# $Ag/Ag_2MoO_4/Bi_2MoO_6$ 复合光催化剂的制备及其光催化性能

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摘要:采用水热、化学沉积和原位光还原的方法成功制备了新型 Ag/Ag2MoO4/Bi2MoO6三元复合光催化剂。通过 X 射线粉末衍 射(XRD)、扫描电子显微镜(SEM)、X 射线光电子能谱(XPS)和紫外可见漫反射光谱(UV-Vis DRS)等技术对材料的组成、形貌、光 吸收特性和光电化学性能等进行系统分析。以四环素为目标污染物,研究 Ag/Ag2MoO4/Bi2MoO6在可见光下的光催化性能。研 究结果表明,相比于纯 Ag2MoO4和 Bi2MoO6, Ag 的表面等离子体共振(SPR)效应显著拓宽了催化体系对可见光的吸收能力及响 应范围。当 Ag2MoO4理论负载量(质量分数)为24.6%时, Ag/Ag2MoO4/Bi2MoO6复合材料在20 min内可将四环素完全降解, 且5次 循环使用后仍保持较高的催化活性, 表现出良好的循环稳定性。

关键词: Ag<sub>2</sub>MoO<sub>4</sub>; Bi<sub>2</sub>MoO<sub>6</sub>; 光催化; 降解; 抗生素 中图分类号: 0643.32; 0614.122; 0614.53<sup>+</sup>2 文献标识码: A 文章编号: 1001-4861(2021)03-0531-10 DOI:10.11862/CJIC.2021.055

# Preparation and Photocatalytic Activity of Ag/Ag<sub>2</sub>MoO<sub>4</sub>/Bi<sub>2</sub>MoO<sub>6</sub> Composite Photocatalyst

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**Abstract:** A novel  $Ag/Ag_2MoO_4/Bi_2MoO_6$  ternary photocatalyst was successfully prepared by hydrothermal, chemical deposition and *in-situ* photoreduction process. The as-prepared photocatalysts were characterized by X-ray diffraction (XRD), scanning electron microscope (SEM), X-ray photoelectron spectroscopy (XPS) and UV-visible diffuse reflection spectroscopy (UV-Vis DRS) to investigate the composition, morphology, optical absorption characteristics and photoelectrochemical properties. The photocatalytic performance of  $Ag/Ag_2MoO_4/Bi_2MoO_6$  photocatalyst was evaluated with tetracycline as the target pollutant under visible light. The research results show that, compared with pure  $Ag_2MoO_4$  and  $Bi_2MoO_6$ , the surface plasmon resonance (SPR) effect of Ag significantly broadens the visible light absorption capacity and response range of the catalytic system. When the theoretical loading (mass fraction) of  $Ag_2MoO_4$  was 24.6%,  $Ag/Ag_2MoO_4/Bi_2MoO_6$  ternary photocatalyst could completely degrade tetracycline within 20 min, and maintained high catalytic activity after 5 cycles of use, showing good cycle stability.

Keywords: Ag2MoO4; Bi2MoO6; photocatalysis; degradation; antibiotic

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## **0** Introduction

Recently, contamination of pharmaceutical compounds especially the antibiotics in wastewater and its harm to living ecosystem have attracted wide attention all over the world<sup>[1]</sup>. Tetracycline (TC) has been widely used to prevent human and animal infections because of its antibacterial, bactericidal effect and low price<sup>[2-3]</sup>. However, drug abuse seriously endangers the ecological environment, as TC could not be completely decomposed in the living, and their residues are detected in surface water, groundwater, and even treated drinking water, which causes the potential pressure on the human health and the safety of entire ecosystem<sup>[4-5]</sup>. In order to effectively remove and degrade TC, various technologies have been developed, such as physical absorption, electrolysis, photocatalysis, microbial decomposition, electrochemical oxidation and membrane separation<sup>[6-8]</sup>. Semiconductor photocatalysis, as an advanced oxidation technology, has become the research hotspot of TC residue treatment in recent years<sup>[9]</sup>. 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.

As a representative member of the Aurivillius family,  $\text{Bi}_2\text{MO}_6$  with a layered structure containing  $\text{O}_2^{-1}$ sandwiched between layered  $\text{Bi}_2\text{O}_2^{2+}$  units and perovskite-like slabs of  $\text{MoO}_4^{2-}$ , is considered to be a promising photocatalyst due to the photostability and environmentally friendly features<sup>[10-11]</sup>. However, the rapid recombination rate of photoinduced charges and inadequate utilization of visible light are still serious problems when using pristine  $\text{Bi}_2\text{MoO}_6$  as a photocatalyst<sup>[12-13]</sup>. Tremendous efforts have thus been made to solve these problems, including the fabrication of heterojunction, doping metal and non-metal ions, and surface modification as well<sup>[14-17]</sup>.

