

## ARTICLE

# Mesh-Like $\text{Bi}_2\text{MoO}_6$ with Enhanced and Stable Visible Light Photocatalytic Activity

Qing-wei Wang<sup>a</sup>, Xiao-yu Guo<sup>b</sup>, Xue Lin<sup>b\*</sup>, Chun-bo Liu<sup>b</sup>, Hong-ju Zhai<sup>b</sup>*a. Key Laboratory of Preparation and Application of Environmentally Friendly Materials, Ministry of Education, Jilin Normal University, Siping 136000, China**b. College of Chemistry, Jilin Normal University, Siping 136000, China*

(Dated: Received on April 25, 2014; Accepted on June 6, 2014)

Mesh-like  $\text{Bi}_2\text{MoO}_6$  product was successfully synthesized by a hydrothermal method without using any surfactant or template. The pH value played an important role in the formation of this morphology. The as-prepared mesh-like  $\text{Bi}_2\text{MoO}_6$  sample exhibited excellent visible-light-driven photocatalytic efficiency. The photocatalytic activity of the mesh-like  $\text{Bi}_2\text{MoO}_6$  sample was much higher than that of bulk  $\text{Bi}_2\text{MoO}_6$  sample prepared by solid-state reaction. Difference in the photocatalytic activities of the mesh-like  $\text{Bi}_2\text{MoO}_6$  sample and bulk  $\text{Bi}_2\text{MoO}_6$  sample was further investigated.

**Key words:**  $\text{Bi}_2\text{MoO}_6$ , Nanostructure, Hydrothermally synthesis, Photocatalytic property

## I. INTRODUCTION

With the rising level of air and water pollution, more and more attention to environmentally friendly materials, especially photodegradation catalysts is given. Since the photocatalytic splitting of water on the  $\text{TiO}_2$  electrodes was discovered by Fujishima and Honda in 1972 [1], the applications of semiconductor photocatalysts on solar energy conversion and degradation of pollution have received great interest. However, the mismatch between the large band gap and the sunlight spectra limits the utilization of solar energy [2–4]. Therefore, new visible light responsive photocatalysts with narrow band gap are highly desired [5–10].

To develop new photocatalysts which are active under visible light, various efforts have been made in the past several years. Especially, there are a number of studies related to the photocatalytic activities of bismuth-containing compounds such as  $\text{Bi}_{12}\text{TiO}_{20}$  [11],  $\text{Bi}_2\text{Ti}_2\text{O}_7$  [12],  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  [13],  $\text{Bi}_2\text{WO}_6$  [14, 15],  $\text{BiVO}_4$  [16–18] and  $\text{Bi}_2\text{MoO}_6$  [19]. Bismuth molybdates have the general chemical formula  $\text{Bi}_2\text{O}_3 \cdot n\text{MoO}_3$  where  $n=3$ , 2, or 1 [20]. Such compounds and their mixtures, especially  $\text{Bi}_2\text{MoO}_6$ , are well known owing to their good catalytic activities for selective oxidation of light hydrocarbons to produce many useful organic compounds: acrolein, methacrolein, butadiene, and so on [21, 22]. Recent studies reveal that  $\text{Bi}_2\text{MoO}_6$  possesses visible-light-driven photocatalytic activity for water splitting and degradation of organic contaminants [20–22].

In heterogeneous photocatalysis, the morphology of

the catalyst plays a key role in catalytic activity [23]. To our knowledge, the morphological control of  $\text{Bi}_2\text{MoO}_6$ -related nanostructures is relatively unexplored due to the lack of synthetic capability. In this work, novel mesh-like  $\text{Bi}_2\text{MoO}_6$  with high photocatalytic activity was successfully prepared by means of a facile template-free hydrothermal method for the first time. There are two significant aspects of the work described in this work. Firstly, the as-prepared  $\text{Bi}_2\text{MoO}_6$  sample exhibited a novel mesh-like morphology. Secondly, the mesh-like  $\text{Bi}_2\text{MoO}_6$  showed excellent photocatalytic performance. The photocatalytic activity of mesh-like  $\text{Bi}_2\text{MoO}_6$  was investigated in comparison with that of bulk  $\text{Bi}_2\text{MoO}_6$  through the photocatalytic degradation of an organic dye of rhodamine B (Rh B) and a colorless model pollutant of ciprofloxacin under visible-light irradiation respectively. The results revealed that the mesh-like  $\text{Bi}_2\text{MoO}_6$  exhibited better photocatalytic performance in the degradation of both Rh B and ciprofloxacin. To the best of our knowledge, investigations on the photocatalytic activity of the mesh-like  $\text{Bi}_2\text{MoO}_6$  have not been attempted yet.

