Morphology, photocatalytic and photoelectric properties of Bi_2MoO_6 tuned by preparation method, solvent, and surfactant

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Abstract:

Bi_2MoO_6 samples with different morphologies have been prepared using co-precipitation and hydrothermal methods. Octahedral-, spherical-, and plate-like particles have been obtained by changing some external factors including preparation methods, solvent types, and surfactants. Our results suggest that pure Bi_2MoO_6 phase with nanoplate morphology are easily obtained via hydrothermal preparation method using ethylene glycol solvent. The photocatalytic and photoelectric properties of these Bi_2MoO_6 samples have also been investigated in detail. Moreover, the photocatalytic activity is enhanced with addition of surfactants, such as Polyvinylpyrrolidone (PVP), Sodium dodecylsulfate (SDS), and cetyltrimethylammonium bromide (CTAB). The excellent photocatalytic activity is found for CTAB addition, which is nearly 100%. It may be ascribed to the specifically exposed facets structure, which is related to larger visible light absorption and improved separation of photogenerated charge carriers.

Keywords: Bismuth molybdate; nanostructure; photocatalyst

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1. Introduction:

Recently, bismuth-based semiconductor photocatalysts have been demonstrated to exhibit superior photocatalytic activity under visible-light irradiation. The interest in such one kind of photocatalyst has continued to grow until now. A series of single-component bismuth-based photocatalysts have been developed, such as CaBi_2O_4 ^[1], Bi_2O_3 ^[2], BiVO_4 ^[3], Bi_2WO_6 ^[4], and Bi_2MoO_6 ^[5-9]. Among all these bismuth-based photocatalysts, bismuth molybdate has one unique layered structure, in which one MoO_4 layer is sandwiched between two $(\text{Bi}_2\text{O}_2)^{2+}$ layers^[10]. This kind of layered structure is demonstrated to be beneficial to charge transfer. Based on the density functional theory (DFT) calculations^[11], the valence band (VB) of Bi_2MoO_6 is composed of Bi 6s and O 2p hybridized orbitals, whereas the conduction band consists of Mo 5d orbital. The hybridization of the Bi 6s and O 2p levels makes VB be largely dispersed. The charge transfer in the photo-excitation process is thus supposed to occur from Bi 6s and O 2p hybrid orbital to Mo 5d orbital. This favors the mobility of the generated charge carriers and thus is beneficial to photocatalytic oxidation of organic pollutants. These excellent geometrical and electronic structure properties make Bi_2MoO_6 exhibit outstanding visible light photocatalytic activities^[12-15]. In particular, it shows good photocatalytic performance for water splitting and organic pollutant degradation. Therefore, it has been received considerable attentions in these recent years.

In these recent experimental studies on bismuth molybdate, some research groups have successfully synthesized Bi_2MoO_6 samples with different morphology via some physical and chemical methods. These techniques include hydrothermal reaction^[16], solution combustion^[17], co-precipitation^[18], citrate complex method^[19], low temperature molten salt method^[20], amorphous precursor method^[21] and ultrasonic assisted method^[22]. Among these various synthesis strategies, the hydrothermal method is considered as the mainstream synthetic approach in the size- and shape-controlled synthesis of inorganic materials with uniform structures. Moreover, during the hydrothermal process, the solvent and surfactant-addition play

an important role. In particular, the chelating agent-assisted route used in the hydrothermal synthesis has been proven to be one promising and popular strategy for the formation of various materials. In such a route, chelating agent usually acts as the shape and morphology modifier. Some chelating agents, such as Polyvinylpyrrolidone (PVP)^[23,24], Sodium dodecyl sulfate (SDS)^[25], ethylenediaminetetraacetic acid (EDTA)^[26,27], and cetyltrimethylammonium bromide (CTAB)^[28] are widely employed to control the nucleation, growth and alignment of crystals. Although Bi₂MoO₆ samples are synthesized by these methods mentioned above, few Bi₂MoO₆ samples are obtained via two synthesis methods at the same time. More importantly, few comparisons have been made to explore the effect different preparation-methods and corresponding synthesis-conditions. However, it is well known that the photocatalytic properties of one specific material are very closely related to its morphology and geometrical structure. Moreover, the sample morphology is generally determined by the sample-synthesis methods and conditions. Therefore, it is of fundamental and practical importance to systematically investigate the effects of these external synthesis methods and conditions on the morphologies and eventually the photocatalytic properties of Bi₂MoO₆ samples.

