Preparation of Bi$3.64$Mo$0.36$O$6.55$ by Reflux Method and Its Application in Photodegradation of Organic Pollution

Chundong Peng  
China University of Geosciences Beijing

Zeyu Jia  
China University of Geosciences Beijing

Yi Zhong  
China University of Geosciences Beijing

Weihua Ao  
China University of Geosciences Beijing

Daimei Chen (chendaimei@cugb.edu.cn)  
China University of Geosciences Beijing  
https://orcid.org/0000-0002-2327-902X

Ruizhe Wang  
China University of Geosciences Beijing

Hao Ding  
China University of Geosciences Beijing

Xiangfeng Wu  
Shijiazhuang Tiedao University

Jiao Wang  
Beijing Polytechnic College

Gaoxiang Du  
China University of Geosciences Beijing

Research Article

Keywords: bismuth molybdate, Bi$3.64$Mo$0.36$O$6.55$, photocatalytic performance.

DOI: https://doi.org/10.21203/rs.3.rs-207069/v1

License: This work is licensed under a Creative Commons Attribution 4.0 International License.  
Read Full License
Abstract

Bismuth molybdate (γ-Bi₂MoO₆) photocatalyst has drawn numerous attentions in the field of photocatalysis because of its band gap (2.5eV ~ 2.8eV) and good visible light response (420 ≤ λ ≤ 500 nm). However, as a kind of bismuth molybdates, there are still few studies on Bi₃.64Mo₀.36O₆.55 (BMO), thus further exploration is needed. Herein, a simple reflux method was developed to synthesize the cubic phase BMO. This method is simple and easy to operate under atmospheric pressure, showing the great potential for large-scale production. In contrast with the nanosheet structure of Bi₂MoO₆, the morphology of BMO is mixture of nanorod and nanoparticle-like structure. The Motts curves show that conduction band position and the valence band position of BMO was 2.77 eV, -0.33eV and 2.44eV, respectively. A new mixed phase of 3Bi₂O₃•2MoO₃ was appeared in BMO crystal, showing that the phase transition of BMO began at 400℃. When BMO was calcined at 300℃, photocatalytic degradation rate is up to maximu. The photocatalytic activity of visible-light range was tested and compared with γ-Bi₂MoO₆. BMO had a better photodegradation activity than that of the Aurigillius phase γ-Bi₂MoO₆ due to its larger band gap and the strong oxidation ability.

1. Introduction

In recent decades, the existence of human being has been threatened by the consumption of fossil energy and the serious pollution of daily environment [1–4]. As a green and clean technology, photocatalysis over semiconductors using solar energy has attracted the attention of more and more scientific researchers in the organic pollutants degradation, heavy metal reduction, hydrogen production, carbon dioxide reduction et al [5–9]. Consequently, many semiconductors such as TiO₂ [2, 10–13], ZnO [14–16] and Bi based compounds (Bi₂O₃ [17–19], Bi₁₂TiO₂₀ [20–22], Bi₂InNbO₇ [23], Bi₂WO₆ [2, 24–27]) have widely reported and exhibited a huge potential to solve above problems. However, the narrow light absorption of the catalyst, the effective separation of photogenerated electron-hole pairs, and the active sites at the reaction interface have always limited the application of photocatalysts [28–31]. Therefore, it is still a challenge and has the significance for exploring a new kind of photocatalyst for really industrial application.

Bismuth molybdates (such as α-Bi₂Mo₃O₁₂, β-Bi₂Mo₂O₉, γ-Bi₂MoO₆, and Bi₃.64Mo₀.36O₆.55) have been drawn much attention because it responds to visible light. Among these different kinds of bismuth molybdates, Bi₃.64Mo₀.36O₆.55 (BMO) is reported to exhibit excellent visible-light photocatalytic activity. Until now, there are a few papers about the preparation and characterization of Bi₃.64Mo₀.36O₆.55 as a visible photocatalyst. Synthetic processes, such as hydrothermal method, low-temperature molten salt, microwave-assisted methods and electrochemical method have been employed to prepare Bi₃.64Mo₀.36O₆.55. However, hydrothermal method was generally carried out at high temperature and high pressure, which limits possible industrialized mass production. While the low-temperature molten salt method induced metal ions in photocatalyst, which might deteriorate the photocatalytic activity [32–38]. The microwave-assisted methods and electrochemical method needing complex equipment cannot
satisfy the large demand of production. Therefore, design and developing a simple method to prepare BMO photocatalyst is needed for really applications.