Silver - based semiconductors, such as  $Ag_2CO_3^{[18]}$ ,  $Ag_3PO_4^{[19]}$ ,  $AgVO_3^{[20]}$ ,  $Ag_2CrO_4^{[21]}$  and  $AgCl^{[22-23]}$ , have been proven to have excellent photocatalytic properties due to the surface plasmon resonance (SPR) effects of

elemental silver and narrow band gap. Ag<sub>2</sub>MoO<sub>4</sub>, as a new silver - based semiconductor photocatalyst, has attracted extensive research interest in recent years due to its unique physicochemical properties and plasticity<sup>[24-25]</sup>. The surface of Ag<sub>2</sub>MoO<sub>4</sub> tends to produce metal Ag when exposed to visible light like other Agbased semiconductors. However, due to the high band gap excitation of Ag<sub>2</sub>MoO<sub>4</sub>, simple binary Ag<sub>2</sub>MoO<sub>4</sub> based composite materials cannot meet the needs of high-efficiency photocatalysis. Therefore, it is reasonable to construct a ternary Ag/Ag<sub>2</sub>MoO<sub>4</sub>/Bi<sub>2</sub>MoO<sub>6</sub> heterojunction photocatalyst which has not been researched before.

Herein, we have firstly synthesized the ternary Ag/ Ag<sub>2</sub>MoO<sub>4</sub>/Bi<sub>2</sub>MoO<sub>6</sub> heterojunction photocatalyst via hydrothermal, chemical deposition and *in-situ* photoreduction method. The as-prepared Ag/Ag<sub>2</sub>MoO<sub>4</sub>/Bi<sub>2</sub>MoO<sub>6</sub> ternary composite exhibited remarkably improved photocatalytic activities in the degradation of representative antibiotic TC in comparison with pure Ag<sub>2</sub>MoO<sub>4</sub> and Bi<sub>2</sub>MoO<sub>6</sub> under visible light irradiation. Moreover, the stability of ternary Ag/Ag<sub>2</sub>MoO<sub>4</sub>/Bi<sub>2</sub>MoO<sub>6</sub> photocatalyst and the mechanism of improving photocatalytic efficiency under visible light were proposed.

# **1** Experimental

## **1.1** Preparation of the samples

Pure Bi<sub>2</sub>MoO<sub>6</sub> was prepared via a simple hydrothermal process according to our previous work<sup>[26]</sup>. Ag2MoO4/Bi2MoO6 was prepared by chemical deposition. Typically, 0.152 5 g Bi<sub>2</sub>MoO<sub>6</sub> (0.25 mmol) was ultrasonically dispersed in 50 mL of ultrapure water, and then a certain amount (2, 4, 6, 8 mL) of AgNO<sub>3</sub> solution (0.05 mol·L<sup>-1</sup>) was dropped into the suspension. The mixture was stirred at a rate of 1 000 r • min<sup>-1</sup> for 30 min to make Ag<sup>+</sup> completely adsorbed on the  $Bi_2MoO_6$  surface. Then a certain amount (1, 2, 3, 4 mL) of  $Na_2MoO_4$  solution (0.05 mol·L<sup>-1</sup>) was added dropwise, and stirred vigorously for 1 h under dark conditions to obtain Ag2MoO4/Bi2MoO6 (AMO/BMO). Subsequently, AMO/BMO sample was irradiated under a 500 W xenon lamp equipped with an ultraviolet filter (>420 nm) for 10 min to change part of the Ag<sup>+</sup> into Ag to obtain Ag/AMO/BMO product. The products were collected, washed several times with deionized water and alcohol, and dried overnight at 65°C in vacuum. The theoretical mass fractions of AMO in the series of samples obtained were 12.3%, 24.6%, 37.0% and 49.2%, respectively, and the corresponding products were named as Ag/AMO/BMO-x (x=1, 2, 3, 4, respectively). For comparison, pure Ag<sub>2</sub>MoO<sub>4</sub> (AMO), Ag/Ag<sub>2</sub>MoO<sub>4</sub> (Ag/AMO) and Ag/Bi<sub>2</sub>MoO<sub>6</sub> (Ag/BMO) were prepared by adopting the similar method.

