Controllable synthesis of Bi₂MoO₆ and effect of morphology and variation in local structure on photocatalytic activities

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ABSTRACT

Highly crystalline orthorhombic Bi₂MoO₆ particles with high visible-light photocatalytic activity have been controllably synthesized via a facile hydrothermal process without adding any surfactant. The morphologies of Bi₂MoO₆ with nanosheet and microrod can be selectively obtained by adjusting the pH value of the reactant. The formation mechanisms of nanosheet and microrod structures were then discussed based on the H⁺ cations adsorption abilities on different crystal faces. The Bi₂MoO₆ samples prepared at acidic condition showed 12 times higher photocatalytic activity than that prepared at basic condition under visible-light irradiation. The reason for the big difference in the photocatalytic activities for the Bi₂MoO₆ samples obtained at different pH values were systematically studied based on their shape, size and the variation of local structure.

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1. Introduction

The photodecomposition of organic compounds and water splitting by semiconductor photocatalysts has attracted intense research interest because of their economic and ecologically safe option for solving energy and pollution problems [1]. In the past several decades, the thoroughly studied conventional TiO₂ displays excellent activities and stabilities. However, the deficiency of requiring UV light for effective photocatalysis severely hinders the overall process to be used in practical. Therefore, the development of a visible-light photocatalyst consequently has become an imperative topic in current photocatalysis research. Considering the relatively slow reaction rate and poor solar efficiency of TiO₂ which hindered its application, many studies have been carried out to exploit new visible light-driven photocatalysts.

As a typical Aurivillius oxide, Bi₂MoO₆ (M=W, Mo) with the layered bismuth oxide family are of special interest due to their dielectric, ion-conductive, luminescent and catalytic properties [2–4]. Recent results revealed that Bi₂MoO₆ could perform as an excellent photocatalyst and solar-energy-conversion material for water splitting and degradation of organic compounds under visible-light irradiation [5–10]. The properties of materials with the same composition but different morphologies could be substantially different. Therefore, the better performance of material is not only depended on the compositions but also on the morphologies of the materials. The dependence of the properties of nanomaterials on both the size and shape is a phenomenon of both fundamental scientific interest and many practical and technological applications [11–13]. In order to advance the basic understanding of the principles that determine the shape and to provide tailored building blocks for nanodevices, a variety of methods have been developed to control the shape, dimensionality, and assembly of nanostructures [14,15]. As known, both the size and the morphology have an influence on the properties of semiconductor oxides. For example, nanoscale photocatalysts are believed to perform better than the bulk materials due to the higher surface-to-volume ratio and separation efficiency of the photogenerated electrons or holes [16,17]. The photocatalytic activities of Bi₂WO₆ and BiVO₄ nanostructures are strongly determined by the shape, size, and structure. Morphology control provides a greater versatility for tuning the photocatalytic properties of semiconductor materials. However, seldom successes in developing approaches to tune the shape and structure of the visible-light-driven photocatalysts have been achieved. As far as we know, the systematic research on the morphology evolutions of Bi₂MoO₆ in different dimensions is rarely concerned. Constructing novel nanostructures by bottom-up techniques may be rationally designed.

In this work, Bi₂MoO₆ nanocrystals were controllably synthesized with tunable morphology by a simple hydrothermal method. The as-prepared Bi₂MoO₆ nanocrystals showed high photocatalytic activity in the decomposition of Methylene blue (MB) under visible-light irradiation. The influence of reaction parameter (pH value) on...
the Bi₂MoO₆ morphology, structure and the relationship between the morphology and photocatalytic activities were investigated. The aim of this research was to develop a method for the fabrication of different-dimensional Bi₂MoO₆ nanomaterials enriching the available methods for preparation of multicomponent metal oxide, and to adjust the properties by modulating the morphology and size of the materials, thus facilitating their applications.