Herein, a refluxed method was developed for preparation of the BMO photocatalyst. This method is simple and easy to operate under atmospheric pressure. It thus shows great potential for large-scale production. The effect calcination temperature on structures and properties was studies. The relationships between the morphologies and structures of BMO and their photocatalytic activity were discussed. BMO exhibited the excellent photodegradation activity, which is higher than that of Bi$_2$MoO$_6$. When the sample was calcined at 300°C, the photodegradation activity of BMO is up to the maximum. The possible photodegradation mechanism of the BMO photocatalyst was finally discussed.

2. Experimental Section

2.1 Preparation of Bi$_{3.64}$Mo$_{0.36}$O$_{6.55}$

The Bi(NO$_3$)$_3$•5H$_2$O and Na$_2$MoO$_4$•2H$_2$O were purchased from Sinopharm Chemical Reagent Co., Ltd. and Xilong Chemical Co., Ltd. respectively, the NaOH was purchased from Lanzhou Institute of Chemistry. All regents were analytically pure and used without further purification. BMO is prepared by boiling reflux method. Typically, 5mmol (2.425g) of Bi(NO$_3$)$_3$•5H$_2$O and 2.5mmol (0.605g) of Na$_2$MoO$_4$•2H$_2$O were put into a 250mL three-necked flask with 120mL of deionized water. After stirring for 10 minutes, 2mol/L NaOH solution was added to adjust the pH value to 9, then the solution was heated to 100°C and refluxed for 12h, after cooling down to room temperature, the product was washed with deionized water and centrifuged at 5000 rpm three times, then dried at 90°C for 8 hours in air. The as-prepared sample were placed in a muffle furnace and heated from ambient temperature to 200°C, 300°C, 400°C, 500°C, 600°C at 2°C/min and held for 1h at each respective temperature. For comparison, we use the same method to prepare Bi$_2$MoO$_6$ under the condition of pH = 9 and calcinated at 300°C for further use.

2.2 Characterizations

The crystallinity of as-prepared sample was characterized by the Bruker D8 Advance X-ray diffractometer (XRD) of Germany at room temperature. The morphologies and structures were observed by 81W/AIS2100 scanning electron microscopy (SEM) of Western Chemical (Beijing) Technology Co., Ltd. and Hitachi HT770 transmission electron microscopy with 100kV of acceleration voltage. Fourier Transform Infrared (FTIR) spectra was carried out on the Spectrum 100 infrared spectrometer of PerlinElmer of USA in the frequency range of 4000cm$^{-1}$-450cm$^{-1}$ with 16 scanning times and a resolution of 4 cm$^{-1}$, the KBr was as the background during the test period. Raman spectra were measured on the OmniRS-532 model Raman spectrometer of Zhuolihan Optical Instrument Co., Ltd. of Beijing. Ultraviolet-visible diffuse reflectance spectra (UV-vis DRS) was tested via Hitachi U-3900 UV-vis spectrophotometer, using BaSO$_4$ as a reference, the slit width, scanning speed and measurement range is 2 nm, 600 nm/min, 200–600 nm respectively. The photoelectrochemical was measured by using the Zennium electrochemical workstation of Zahner Company of Germany, the Mott-Schottky curve was
carried out, then the band positions can be calculated combined with UV-vis DRS, the testing, the ITO glass was boiling in a mixed solution consists of NH$_3$•H$_2$O, H$_2$O$_2$, H$_2$O with the ratio of 1:1:6 for 30min, then clean it with ethanol, after irradiated the resistance side upward with UV for 1 hour, and 10 mg of the sample was dispersed in 1ml of ethanol by ultrasonication for 15min, then the samples were spread onto the ITO glass by dropping and dried in the air for 12h before drying at the oven.