Hence, to systematically investigate the effects of the external synthesis conditions on the morphologies and photocatalytic properties of Bi₂MoO₆, in the current work two aspects are considered. One is that Bi₂MoO₆ samples are synthesized via two preparation techniques at the same time, and the other is that some external conditions including solvent and surfactant types are also changed in the synthesis process. The adopted preparation techniques are chemical co-precipitation(CP) method and hydrothermal(HY) method. Via these two different preparation methods, Bi₂MoO₆ samples with different morphology have been successfully synthesized. The crystallizability, morphology, band gap, and photocatalytic activities of Bi₂MoO₆ samples under different external synthesis conditions have been also systematically probed. Some interesting results have been obtained and discussed. For example, our results clearly suggest that the Bi₂MoO₆ samples, which are synthesized in the presence of surfactant CTAB, exhibit the most

excellent photocatalytic activity in decomposition of methylene blue (MB) under simulated sunlight irradiation.

2. Experimental part:

2.1 Materials

The synthesis of Bi_2MoO_6 was carried out by two different preparing methods. The raw materials include $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$, NaOH , HNO_3 , ethylene glycol, SDS, PVP, CTAB, and de-ionized water.

2.2 Preparation

Two different methods are used to prepare the current samples. The detailed processes are introduced as follows.

One is the simply chemical co-precipitation method. At first, stoichiometric amounts of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ were dissolved in the deionized water to form aqueous solution, respectively. Then $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ solution was added to the aqueous $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ solution to form mixture. The solution pH value was adjusted to 7 by addition of dilute NaOH solution. Finally, the aqueous solution was transferred into the prepared precipitator and stirring it for 7h, and the solution was centrifuged and washed with deionized water several times. The washed powder was dried at 80°C .

The other is hydrothermal preparation method. Stoichiometric amounts of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ were dissolved in the HNO_3 and glycol, respectively. $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$, and NaOH were separately dissolved in the deionized water with stirring for 30min using a magnetic stirrer. NaOH solution was added to adjust pH value to 7. An amount of SDS, PVP, and CTAB were dissolved in the deionized water with magnetic stirring and added dropwise to the above mixed solution under vigorous magnetic stirring for 30min. Finally, the mixture was placed in a 1000ml hastelloy autoclave (Parr 4577) and reacted at 160°C for 12h. After the autoclave was cooled to

room temperature naturally, the products were separated by centrifugation, washed with ethanol and deionized-water several times, and subsequently dried at 80°C to obtain the final samples.

Via these two synthesis methods, the obtained samples are summarized in Table 1. Sample S1 is synthesized via co-precipitation method. In the synthesis process, the solvent H₂O is adopted to solve Bi(NO₃)₃·5H₂O. However, no surfactant is used. Samples S2-S6 are obtained via hydrothermal preparation. Therefore, the comparisons and discussions between S1 and S2-S6 are used to probe the effect of different synthesis methods. In the hydrothermal synthesis process of sample S2, the used solvent is HNO₃, and the adopted solvent for S3 is Ethylene glycol. For S2 and S3, no surfactant is used in both synthesis procedures. Therefore, although similar synthesis method is adopted, the used solvent is different between S2 and S3. Via the comparisons and analyses between S2 and S3, the effect of solvent type in the similar synthesis procedure will be involved. Besides the similar solvent environment ethylene glycol with S3, different surfactants are used in the synthesis process of samples S4-S6. The used surfactant for S4 is SDS, PVP for S5, and CTAB for S6. Therefore, the comparisons of S3, S4, S5, and S6 are used to probe the effect of assisted-surfactant on the Bi₂MoO₆ system.

