Microwave Solvothermal Synthesis of Three-Dimensional Bi₂MoO₆ Microspheres with Enhanced Photocatalytic Activity

Shuaishuai Ma, ‡ Jiandong Gu, ‡ Yuqing Zong, Jinjuan Xue, * and Zhaolian Ye, *

ABSTRACT: In this study, three-dimensional (3D) Bi₂MoO₆ microspheres were successfully fabricated by a facile, rapid, and mild microwave solvothermal strategy for the first time. The resultant 3D Bi₂MoO₆ microspheres exhibited superior adsorption capacity and photocatalytic efficiency in the degradation of the representative antibiotic ciprofloxacin under visible light, for which the reaction kinetic rate constant is 7.5 times as high as that of the as-synthesized zero-dimensional Bi₂MoO₆ nanoparticles. The 3D hierarchical porous structure and the high Brunauer–Emmett–Teller surface area providing abundant reactive sites mainly contributed to the enhanced photocatalytic activity. The results highlight the feasibility of 3D Bi₂MoO₆ microspheres as an efficient visible-light-responsive photocatalyst for antibiotic removal in an aqueous system.

1. INTRODUCTION

During the past several decades, the existence of pharmacuetical residues in wastewater and its harm to the living ecosystem has attracted wide attention all over the world. ¹ Ciprofloxacin (CIP), as a broad-spectrum antibiotic, has been widely used to prevent human and animal infections because of its antibacterial, bactericidal effect, and low price. ²,³ However, drug abuse seriously endangers the ecological environment as CIP could not be completely decomposed in the living, and its residues are detected in surface and groundwater around the world, which causes potential pressure on human health and the safety of the entire ecosystem. ⁴,⁵ Therefore, it is urgent to develop an effective CIP removal technology. Semiconductor photocatalysis, as an advanced oxidation technology, can directly capture solar energy to remove organic pollutants from aqueous solutions and is an ideal way to solve environmental problems. ⁶,⁷ From the perspective of solar energy utilization, visible light accounts for 44% of the total solar spectrum. Therefore, many people devote themselves to the development of superior visible light-driven photocatalysts. ⁸⁻¹⁰

Recently, bismuth molybdate (Bi₂MoO₆), with a layered Aurivillius structure, has been studied as a potential visible-light-responsive photocatalyst because of its appropriate band gap, good optical property, and high chemical inertness. ¹¹⁻¹³ It is well known that the specific morphology, particle size, and microstructure of a semiconductor would have a great influence on its photocatalytic performance. ¹⁴⁻¹⁶ Previous studies have demonstrated that semiconductors with spherical and other hierarchical 3D structures constructed from secondary units show preferable photocatalytic activities owing to their large specific surface area, radial open-up structures, unfavorable agglomeration properties, and abundant active sites. ¹⁹,²⁰ In a previous report, 3D hierarchical Bi₂MoO₆ microspheres have been synthesized by a conventional solvothermal method with relatively long reaction time and high temperature. ²¹,²² Nevertheless, exploitation of new strategies to fabricate 3D Bi₂MoO₆ through a facile, fast, and mild process is still needed. More recently, microwave-assisted heating strategy exhibited several advantages in material synthesis, including the rapid heating rate in a short time, low reaction temperature, and higher crystallinity with better control of the morphology over the synthesized materials. ²³⁻²⁷

Herein, we report a facile template-free microwave solvothermal approach to fabricate 3D Bi₂MoO₆ microspheres for the first time. The 3D Bi₂MoO₆ microspheres can be obtained in 15 min of rapid microwave-assisted solvothermal process, exhibiting high efficiency compared to the time-consuming conventional solvothermal method. The as-prepared 3D Bi₂MoO₆ microspheres exhibited superior performance in the photodegradation of representative antibiotic CIP under visible-light irradiation.