## **1.2** Characterization of the samples

X-ray diffraction (XRD) data were obtained on an X-ray diffractometer (SmartLab, Rigaku) operated at 40 kV and 30 mA with Cu  $K\alpha$  X-ray radiation source, a nickel filter ( $\lambda = 0.154$  nm), and  $2\theta$  range of  $20^{\circ} \sim 70^{\circ}$ . The morphologies and microstructures of the samples were investigated by field emission scanning electron microscopy (FE - SEM, SUPRA55, SAPPHIRE, Zeiss) at the acceleration voltage of 5 kV. UV-Vis spectrophotometer (UV-3600, Shimadzu) equipped with an integrating sphere was used to investigate the UV-visible diffuse-reflectance spectra (UV-Vis DRS). The X-ray photoelectron spectra (XPS) were carried out on Thermo Scientific Escalab 250Xi, equipped with an Al  $K\alpha$ monochromatic X-ray source ( $h\nu = 1$  486.7 eV) with a line width of 0.20 eV in an analysis chamber at a bass pressure of less than 4.3×10<sup>-8</sup> Pa. The electrochemical measurement was performed with an electrochemical workstation (CHI660B, Chenhua Instruments, Shanghai, China).

#### **1.3** Photocatalytic activity

The photocatalytic activities of the samples were evaluated by the degradation of TC aqueous solution under irradiation of a 500 W xenon lamp with a 420 nm cutoff filter. Typically, 10 mg of as-prepared photocatalyst was suspended in a 50 mL of TC solution (10 mg·L<sup>-1</sup>) and stirred magnetically for 60 min in the dark to ensure the establishment of the adsorption/desorption equilibrium between the catalyst and the simulated pollutant. In the course of the experiment, 1 mL of the sample was taken out every 5 min and PTFE syringe filter (0.22  $\mu$ m) was used to remove the particles. Then the photodegradation rate (DR) of TC was tested by the high performance liquid chromatography (HPLC, Shimadzu LC-20A, Japan).

## 2 Results and discussion

#### 2.1 Characterization of the samples

The XRD analysis was conducted to determine the crystalline structures and the corresponding patterns of Ag/AMO/BMO-x samples, and the results are demonstrated in Fig.1. The intensive diffraction angels 20 at 23.5°, 28.3°, 32.6°, 33.1°, 36.1°, 39.7°, 46.7°, 47.2°, 55.6°, 56.3° and 58.5° can be assigned to (111), (131), (002), (060), (151), (042), (202), (062), (133), (191) and (262) crystallographic planes of orthorhombic Bi<sub>2</sub>MoO<sub>6</sub> (PDF No.72-1524). Meanwhile, other peaks at  $2\theta = 27.1^{\circ}, 31.8^{\circ}, 33.3^{\circ}, 38.7^{\circ}, 47.8^{\circ}, 50.9^{\circ}, 55.8^{\circ},$ 65.6° and 66.5° are assigned to the (220), (311), (222), (400), (422), (511), (440), (533) and (622) planes of cubic Ag<sub>2</sub>MoO<sub>4</sub> (PDF No.08-0473), respectively. With the increase of AMO content, the intensity of the cubic AMO peak gradually increased. Cubic/hexagonal Ag<sup>0</sup> peaks were difficult to find, which may be due to the low metallic Ag content and low crystallinity.



Fig.1 XRD patterns of Ag/AMO/BMO-x (x=1, 2, 3, 4) samples and standard XRD patterns of Bi<sub>2</sub>MoO<sub>6</sub> (PDF No.72-1524) and Ag<sub>2</sub>MoO<sub>4</sub> (PDF No.08-0473)

The elemental compositions and the surface chemical states of AMO/BMO and Ag/AMO/BMO-2 were obtained by XPS spectra. As depicted in Fig. 2a, the XPS survey spectra of AMO/BMO and Ag/AMO/BMO-2 illustrated that the prepared samples were composed of Bi, Mo, O and Ag elements. In Fig.2b~2d, no obvious difference was found about the high-resolution XPS spectra of Bi4*f*, Mo3*d* and O1*s* over AMO/BMO and Ag/AMO/BMO-2 samples. The Bi4*f* spectrum in Fig.2b for Ag/AMO/BMO-2 composite displayed two characteristic peaks at 159.4 and 164.8 eV attributed to Bi4 $f_{7/2}$  and Bi4 $f_{5/2}$ , revealing that Bi exist as the form of Bi<sup>3+[27]</sup>. In Fig.2c, the peaks of Mo3*d*<sub>3/2</sub> and Mo3*d*<sub>3/2</sub> at 232.8 and 235.8 eV in the Mo3*d* spectrum can be attributed to the oxidation states of Mo<sup>6+[28]</sup>. Generally, the O1*s* peaks in Fig.2d can be divided into two different peaks at 530.3 and 531.2 eV, which should be attributed to the presence of Mo—O and surface —OH groups,