## II. EXPERIMENTS

### A. Preparation of $\text{Bi}_2\text{MoO}_6$ photocatalyst

All reagents used in our experiment were of analytical purity and used without further purification. In a typical synthesis of  $\text{Bi}_2\text{MoO}_6$ , 2 mmol of  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  was dispersed into 10 mL of distilled water. Then an emulsion of  $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$  (2 mmol of  $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ , 5 mL of distilled water) was added to the above mixture under magnetic stirring. The amorphous yellow slurry formed immediately. Four slurries

\* Author to whom correspondence should be addressed. E-mail: jlsdlinxue@126.com, FAX: +86-434-3291890

were prepared and transferred into four 25 mL Teflon-lined autoclaves and the pH value of the reaction mixture was adjusted with NaOH solution to 1, 5, 7, and 9, respectively. Subsequently, the autoclave was heated to 160 °C in an oven. After crystallizing for 24 h, the resulting yellow products were filtered, washed with ethanol and distilled water several times, and dried at 100 °C for 10 h. The sample prepared for comparison was bulk  $\text{Bi}_2\text{MoO}_6$  sample, which was synthesized according to Jung *et al.*'s report [24].

### B. Characterization of $\text{Bi}_2\text{MoO}_6$ photocatalyst

The crystal structures of the samples were characterized by X-ray diffraction (XRD, D/max 2500) with Cu  $K\alpha$  radiation. The morphologies of the as-prepared samples were detected by using a field emission scanning microscopy (FESEM, Japan JEOL JSM-6700F). The chemical composition of the compound was determined by scanning electron microscope-X-ray energy dispersion spectrum (SEM-EDX). The specific surface area of  $\text{Bi}_2\text{MoO}_6$  samples was measured through nitrogen adsorption BET method (BET/BJH Surface Area, 3H-2000PS1). The UV-Vis diffuse reflectance spectra (DRS) were recorded for the dry-pressed disk sample using a scan UV-Vis spectrophotometer (UV-Vis, UV-2550) equipped with an integrating sphere assembly.

### C. Photocatalytic activities studies

The photocatalytic activities of the as-prepared  $\text{Bi}_2\text{MoO}_6$  samples were evaluated using Rh B dye and ciprofloxacin model compound. In experiments, the Rh B dye or ciprofloxacin solution (0.005 mmol/L, 100 mL) containing 0.02 g of  $\text{Bi}_2\text{MoO}_6$  photocatalyst were mixed in a pyrex reaction glass. A 500 W Xe lamp ( $\lambda > 420$  nm) was used to provide VLR. A glass sheet was inserted between the lamp and the sample to filter out UV light ( $\lambda < 420$  nm). Prior to visible light illumination, the suspension was strongly magnetically stirred for 30 min in the dark for adsorption/desorption equilibrium. Then the solution was exposed to visible light irradiation under magnetic stirring. At given time intervals, about 4 mL of the suspension was periodically withdrawn and analyzed after centrifugation. The Rh B concentration was analyzed by a UV-2550 spectrometer to record intensity of the maximum band at 552 nm in the UV-Vis absorption spectra. The ciprofloxacin concentration was analyzed by a UV-2550 spectrometer to record intensity of the maximum band at 275 nm in the UV-Vis absorption spectra.

## III. RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns of the bulk  $\text{Bi}_2\text{MoO}_6$  sample prepared by solid-state method

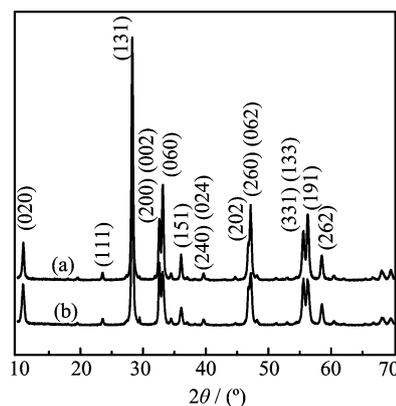


FIG. 1 XRD patterns of (a)  $\text{Bi}_2\text{MoO}_6$ (s) and (b)  $\text{Bi}_2\text{MoO}_6$  (pH=5).