2. RESULTS AND DISCUSSION

X-ray diffraction (XRD) patterns of 3D Bi₂MoO₆ microspheres (denoted as 3D BMO) and zero-dimensional (0D) Bi₂MoO₆ nanoparticles (denoted as 0D BMO) are shown in Figure 1a. It
is revealed from Figure 1a that all the peaks of both 3D BMO and 0D BMO could be readily indexed to the orthorhombic phase of bismuth molybdate, with lattice constants of $a = 5.502$ Å, $b = 16.213$ Å, and $c = 5.483$ Å (JCPDS no. 21-0102). The Raman spectrum further confirmed the formation of 3D BMO crystals. In Figure 1b, the Raman modes are found around 59, 76, 145, and 184 cm$^{-1}$ corresponding to the lattice of (Bi$_2$O$_2$)$_2^+$. The Raman modes at 295, 350, 725, 806, and 848 cm$^{-1}$ are assigned to the asymmetric and symmetric stretching vibrations of the MoO$_6$ octahedrons referring to the
motion of apical oxygen atoms, normally directed to the \((\text{Bi}_2\text{O}_2)^{2+}\) layers.\(^{30,31}\) UV–vis diffuse reflectance spectroscopy (UV–vis DRS) was performed to study the optical property of 3D BMO and 0D BMO samples (Figure 1c). As can be observed, both of the samples exhibit a similar optical absorption edge. Figure 1d is \((a h u)^2\) versus \(h u\) plots, and the bad gap for 3D BMO is estimated to be 2.79 eV, which is quite close to that of 0D BMO. Thus, the light harvesting ability would not be an important factor for the enhancement of photocatalytic performance of the as-prepared 3D BMO.

The morphological and microstructural feathers of 3D BMO and 0D BMO samples were observed by field emission scanning electron microscopy (FE-SEM). The FE-SEM image (Figure 2a–c) displays that the 3D BMO sample possesses near-spherical morphology with a hierarchical structure consisting of many nanosheets. As shown in Figure 2d, the 0D BMO sample presents granular morphology with size around 100–200 nm. The Brunauer–Emmett–Teller surface area and porosity of the as-synthesized samples were further investigated by \(\text N_2\) absorption–desorption isotherms and the corresponding pore size distribution curves. It can be identified from Figure 2c that both 3D BMO and 0D BMO samples exhibit type-IV isotherms, indicating the presence of the mesoporous structure within the samples.\(^{32}\) The pore size distribution curves (Figure 2f) illustrate a relatively wide distribution range of 2–60 nm, with the average pore size of 8.84 and 10.60 nm for 3D BMO and 0D BMO samples, respectively.

The specific surface area of 3D BMO is 66.27 m\(^2\)/g, which is much larger than that of 0D BMO (10.50 m\(^2\)/g). In addition, the pore volume value of 3D BMO reaches 0.21 cm\(^3\)/g, while the value of 0D BMO is only 0.04 cm\(^3\)/g. As expected, the increased specific surface area and pore volume would
provide more active sites for reaction, thus contributing to the enhanced photocatalytic activity.

The elemental compositions and the surface chemical states of 3D BMO and 0D BMO were obtained by X-ray photoelectron spectroscopy (XPS). As depicted in Figure 3a, the XPS survey spectra of 3D BMO and 0D BMO illustrated the prepared samples were composed of Bi, Mo, and O elements. In Figure 3b–d, no obvious difference is found between the high-resolution XPS spectra of Bi 4f, Mo 3d and O 1s over 3D BMO and 0D BMO. In the high-resolution picture, the binding energies located at 159.3 and 164.6 eV belong to Bi 4f7/2 and Bi 4f5/2, revealing Bi exists in the form of Bi3+.33,34 The two peaks of Mo 3d5/2 and Mo 3d3/2 at 232.4 and 235.7 eV in the Mo 3d spectrum can be attributed to the oxidation states of Mo6+.35 Generally, the O 1s peaks can be divided into two different peaks at 530.3 and 531.6 eV, which should be attributed to the presence of Mo−O and surface −OH groups, respectively.36

