>0.0335</td>
<td>[74]</td>
</tr>
<tr>
<td>Bi:MoO6/rGO</td>
<td>20 mg</td>
<td>150W Xe lamp</td>
<td>180 min</td>
<td>RhB, 10 mg/L,50mL</td>
<td>100%</td>
<td>/</td>
<td>[75]</td>
</tr>
<tr>
<td>Gd³⁺-doped Bi2MoO6</td>
<td>100 mg</td>
<td>300W Xe lamp</td>
<td>180 min</td>
<td>RhB, 10 mg/L,50mL</td>
<td>90.2%</td>
<td>0.0122</td>
<td>[24]</td>
</tr>
<tr>
<td>Ho³⁺-doped Bi2MoO6</td>
<td>100 mg</td>
<td>300W Xe lamp</td>
<td>180 min</td>
<td>RhB, 10 mg/L,50mL</td>
<td>81.9%</td>
<td>0.0078</td>
<td>[24]</td>
</tr>
<tr>
<td>Yb³⁺-doped Bi2MoO6</td>
<td>100 mg</td>
<td>300W Xe lamp</td>
<td>180 min</td>
<td>RhB, 10 mg/L,50mL</td>
<td>79.8%</td>
<td>0.0091</td>
<td>[24]</td>
</tr>
<tr>
<td>Dy³⁺-doped Bi2MoO6</td>
<td>100 mg</td>
<td>300W Xe lamp</td>
<td>40 min</td>
<td>RhB, 10 mg/L, 100mL</td>
<td>100%</td>
<td>/</td>
<td>[19]</td>
</tr>
</tbody>
</table>

Figure 9 displays the absorption spectra of RhB over time in the presence of 0.5%Y-BC under visible light. As the irradiation time increased, the absorbance of RhB at 550 nm decreased rapidly. This decrease was accompanied by a blue shift in the absorption band, which is due to the formation of a series of N-de-ethylated intermediates as RhB degrades [76]. After 60 min, RhB was entirely degraded, indicating that the dye-conjugated structure of the RhB molecule was destroyed.
Figure 9. Time-dependent UV-vis adsorption spectral of RhB degraded by 0.5%Y-BC.

3.5. Cycle Experiment

The stability and reusability of 0.5%Y-BC was investigated via a recycling experiment, and the results are presented in Figure 10. As shown in Figure 10a, the degradation efficiency of 0.5%Y-BC for RhB decreased slightly, from 99.7% to 83.3%, after four cycles of experiments. Two factors could lead to the decrease in degradation efficiency. Firstly, there could have been a loss of catalyst mass during the centrifugation collection process. Secondly, the adsorption of the intermediate onto the photocatalyst’s surface may have resulted in a reduction in the number of exposed reactive sites, leading to a decrease in the removal efficiency for RhB. Additionally, the stability of 0.5%Y-BC was analyzed via XRD, and the results are presented in Figure 10b. Notably, the XRD data revealed that the phase of the 0.5%Y-BC remained unchanged even after four cycles of experiments, indicating its stability and reusability in conducting photocatalytic reactions.

Figure 10. (a) Recyclability of 0.5%Y-BC for the degradation of RhB under visible light for four cycles; (b) the XRD patterns of the original and recycled 0.5%Y-BC.

3.6. Possible Photocatalytic Mechanism of Photocatalysts

To determine the primary active radicals and explain the photocatalytic mechanism in the photocatalytic degradation of RhB by 0.5%Y-BC, active species trapping experiments were conducted. IPA, Na$_2$C$_2$O$_4$, and BQ were used as scavengers of ·OH, h$, and ·O$_2^-$, respectively [77]. The results, depicted in Figure 11, reveal that the photocatalytic
activity of 0.5%Y-BC decreased with the addition of different active species scavengers. Specifically, the introduction of BQ and Na2C2O4 significantly lowered the photocatalytic activity of 0.5%Y-BC, suggesting that ·O2− and h+ are the primary active species involved in the RhB degradation by 0.5%Y-BC. We also observed a slight decrease in photocatalytic efficiency with the addition of IPA, indicating that ·OH also plays a crucial role in the photocatalytic reaction.