(Fig.1(a), denoted as  $\text{Bi}_2\text{MoO}_6$ (s)), and the mesh-like  $\text{Bi}_2\text{MoO}_6$  sample prepared by the hydrothermal procedure (pH=5) (Fig.1(b), denoted as  $\text{Bi}_2\text{MoO}_6$  (pH=5)). The XRD pattern of  $\text{Bi}_2\text{MoO}_6$  (pH=5) exhibits diffraction peaks similar to those for  $\text{Bi}_2\text{MoO}_6$ (s). These diffraction peaks can be assigned to the  $\text{Bi}_2\text{MoO}_6$  phase (JCPDS 21-0102). No peaks of impurities were detected from these patterns. The strong and sharp peaks indicate high crystallinities of the samples. Furthermore, the  $\text{Bi}_2\text{MoO}_6$ (s) sample has stronger peak intensity which means the crystallinity of the bulk  $\text{Bi}_2\text{MoO}_6$  sample was higher.

It has been reported that although the crystal growth habit is mainly determined by the intrinsic structure, it is also affected by the external conditions such as pH value of the solution, saturation, and temperature [24]. In this work, pH value played an important role in determining the morphologies of  $\text{Bi}_2\text{MoO}_6$  crystals. The influence of different pH values on the morphologies of  $\text{Bi}_2\text{MoO}_6$  samples was investigated, NaOH was used to adjust the pH values in the range from 1 to 9. Figure 2 shows the FESEM images of samples prepared at different pH value. At lower pH value (pH=1),  $\text{Bi}_2\text{MoO}_6$  nuclei produced in solution could aggregate to form small nanospheres (as shown in Fig.2(a)). At pH value of 5, the morphology of the product was mesh-like nanostructure (Fig.2(b)). With the increase of pH to 7, as shown in Fig.2(c), a large number of  $\text{Bi}_2\text{MoO}_6$  nanoplates were formed, accompanied by the disappearance of the mesh-like nanostructure. When the pH value was further increased to 9,  $\text{Bi}_2\text{MoO}_6$  nanoplates were obtained (as illustrated in Fig.2(d)). It should be noted that all the hydrothermally synthesized  $\text{Bi}_2\text{MoO}_6$  crystals with different particle shapes and morphologies were formed simply by changing the pH in the synthesis process. Thus, the pH value played an important part in controlling the formation of seeds and the growth rates to shape the  $\text{Bi}_2\text{MoO}_6$  particles. Figure 3 displays the EDX spectrum of the as-prepared  $\text{Bi}_2\text{MoO}_6$  (pH=5) sample. It reveals that the mesh-like nanos-

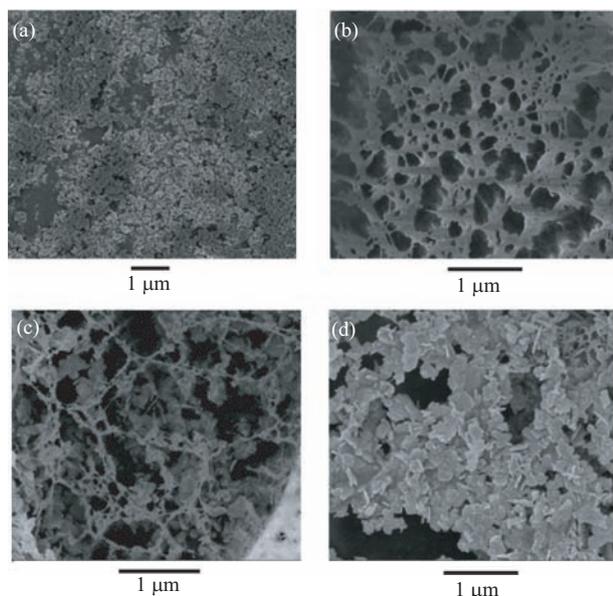


FIG. 2 FESEM images of  $\text{Bi}_2\text{MoO}_6$ . (a)  $\text{pH}=1$ , (b)  $\text{pH}=5$ , (c)  $\text{pH}=7$ , and (d)  $\text{pH}=9$ .