Figure 4a displays the transient photocurrent responses of 3D BMO and 0D BMO samples in several light on−off cycles. It can be found that 3D BMO enhances photocurrent performance only little compared to 0D BMO, indicating that both of them have similar electron and hole recombination rates. Electrochemical impedance spectroscopy measurements were subsequently employed to investigate the interface layer resistance. It can be seen from Figure 4b that the diameter of the Nyquist circle of 3D BMO is similar with 0D BMO. Similar arc radius indicates similar charge transfer efficiency, which means that electron−hole pair separation and electron transfer efficiency are not the main factors to improve the photocatalytic performance of 3D BMO.

The performance of the as-synthesized 3D BMO photocatalyst was evaluated by the degradation of the representative antibiotic CIP in aqueous solution under visible light. Moreover, 0D BMO photocatalyst also conducted the degradation reaction under identical conditions as a comparison. As depicted in Figure 5a, in the dark adsorption step, adsorption−desorption equilibrium was reached within 60 min and 48.3 and 4.8% of CIP can be adsorbed by 3D BMO and 0D BMO photocatalysts, respectively. It is noted that 3D BMO photocatalyst exhibited a much higher adsorption ability, which is related to its special 3D hierarchical structure and larger specific surface area compared to that of 0D BMO. In Figure 5b, blank experiments show that the photolysis of CIP can be neglected under visible light irradiation without the photocatalyst. 3D BMO photocatalyst degraded around 98.2% of CIP after 30 min illumination, while the degradation efficiency just reached 42.6% over the 0D BMO photocatalyst in the same reaction time. Obviously, the photocatalytic performance can be significantly improved by the fabrication of 3D Bi2MoO6 microspheres. The kinetics of CIP photo-degradation is fitted by the pseudo-first-order model (Figure 5c), which can be described as ln(C0/Ct) = kt, where, C0 and Ct represent the initial concentration and the concentration of CIP after irradiation, respectively, and k is the kinetic rate constant.37 The calculated kinetic rate constant for the 3D BMO photocatalyst is 0.135 min−1, which is 7.5 times as high as that of the 0D BMO photocatalyst (0.018 min−1). It can be concluded from the above results that the 3D BMO photocatalyst has superior activity and has potential application in the efficient degradation of antibiotics. In the actual application of photocatalysts, in order to avoid
secondary pollution, the mineralization of pollutants is very important. Therefore, it is necessary to test the total organic carbon (TOC) during the photocatalytic process. The TOC removal is shown in Figure 5d, which increase with the irradiation time. Interestingly, the TOC removal efficiency is lower than the degradation efficiencies, indicating that it was easier to destruct the chromophore of the organic pollutant rather than to mineralize them down to CO₂.

Figure 6a represents the effect of the initial pH of solution on the degradation of CIP over the 3D BMO photocatalyst. The pH experiments were investigated at 2, 7, and 11 as initial pH, and the photodecomposition efficiency was determined 74.9, 98.2, and 54.3%, respectively. Adsorption is a prerequisite for photocatalytic degradation. The pH at which the surface of the catalyst is uncharged is defined as the zero point charge (pHₜₚₖ). The pKₐ of the four groups in CIP are different (as shown in Figure S1), and it can exist as H₄CIP³⁺, H₃CIP²⁺, H₂CIP⁺, HCl⁻, and CIP⁻ at different pHs. At low pH (pH < pHₜₚₖ), the degradation of photocatalytic degradation efficiency may be because of the fact that the catalyst surface facilitates the adsorption of hydrogen ions, and the repulsion between the positively charged surface of the catalyst and CIP reduces the adsorption of CIP on the photocatalyst surface. At high pH values (pH > pHₜₚₖ), both the photocatalyst and CIP were negatively charged, leading to electrostatic repulsion between them and low photocatalytic degradation efficiency of CIP.