2.3 Characterization

The crystal structure of the products was characterized by X-ray diffraction using an X-ray diffractometer (XRD dx-2000 SSC) with Cu K α radiation ($\lambda=1.5418\text{\AA}$) over a scanning range of 10-80° with a step of 0.02°. Surface morphologies and microstructure were observed using a scanning electron microscope (SEM, S-4800, Hitachi) and transmission electron microscopy (high resolution) (TEM, JEOL JEM-2100). The optical diffuse reflectance spectra were recorded on a Japan Shimadzu UV-3600 (Japan) using BaSO₄ as a reference. Electrochemical impedance spectroscopy (EIS) measurement was carried out on an electrochemical work-station under dark condition using a three electrode configuration with a Pt foil as counter electrode and a standard calomel electrode as reference electrode. EIS was recorded in

the frequency range of 0.1Hz-1MHz, and the applied bias voltage and ac amplitude was set at open-circuit voltage and 10mV.

2.4 Photocatalytic reactions

The photocatalytic activities of Bi_2MoO_6 samples were evaluated by the degradation of methyl blue under a 350W Xe lamp light. In each experimental, 200mg of the photocatalyst was added to 80ml of methyl blue solution (10mg/L) in test tube. Before illumination, the suspensions were magnetically stirred in the dark for 60min to ensure the establishment of an adsorption-desorption equilibrium between the photocatalysts and methyl blue. And then, the solution under magnetic stirring was exposed to Xe lamp light irradiation. At given interval time, the test tubes were sampled and then centrifuged to remove the photocatalyst particles.

3. Results and Discussions

A. The effect of different preparation method

Here, the Bi_2MoO_6 samples with different morphology are obtained via two different methods, including the chemical co-precipitation and the hydrothermal method. The obtained samples are summarized in Table 1. The geometrical structure, band gap, morphology characteristics and photocatalytic performance of these samples are further investigated.

In Fig. 1, it is shown that XRD patterns of these products obtained using different preparation methods. In this figure, S1 is obtained via the co-precipitation method, and S2 is corresponding to the hydrothermal method. Obviously, it is observed that in both S1 and S2 samples, the characteristic diffraction peaks are assigned to two different crystal phases. One corresponds to cubic phase $\text{Bi}_{3.64}\text{Mo}_{0.36}\text{O}_{6.55}$ (JCPDS 43-446), and the other is orthorhombic Bi_2MoO_6 (JCPDS 76-2388). That is to say, S1 and S2 samples are both composed of two phases, except that $\text{Bi}_{3.64}\text{Mo}_{0.36}\text{O}_{6.55}$ is the main phase in these two samples. Similar result has been reported in reference ^[29]. However, there also exist some obvious differences between S1 and S2. For S1 samples, there are two weaker peaks at 28.30° and 33.14° , which match well with (131) and (060) crystal planes of Bi_2MoO_6 . For S2 sample, the above

two peaks become more distinct and one new peak at 10.87° appears, corresponding to (020) plane of Bi_2MoO_6 .

The morphologies of these as-prepared S1 and S2 samples are further examined by SEM and TEM. The results are shown in Fig. 2(a)-(d). From the SEM images presented in Fig. 2(a) and (b), it is clearly found that there exist two different kinds of morphologies in these samples. S1 sample is mostly octahedral in shape. S2 sample is the mixture of sphere-like nanoparticles and flake-like nanoplates. Fig. 2(c) and (d) presents the TEM images for S1 and S2 samples which are corresponding to the SEM result.