### 2.3 photocatalytic performance test

The photocatalytic performance of the as-sample was carried out on a photoreactor with a 500W xenon lamp as the light source, and a 420nm cutoff filter was used to make sure the reaction at a visible-light condition. The photocatalytic activity of the sample was evaluated by the MB degradation experiment. 50mg of photocatalyst was dispersed into 50mL of MB (2×10$^{-5}$ mol/L) solution in a 50mL quartz tube via ultrasonication for 10min. Before light irradiation, the suspension was kept stirring at dark to reach the adsorption desorption equilibrium then exposed to visible light for reaction under stirring. At each given time interval, 3 mL suspension was sampled and centrifuged to remove the solid photocatalyst. Methylene blue (MB) concentration during the degradation was detected by colorimetry using a UV2550 ultraviolet-visible spectrophotometer of Shanghai Jingyan Instrument Company.

### 3. Results And Discussion

Figure 1 shows the XRD patterns of BMO samples calcined at different temperatures. The peaks at 27.7°, 31.7°, 45.6° and 53.9° are ascribed to (111), (200), (220), and (311) planes of BMO (PDF No.43–0446), suggesting the successful preparation of BMO by the reflux method. When the temperature was exceeded the 400°C (500°C and 600°C), new peaks attributed to 3Bi$_2$O$_3$•2MoO$_3$ phase can be observed, indicating the phase transition occurred as the temperature of 500°C.

Figure 2 is the SEM images of Bi$_2$MoO$_6$ and BMO samples calcined at different temperatures. The image of Bi$_2$MoO$_6$ is mainly sheet-like structure (Fig. 2a), which is consistent with the results of previous reports [2]. Figure 2b shows that BMO sample appears the mixture of granular and rod-like structure. As the temperature increases, the amount of rod-like BMO decreases while that of particle-like BMO increase, suggesting that parts of nanorods might be changed to nanoparticles. Furthermore, with the calcination temperature increasing from 200 to 500°C, the particle size increase from the several decade nanometers to several hundred nanometers, and the particle shape changes from irregular to uniform.

Figure 3 shows the TEM and HTEM of Bi$_2$MoO$_6$ and BMO samples. Figure 3a, b, c showed the morphology of BMO sample presents the mixture rod-like and particle-like structure, which was consistent with the SEM analysis. With the calcination temperature increasing from 200 to 400°C, most of nanorods were changed into nanoparticles, and the shape changes from irregular to uniform. The high-resolution TEM (HRTEM) pictures of Bi$_2$MoO$_6$ and BMO calcined at 300°C were shown in the Fig. 3d, 3e, 3f. In Fig. 3d, clear lattice fringe with d-spacing of 0.268 nm corresponds to the (040) plane of Bi$_2$MoO$_6$ (PDF#76-2388) The clear interplane spacing of 0.312 nm in Fig. 3e corresponding to (111) plane of BMO.
phase. A new interplanar space of 0.305 nm in the Fig. 3f, attribute to metal Bi, was found because the bismuth salt is unstable and bismuth oxide is easy to reduce into metal Bi when the TEM electron beam hits the sample [39, 40].

Figure 4 showed the FTIR of Bi$_2$MoO$_6$, Bi$_2$MoO$_6$ calcined at 300°C, BMO, and BMO calcinated at 200, 300, 400, and 500°C, respectively. The band range at 950 – 700 cm$^{-1}$ is the stretching mode of Mo-O bond, and the band at 600 – 400 cm$^{-1}$ is assigned to the stretching and deformation mode of Bi-O bond. These groups between BMO samples and Bi$_2$MoO$_6$ are similar, even for the Bi$_2$MoO$_6$ sample calcinated at 300°C, there was still no difference among their peak position. However, attributed to the distort of Bi-O bond and the Mo-O bond as the increase of calcined temperature of BMO, the absorption peak of Bi-O bond shifts to higher frequency and gradually became sharper. It is observed that the absorption peak of Mo-O bond gradually divided into two absorption peaks above 300°C. Based on the result of XRD, this phenomenon is due to the occurrence of new phase of 3Bi$_2$O$_3$•2MoO$_3$.