Natural organic matter (NOM) and some anions are ubiquitous in natural water bodies, affecting the production and consumption of active substances in the photocatalytic process. Therefore, this study investigated the influence of four main anions (HCO₃⁻, SO₄²⁻, Cl⁻, and NO₃⁻) and humic acid (HA) as representatives of NOM on the efficiency of 3D BMO processes. An amount of 100 mg L⁻¹ was used for the inorganic anions. As shown in Figure 6b, the presence of these anions slightly inhibited the CIP degradation process. The
results show that, compared with HCO$_3^-$, SO$_4^{2-}$, and NO$_3^-$, the interference effect of Cl$^-$ on the degradation of CIP is negligible. Additionally, among the investigated anions, HCO$_3^-$ resulted in the highest inhibition with 8.1% decrease in degradation efficiency. Consistently, previous studies have also shown that bicarbonate ions can scavenge $^\cdot$OH and h$^+$ from the surrounding environment to form carbonate radicals ($^\cdot$CO$_3^-$), which is a weaker oxidizing agent. 43 The effect of different concentrations of HA on the degradation of CIP was studied, as revealed in Figure 6c. The degradation efficiencies at optimum conditions for 5, 15, and 30 mg L$^{-1}$ were 93.4, 81.3, and 66.8%, respectively, suggesting that HA had a significant inhibitory effect on the CIP degradation in higher concentrations. This result may be because of the fact that HA can interfere with the adsorption of CIP to 3D BMO surface activation sites, thereby reducing 3D BMO activity. 44

Photocatalytic stability and recyclability are the main parameters of its practical application. Figure 7a shows the photocatalytic CIP degradation performance of the 3D BMO sample under visible light for five successive runs. It can be seen that after five cycles, the removal rate of CIP remains at 88.1%, indicating that the 3D BMO photocatalyst possesses high stability and can be used for repeated treatment of CIP. In order to further explore the stability of 3D BMO, the leaching of Bi and Mo ions in the reaction solution was determined by atomic absorption spectrophotometry (Figure 7b). It can be found that as the photocatalytic process progresses, some Bi and Mo ions are leached from the material. After 30 min, the maximum leaching concentrations of Bi and Mo ions in the material were 0.36 and 0.11 mg L$^{-1}$, respectively, which further confirmed the good stability of these photocatalysts.

In order to reveal the primary active species participating in the photodegradation of CIP, scavenging experiments were also carried out over the 3D BMO photocatalyst. In this study, ethylenediaminetetraacetic acid (EDTA), p-benzoquinone, and t-BuOH were used to scavenge h$^+$, $^\cdot$O$_2^-$, and $^\cdot$OH, respectively. 45-47 As shown in Figure 8, the degradation efficiency of CIP has no significant change with the addition of t-BuOH, which is close to the activity in the absence of any scavenger, indicating that $^\cdot$OH is barely involved in CIP photodegradation. However, the CIP degradation efficiencies decreased upon adding EDTA and p-benzoquinone scavengers, reducing to 42.6 and 82.3%, respectively. The facts suggest that h$^+$ and $^\cdot$O$_2^-$ are the main active species responsible for CIP photodegradation over the 3D BMO sample.

In order to clarify the photodegradation pathway of CIP in the presence of 3D BMO, the main intermediate products of CIP transformation in the photodegradation process were precisely identified by high-performance liquid chromatography–mass spectrometry (HPLC–MS). The mass spectra of CIP after reacting for 30 min by 3D BMO are displayed in Figure S2. As shown in Figure S2, CIP completely transforms to seven main photoproducts, which are designated as P1–P6 in the order of retention time. The possible molecular structures of these products are described in Table S1. Combining with these detection results and references, 38–50 the degradation removal process could be proposed as three main pathways (Figure 9). The oxidative degradation of the piperazine moiety is the main degradation pathway. First, piperazine was oxidized, and it lost a formaldehyde group, generating the intermediate with m/z of 333.1 (P1). Second, P1 underwent secondary amine nitrogen loss, oxidation, and formaldehyde loss from the amine side chain and successively formed P2 (m/z 290.3) and P3 (m/z 258.1). In pathway 2, the reaction was initiated by $^\cdot$O$_2^-$ and $^\cdot$OH on the attack of F, which underwent a hydroxyl radical substitution, resulting in the formation of the P4 (m/z 330.1) defluorination product. Under the action of h$^+$ and $^\cdot$OH, the fractured quinolonic ring closed up afterwards with the loss of carbonyl, leading to the formation of intermediate P5 (m/z 280.3) (pathway 3). Subsequently, the piperazine and quinolone of intermediate P5 could be oxidized, and then closing of a five-membered ring loss of the lateral groups with cleavage of the five-membered ring yields intermediate P6 (m/z 171.3). Thus, it can be seen that CIP has been gradually disintegrated, and the relevant degradation intermediates are produced and then decomposed. Finally, these substances can convert into CO$_2$, H$_2$O, and the other degradation products.