And then, the UV-visible absorption properties of the S1 and S2 products are probed, as shown in Figure 3. From this figure, it is observed that for these two samples, the absorption regions are both from visible light region to UV light region. This suggests that the current Bi_2MoO_6 samples possibly have photocatalytic activity under visible light radiation. In this figure, it is also found that there exists one steep absorption edge. Such one steep absorption edge indicates the absorption is relevant to energy gap, resulting from intrinsic transition. For crystalline semiconductors, one classic Tauc approach is employed to estimate the photonic energy gap via the following equation $\alpha h\nu = A(h\nu - E_g)^{n/2}$, where α , h , ν , E_g and A are absorption coefficient, Planck constant, photon frequency, photonic energy gap and one constant, respectively^[30]. The parameter n depends on the characteristics of the transitions in the semiconductor. For a direct transition, $n=1$, whereas for an indirect transitions, $n=4$ ^[31]. For $n=1$, energy gap for the absorption edge is able to be determined by extrapolating the linear portion of the plot $(\alpha h\nu)^2$ vs $h\nu$ to zero absorbance. Based on the formula mentioned above, the calculated energy gaps of S1 and S2 samples are 2.97 and 2.87 eV, respectively.

The photocatalytic performances of the S1 and S2 samples are presented in Fig. 4. MB was chosen as the representative model pollutant. Before light irradiation, dark absorption equilibrium between MB molecules and photocatalyst was achieved after stirring the suspension. 15% and 18% degradations after 120 min of UV-irradiation

are observed for S1 and S2 samples. Compared with those S2 samples, those S1 samples are found to have slightly lower photocatalytic activity.

B. The effect of different solvent type in the hydrothermal method

As mentioned in other reports^[32,33], solvents can be used to precisely control the morphology of nanosystems. For example, ZnO^[32] and Bi₂WO₆^[33] have been successfully synthesized by the solvothermal process, and the size and shape of produced nanostructures are precisely tuned by using different solvents. Therefore, the solvent may be one important factor in the synthesis process. Therefore, in the current work different solvent types including HNO₃ and ethylene glycol are also introduced in the synthesis process of hydrothermal method. In these samples, S2 is obtained with Bi(NO₃)₃·5H₂O being dissolved in the HNO₃, and S3 is generated via Bi(NO₃)₃·5H₂O being dissolved in the ethylene glycol. The structure, morphology, energy band gap, and photocatalytic properties of sample S2 and S3 are analyzed. Hence, the effects of solvents types (HNO₃ and ethylene glycol) are systematically investigated and discussed in this portion.

Figure 5 shows the XRD patterns of these two samples. As discussed above, in S2 sample there exist two mixed phases. One is cubic Bi_{3.64}Mo_{0.36}O_{6.55}, and the other is orthorhombic Bi₂MoO₆. The former is main phase. In the synthesis process of S3 sample, solvent is changed into ethylene glycol. Surprisingly, in the obtained S3 sample, only one pure orthorhombic phase is observed. The following peaks, located at 10.87°, 27.32°, 28.30°, 32.56°, 33.14°, 36.01°, 46.71°, 47.91°, 55.41°, 56.21° and 58.50°, are found. These peaks match well with (020), (140), (131), (200), (060), (151), (202), (062), (133), (082), (262) crystal planes of Bi₂MoO₆, respectively. Therefore, compared with HNO₃ used in the S2 sample, our results clearly suggest that ethylene glycol is more suitable to synthesize the pure-phase Bi₂MoO₆ material.

The effect of solvent on the morphology and structure was further analyzed by SEM and TEM. The corresponding images are shown in Fig. 6(a) and (c). As mentioned above, for Sample S2 shown in Fig. 2(b) and (d), both sphere-like

$\text{Bi}_{3.64}\text{Mo}_{0.36}\text{O}_{6.55}$ and flake-like Bi_2MoO_6 nanostructures are formed in S2 sample, which is synthesized in the HNO_3 medium. The sphere-like $\text{Bi}_{3.64}\text{Mo}_{0.36}\text{O}_{6.55}$ nano-particles are also observed in reference^[34,35]. When the solvent is changed from HNO_3 to ethylene glycol, as presented in Fig. 6(b) and (d), the morphology of the products is completely changed. Two-dimensional nanoplates are observed in S3 sample. These nanoplates belong to pure Bi_2MoO_6 phase samples, as discussed below.