2. Experimental

2.1. Preparation

All chemicals were analytically pure and used without further purification. For the synthesis of Bi₂MoO₆, 2 mmol Bi(NO₃)₃·5H₂O (0.97 g) was dissolved in 20 mL nitric acid solution (2 mol L⁻¹) and stirred for several minutes. Then 0.1 mol L⁻¹ Na₂MoO₄ solution (10 mL) was slowly added into the above solution. The amorphous white precipitate formed immediately. The different pH values of the solution (1, 3, 5, 7, 9, 11, 13) were then adjusted with concentrated ammonia under stirring. After being vigorously stirred for 30 min, the resulting precursor suspension was transferred into a 40 mL capacity Teflon-lined stainless steel autoclave, which was subsequently heated to 180 °C and maintained for 24 h. Subsequently, the autoclave was cooled to room temperature naturally. The obtained samples were filtered, washed with deionized water and dried at 80 °C in air.

2.2. Characterization

X-ray powder diffraction (XRD) patterns were obtained on a Bruker D8 Advance X-ray diffractometer at 40 kV and 40 mA with Cu Kα radiation. The crystallite size was calculated from X-ray line broadening via the Scherrer equation: \( D = \frac{0.9λ}{β cos θ} \), where \( D \) is the crystal size in nm, \( λ \) the Cu Kα1 wavelength (1.5406 Å), \( β \) is the half-width of the peak in radians, and \( θ \) is the corresponding diffraction angle. Scanning electron microscopy (SEM) was operated on a JEOL JSM-6700F field-emission scanning electron microscope. Transmission electron microscopy (TEM) was performed using a JEOL JEM 2010 EX instrument at an accelerating voltage of 200 kV. The powder particles were supported on a carbon film coated on a 3 mm diameter fine-mesh copper grid. A suspension in ethanol was sonicated, and a drop was dripped on to the support film. A suspension in ethanol was sonicated, and a drop was dripped on to the support film. The UV–vis diffuse reflectance spectra (UV–vis DRS) of the samples were obtained on a UV–vis spectrophotometer (UV-3010, Shimadzu) using an integrating-sphere accessory. BaSO₄ was used as the reference. The UV–vis diffuse reflectance spectra of the samples prepared at acid conditions (pH 1, pH 3 and pH 5), the samples prepared at alkaline conditions (pH 9, pH 11, and pH 13) were obtained on a UV–vis spectrophotometer. The UV–vis diffuse reflectance spectra of the samples were recorded for KBr disks containing the powder sample.

2.3. Photocatalytic activity measurements

The photocatalytic activities of Bi₂MoO₆ samples were evaluated by the degradation of MB in an aqueous solution. A 500 W Xe lamp with a cutoff filter (λ > 420 nm) was used as light resource to ensure the photoreaction proceeded under visible-light irradiation. The reaction cell was placed in a sealed black box of which the top was open and the cutoff filter was set on the window face of the reaction cell to ensure the desired irradiation condition. In each experiment, photocatalyst powders (0.10 g) were added into MB solution (10⁻⁵ mol L⁻¹, 100 mL). Before illumination, the suspensions were magnetically stirred for 60 min to reach the adsorption–desorption equilibrium between the photocatalysts and MB. At given time intervals, 3 mL of the aliquots were sampled and centrifuged to remove photocatalyst powders. The degraded solution was analyzed using a UV–vis spectrophotometer and absorption peak at 663 nm was monitored.

3. Results and discussions

3.1. Structure, morphology and formation mechanism

The effects of pH values on the structure and morphology of Bi₂MoO₆ prepared without any surfactant were studied. The precursor suspensions were adjusted to the desired pH values by adding NH₃·H₂O solution, and then were hydrothermally treated at 180 °C for 24 h. The Bi₂MoO₆ samples prepared from the precursor suspensions with pH values of 1, 3, 5, 7, 9, 11, and 13 are denoted as pH 1, pH 3, pH 5, pH 7, pH 9, pH 11, and pH 13, respectively.