Figure 10 displays the schematic representation of the proposed mechanism for target pollutant degradation over 3D BMO. Under visible light irradiation, because of the narrow band gap, photoelectrons (e$^-$) can be excited from the valence band (VB) to conduction band, while holes (h$^+$) stay at VB. The h$^+$ and e$^-$ can be effectively separated because of its 3D feature, resulting in the decrease of electron–hole recombination rate and the prolongation of positive hole half-life; along these lines, high photocatalytic activity was expected in the test of 3D BMO. The photogenerated electrons could be readily trapped by absorbed O$_2$ at the catalyst surface or the dissolved oxygen to form active species $^\cdot$O$_2^-$, and $^\cdot$OH radicals also can be produced via the multistep reduction of O$_2$. In addition, the redox potential of Bi$^{3+}$/Bi$^{4+}$ ($E^\circ = +1.59$ eV) is much lower than $^\cdot$OH/H$_2$O ($+1.99$ eV), indicating that photoinduced holes on the VB of the Bi$_2$MoO$_6$ cannot react with $^\cdot$OH/H$_2$O to form $^\cdot$OH. 43 However, the h$^+$ produced by the VB of 3D BMO has the ability to oxidize pharmaceutical molecules directly. Finally, the CIP was effectively degraded into small molecules by 3D BMO.

### 3. CONCLUSIONS

In conclusion, we have successfully fabricated 3D Bi$_2$MoO$_6$ microspheres via a facile and rapid microwave solvothermal method. For comparison, 0D Bi$_2$MoO$_6$ nanoparticles were also synthesized. The as-prepared 3D Bi$_2$MoO$_6$ microspheres and 0D Bi$_2$MoO$_6$ nanoparticles were applied as visible-light-driven photocatalysts in the degradation of representative antibiotic CIP to test their photocatalytic performances. 3D Bi$_2$MoO$_6$ microspheres exhibit superior photodegradation efficiency.
which the reaction kinetic rate constant is 7.5 times as high as that of 0D Bi$_2$MoO$_6$ nanoparticles. The enhanced photocatalytic activity mainly can be attributed to the unique 3D hierarchical pore structure and large specific surface area, which can create more active sites for reaction.

4. EXPERIMENTAL SECTION

4.1. Preparation of Photocatalysts.

Synthesis of 3D Bi$_2$MoO$_6$ microspheres (denoted as 3D BMO) is as follows. A total of 1.6866 g of Bi(NO$_3$)$_3$·5H$_2$O and 0.4210 g of Na$_2$MoO$_4$·2H$_2$O was dissolved in 5 mL of ethylene glycol (EG) under ultrasound, respectively. Then, the two solutions were mixed, and another 20 mL of EG was added. The reaction mixture was placed into a microwave reactor and heated at 100°C for 15 min with a power of 800 W. After naturally cooling to room temperature, the obtained sample was collected, washed several times, and dried at 65°C in a vacuum oven overnight.