Therefore, based on the above XRD and SEM results, our results clearly suggest that the solvent type plays an important role on the morphology of the products in the hydrothermal processes. When $\text{Bi}(\text{NO}_3)_3$ is dissolved in HNO_3 medium, the reaction between Bi^{3+} and MoO_6^{6-} starts when two micro emulsions are mixed together. One mixture phase of sphere-like $\text{Bi}_{3.64}\text{Mo}_{0.36}\text{O}_{6.55}$ and flake-like Bi_2MoO_6 nanostructure is generated. When organic solvent ethylene glycol was used, instead of HNO_3 , there exists only one flake-like Bi_2MoO_6 nanostructure. Figure 6(c) and (d) presents the TEM image, which is well corresponding to the SEM result.

As we all know, the ethylene glycol exhibits strong chelating ability. When $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ are dissolved in ethylene glycol. They may be chelated with glycol to form Bi_2MoO_6 . One of the critical factors, which is responsible for the shape determination of the nano- and microcrystals, is the crystallographic phase of the initial seed. Once the crystalline phase is determined, the characteristic cell structures of the seeds will strongly affect the further crystal growth^[36]. As for Bi_2MoO_6 , the structure consists of alternating $(\text{Bi}_2\text{O}_2)_n^{2+}$ layers and perovskite-like $(\text{MoO}_4)_n^{2-}$ layers, and octahedral Mo chains usually play an important role on the high intrinsic anisotropic growth in various molybdates^[37]. Crystal growth is strongly related to the intrinsic crystal structure of Bi_2MoO_6 and the relative chemical potential. It is believed that two-dimensional growth occurs only if the chemical potential of two surfaces is much higher than others. On the basis of Bi_2MoO_6 structure, the chains of octahedral-Mo equally exist along a and c axes. The facts which are perpendicular to these chains usually have a much higher chemical potential in

comparison with other facets. The above features will result in faster growth rates of these faces, and thus the crystal growth is preferentially along the layer.

UV-visible absorption spectra of S2 and S3 samples are also measured and presented in Fig.7. This figure clearly suggests that there also exist strong photo-absorption range from ultraviolet to visible light with wavelength being shorter than 500nm. In addition, the calculated band gap E_g is about 2.87eV and 2.80eV for S2 and S3 sample, respectively. There is no obvious difference in E_g gap for these two samples.

Figure 8 presents the photocatalytic performances of S2 and S3 samples for the degradation of MB. Comparing with S2 sample ($C/C_0=18\%$), S3 sample behaves high photocatalytic performance. MB can be almost decomposed within 120 minutes over S3 sample ($C/C_0=85\%$). This may be ascribed to two following aspects. One is that Bi_2MoO_6 flake-like morphology has more active surface sites, and thus exhibits high efficiency of surface charge carrier transfer in photocatalysis. The absorption ratio reaches 15% and 85% for S2 and S3 sample, respectively. On the other hand, ethylene glycol has abundant hydroxyl which facilitates the capture of photo-generated holes in S3 sample. As a result, all these factors further oxidize the absorbed dye molecules and the photocatalytic performance is enhanced.

C. Different assisted-surfactants in the hydrothermal method

To systematically investigate the synthesis and the photocatalyst properties of Bi_2MoO_6 system, the effects of different assisted-surfactants are also probed. As presented in Table 1, the Bi_2MoO_6 samples are prepared from the precursor suspensions without surfactant, and with SDS, PVP and CTAB addition. These samples are labeled as S3, S4, S5 and S6, respectively. In this portion, via discussing the difference between S3, S4, S5, and S6, the effects of assisted-surfactants on the structure, morphology, and photocatalyst are investigated.