Fig. 1 shows the XRD patterns of Bi₂MoO₆ samples prepared by hydrothermal procedure at different pH values (A–G: pH 1–13). The diffraction peaks of all the samples can be indexed as a pure koechlinite phase, which are consistent with the literature values (JCPDS 76-2388). As can be seen from the XRD patterns, the high crystallinity can be obtained at a relatively low hydrothermal treatment temperature (180 °C). When the pH value is maintained at pH 1, pH 3, pH 5, the expanded diffraction peaks obviously reveal that the crystalline phase would be nanosized. The influence of pH value on the crystalline phase was demonstrated through the changes of XRD patterns. As the pH value increases from 1 to 13, the shape of diffraction peaks become more clean-cut and the intensities increases gradually, indicating better crystallines formed. The crystallines grow larger as estimated according to the width of peak on the basis of the Scherrer equation. It is noteworthy that the XRD patterns also indicate that there are large differences in the relative intensities based on the (0 2 0), (1 3 1), (2 0 0), (0 0 2) and (0 6 0) peaks for all the samples, indicating the possibility of different preferential orientation growth under different pH conditions. For the samples prepared at acid conditions (pH 1, pH 3 and pH 5), the ratio of intensity of (1 3 1)/(2 0 0) is about three, while the standard intensity of the (1 3 1) peak of the XRD pattern is about five times
stronger than that of the (2 0 0) peak. This implies that the crystal has special anisotropic growth. These results can be attributed to the square-plate structure of the crystallites, which is proved by further study of morphologies of the crystallites. However, the changes of diffraction peaks for the samples (D–G) obtained at base conditions are different with the samples at acid conditions (A–C). As is shown in Fig. 1, the intensities of (1 3 1) peak are similar for all the four samples (D–G), while the intensities of (0 2 0) and (0 6 0) peaks increased greatly, indicating that there must be a different preferential growth orientation in Bi\textsubscript{2}MoO\textsubscript{6} under basic conditions. The crystal would grow along the (0 1 0) direction and form 1D rod-like materials.

As a further confirmation of the XRD analysis, Fig. 2 shows the morphological evolution of Bi\textsubscript{2}MoO\textsubscript{6} samples with different pH values of the precursor suspensions (A–G: pH 1, pH 3, pH 5, pH 7, pH 9, pH 11, pH 13). When the pH values in the reaction system are kept at 1, 3 and 5, sheet-like Bi\textsubscript{2}MoO\textsubscript{6} crystals with the thickness of several nanometers are observed. Interestingly, under acidic condition, the size of the as-obtained Bi\textsubscript{2}MoO\textsubscript{6} nanosheets grows smaller with the increasing of the pH values of the reaction system. The width of the nanosheets is about 150, 80 and 50 nm for samples (A–C), respectively. Further increasing the pH value leading to the shape of the as-obtained nanostructures evolved from nanosheets to nanoplates with the thickness of tens of nanometers (D: pH 7). The pH-dependent experiments are taken subsequently by increasing the pH values to 9, 11 and 13. Fig. 2 indicates that the as-prepared Bi\textsubscript{2}MoO\textsubscript{6} almost exhibits a rod shape with an average diameter of about 1 μm and length of about 3 μm, which is very different from the morphologies of samples obtained under acid conditions. The above results suggest that the morphology of Bi\textsubscript{2}MoO\textsubscript{6} nanosheets/microrods strongly depends on the initial pH of the dispersion. Similar results were also observed in the synthesis of some tungstates [18]. Therefore, the morphology of the as-prepared molybdate nanosheets/microrods can be controlled by tuning the pH value of colloidal precursor.

Fig. 3 shows the HRTEM images of Bi\textsubscript{2}MoO\textsubscript{6} samples prepared at different pH values (Fig. 3A–C) and SEM image of Bi\textsubscript{2}MoO\textsubscript{6} sample prepared at pH 7 (Fig. 3D). The nanoplate structure is clearly observed from Fig. 3D, which is in accordance with the TEM results. HRTEM images indicate the single-crystalline nature of the samples. For the sample prepared at pH <7, the d spacing of 0.305 nm corresponding to the lattice spacing of (1 3 1) of orthorhombic
B$_2$MoO$_6$ is observed from Fig. 3A and B. For the sample prepared at basic condition (pH 11), it can be measured that the d spacings are 0.274 and 0.275 nm, which agree well with the lattice spacings of (0 0 2) and (2 0 0), respectively.

One of the critical factors 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 strongly affect the further crystal growth [19]. As is known, the structure of koechlinite B$_2$MoO$_6$ consists of alternating (Bi$_2$O$_2$)$_n^{2+}$ layers and perovskite-like (MoO$_4$)$_n^{2-}$ layers, and octahedral Mo chains usually play an important role in the high intrinsic anisotropic growth in various molybdates [20].