respectively<sup>[29]</sup>. The Ag3*d* spectrum shown in Fig. 2e had two distinct peaks at 374.3 and 368.3 eV, which are connected to the Ag3*d*<sub>3/2</sub> and Ag3*d*<sub>5/2</sub> orbitals. The curves could be further divided into four peaks. The strong peaks of 368.3 and 374.3 eV can be attributed to Ag<sup>+</sup>, which proves that Ag<sup>+</sup> is the dominant species of Ag<sup>[30]</sup>. As for Ag/AMO/BMO-2, the binding energies at 369.4 and 375.2 eV can be indexed to Ag NPs (nanopartides)<sup>[31]</sup>, confirming the existence of a small amount of Ag<sup>0</sup> in Ag/AMO/BMO-2.

The FE-SEM images of AMO, Ag/AMO, BMO, Ag/ AMO/BMO - 2 and AMO/BMO are depicted in Fig. 3. Pure AMO had an irregular cashew shape with a parti-



Fig.2 XPS survey spectra (a), high resolution XPS spectra of Bi4*f* (b), Mo3*d* (c), O1*s* (d) and Ag3*d* (e) core level electrons of AMO/BMO and Ag/AMO/BMO-2 samples



Fig.3 FE-SEM images of AMO (a), Ag/AMO (b), BMO (c), Ag/AMO/BMO-2 (d) and AMO/BMO (e)

cle size of  $2~3 \mu m$  and a smooth surface (Fig.3a). After being irradiated with visible light, some particles believed to be silver were deposited on the surface of AMO (Fig.3b). As shown in Fig.3c, BMO sample showed nanoplate-like morphology with side length of 100~200 nm. As indicated in Fig.3d and 3e, Ag/AMO/BMO-2 and AMO/BMO processed similar morphology. It can be seen that BMO nanoplates and irregular block AMO coexisted in the composite material, and most of them had good contact, which proves that the heterojunction photocatalyst has been successfully synthesized. Furthermore, we could also observe that the surface of AMO became rough after forming a heterojunction with BMO, thus increasing the contact area between each other.

The optical properties of AMO, BMO, AMO/BMO and Ag/AMO/BMO-2 were investigated by UV-Vis DRS and the results are shown in Fig. 4. Pure AMO only has obvious absorption in the ultraviolet region, and the absorption edge was around 380 nm (band gap: 3.26 eV). It was observed that pure BMO had an adsorption edge at about 460 nm, which corresponds to the reported optical band gap of about 2.64 eV. The formation of the heterojunction between AMO and BMO broadened and increased the visible light absorption, and the wavelength thresholds of AMO/BMO sample was estimated to be about 475 nm, corresponding to the band gaps of 2.56 eV. Whereas compared with the absorption spectrum of AMO and BMO, Ag/AMO/BMO-2 sample displayed a more intense absorption ranging from 300 to 700 nm and exhibited a broad absorption peak at around 530 nm which can be attributed to the SPR effect of Ag nanoparticles<sup>[32]</sup>. Due to the expansion of the light absorption range and light intensity of Ag/ AMO/BMO-2 photocatalyst, it is expected to achieve more effective utilization of the solar spectrum and show enhanced photocatalytic activity.



Fig.4 UV-Vis absorption spectra of AMO, BMO, AMO/BMO and Ag/AMO/BMO-2

The edge position can be determined by the following empirical equation<sup>[33]</sup>:  $E_{\rm VB}=X-E_0+0.5E_g$ ,  $E_{\rm CB}=E_{\rm VB}-E_g$ , where  $E_{\rm VB}$  is the VB edge potential and X is the absolute electronegativity of the semiconductor;  $E_0$  is the energy of free electrons on the hydrogen scale (~4.5 eV) and  $E_g$  is the band gap energy of the semiconductor. The X values for AMO and BMO were calculated to be 5.92 and 5.50 eV, respectively. Therefore, the  $E_{\rm VB}$  and  $E_{CB}$  values of AMO were determined to be 3.05 and -0.21 eV (vs NHE), and those of BMO were calculated to be 2.32 and -0.32 eV (vs NHE), respectively.