![Figure 11](image-url)  

**Figure 11.** The effects of photogenerated carriers trapping on photocatalytic degradation activity of 0.5%Y-BC.

The Y3+ ion significantly enhanced the photocatalytic efficiency of Y-doped Bi2MoO6/CMS through several mechanisms. Firstly, Y doping narrowed the band gap of the photocatalysts, making it easier for photo-excited electrons to move from the CB to VB. Second, Y doping substantially increased the specific surface area of the catalyst (from 28.6385 to 42.4971 m²/g), providing more reaction sites and promoting photocatalytic degradation. Thirdly, Y doping triggered the formation of new defect sites and oxygen vacancies, which acted as electron traps to prevent the recombination of electron–hole pairs. Furthermore, mussel shells, as photocatalyst supports, have unique pores and surface structures which could offer more active sites for pollutant attachment in photocatalytic reactions than stacked catalysts [38,43]. Moreover, shells contained various trace metal elements (e.g., Se, Mn, Zn, Ti, and Sr) that could serve as doping elements, facilitating electron transfer in photocatalytic reactions, thus enhancing the photocatalytic capability of the composites [37,42]. Therefore, CMS and Y3+ ions synergistically enhanced the performance of composite photocatalysts.

A proposed mechanism, based on experimental results and the literature, explains the possible reactions in photocatalysis, as shown in Figure 12. Under visible light irradiation, Bi2MoO6 was excited, generating electron–hole pairs, with the electrons excited to the conduction band and the holes remaining in the valence band. The presence of Y3+ on the Bi2MoO6, and its specific electronic configuration with vacant 4d and 5s orbitals, could capture electrons and form Y3+, hindering the recombination of electron–hole pairs. And then, these Y3+ ions reacted with oxygen molecules to produce superoxide radicals (O2·−) [78–81]. Simultaneously, the holes in the valence band directly participate in the photo-oxidation reaction with water molecules to produce hydroxyl radicals (·OH). These active species, i.e., ·O2−, h+, and ·OH, could directly attack RhB molecules, breaking down their conjugated structure. The overall reaction could be expressed as follows:

\[
\text{Bi}_2\text{MoO}_6 + \text{hv} \rightarrow \text{Bi}_2\text{MoO}_6 (e^- + h^+) \]
\[ \text{Y}^{3+} + e^- \rightarrow \text{Y}^{2+} \]
\[ \text{Y}^{2+} + \text{O}_2 \rightarrow \text{Y}^{3+} + \cdot \text{O}_2^- \]
\[ \text{h}^+ + \text{H}_2\text{O} \rightarrow \cdot \text{OH} + \text{H}^+ \]

\[ \text{RhB} + \cdot \text{O}_2^-/\text{h}^+/\cdot \text{OH} \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{Degradation products} \]

**Figure 12.** The mechanism of photodegradation RhB by Y-doped Bi₂MoO₆ composites.

### 4. Conclusions

In this study, a series of Y-doped Bi₂MoO₆/CMS was successfully developed via a simple solvothermal method based on the mussel shell. XPS results showed that Y was successfully doped into Bi₂MoO₆/CMS, and XRD demonstrated that Y-doped Bi₂MoO₆/CMS consisted of orthorhombic phase Bi₂MoO₆ and calcite phase CaCO₃. Y-doped Bi₂MoO₆/CMS exhibited superior visible-light-driven catalytic performance in the degradation of RhB solution, as compared to the undoped sample. Specifically, 0.5%Y-BC with excellent stability and reusability showed the maximum degradation rate of 99.7% in 60 min, and -\text{O}_2^- and \text{h}^+ are the primary active species in the RhB degradation. Moreover, the improved photocatalytic activity of 0.5%Y-BC was mainly attributed to its higher surface area, narrower bandgap, and enhanced separation of electron–hole pairs. Therefore, this study provided a new approach for the high-value utilization of mussel shells, and developing high-performance photocatalysts for removing organic pollutants from wastewater.

**Author Contributions:** Conceptualization, L.C. and L.J.; methodology, L.C., Y.Z. and L.J.; software, L.C., Y.Z. and J.S.; validation, L.J., Y.Z. and J.G.; formal analysis, L.C. and Y.Z.; investigation, J.G. and L.C.; resources, J.G. and L.J.; data curation, L.C.; writing—original draft preparation, L.C.; writing—review and editing, L.J.; visualization, L.C. and Y.Z. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research was funded by the Demonstration Project of Marine Economic Innovation and Development of Zhoushan City of China (NO.2016-496), the Scientific Research Fund of Zhejiang Provincial Education Department (Y201942627) and China Scholarship Council (NO.202008330459).
Data Availability Statement: All data that support the findings of this study are available from the corresponding author upon reasonable request.

Conflicts of Interest: The authors declare no conflicts of interest.

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