In our experiments, it was noted that there was no phase transformation process for all the samples accompanied with morphology variation during the crystal growth. However, the pH value of the growth solution was a crucial parameter in the control of morphology of B$_2$MoO$_6$ nano- and micro-crystals. The main effect of tuning the pH value was to modulate the kinetics of nucleation and growth of the crystal by controlling experimentally the surface free energy. The preferential adsorption of molecules and ions in solution onto different crystal facets directed the growth of particles into various shapes by controlling the growth rates along different crystal axes [21–24]. The crystal plane with a higher surface energy is expected to have a faster growth rate. Herein, the differences in the pH values showed a significant effect on the selective adsorption of H$^+$ onto the different surfaces of growing B$_2$MoO$_6$ crystallites, giving rise to the difference of the growth rates between the different crystallographic directions. At pH 1, pH 3, pH 5 there would be abundant H$^+$ in the system to adsorb on the (0 1 0) faces and even on (0 0 1) and (1 0 0) faces. Therefore, the surface energy of these faces would all be markedly reduced. Thus, it is possible to form a relatively thin nature along [0 1 0] direction [25]. It is well known that under the hydrothermal environment, nuclei could grow freely in aqueous solution (an open space) to form the nanocrystals with their natural habit, i.e., nanorods, nanoflowers, nanocubes, etc. Further crystal growth for the formation of 2D nanostructures was strongly related to the intrinsic crystal structure of B$_2$MoO$_6$. It has been reported that orthorhombic B$_2$MoO$_6$ is constructed by a cornershared MoO$_6$ octahedral layer and [Bi$_2$O$_2$]$^{2-}$ atom layers sandwiched between MoO$_6$ octahedral layers. It is well known that the shape of the nanostructures is strongly dependent on 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 B$_2$MoO$_6$ structure, the chains of octahedral-Mo equally exist along the a and c axes. The facets which are perpendicular to these chains usually have a much higher chemical potential in comparison with other facets. The above feature resulted in faster growth rates of these faces, and thus the crystal growth was preferentially along the layer. Because the B$_2$MoO$_6$ have an orthorhombic crystal structure, crystal symmetries along a, c axes should be equivalent. Therefore, the direction of the nanosheets stacking is along the b axis, perpendicular to a and c axes of the planes, and each layer has the same a and c axes. Based on the experimental results, it can be concluded that under a low pH value condition, there existed higher surface energy on the (1 0 0) and (0 0 1) faces compared with other crystal planes, and the growth of nanocrystal along the (0 1 0) plane was inhibited. The surface cleavage of B$_2$MoO$_6$ crystal also provides further information for explaining the adsorption of H$^+$ cations (Fig. 4). As seen from the figure, the (1 0 0), (0 1 0) and (0 0 1) crystal planes are terminated with Mo, O and Bi atoms, respectively. The zigzag
orientations of Mo octahedral anions on (1 0 0) face results in this face becoming unfavorable for the adsorption of H\(^+\) cations. The amount of O atoms on the (0 1 0) plane is much higher than other planes (Fig. 4C). Therefore, H\(^+\) cations would prefer to absorb on the (0 1 0) planes because of the high density of oxygen atoms on this face, resulting in the crystal growth rate along the (0 1 0) orientation is slowed and formed nanosheets.

However, when NH\(_3\)·H\(_2\)O (1 M) was added to the growth suspension, the H\(^+\) ions were partially neutralized, which makes the localized concentration of H\(^+\) varied on the nanocrystal surface and results in the surface free energies of the various crystallographic planes differing significantly. Obviously, the growth rate of those facets possessing higher free energy would be relatively faster, which affords the possibility of breaking the natural growth habit of the crystal and creating additional growth anisotropy. As revealed in the experiments, Bi\(_2\)MoO\(_6\) microrods can be obtained by tuning the pH of the growth solution [26]. Under the alkaline condition (pH 9, pH 11, pH 13), the dominant adsorption of OH\(^-\) onto the facets lowers the surface energy of these facets, subsequently prohibits the enlargement in \(a, b\) planes and drives the growth of nuclei along the directions of [0 1 0] [27]. This is coincident with the XRD results. In the XRD pattern of the corresponding samples (Fig. 1F–H), the strongest reflection is (0 2 0), which is quite different from the literature data. This abnormal intensity of the (0 1 0) peak suggests the preferential orientation growth along the [0 1 0] direction to a great degree.