In order to determine the separation efficiency of the carrier, the photochemical measurements were performed. Fig. 5a displays the transient photocurrent responses of AMO, BMO, AMO/BMO and Ag/AMO/ BMO-2 samples in several light on-off cycles. The intensity of photocurrent for AMO and BMO was weak, indicating pure photocatalyst is faced with the headache that the quantity and migration speed of charge carriers is low. AMO/BMO composites showed a higher transient photocurrent intensity compared with pure AMO and BMO, indicating that the heterojunction of AMO/BMO composites not only boost the generation but also accelerate separation of charges carriers. Obviously, it can be found that Ag/AMO/BMO-2 significantly enhanced the photocurrent performance compared to AMO/BMO, which indicates that the introduction of Ag NPs can further reduce the electron and hole recombination rate. Moreover, the charge migration rate was evaluated according to the arc radius in the EIS (electrochemical impedance spectroscopy). Fig. 5b shows the EIS Nyquist plots of AMO, BMO, AMO/BMO and Ag/AMO/BMO-2 under the identical experimental conditions. Obviously, Ag/AMO/BMO-2 showed the minimum radius of curvature, indicating its highest electron -hole pairs separation and electrons transfer efficiency, which agreed well with the results of photocurrent response.



Fig.5 Photocurrent response curves (a) and Nyquist plots (b) of AMO, BMO, AMO/BMO and Ag/AMO/BMO-2

#### 2.2 Photocatalytic activity

The performance of degradation of TC by all synthesized samples under visible light irradiation are shown in Fig.6a, where  $c_0$  and c are the initial concentration of TC and the concentration remaining in the solution after the irradiation time (t), respectively. As shown in Fig.6a, TC was rarely degraded without photocatalysts in the control test, indicating that the self-photolysis of TC could be ignored. In Fig.6a, the degradation rates of TC over Ag/AMO/BMO - x (x=1, 2, 3, 4) samples were higher than that of AMO, BMO, Ag/AMO, Ag/BMO and AMO/BMO, respectively. The photocatalytic activity of Ag/AMO/BMO composite first increased and then decreased with the increase of Ag/AMO/BMO-2 showed the best photocatalytic performance, and the photodegradation rate of

TC reached almost 100% after 20 min of irradiation. In addition, if the initial TC concentration is within the millimolar concentration range, photocatalytic degradation of organic pollutants generally follows pseudofirst-order kinetics and the kinetic model can be expressed by equation  $\ln(c_0'/c) = kt$ , where  $c_0'$  is the initial TC concentration at the beginning of photocatalitic degradation, and k is the kinetic rate constant<sup>[34-35]</sup>. As depicted in Fig. 6b, Ag/AMO/BMO-2 photocatalyst exhibited the highest rate constant  $(0.168 \ 2 \ min^{-1})$ among all of the samples for the degradation of TC, which was 7.2 and 17.7 times higher than those of pure BMO (0.022 6 min<sup>-1</sup>) and Ag/AMO (0.009 2 min<sup>-1</sup>), respectively. The enhanced activity of Ag/AMO/BMO-2 can be attributed to the formation of heterojunctions that can effectively separate photocarriers, and the introduction of Ag NPs in the composite material also helps to expand the optical response range and realize more effective electron transfer. Furthermore, Table 1 list the photocatalytic performance of the reported photocatalysts compared to the as-prepared samples. As expected, Ag/AMO/BMO-2 photocatalyst toward TC degradation possessed distinct advantage over the reported Bi<sub>2</sub>MoO<sub>6</sub>-based catalysts. Although a direct comparison is difficult owing to the differences in photocatalytic reaction parameters, Ag/AMO/BMO-2 photocatalyst indeed displayed excellent visible-light-driven photocatalytic activity for TC degradation. Consequently, the results further proved that Ag/AMO/BMO-2 sample could be acted as a promising photocatalyst to remove the antibiotic pollutants in the aqueous solution.

Photocatalytic stability and recyclability are the main parameters for the practical application of photocatalyst. Fig.7 shows the photocatalytic TC degradation performance of Ag/AMO/BMO-2 sample under visible light for five runs. It can be seen that after five cycles, the removal rate of TC remained at 89.8%, indicating that Ag/AMO/BMO-2 photocatalyst possesses good stability and can be used for repeated treatment of TC. The photodecomposition of Ag/AMO/BMO-2 and the formation of more Ag NPs may be the reason for the decrease of its photocatalytic activity. A small amount of Ag NPs can promote the visible light absorption and photocatalytic activity of the catalyst, while excessive Ag NPs deposited on the surface of the catalyst will block the incidence of light and reduce the photocatalytic performance<sup>[24,42]</sup>. The XRD pattern of the used Ag/ AMO/BMO-2 collected after the cycling runs showed small peaks at  $2\theta$ =38.1°, 44.2° and 64.4°, corresponding to the (111), (200) and (220) facets of cubic Ag<sup>0</sup> (Fig. 8), while the fresh Ag/AMO/BMO-2 had no obvious Ag<sup>0</sup> peaks.