Figure 5 showed the Raman spectra of Bi$_2$MoO$_6$ and BMO samples. Firstly, Bi$_2$MoO$_6$ showed a strong band at 796 cm$^{-1}$, which was attributed to A$_{1g}$ mode of a typical symmetrical expansion and contraction of the MoO$_6$ octahedron. The peak at 845 cm$^{-1}$ was due to the orthogonal distortion of the octahedron. And the peaks range between 270cm$^{-1}$ and 360cm$^{-1}$ with Eg characteristics, which was corresponding to the rocking vibration mode of octahedral of MoO$_6$. The peak at 145cm$^{-1}$ indicated the lattice mode of Bi$^{3+}$ was perpendicular to the layered structure [41, 42], This was basically consistent with the characteristics of γ-Bi$_2$MoO$_6$. Comparing to BMO, two bands at 796 cm$^{-1}$ and 845 cm$^{-1}$, the characteristic band of the MoO$_6$ octahedron on the Bi$_2$MoO$_6$, shift to a higher wavenumber, and merged into one band at 878 cm$^{-1}$. Meanwhile, the two bands from 270 cm$^{-1}$ to 360 cm$^{-1}$ exhibited lower wavenumber shift, and merged into one band at 305 cm$^{-1}$. However, the characteristic band of Bi$^{3+}$ was still at 145 cm$^{-1}$ and without any shift. This suggested that the octahedral structure of the Mo-O bond in the Bi$_2$MoO$_6$ phase disappeared in the BMO phase, which resulting in a formation of new structure. The peak of MoO$_6$ gradually became wider as the increase of calcinated temperature of BMO. When the temperature reached above 300°C, the intensity of the peak decreases, After the temperature reaches 500°C, the crystal phase changes to 3Bi$_2$O$_3$•2MoO$_3$, and the peak suddenly became wider and sharper.

The light absorption of Bi$_2$MoO$_6$ and BMO calcinated at different temperature was investigated by DRS in Fig. 7. Bi$_2$MoO$_6$ is obviously a visible-light photocatalyst, which has the absorption edge of 480 nm. After Bi$_2$MoO$_6$ is calcinated at 300°C, the light absorption has a little blue shift. Compared with Bi$_2$MoO$_6$, the absorption edges of all the BMO samples shift to the lower wavelength, suggesting that BMO samples have a larger bang gap. It can be seen form Fig. 7 that the calcination temperature has great effect on the light absorption for BMO samples. Before 300°C, the light absorption exhibits a red shift compared with untreated BMO, after that, it shifts to the lower wavelength. Figure 7b compared the UV-vis DRS of Bi$_2$MoO$_6$ calcinated at 300°C and BMO calcinated at 300°C. The band gap of semiconductor can be obtained from the formula $E_g(\text{eV}) = 1240/\lambda_g \ (\text{nm})$ [43] (\(\lambda_g\): the abscissa wave number of the point of
intersection). Therefore, the band gap of BMO and Bi$_2$MoO$_6$ is calculated to be 2.77 eV and 2.64 eV, respectively. This result shows that BMO has the larger band gap than Bi$_2$MoO$_6$. In generally, the high band gap means the larger redox ability.

Figure 8 was Mott-Schottky curve of BMO calcinated at 300°C. The specific algorithm of the conduction band position of the sample can be roughly obtained by the tangent method [44], two tangent lines are drawn at the two inflection points of the curve to intersect at a point, and the abscissa of this point is the conduction position (CB) position, which is around -0.55 eV. According to the formula of VB = $E_g + CB$, the position of the valence band (VB) of the BMO sample is 2.22 eV (CB = -0.33 eV, VB = 2.44 eV vs NHE). According to the references, the positions of CB and VB are -0.37 eV, 2.27 eV, respectively [45]. Compared with Bi$_2$MoO$_6$, BMO sample has the lower VB position, indicating it has the stronger oxidation ability (Figure 9).