Figure 9 presents the XRD pattern of the as-prepared bismuth molybdate with various surfactants in the process of hydrothermal synthesis at 160°C. As observed

from this figure, there exist no other diffraction peaks in these XRD patterns, demonstrating that these samples (S3, S4, S5, and S6) are purity. The diffraction peaks of four as-prepared samples can be well indexed to those corresponding to the pure orthorhombic phase of Bi_2MoO_6 . Therefore, our results clearly suggest that the assisted-surfactant has little influence on the pure orthorhombic crystal structure.

The morphologies and microstructures of these bismuth molybdate samples were further presented by SEM images, shown in Fig.10. Fig.10(a) clearly suggests that the morphology of S3 sample has the following two characters. One is that the sample has inhomogeneous and irregular flake-like structure, and the other is that all these plate-like samples are very thin. The sizes of some of plate-like samples reach 1-2 μm . With surfactants SDS, PVP and CTAB being added in the synthesis process, S4-S6 samples are obtained. From Fig.10(b)-(c), the morphology images are presented. Compared with Fig.10(a), the main difference between S3 and S4-S6 is summarized as three following points. One is about shape, the other is related to size, and another is about arrangement. In the case of S3, the sample shape is irregular. However, after assisted-surfactants are added in the synthesis process, the shapes of these obtained S4-S6 samples become almost regular. In particular, as for the shape of S6 shown in Fig. 10(d), when the surfactant CTAB is adopted, irregular plate-like structure has been changed into homogeneous and regular rectangle. Compared S3 with S4-S6, the sizes of flakes are also found to be reduced, whose radii are all changed to about 0.1 μm . Moreover, the average sizes and the shapes of flakes become very uniform. More importantly, in the case of S3 the arrangement of these flakes seems to resemble chaotically. On the contrary, in the cases of S4 and S5, the flakes are regularly positioned across each other. As for S6, these rectangles tend to stack horizontally one by one and blend each other into big pieces. Therefore, S4-S6 tends to assemble regularly. Based on our results mentioned above, the assist-surfactants will result in two main effects. One is the decrease of sample size, and the other is that the sample arrangement tends to be more uniform and regular. More interestingly, horizontally-stacked structure is believed to be more benefit to photo-catalyst. In other words, the photocatalyst properties of sample S6

will be more efficient, as demonstrated in the following. The structure characterization has been further investigated by TEM measurement. Figure 11 shows several laminar plates of these as-prepared bismuth molybdate products, which is well accordance with the SEM result.

The main effect of adding different surfactant is to modulate the particle surface condition. In the synthesis process, the surface of crystal nucleus is covered with surfactant ions in solution, and these surfactant ions are attached onto different crystal facets, and eventually they will guide the growth of particles with the various shapes by controlling the growth rates along the different crystal axes^[38-41]. SDS is an anionic surfactant with a hydrophobic short chain connected to a negative ionic group. During the hydrothermal treatment, the $(\text{Bi}_2\text{O}_2)_n^{2+}$ cations strongly attached on the $\text{C}_{12}\text{H}_{25}\text{SO}_4^{2-}$ anions and formed micelles due to electrostatic interaction. The MoO_4^{2-} anions continuously react with the $(\text{Bi}_2\text{O}_2)_n^{2+}$ cations of the micelles to form the $-\text{Mo}-\text{O}-\text{Bi}-$ networks^[42]. PVP plays an important role as a template in optimizing the growth rate and orientation in the formation of crystallites. PVP as non-ionic polymer is easily dissolved in water and can form by uncountable N-vinylpyrrolidone monomers^[43]. The molecules can attach on the planes of Bi_2MoO_6 leading the formation of nanoplates^[44]. Since CTAB is one kind of strong-acid-weak base salt, it can accelerate the ionization process of MoO_4^{2-} . The $\text{CTA}^+-\text{MoO}_4^{2-}$ ion pairs are combined with $\text{Bi}_2\text{O}_2^{2+}$, consequently Bi_2MoO_6 is synthesized. The Br^- ions from CTAB strongly absorb on the nanoflakes and thus make the surface negatively charged. In the self-assembly process, the large size nanoflake is blocked by Coulomb repulsion forces and the hydrophobic chains of CTA^+ ions. With prolonged hydrothermal reaction time, the system finds its minimum energy configuration by adopting the small size nanoplate-like structure^[38]. The above results suggest that the morphology of Bi_2MoO_6 nanoplates strongly depends on the surfactant addition of the dispersion.