In order to deeply investigate the active species involved in photocatalysis, a series of radical captured experiments were performed. In this study, EDTA-2Na



Fig.6 Visible light photocatalytic activities (a) and pseudo-first-order kinetics linear fitting (b) for TC degradation over the as-prepared samples

Table 1	Comparison of	photocatalytic	performance of Bi <sub>2</sub>	MoO <sub>2</sub> -based	photocataly	vsts for deg	radation of TC	2

Photocatalyst	$c_{\rm catalyst}/({\rm g}{\boldsymbol{\cdot}}{\rm L}^{-1})$	$c_{\rm TC}/({\rm mg}{\boldsymbol{\cdot}}{\rm L}^{-1})$	DR, time	Light power	Ref.
Bi <sub>2</sub> MoO <sub>6</sub> /Ti <sub>3</sub> C <sub>2</sub>	0.5	15	97%, 60 min	15 W LED	[36]
$Fe(\mathbb{II})/Bi_2MoO_6$	0.2	10	99%, 60 min	500 W Xe lamp	[26]
$\rm TNCuPc/CeO_2/Bi_2MoO_6$	1.5	50	95%, 120 min	800 W Xe lamp	[37]
$WO_3/Bi_2MoO_6$	1.0	20	77%, 120 min	300 W Xe lamp	[38]
N-TiO <sub>2</sub> /Bi <sub>2</sub> MoO <sub>6</sub>	0.25	20	94%, 150 min	5 W LED	[39]
CuBi <sub>2</sub> O <sub>4</sub> /Bi <sub>2</sub> MoO <sub>6</sub>	0.3	20	73%, 60 min	300 W Xe lamp	[40]
Bi <sub>2</sub> MoO <sub>6</sub> /BiFeO <sub>3</sub>	1.0	10	93%, 300 min	150 W Xe lamp	[41]
$Ag/Ag_2MoO_4/Bi_2MoO_6$	0.2	10	100%, 20 min	500 W Xe lamp	This work



Fig.7 Cycling runs for photodegradation of TC over Ag/AMO/BMO-2



Fig.8 XRD patterns of Ag/AMO/BMO-2 before and after five cycling runs

(1 mmol·L<sup>-1</sup>), *p*-benzoquinone (1 mmol·L<sup>-1</sup>) and *t*-BuOH (1 mmol·L<sup>-1</sup>) were used to scavenge h<sup>+</sup>,  $\cdot O_2^{-1}$ and  $\cdot OH$ , respectively<sup>[26]</sup>. As shown in Fig.9, it is obvious that the degradation rate for TC significantly reduced after addition of *p*-benzoquinone and EDTA -2Na, indicating the  $\cdot O_2^{-1}$  and h<sup>+</sup> play significant roles during the degradation process. However, little efficiency reduction with the addition of *t*-BuOH demonstrated that  $\cdot OH$  might not the predominant active species. These facts confirm that h<sup>+</sup> is the main active species and  $\cdot O_2^{-1}$  plays a secondary role in the photocatalytic degradation process.

On the basis of the results described above, we proposed a possible mechanism of degradation of TC over Ag/AMO/BMO-2 photocatalyst under visible light irradiation in Fig. 10. From Fig. 4, we know that AMO has no response to visible light due to its large energy gap, whereas BMO can be excited to produce photoelectrons ( $e^-$ ) and holes ( $h^+$ ) pairs on its surface due to the narrow energy gap. The  $E_{CB}$  values of BMO was calculated to be -0.32 eV (vs NHE), which was lower than



Fig.9 Photocatalytic performance of Ag/AMO/BMO-2 in the presence of different scavengers