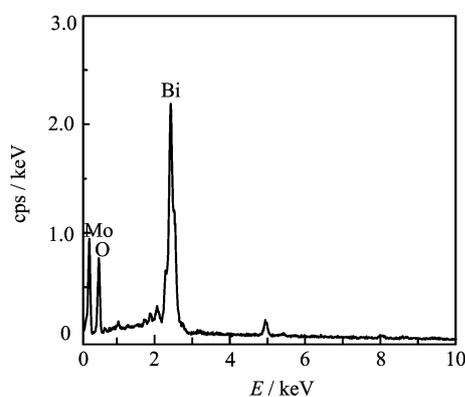


FIG. 3 EDX spectrum of the as-prepared  $\text{Bi}_2\text{MoO}_6$  ( $\text{pH}=5$ ) sample.

structure is only composed of Bi, Mo, and O elements. The molar ratio of Bi to Mo is calculated to be 2.0, which is in accordance with the nominal molar ratio of  $\text{Bi}_2\text{MoO}_6$ .

$\text{N}_2$  adsorption-desorption isotherms were performed to determine the surface areas of the  $\text{Bi}_2\text{MoO}_6(\text{s})$  and  $\text{Bi}_2\text{MoO}_6(\text{pH}=5)$  sample, as shown in Fig.4(a). The as-fabricated samples exhibit a type-IV isotherm, which is a more efficient photocatalyst structure for degrading organic pollutants in water. The BET surface area of  $\text{Bi}_2\text{MoO}_6(\text{pH}=5)$  sample ( $22.70 \text{ m}^2/\text{g}$ ) is about 5 times as large as that of  $\text{Bi}_2\text{MoO}_6(\text{s})$  ( $4.54 \text{ m}^2/\text{g}$ ). In addition, the corresponding pore size distribution curves for the as-prepared  $\text{Bi}_2\text{MoO}_6$  samples were obtained by the BJH method, as illustrated in Fig.4(b). The pore size distribution center of  $\text{Bi}_2\text{MoO}_6(\text{pH}=5)$  is about 5 nm based on BJH desorption pore distribution, which is

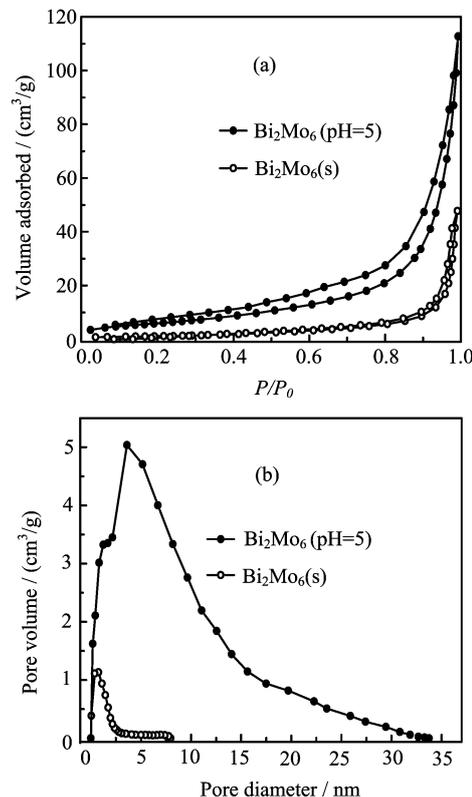
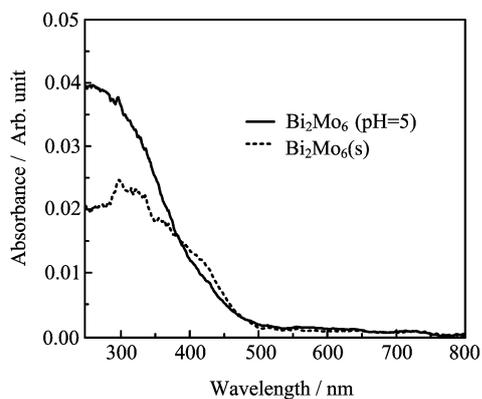
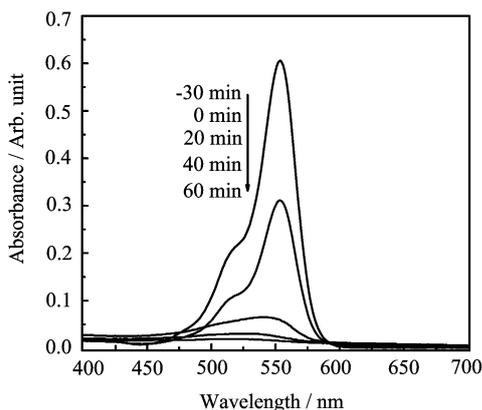


FIG. 4 (a)  $\text{N}_2$  adsorption-desorption isotherm curves of different samples. (b) Pore size distribution of different samples.

much higher than that of  $\text{Bi}_2\text{MoO}_6(\text{s})$ . The larger BET surface area and porous structure can facilitate more efficient contact of  $\text{Bi}_2\text{MoO}_6(\text{pH}=5)$  with organic contaminants and thus improve its photocatalytic activity. In this work, we focus on the effect of the BET surface upon the photocatalytic activities of the mesh-like  $\text{Bi}_2\text{MoO}_6$  sample and bulk  $\text{Bi}_2\text{MoO}_6$  sample. Further study on the effects of the BET surface on the photocatalytic properties of  $\text{Bi}_2\text{MoO}_6$  samples prepared under different pH values is of great interest.