### 3.2. Optical properties and photocatalytic performances

Optical absorption of Bi\(_2\)MoO\(_6\) samples was measured by UV–vis spectroscopy. Fig. 5 exhibits the diffuse reflectance spectra of the Bi\(_2\)MoO\(_6\) samples (A–G: pH 1–13). As can be seen, all the Bi\(_2\)MoO\(_6\) samples showed strong photoabsorption properties from the UV light region to the visible-light region with the wavelength shorter than 490 nm. The steep shape of the spectra indicated that the visible-light absorption is arisen from the band-gap transition but not from the impurity level [28]. In this system, slight red shift of the absorption band edge of Bi\(_2\)MoO\(_6\) samples (from 2.81 to 2.85 eV) can be observed with the pH value increasing from 1.
to 13. It is well known that the band gap energy of semiconductor nanoparticles decreases with the decrease of grain size. Herein, Bi$_2$MoO$_6$ with a 1D microstructure (pH 9, pH 11, pH 13) had a red shift in the band-gap transition compared with sheet-like Bi$_2$MoO$_6$ (pH 1, pH 3, pH 5, pH 7), attributed to the smaller grain sizes of the building blocks of the 2D nanostructures than that of the 1D microrods.

Methylene blue was used as a probe in the heterogeneous photocatalysis, the dark adsorption (on the surface of semiconductor oxide), subsequent decoloration and decomposition can be monitored via visible-light absorption signature (at $\lambda_{\text{max}} = 664$ nm). Fig. 6 shows the dependence of visible-light photocatalytic activity of the Bi$_2$MoO$_6$ samples upon pH values (A–G: pH 1–13) of the precursor suspensions. The blank test demonstrates that the degradation of MB is extremely slow without a photocatalyst under visible-light illumination. The first-order linear relationship was revealed by the plots of $\ln(C/C_0)$ versus irradiation time ($t$). It was found that the obtained Bi$_2$MoO$_6$ samples under acid conditions exhibited much higher photocatalytic activity than other samples. More than 90% of MB could be decomposed with the Bi$_2$MoO$_6$ samples prepared at acid condition under visible-light irradiation within 120 min, while only 9% of MB was photodegraded with the sample prepared at basic condition. The calculated apparent reaction rate constant $k$ for the sample prepared at pH 5 was 0.016 min$^{-1}$, which is more than 12 times faster than that of Bi$_2$MoO$_6$ prepared at pH 11 ($k = 0.0013$ min$^{-1}$). The vastly different photodegradation rates of MB by different Bi$_2$MoO$_6$ samples (A–G) indicated that the photocatalytic performances of these Bi$_2$MoO$_6$ samples are greatly different and are strongly dependent on shape, crystal size, and structure.

The lower pH values of the precursor suspensions the higher the photocatalytic activities of the Bi$_2$MoO$_6$ samples exhibited. Table 1 shows the average size, Brunauer–Emmett–Teller (BET) surface areas and the adsorption percentages of MB on the photocatalysts in the dark for 60 min. It is clearly revealed that the samples with small size (pH 3, pH 5) can more efficiently absorb the MB due to their higher BET surface area than other samples with larger sizes. The decrease of grain radius reduces the opportunities for recombination and promotes the transfer of the light-generated charge to the surface to degrade the absorbed MB molecules [29]. In addition, with the transformation of Bi$_2$MoO$_6$ from a 2D plate-like structure to a 1D rod-like microstructure (samples prepared at pH 1–13), the BET surface area of the samples decreases, resulting in a decrease of adsorption percentages of MB molecules. The increasing of BET surface areas and the decrease of crystalline grains were both beneficial to the enhancement of the photocatalytic activity of Bi$_2$MoO$_6$ [30].