Fig.10 Proposed photocatalytic mechanism of Ag/AMO/BMO-2

the standard redox potential of  $O_2/ \cdot O_2^-$  (-0.33 eV)<sup>[43]</sup>. However, in the above free radical trapping experiment, we confirmed that  $\cdot O_2^-$  is the main active substance on Ag/AMO/BMO-2 photocatalyst, indicating that the formation of  $\cdot O_2^-$  in the reaction is definite. The reason can be explained as follows: Ag NPs can absorb the visible light and generate electron-hole pairs due to SPR effect<sup>[44]</sup>. With visible light irradiation, photogenerated electron-hole pairs are separated on the surface of Ag NPs. The energy of hot electrons waved around its own Fermi level and the range of the vibration is from 1.0 to 4.0 eV<sup>[45]</sup>. Therefore, the excited electrons have enough energy to transfer from Ag NPs to CB of AMO and BMO. Subsequently, the electrons accumulated on the surface of AMO and BMO will be captured by absorbed  $O_2$  to form  $\cdot O_2^{-}$ , then further oxidized the organic contaminants. Since  $E_{CB}$  of BMO was negative than that of AMO, the photogenerated electrons in BMO have a tendency to diffuse to the CB of AMO via the interface. This causes an efficient separation of photogenerated electrons and holes and the lifetime of the excited electrons and holes can be prolonged in the transfer process. On the other hand, because the  $E_{\rm VB}$  value of BMO (+2.32 eV (vs NHE)) was lower than the standard redox potentials of  $\cdot$ OH/ H<sub>2</sub>O (+2.68 eV (vs NHE)), indicating that photoinduced holes on the VB of BMO cannot react with •OH/  $H_2O$  to form •OH, hence  $h^+$  on the VB of BMO would be consumed by directly decomposing TC.

#### **3** Conclusions

In summary, the Ag/AMO/BMO composites with different Ag/AMO mass fractions were synthesized via hydrothermal, chemical deposition and *in-situ* photoreduction method. The as-prepared Ag/AMO/BMO-2 photocatalyst exhibited significantly enhanced photocatalytic activities toward antibiotic TC degradation and the degradation rate was nearly 7.2 and 17.7 times higher than that of pure BMO and Ag/AMO, respectively. The Ag SPR effect that enlarged the optical adsorption range combining with AMO to efficiently separate photogenerated charge carriers synergistically account for the enhancement of photocatalytic activity. The optimal photocatalyst showed reasonable stability during five successive runs. Part of the catalyst deactivation is due to the excessive reduction of  $Ag^+$  to  $Ag^0$  during exposure to visible light. The main active substances responsible for photocatalytic degradation are photoinduced holes and  $\cdot O_2^-$  free radicals.

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#### **References:**

- [1] Xu J, Zhang B B, Jia L, Bi N, Zhao T Q. J. Hazard. Mater., 2020,386: 121630
- [2] Liu X H, Guo X C, Liu Y, Lu S Y, Xi B D, Zhang J, Wang Z, Bi B. Environ. Pollut., 2019,254:112996
- [3] Yang Y Y, Song W J, Lin H, Wang W B, Du L N, Xing W. Environ. Int., 2018,116:60-73
- [4] Wu Q F, Li Z H, Hong H L. Appl. Clay Sci., 2013,74:66-73
- [5] 张宇晴,曾雪玉,于凯,刘桂芳,曹海雷,吕健,曹荣. 无机化学学报, 2019,35(11):2185-2191
  ZHANG Y Q, ZENG X Y, YU K, LIU G F, CAO H L, LÜ J, CAO R. Chinese J. Inorg. Chem., 2019,35(11):2185-2191
- [6] Yan X, Wang X Y, Gu W, Wu M M, Yan Y, Hu B, Che G B, Han D L, Yang J H, Fan W Q, Shi W D. Appl. Catal. B, 2015,164:297-304
- [7] Xu W H H, Zhang G, Wai O W H, Zou S C C, Li X D D. J. Soils Sediments, 2009.9:364-373
- [8] Jiang D L, Xiao P, Shao L Q, Li D, Chen M. Ind. Eng. Chem. Res., 2017,56:8823-8832
- [9] 梁梦君, 邓楠, 向心怡, 梅英, 杨志远, 杨赟, 杨水金. 无机化学学 报, 2019,35(2):263-270
- LIANG M J, DENG N, XIANG X Y, MEI Y, YANG Z Y, YANG Y, YANG S J. Chinese J. Inorg. Chem., **2019**,**35**(2):263-270
- [10]Zhang L W, Xu T G, Zhao X, Zhu Y F. Appl. Catal. B, 2010,98:138-146
- [11]Wang S Y, Ding X, Yang N, Zhan G M, Zhang X H, Dong G H, Zhang L Z, Chen H. Appl. Catal. B, 2020,265:118585
- [12]Dai Z, Qin F, Zhao H Q, Ding J, Liu Y L, Chen R. ACS Catal., 2016, 6:3180-3192
- [13]Guo L, Zhao Q, Shen H, Han X X, Zhang K L, Wang D J, Fu F, Xu B. Catal. Sci. Technol., 2019,9:3193-3202
- [14]Zhang J J, Wang T, Chang X X, Li A, Gong J L. Chem. Sci., 2016,7: 6381-6386