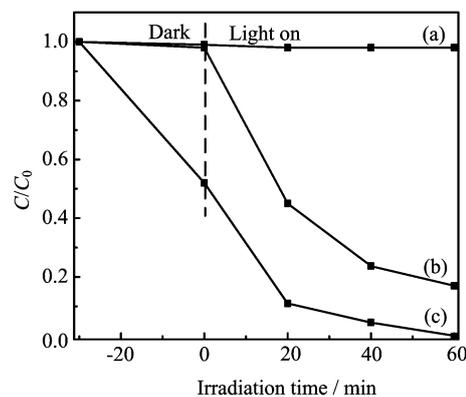
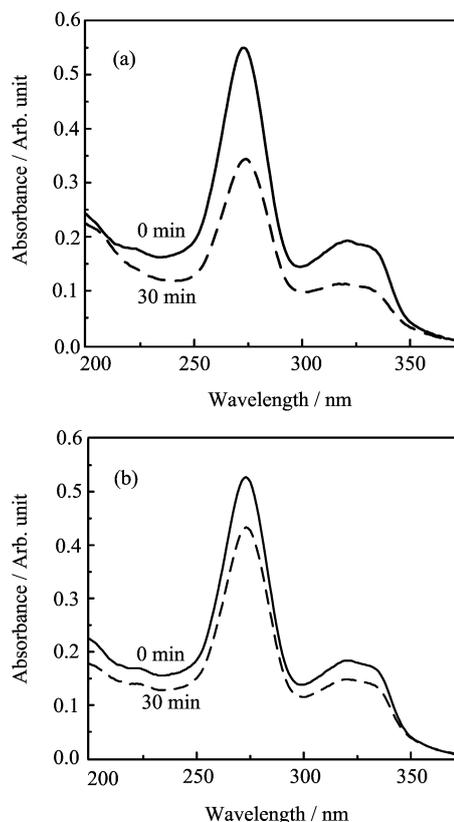
Figure 5 shows the UV-Vis DRS of the as-prepared  $\text{Bi}_2\text{MoO}_6(\text{pH}=5)$  and  $\text{Bi}_2\text{MoO}_6(\text{s})$  photocatalyst. The band gap adsorption edge of  $\text{Bi}_2\text{MoO}_6(\text{pH}=5)$  is estimated to be 477 nm corresponding to the band gap energy about 2.60 eV. Furthermore, the visible-light absorption intensity of  $\text{Bi}_2\text{MoO}_6(\text{pH}=5)$  is much higher than that of  $\text{Bi}_2\text{MoO}_6(\text{s})$ . It can be expected that the as-prepared mesh-like  $\text{Bi}_2\text{MoO}_6$  sample prepared in the present study should have a good photocatalytic potential not only in the ultraviolet light but also in the visible-light region.

The temporal evolutions of the spectral changes during the photodegradation of Rh B over  $\text{Bi}_2\text{MoO}_6(\text{pH}=5)$  under visible-light illumination are displayed in Fig.6. It shows that the absorbance is gradually decreased along with a slight blue shift in  $\lambda_{\text{max}}$  dur-

FIG. 5 UV-Vis DRS of the as-prepared  $\text{Bi}_2\text{MoO}_6$  samples.FIG. 6 UV-Vis spectral changes of Rh B in an aqueous  $\text{Bi}_2\text{MoO}_6$  (pH=5) before irradiation of 30 min (-30 min) and after irradiation for 0, 20, 40, 60 min under visible-light illumination.