Visible-light irradiation of aqueous MB/Bi$_2$MoO$_6$ dispersions leads to a decrease in absorption intensity and a blue-shift of the wavelength as the MB degrades. UV–vis spectra taken over time during the photodegradation of MB mediated by Bi$_2$MoO$_6$ nanosheets versus microrods are shown in Fig. 6B and C, respectively. A control experiment on an aqueous MB solution in the absence of Bi$_2$MoO$_6$ photocatalyst was carried out under the same experimental conditions, but the absorption intensity and absorption wavelength hardly changed with increasing irradiation time. From Fig. 6A it can be concluded that the degradation rate of MB mediated by nanosheets is much faster than that mediated by

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Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>pH 1</th>
<th>pH 3</th>
<th>pH 5</th>
<th>pH 7</th>
<th>pH 9</th>
<th>pH 11</th>
<th>pH 13</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average size ($\mu$m)</td>
<td>$\sim$0.1</td>
<td>$\sim$0.07</td>
<td>$\sim$0.05</td>
<td>$\sim$0.4</td>
<td>$\sim$1</td>
<td>$\sim$3</td>
<td>$\sim$2</td>
</tr>
<tr>
<td>BET surface areas (m$^2$ g$^{-1}$)</td>
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<td>17.32</td>
<td>18.75</td>
<td>6.03</td>
<td>5.78</td>
<td>4.41</td>
<td>0.79</td>
</tr>
<tr>
<td>Adsorption (%) in dark</td>
<td>45</td>
<td>74</td>
<td>76</td>
<td>32</td>
<td>27</td>
<td>18</td>
<td>9</td>
</tr>
</tbody>
</table>

Fig. 6. Photocatalytic degradation of MB in the presence of as-prepared photocatalysts (A–G: pH 1, pH 3; pH 5, pH 7, pH 9, pH 11 and pH 13).
the microrods. The blue-shift of the absorption band from 664 to 610 nm arises from the degradation of MB [31]. After irradiation for 120 min the absorption blue-shifts from 664 to 629 nm in the presence of the prepared nanosheets, indicating that MB has accomplished a demethylation step, while in the same time period it only blue-shifted from 664 to 661 nm using microrods as catalyst. The results confirm that the Bi$_2$MoO$_6$ nanosheets had superior photocatalytic activities compared with the microrods. This high photocatalytic activity must be related to the higher surface area of the nanosheets. Moreover, The thickness of the nanosheets results in a relatively large distortion of the unit cell due to the large surface strain, and the nanosheet structure means that electron–holes generated inside the crystal easily transfer to the surface and react with MB [30]. Thus, a higher photocatalytic activity was exhibited compared to the microrods. In addition, XRD and TEM techniques are applied to evaluate the stability of Bi$_2$MoO$_6$ after photocatalytic reaction cycles. Results showed that the photocatalytic activity of the pH 5 sample remains almost the same in several consecutive runs for the photodegradation of MB under visible-light illumination ($\lambda > 420$ nm).

The photocatalytic property of Bi$_2$MoO$_6$ is also related to the distortion of the M–O polyhedron in crystal structure. Raman spectroscopy is effective to probe the local structure of materials because the Raman spectrum reflects the bonding states in the coordination polyhedra of a material. Raman spectra of Bi$_2$MoO$_6$ samples obtained at different pH value by hydrothermal method are shown in Fig. 7. All the typical vibrational bands for Bi$_2$MoO$_6$ samples are observed: 845 cm$^{-1}$ (s), 815 cm$^{-1}$ (w, sh), 797 cm$^{-1}$ (vs), 715 cm$^{-1}$ (m), 402 cm$^{-1}$ (m), 354 cm$^{-1}$ (s), 328 cm$^{-1}$ (w), 292 cm$^{-1}$ (m, sh), 282 cm$^{-1}$ (s), 262 cm$^{-1}$ (w, sh), 233 cm$^{-1}$ (w), 200 cm$^{-1}$ (m), 139 cm$^{-1}$ (m) (Fig. 7A). All the samples showed the similar Raman vibration modes in the range of 100–450 cm$^{-1}$, and no apparent change of Raman shifts can be found. However, an obvious change of the Raman band intensity occurred in this range varying with the increasing of pH values in reaction system. As is shown in Fig. 7B, the intensity of band at 354 cm$^{-1}$ remains the same all the time, while the intensity of 282 cm$^{-1}$ increases gradually and the relative ratio of intensity at 282 and 354 cm$^{-1}$ varies from 0.6 to 1.4, reflecting the difference in deformation degree of MoO$_6$ octahedra in different samples. It is well known that the bands in the 180–500 cm$^{-1}$ region originates from the bending modes of the MoO$_6$ octahedra coupled with stretching and bending modes of the bismuth–oxygen polyhedra. The modes near 326, 345 and 402 cm$^{-1}$ are corresponded to the $E_g$ symmetry bending modes. And the intense Raman modes near 292, and 282 cm$^{-1}$ originate most likely from the $E_g$ mode bending vibration [32]. The dependence of the relative intensities of the asymmetric and symmetric deformational vibrations (282 and 354 cm$^{-1}$) of the MoO$_6$ octahedron on the synthesis conditions is observed, demonstrating that MoO$_6$ octahedra with different space symmetries are formed and the variation or rearrangement of the crystal structure exist under the influence of reaction conditions (pH value). The band at 139 cm$^{-1}$ is assigned to the lattice modes of Bi$^{3+}$ atoms mainly in the direction perpendicular to the layers.