The photodegradation activities and their corresponding degradation kinetic rate constants of Bi$_2$MoO$_6$, Bi$_2$MoO$_6$ calcinated at 300°C, BMO and BMO calcinated at different temperatures were shown in Fig. 10 (a) and 10 (b), respectively. Figure 10(a) shows that Bi$_2$MoO$_6$ calcinated at 300°C has the higher photodegradation activity than that of Bi$_2$MoO$_6$ due to the improved crystallinity at high calcination temperature. The same result can also be observed in BMO samples. With the increase of calcination temperature, the photodegradation activity increase, and it is up to the maximum at 300°C. After 300°C, the photocatalytic activity is gradually decreased due to the formation of new phase in BMO sample. The histogram of the K value of MB degradation of BMO and Bi$_2$MoO$_6$ calcinated at different temperatures were illustrated in Fig. 10(b). The Bi$_2$MoO$_6$ calcinated at 300°C has the largest kinetic rate constant among the BMO samples. In addition, the kinetic rate constant of BMO calcined at 300°C is about 1.27 times higher than that of Bi$_2$MoO$_6$ calcinated at 300°C. The enhanced photocatalytic activity of BMO calcined at 300°C is that BMO has the larger band gap and stronger oxidation ability than that of Bi$_2$MoO$_6$.

**Conclusion**

In conclusion, BMO is successfully synthesized by a simple reflux method. The BMO sample consists of the nanorod and nanoparticle-like structure. With the increase of calcinated temperature, the nanoparticle size of BMO gradually grows larger and the amount of rod-like BMO decreases. The phase transition of BMO begins at 400°C, and a new mixed phase of 3Bi$_2$O$_3$・2MoO$_3$ was appeared. With increase the calcination temperature from 200 to 300°C, the photocatalytic activity increases due to the enhanced visible absorption and crystallinity. After that, the photocatalytic activity largely decreases because of the appearance of new mixed phase in BMO sample. BMO sample calcinated at 300°C exhibited the best activity, which is 1.5 times higher than uncalcinated BMO. Compared to Bi$_2$MoO$_6$, the photodegradation activity of BMO is much higher because of the larger band gap and strong oxidation ability.

**Declarations**
Acknowledgment

This work was partly supported by the National Natural Science Foundations of China (Grant No. 21978276), the Fundamental Research Funds for the Central Universities (Grant No. 2652017377, 2652017378), the Beijing Municipal Education Commission Key Science and Technology Project Fund (No. KZ201910853043), and the Innovation Ability Improvement Project of Hebei Province, China (No. 20543601D).

References

1. J. Ma, R. Guo, Engaging in Curriculum Reform of Chinese Chemistry Graduate Education: An Example from a Photocatalysis—Principles and Applications Course. J. Chem. Educ. 91, 206–210 (2014)
2. D. Chen, Q. Hao, Z. Wang, H. Ding, Y. Zhu, Influence of phase structure and morphology on the photocatalytic activity of bismuth molybdates. CrystEngComm 18, 1976–1986 (2016)
3. A. Kumar, A. Kumar, V. Krishnan, Perovskite Oxide Based Materials for Energy and Environment-Oriented Photocatalysis. ACS Catalysis 10, 10253–10315 (2020)
4. C. Guo, M. Ge, L. Liu, G. Gao, Y. Feng, Y. Wang, Directed Synthesis of Mesoporous TiO$_2$ Microspheres: Catalysts and Their Photocatalysis for Bisphenol A Degradation, Environmental Science & Technology, 44 (2010) 419–425
5. X. Zhang, X.-B. Wang, L.-W. Wang, W.-K. Wang, L.L. Long, W.-W. Li, H.-Q. Yu, Synthesis of a Highly Efficient BiOCl Single-Crystal Nanodisk Photocatalyst with Exposing {001} Facets. ACS Appl. Mater. Interfaces. 6, 7766–7772 (2014)
6. X.-S. Wang, C.-H. Chen, F. Ichihara, M. Oshikiri, J. Liang, L. Li, Y. Li, H. Song, S. Wang, T. Zhang, Y.-B. Huang, R. Cao, J. Ye, Integration of adsorption and photosensitivity capabilities into a cationic multivariate metal-organic framework for enhanced visible-light photoreduction reaction. Appl. Catal. B 253, 323–330 (2019)
7. H. Xu, X. She, T. Fei, Y. Song, D. Liu, H. Li, X. Yang, J. Yang, H. Li, L. Song, P.M. Ajayan, J. Wu, Metal-Oxide-Mediated Subtractive Manufacturing of Two-Dimensional Carbon Nitride for High-Efficiency and High-Yield Photocatalytic H$_2$ Evolution. ACS Nano 13, 11294–11302 (2019)
8. S. Wang, W. Yao, J. Lin, Z. Ding, X. Wang, Cobalt Imidazolate Metal–Organic Frameworks Photosplit CO$_2$ under Mild Reaction Conditions. Angew. Chem. Int. Ed. 53, 1034–1038 (2014)
9. L. Zhu, X.-Q. Liu, H.-L. Jiang, L.-B. Sun, Metal–Organic Frameworks for Heterogeneous Basic Catalysis. Chem. Rev. 117, 8129–8176 (2017)
10. W. Jiang, Y. Liu, J. Wang, M. Zhang, W. Luo, Y. Zhu, Separation-Free Polyaniline/TiO$_2$ 3D Hydrogel with High Photocatalytic Activity. Advanced Materials Interfaces 3, 1500502 (2016)
11. J. Zuo, H. Wu, A.J. Chen, J.Q. Zhu, M.D. Ye, J.D. Ma, Z.B. Qi, Shape-dependent photogenerated cathodic protection by hierarchically nanostructured TiO$_2$ films. Appl. Surf. Sci. 462, 142–148 (2018)
12. L.M. Lobanov, A.I. Ustinov, V.S. Volkov, A.A. Mokhniuk, V.A. Telichko, S.A. Demchenkov, Al/TiO$_2$ bilayer coatings for space applications: Mechanical and thermoradiation properties. Thin Solid Films **668**, 30–37 (2018)