The band structure of semiconductor material is one key factor in estimating its photocatalytic activity. To further probe the effect of surfactants, the optical properties of the as-prepared bismuth molybdate catalysts were characterized by UV-vis diffuse reflectance spectra technique. And E_g can be obtained correspondingly. The band gap

of the Bi_2MoO_6 was estimated to be 2.80, 2.82, 2.81, and 2.70 eV for S3, S4, S5, and S6 samples. The band gap is almost equal for S3, S4, and S5. However, for S6 sample, the band gap is decreased largely. The Br^- ions on surface induce a decrease in the band gap energy of nanoplates in S6 sample. According to the reference^[44] about the synthesis of Bi_2WO_6 samples, the bottom of conduction band is originated from W 5d orbital, whereas the top of valence band is composed of hybridized orbital of Bi 6s, O 2p and Br 4p. Due to more negative potential of their top of valence, as one similar main group element with Bi, it is believed that in Bi_2MoO_6 system there is also narrower band gap for CTAB-assisted samples S6.

To estimate the photocatalytic activities of Bi_2MoO_6 nanoflakes, the degradation of MB aqueous solution is also measured under visible light irradiation. Figure 13 shows the degradation of dyes in the presence of different samples. The results suggest that, after 120 min irradiation of visible light, 83%, 67%, 74% and 100% of MB were removed in the presence of the samples (S3, S4, S5 and S6). The results showed that the catalytic activity is in the order of $\text{S4} < \text{S5} < \text{S3} < \text{S6}$.

The photocatalytic activity of S4 and S5 is lower than that of S3, which may be ascribed to the weaker absorption of smaller size nanoflakes. Similarly, the excellent photocatalytic activity of S6 can be attributed to the enhanced visible light absorption, improved separation of photogenerated charge carriers and the specific exposed facets structure. One larger specific surface area of photocatalysts can supply more surface active sites, and make charge carriers transport easier, leading to the enhancement of the photocatalytic performance. On the other hand, the Br^- ions surfaces induce a decrease in the bandgap energy of the nanoplates. The surface Bi atoms are coordinatively unsaturated and thus the monolayers surfaces expose a huge number of active sites. On irradiation, holes are directly generated on the active surfaces and electrons in the middle.

To further investigate the influence of preparation methods and other synthesis conditions including solvent type etc., the electrochemical impedance spectroscopy (EIS) technique was used to study the solid-electrolyte interfaces of S1-S6 samples.

The results are shown in Fig.14. From this figure, it is found that the shapes are similar, however the arc radius of the EIS Nyquist plot is different. One smaller radius indicates one lower electric charge transfer resistance of the sample. Thus, in the case of PVP-surfactants, the photo-induced electron-hole pairs are more easily separated and transferred on the sample surface. While, the highest EIS values is found in the S1 sample. The EIS magnitude of S2, S3, S4, and S6 samples is almost same. In addition, compared with the other samples, it is noted the EIS magnitude for S5 is lowest. Analyzing these experimental results, we presume that these features are directly associated to the preferential orientation and/or structural defects arising from imperfectly attached interfaces between nanocrystals, crystal sizes, and shapes. Theoretically, the existence of defects are able to modulate the density of intermediary energy states within the forbidden band gap due to order-disorder effects and distortion of the octahedral MoO_6^{4-} . All these will affect the photocatalytic and photoelectric properties of Bi_2MoO_6 sample.