ing VLR. The photodegradation for the two kinds of photocatalysts is shown in Fig.7. The photolysis test demonstrated that the self-degradation of Rh B was extremely slow, only 2% of Rh B was photodegraded after 60 min VLR. However, with  $\text{Bi}_2\text{MoO}_6$  (pH=5) as photocatalyst, 100% of the Rh B was decolorized after 60 min irradiation (Fig.7(c)), showing a high photocatalytic activity under VLR. The as-prepared  $\text{Bi}_2\text{MoO}_6$  (pH=5) sample revealed a higher photocatalytic activity compared with other reports [25, 26], which may be associated with the large BET surface area and the extension to visible light in absorption spectrum. For comparison, the photocatalytic property of  $\text{Bi}_2\text{MoO}_6$ (s) was also tested. After 60 min of VLR, the degradation rate of Rh B by  $\text{Bi}_2\text{MoO}_6$ (s) was 90% (Fig.7(b)), less efficient than that of the as-prepared mesh-like  $\text{Bi}_2\text{MoO}_6$  (pH=5) under the same condition.

The photocatalytic activities of as-prepared  $\text{Bi}_2\text{MoO}_6$  samples were also evaluated by the degradation of ciprofloxacin under irradiation with visible light ( $\lambda > 420$  nm). The temporal evolutions of the spectral changes during the photodegradation of ciprofloxacin

FIG. 7 Photodegradation efficiencies of Rh B as a function of irradiation time for different photocatalysts. (a) Without any catalyst, (b)  $\text{Bi}_2\text{MoO}_6$ (s), and (c)  $\text{Bi}_2\text{MoO}_6$  (pH=5).FIG. 8 UV-Vis spectral changes of ciprofloxacin in (a) an aqueous  $\text{Bi}_2\text{MoO}_6$  (pH=5) and (b)  $\text{Bi}_2\text{MoO}_6$ (s) dispersion for different irradiation time under visible-light illumination.

over  $\text{Bi}_2\text{MoO}_6$  (pH=5) and  $\text{Bi}_2\text{MoO}_6$ (s) under visible-light illumination are shown in Fig.8. The as-prepared  $\text{Bi}_2\text{MoO}_6$  (pH=5) sample revealed a higher photocatalytic activity than that of  $\text{Bi}_2\text{MoO}_6$ (s).

It is worth pointing out that the stability of a given photocatalyst during photoreaction is a crucial factor for any practical applications. To test the stability of photocatalyst, the  $\text{Bi}_2\text{MoO}_6$  (pH=5) sample was reused

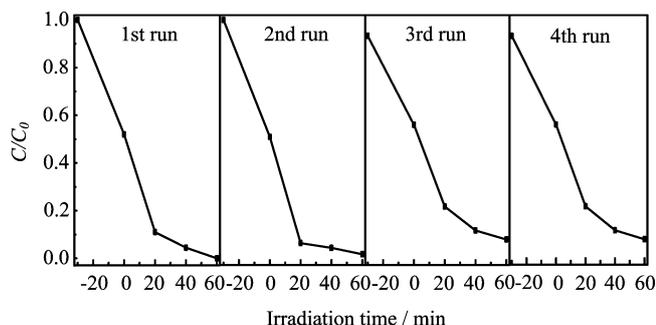


FIG. 9 Cycling runs for the photocatalytic degradation of Rh B over  $\text{Bi}_2\text{MoO}_6$  (pH=5) under VLR.

four times, as shown in Fig.9. It is found that no significant deactivation occurred for the photodecolorization of Rh B over  $\text{Bi}_2\text{MoO}_6$  (pH=5) under VLR, indicating that the as-obtained  $\text{Bi}_2\text{MoO}_6$  (pH=5) sample can be deemed as an attractive candidate for industrial water purification.

#### IV. CONCLUSION

Mesh-like  $\text{Bi}_2\text{MoO}_6$  product was successfully synthesized by a facile hydrothermal method. Photocatalytic evaluation revealed that the as-prepared mesh-like  $\text{Bi}_2\text{MoO}_6$  sample exhibited a high photocatalytic performance. For the degradation of rhodamine (Rh B) under VLR ( $\lambda > 420$  nm), almost 100% of the Rh B was degraded within 60 min VLR. In the very facile route only common and inexpensive reagents was used, which might be suitable for the large-scale production of the mesh-like  $\text{Bi}_2\text{MoO}_6$  product as an highly active visible-light-driven photocatalyst.

#### V. ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (No.21407059 and No.61308095), the China Postdoctoral Science Foundation (No.2013M531286), the Key Laboratory of Preparation and Application Environmentally Friendly Materials of the Ministry of Education of China, and the Science Development Project of Jilin Province China (No.20130522071JH and No.20130102004JC).

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