13. Z.L. Cheng, S. Han, Preparation of a novel composite electrode based on N-doped TiO$_2$-coated NaY zeolite membrane and its photoelectrocatalytic performance. Chin. Chem. Lett. **27**, 467–470 (2016)

14. H. Wang, X.Q. Qiu, W.F. Liu, D.J. Yang, Facile preparation of well-combined lignin-based carbon/ZnO hybrid composite with excellent photocatalytic activity. Appl. Surf. Sci. **426**, 206–216 (2017)

15. M.M. Rahman, H.B. Balkhoyor, A.M. Asiri, Removal of a melamine contaminant with Ag-doped ZnO nanocomposite materials. New J. Chem. **43**, 18848–18859 (2019)

16. Q. Zhu, X. Shen, L. Wang, L. Zhu, L. Wang, G. Liao, Polyvinylpyrrolidone-assisted growth and optical properties of ZnO hexagonal bilayer disk-like microstructures. Chin. Chem. Lett. **29**, 1310–1312 (2018)

17. J. Divya, N.J. Shivaramu, W. Purcell, W.D. Roos, H.C. Swart, Multifunction applications of Bi$_2$O$_3$:Eu$^{3+}$ nanophosphor for red light emission and photocatalytic activity. Appl. Surf. Sci. **497**, 12 (2019)

18. Y.L. Ren, Y.Y. Yang, X. Jing, X. Wang, H. Song, Facile one step solvothermal synthesis and high visible light photocatalytic property of flower-like Bi$_2$O$_3$/BiOBr microspheres. Mater. Lett. **257**, 4 (2019)

19. F. Rao, G.Q. Zhu, M.M. Wang, S.M. Zubairu, J.H. Peng, J.Z. Gao, M. Hojamberdiev, Constructing the Pd/PdO/beta-Bi$_2$O$_3$ microspheres with enhanced photocatalytic activity for Bisphenol A degradation and NO removal. J. Chem. Technol. Biotechnol. **95**, 862–874 (2020)

20. F. Zhou, X.H. Ren, Reversible photochromic photocatalyst Bi$_2$O$_3$/TiO$_2$/Al$_2$O$_3$ with enhanced visible photoactivity: application toward UDMH degradation in wastewater. J. Environ. Sci. Health Part A-Toxic/Hazard. Subst. Environ. Eng. **55**, 239–255 (2020)

21. L.Z. Cao, Y.F. Li, Y.Y. Tong, R. Yang, L. Sun, Q. Cao, R. Chen, A novel Bi$_{12}$TiO$_{20}$/g-C$_3$N$_4$ hybrid catalyst with a bionic granum configuration for enhanced photocatalytic degradation of organic pollutants. J. Hazard. Mater. **379**, 12 (2019)