Conclusion:

In the current research, to systematically probe the effect of synthesis methods and conditions on the morphologies and eventually the photocatalytic properties of one specific material, Bi_2MoO_6 samples are synthesized via two preparation techniques at the same time. Moreover, some external conditions including solvent and surfactant types are also considered in the synthesis processes. Bi_2MoO_6 photocatalyst with different morphologies such as octahedral-like, spherical-like, and nanoplate-like have been successfully synthesized. Mixed phases (cubic phase $\text{Bi}_{3.64}\text{Mo}_{0.36}\text{O}_{6.55}$ and orthorhombic Bi_2MoO_6) are also obtained by co-precipitation and hydrothermal method (using HNO_3 solvent). When HNO_3 is changed to ethylene glycol in the hydrothermal preparation, pure Bi_2MoO_6 phase is achieved. The photo-degradation efficiency of the as-prepared samples was investigated by monitoring the degradation of MB under visible light irradiation. The experimental results indicate that Bi_2MoO_6 nanoplates hydrothermally prepared with CTAB

surfactant show highest photocatalytic activity (nearly 100%) in all samples due to the enhanced visible light absorption, improved separation of photogenerated charge carriers and the specific exposed facets structure.

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Figure captions

Figure 1 XRD pattern for the samples obtained with different preparation method, S1 (co-precipitation method) and S2 (hydrothermal method)

Figure 2 SEM and TEM images of (a)(c) for S1 and (b)(d) for S2 sample

Figure 3 UV-vis diffuse reflectance spectra of S1 and S2 samples, Inset plots of $(ah\nu)^2$ vs photo energy $(h\nu)$ for S1 and S2 samples

Figure 4 Photo-degradation of MB in the presence of S1 and S2 samples

Figure 5 XRD pattern for the samples obtained with different solvent in the hydrothermal preparation, S2 (HNO₃) and S3 sample (ethylene glycol)

Figure 6 SEM and TEM images of (a)(c) for S2 and (b)(d) for S3 sample

Figure 7 UV-vis diffuse reflectance spectra of S2 and S3 samples, Inset plots of $(ah\nu)^2$ vs photo energy $(h\nu)$ for S2 and S3 samples

Figure 8 Photo-degradation of MB in the presence of S2 and S3 samples

Figure 9 XRD pattern for the samples obtained with different surfactant S3 (without surfactant), S4 (SDS as surfactant), S5 (PVP as surfactant), and S6 (CTAB as surfactant)

Figure 10 SEM images for the samples obtained with different surfactant S3 (a), S4 (b), S5 (c), and S6 (d)

Figure 11 TEM images for the samples obtained with different surfactant S3 (a), S4 (b), S5 (c), and S6 (d)

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Figure 13 Photo-degradation of MB in the presence of S3, S4, S5 and S6 samples

Figure 14 EIS profiles of S1(a), S2(b), S3(c), S4(d), S5(e), and S6(f) samples

Table 1 Various preparation method, solvent, surfactant, and the corresponding obtained phases

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Table 1 Various preparation method, solvent, surfactant, and the corresponding obtained samples

Sample	S1	S2	S3	S4	S5	S6
Preparation method	CP	HY	HY	HY	HY	HY
solvent	H ₂ O	HNO ₃	EG	EG	EG	EG
surfactant	---	---	---	SDS	PVP	CTAB
phase	Bi _{3.64} Mo _{0.36} O _{6.55} Bi ₂ MoO ₆	Bi _{3.64} Mo _{0.36} O _{6.55} Bi ₂ MoO ₆	Bi ₂ MoO ₆	Bi ₂ MoO ₆	Bi ₂ MoO ₆	Bi ₂ MoO ₆

CP---co-precipitation, HY---hydrothermal, EG---ethyleneglyco