In general, The Raman modes mainly at 797 cm$^{-1}$ ($A_{1g}$ mode) with two shoulders (782, 812 cm$^{-1}$) and 845 cm$^{-1}$ ($A_{2u}$ mode) can be assigned to the symmetric and asymmetric stretching vibrations of the WO$_6$ octahedra that involve motions of the apical oxygen atoms which are perpendicular to the layers [33]. The differences in the stretching vibrational bands provide interesting information on the structural variations. Variations in the width and the relative intensity of these two bands suggested that the stretching modes of the Mo–O bond are different (Fig. 7C). As the pH value increased, the strong band at 797 cm$^{-1}$ was found to be shifted to 792 cm$^{-1}$ and broadened. And the two shoulders at 782 and 812 cm$^{-1}$ became prominent from pH 9 to pH 13. The shifts observed for Bi$_2$MoO$_6$ (pH 7, pH 9, pH 11, pH 13) were especially pronounced. The medium-intensity band was also broadened and also shifted in the position from 845 to 848 cm$^{-1}$. The absence of significant spectral variation from the samples (pH 1–7) revealed that the skeleton structure of the Bi$_2$MoO$_6$ phase was not dramatically disturbed. A similar Raman-band shift of the V–O stretching vibration was also observed in the Raman spectrum of BiVO$_4$ [12]. However, the observation of minute changes, such as the appearance of the triplet nature of the dominant Mo–O stretching bands at around 797 cm$^{-1}$, shift in position and broadening of the remaining Raman bands, suggested that there might be some subtle rear-
rangements in the structure [34]. The obvious change of Raman modes for MoO$_6$ confirmed that the reaction condition (pH value) could result in the structure change of MoO$_6$ octahedra related to the apical oxygen atoms. However, the mode at 715 cm$^{-1}$ exhibit no evident shift and broaden, which is due to the asymmetric stretching vibration ($E_u$ mode) of the MoO$_6$ octahedra involving the motion of the equatorial oxygen atoms within layers, further confirming that the variation of MoO$_6$ structure only exist in the apical oxygen atoms not equatorial oxygen atoms.

The relationship between Raman stretching frequency and bond length was found to follow a simple exponential form:

$$R_{\text{Mo-O}} = 0.48239 \ln \left( \frac{32.895}{\nu} \right)$$

(1)

where $\nu$ is the Raman stretching frequency in wavenumbers and $R$ is the metal–oxygen bond length in angstroms [35]. It can be concluded that the lower frequencies of the Raman stretching band correspond to the longer bond lengths. A calculation of the Mo–O bond length for Bi$_2$MoO$_6$ based on the expression suggests that one of the Mo–O (apical) bond length (797 cm$^{-1}$) increased from 1.793 Å in Bi$_2$MoO$_6$ (pH 1) to 1.798 Å in Bi$_2$MoO$_6$ (pH 9). While the other apical Mo–O bond length (845 cm$^{-1}$) decreased from 1.767 Å in Bi$_2$MoO$_6$ (pH 1) to 1.764 Å in Bi$_2$MoO$_6$ (pH 13). The observation of the gradual increase and decrease in the bond lengths of the apical Mo–O distance strongly suggested the loose structure (weak symmetry constraint) existed in the samples synthesized at higher pH values. Several differences in half-widths and intensities of the diffraction peaks were observed in the XRD patterns of Bi$_2$MoO$_6$ synthesized hydrothermally at various pH values (Fig. 1), indicating that slight changes in the structure, even though all the powders exhibited the monoclinic koechlinite phase.