22. T.Y. Wang, F.Z. Lv, Z. Chen, R. Li, Y.H. Zhang, Flexible Bi$_{20}$TiO$_{32}$/TiO$_2$/C electrospun membranes with excellent catalysis. Mater. Res. Express **6**, 10 (2019)

23. J. Zhao, X. Guo, X.L. Zhang, Q. He, Y.Y. Yao, X.K. Feng, Z.J. Dan, L.L. Lu, Q. Zhang, Preparation and photocatalytic properties of Bi$_2$InNbO$_7$ nanorods obtained by the sol-gel method. Mater. Technol. **32**, 668–674 (2017)

24. X. Tang, Y. Yu, C.C. Ma, G.S. Zhou, X.L. Liu, M.S. Song, Z.Y. Lu, L. Liu, The fabrication of a biomass carbon quantum dot-Bi$_2$WO$_6$ hybrid photocatalyst with high performance for antibiotic degradation. New J. Chem. **43**, 18860–18867 (2019)

25. B. Li, L. Tan, X.M. Liu, Z.Y. Li, Z.D. Cui, Y.Q. Liang, S.L. Zhu, X.J. Yang, K.W.K. Yeung, S.L. Wu, Superimposed surface plasma resonance effect enhanced the near-infrared photocatalytic activity of Au@Bi$_2$WO$_6$ coating for rapid bacterial killing. J. Hazard. Mater. **380**, 10 (2019)
26. M. Ran, X.X. Zou, Q.W. Tian, L. Liang, T. Wu, A.X. Pan, Y.J. Deng, G.G. Fang, L.B. Ding, Shapes Control of Bi$_2$WO$_6$ Nano-Structures as Photo-Fenton Catalysts for Pulping Wastewater Treatment, Catalysts, 9 (2019) 10

27. H.M. Zhang, J. He, C.Y. Zhai, M.S. Zhu, 2D Bi$_2$WO$_6$/MoS$_2$ as a new photo-activated carrier for boosting electrocatalytic methanol oxidation with visible light illumination, Chin. Chem. Lett., 30 (2019) 2338–2342

28. D. Xu, P. Xu, Y. Zhu, W. Peng, Y. Li, G. Zhang, T.E. Mallouk, X. Fan, High Yield Exfoliation of WS$_2$ Crystals into 1–2 Layer Semiconducting Nanosheets and Efficient Photocatalytic Hydrogen Evolution from WS$_2$/CdS Nanorod Composites. ACS Appl. Mater. Interfaces. 10, 2810–2818 (2018)

29. X.-J. Wen, C.-G. Niu, L. Zhang, G.-M. Zeng, Fabrication of SnO$_2$ Nanoparticles/BiOI n–p Heterostructure for Wider Spectrum Visible-Light Photocatalytic Degradation of Antibiotic Oxytetracycline Hydrochloride. ACS Sustainable Chemistry & Engineering 5, 5134–5147 (2017)

30. B. Long, Y. Huang, H. Li, F. Zhao, Z. Rui, Z. Liu, Y. Tong, H. Ji, Carbon Dots Sensitized BiOI with Dominant {001} Facets for Superior Photocatalytic Performance. Industrial & Engineering Chemistry Research 54, 12788–12794 (2015)

31. T.X. Xu, J.P. Wang, Y. Cong, S. Jiang, Q. Zhang, H. Zhu, Y.J. Li, X.K. Li, Ternary BiOBr/TiO$_2$/Ti$_3$C$_2$T$_x$ MXene nanocomposites with heterojunction structure and improved photocatalysis performance. Chin. Chem. Lett. 31, 1022–1025 (2020)

32. J. Ren, W. Wang, M. Shang, S. Sun, E. Gao, Heterostructured Bismuth Molybdate Composite: Preparation and Improved Photocatalytic Activity under Visible-Light Irradiation. ACS Appl. Mater. Interfaces. 3, 2529–2533 (2011)