For comparison, 0D Bi$_2$MoO$_6$ nanoparticles (denoted as 0D BMO) were also prepared. Typically, 0.9705 g of Bi(NO$_3$)$_3$·5H$_2$O and 0.2420 g of Na$_2$MoO$_4$·2H$_2$O were dispersed in 80 mL of deionized water and stirred for 30 min. After that, the solution was sealed in a 100 mL Teflon-lined autoclave and heated at 180°C for 16 h. After naturally cooling to room temperature, the powder product was collected, washed several times, and then dried at 65°C in a vacuum oven overnight.

4.2. Characterization.

XRD data were obtained on an X-ray diffractometer (SmartLab, Rigaku) with Cu Kα radiation. FE-SEM (SUPRAS5, SAPPHIRE, Zeiss) was used to investigate the morphologies and microstructures of the samples. XPS was carried out on a Thermo Scientific Escalab 250Xi. The N$_2$ adsorption–desorption isotherms were measured on a surface aperture adsorption instrument (ASAP 2020, Micromeritics, USA) by N$_2$ physisorption at 77 K. Raman spectra were collected using a DXR Raman microscope (Thermo Fisher Scientific Inc., USA, $\lambda_{ex} = 532$ nm). The UV–vis diffuse reflectance spectra were obtained on a UV–vis spectrophotometer (UV-3600, Shimadzu, Japan) by using BaSO$_4$ as the reflected sample. The intermediate analysis was performed by a HPLC–MS system (Agilent 1290/6640, Triple Quad MS) equipped with a Zorbax XDB-C18 column (150 × 2.1 mm, 3.5 μm). The electrochemical measurement was performed with an electrochemical workstation (CHI660B, Chen Hua Instruments, Shanghai, China).

4.3. Photocatalytic Activity. The photodegradation of CIP was performed in a photochemical reactor at room temperature, and a 500 W xenon lamp was used as the visible light source. A total of 10 mg of the photocatalyst was dispersed in 50 mL of CIP aqueous solution with an initial concentration of 10 mg L$^{-1}$. Before illumination, the suspension was stirred for 60 min in the dark to reach the adsorption–desorption equilibrium. In the course of the experiment, 1 mL of the sample was taken out every 5 min and a poly(tetrafluoroethylene) syringe filter (0.45 μm) was used to remove the particles. Then, the photodegradation rate of CIP was tested by HPLC (Shimadzu LC-20A, Japan). The TOC was measured on a TOC analyzer (Multi N/C 2100, Analytik Jena, Germany). This experiment was carried out under the same condition with the photocatalytic activity test. Most degradation experiments were conducted in triplicates, and the average data with their standard deviations were displayed.

ASSOCIATED CONTENT

* Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c03595.

Molecular structure and dissociation positions of CIP, mass spectra of the CIP and intermediates eluted at different retention times, and the identified CIP and its possible transformation products during photodegradation (PDF)

AUTHOR INFORMATION

Corresponding Authors

Jinjuan Xue – School of Environmental and Safety Engineering, Changzhou University, Changzhou 213164, PR China; orcid.org/0000-0001-6133-1581; Email: xuechem@163.com

Zhaolian Ye – College of Chemistry and Environmental Engineering, Jiangsu University of Technology, Changzhou
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213001, PR China; Collaborative Innovation Center of Atmospheric Environment and Equipment Technology, Jiangsu Key Laboratory of Atmospheric Environment Monitoring and Pollution Control (AEMPC), Nanjing University of Information Science & Technology, Nanjing 210044, China; Email: bess_ye@jsut.edu.cn

Authors
Shuaishuai Ma — College of Chemistry and Environmental Engineering, Jiangsu University of Technology, Changzhou 213001, PR China; orcid.org/0000-0001-8394-1372
Jiandong Gu — College of Chemistry and Environmental Engineering, Jiangsu University of Technology, Changzhou 213001, PR China
Yuqing Zong — School of Environmental and Safety Engineering, Changzhou University, Changzhou 213164, PR China

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.0c03595

Author Contributions
S.M. and J.G. contributed equally to this work.

Notes
The authors declare no competing financial interest.

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