Fig. 8 shows the FTIR spectra of Bi$_2$MoO$_6$ samples obtained at different pH values. The main absorption bands at 400–900 cm$^{-1}$ are mainly related to Bi–O, Mo–O stretching and Mo–O–Mo bridging stretching modes, which can reflects the variation of structure in crystal [33]. The bands at around 843 and 797 cm$^{-1}$ can be assigned as the asymmetric and symmetric stretching mode of MoO$_6$ involving vibrations of the apical oxygen atoms, respectively. The band at 734 cm$^{-1}$ is attributed to the asymmetric stretching mode of MoO$_6$ involving vibrations of the equatorial oxygen atoms and the bands at 603, 570 cm$^{-1}$ correspond to the bending vibration of MoO$_6$. As seen from the figure, the bands of MoO$_6$ at 797 and 603 cm$^{-1}$ for all the samples are similar and no shifts can be found. Minor downshifts of wavenumber at 843 cm$^{-1}$ and great upshifts at 570 cm$^{-1}$ are observed, indicating that the variation of structure for MoO$_6$ octahedra may be occurred with the increasing of pH values in this system. Furthermore, a small change of the band occurred at 454 cm$^{-1}$, which is attributed to the stretching and bending vibrations of BiO$_6$ octahedra, further confirming the changes of crystal structure. Based on the above results and analysis, it can be concluded that the changing of pH value in reaction system may influence the crystal structure and corresponding photocatalytic performance.

In orthohombic Bi$_2$MoO$_6$, the molybdenum cation is located in a distorted MoO$_6$$^{2-}$ octahedron with different bond lengths, and the bismuth cation is coordinated with the MoO$_6$$^{2-}$ octahedrons. Consequently, the lone-pair distortion existed in the orthohombic structure due to the difference in the Bi–O bond lengths around the bismuth cation. Based on the above discussion, it can be concluded that the lone-pair distortions around the bismuth cation in Bi$_2$MoO$_6$ prepared at higher pH values (pH 9, pH 11, pH 13) are less than those of Bi$_2$MoO$_6$ (pH 1, pH 3, pH 5). Therefore, the delocalization of photogenerated electron and hole pairs for Bi$_2$MoO$_6$ prepared at higher pH values is less than that at low pH value. The distortion degree of the MoO$_6$ octahedron in the local structure of Bi$_2$MoO$_6$ could result in a distinct variation in the electronic structure [12]. The greater the degree of distortion of the local structure, the more the Bi 6s and O 2p orbitals overlap, which enhances the migration of photogenerated holes [12]. It is reasonable that the Bi$_2$MoO$_6$ samples obtained under basic conditions showed the lower photocatalytic activities. The order of the photocatalytic activities for the hydrothermally synthesized Bi$_2$MoO$_6$ samples agrees well with the degree of lone-pair distortion indicated by Raman shifts. The degree of distortion of Bi$_2$MoO$_6$ (pH 3) was similar to that of Bi$_2$MoO$_6$ (pH 5), and thus their photocatalytic activities are comparable. The photocatalytic activity of Bi$_2$MoO$_6$ (pH 1) was lower than that of Bi$_2$MoO$_6$ (pH 3, pH 5) can be attributed to the relatively small BET surface area (6.38 m$^2$/g).

4. Conclusions

The transformation of the Bi$_2$MoO$_6$ morphology from a 2D sheet-like structure to a 1D rod-like has been realized through a facile, pH-controlled, surfactant-free hydrothermal route. The Bi$_2$MoO$_6$ sample prepared at acidic condition exhibited a photocatalytic activity 12 times higher than that prepared at basic condition for the photodegradation of MB under visible-light irradiation. The relationship between the initial pH value, morphology, variation of local structure, and photocatalytic activity of Bi$_2$MoO$_6$ was elucidated. Our work suggests that the photocatalytic performance of Bi$_2$MoO$_6$ is greatly dependent on the local structure and the morphology. The hydrothermal technique presented here seems an economical and easy way for the morphology and local structure control of such material.

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