33. J.-P. Zou, S.-L. Luo, L.-Z. Zhang, J. Ma, S.-L. Lei, L.-S. Zhang, X.-B. Luo, Y. Luo, G.-S. Zeng, C.-T. Au, One-pot solvothermal syntheses of ternary heterostructured TiO$_2$–Bi$_2$MoO$_6$/Bi$_{3.64}$Mo$_{0.36}$O$_{6.55}$ controllable in terms of composition, morphology and structure: Materials of high visible-light driven photocatalytic activity, Applied Catalysis B: Environmental, 140–141 (2013) 608–618

34. X. Lin, X. Guo, W. Shi, H. Zhai, Y. Yan, Q. Wang, Quaternary heterostructured Ag–Bi$_2$O$_2$CO$_3$/Bi$_{3.64}$Mo$_{0.36}$O$_{6.55}$/Bi$_2$MoO$_6$ composite: Synthesis and enhanced visible-light-driven photocatalytic activity. J. Solid State Chem. 229, 68–77 (2015)

35. X. Lin, S. Yu, Z. Gao, X. Zhang, G. Che, Heterostructured RGO/Bi$_{3.64}$Mo$_{0.36}$O$_{6.55}$ nanospheres: Synthesis and enhanced visible-light-driven photocatalytic activity. J. Mol. Catal. A: Chem. 411, 40–47 (2016)

36. X. Lin, B. Wei, X. Zhang, M. Song, S. Yu, Z. Gao, H. Zhai, L. Zhao, G. Che, Construction of heterostructured g-C$_3$N$_4$/Ag/Bi$_{3.64}$Mo$_{0.36}$O$_{6.55}$ nanospheres with enhanced visible-light photocatalytic activity. Sep. Purif. Technol. 169, 9–16 (2016)

37. J.J. Mu, G.H. Zheng, Z.X. Dai, L.Y. Zhang, Z.F. Yao, Y.Q. Ma, A superior visible light-driven photocatalyst: rare earth-loaded Bi$_2$MoO$_6$ catalysts. J. Mater. Sci.-Mater. Electron. 28, 14747–14757 (2017)
38. M. Wang, M. You, K. Zhang, Y. Zhang, J. Han, R. Fu, S. Liu, T. Zhu, Bi$_{3.64}$Mo$_{0.36}$O$_{6.55}$/Bi$_2$MoO$_6$ heterostructure composite with enhanced photocatalytic activity for organic pollutants degradation. J. Alloy. Compd. 766, 1037–1045 (2018)

39. A.M. Beale, G. Sankar, In situ study of the formation of crystalline bismuth molybdate materials under hydrothermal conditions. Chem. Mat. 15, 146–153 (2003)

40. G. Zhen, H. Liu, N. Gu, H. Zhang, Y. Xu, Z. Zhang, G. Zhen, H. Liu, N. Gu, H. Zhang, Y. Xu, Z. Zhang. Mesenchymal stem cells transplantation protects against rat pulmonary emphysema. Front Biosci 13: 3415–3422, Frontiers in bioscience: a journal and virtual library, 13 (2008) 3415–3422

41. Y. Pang, G. Xu, Q. Feng, J. Liu, J. Lv, Y. Zhang, Y. Wu, Synthesis of α-Bi$_2$Mo$_3$O$_{12}$/TiO$_2$ Nanotube Arrays for Photoelectrochemical COD Detection Application, Langmuir, 33 (2017)

42. H.H. Li, K.W. Li, H.J.C.J.o.IC. Wang, Physics, Hydrothermal synthesis and photocatalytic properties of bismuth molybdate materials, 116 (2009) 134–142

43. X. Zhao, T. Xu, W. Yao, Y. Zhu, Synthesis and photoelectrochemical properties of thin bismuth molybdates film with various crystal phases. Thin Solid Films 517, 5813–5818 (2009)

44. H.H. Li, K.W. Li, H.J.C.J.o.IC. Wang, Hydrothermal Synthesis and Visible-light Photocatalytic Properties of α-Bi$_2$Mo$_3$O$_{12}$and γ-Bi$_2$MoO$_6$, 25 (2009) 512–516

45. J. Zhang, Z. Liu, Z. Ma, Facile Formation of Bi$_2$O$_2$CO$_3$/Bi$_2$MoO$_6$ Nanosheets for Visible Light-Driven Photocatalysis. ACS Omega 4, 3871–3880 (2019)