- [15]Zhao Z W, Zhang W D, Sun Y J, Yu J Y, Zhang Y X, Wang H, Dong F, Wu Z B. J. Phys. Chem. C, 2016,120:11889-11898
- [16]Long J L, Wang S C, Chang H J, Zhao B Z, Liu B T, Zhou Y G, Wei W, Wang X X, Huang L, Huang W. Small, 2014,10:2791-2795
- [17]Ding X, Zhao K, Zhang L Z. Environ. Sci. Technol., 2014,48:5823-5831
- [18]Dong H J, Chen G, Sun J X, Li C M, Yu Y G, Chen D H. Appl. Catal. B, 2013,134:46-54
- [19]Zheng B J, Wang X, Liu C, Tan K, Xie Z X, Zheng L S. J. Mater. Chem. A, 2013,1:12635-12640
- [20]Li D, Duan X C, Qin Q, Fan H M, Zheng W J. CrystEngComm, 2013, 15:8933
- [21]Liu Y, Yu H B, Cai M, Sun J W. Catal. Commun., 2012,26:63-67
- [22]Gao S T, Feng T, Feng C, Shang N Z, Wang C. J. Colloid Interface Sci., 2016,466:284-290
- [23]Gao S T, Liu W H, Shang N Z, Feng C, Wu Q H, Wang Z, Wang C. RSC Adv., 2014,4(106):61736-61742
- [24]Jiao Z Y, Zhang J L, Liu Z D, Ma Z. J. Photochem. Photobiol. A, 2019,371:67-75
- [25]Zhang J L, Ma Z. J. Taiwan Inst. Chem. Eng., 2017,71:156-164
- [26]Xue J J, Huang C J, Zong Y Q, Gu J D, Wang M X, Ma S S. Appl. Organomet. Chem., 2019,33:e5187
- [27]Li H P, Deng Q H, Liu J Y, Hou W G, Du N, Zhang R J, Tao X T. Catal. Sci. Technol., 2014,4:1028-1037
- [28]Zhang M Y, Shao C L, Mu J B, Huang X M, Zhang Z Y, Guo Z C, Zhang P, Liu Y C. J. Mater. Chem., 2012,22:577-584
- [29]Li Z Q, Chen X T, Xue Z L. CrystEngComm, 2013,15:498-508
- [30]Gao X M, Shang Y Y, Liu L B, Nie W, Fu F. J. Phys. Chem. Solids, 2018,127:186-193

[31]Wen X J, Shen C H, Niu C G, Lai D C, Zhu M S, Sun J, Fei Z H. J. Mol. Liq., 2019,288:111063

报

- [32]Zhu M S, Chen P L, Liu M H. J. Mater. Chem., 2012, 22: 21487-21494
- [33]Zong X, Yan H J, Wu G P, Ma G J, Wen F Y, Wang L, Li C. J. Am. Chem. Soc., 2008,130:7176-7177
- [34]Zhang J L, Zhang L S, Shen X F, Xu P F, Liu J S. CrystEngComm, 2016,18:3856-3865
- [35]杨冰叶,李航商,宁昭,冯成,高书涛,王春. 无机化学学报, 2017, 33(3):396-404

YANG B Y, LI H S, NING Z, FENG C, GAO S T, WANG C. *Chinese* J. Inorg. Chem., **2017**,**33**(3):396-404

- [36]Zhao D X, Cai C. Inorg. Chem. Front., 2020,7(15):2799-2808
- [37]Kang L, Pang Y P, Lu Q F. Inorg. Chem. Front., 2019,6(11):3215-3224
- [38]Li S J, Hu S W, Jiang W, Zhang J L, Xu K B, Wang Z H. J. Colloid Interface Sci., 2019,556:335-344
- [39]Zhang L H, Shen Q H, Yu L X, Huang F L, Zhang C T, Sheng J S, Zhang F, Cheng D, Yang H. CrystEngComm, 2020,22(33):5481-5490
- [40]Shi W L, Li M Y, Huang X L, Ren H J, Guo F, Tang Y B, Lu C Y. Chem. Eng. J., 2020,394:125009
- [41]Tao R, Shao C L, Li X H, Li X W, Liu S, Yang S, Zhao C C, Liu Y C. J. Colloid Interface Sci., 2018,529:404-414
- [42]Li Z Q, Chen X T, Xue Z L. Sci. China Chem., 2013,56:443-450
- [43]Wang Z L, Huo Y, Zhang J F, Lu C, Dai K, Liang C H, Zhu G P. J. Alloys Compd., 2017,729:100-108
- [44]Wang J J, Tang L, Zeng G M, Liu Y N, Zhou Y Y, Deng Y C, Wang J J, Peng B. ACS Sustainable Chem. Eng., 2017,5:1062-1072
- [45]Linic S, Christopher P, Ingram D B. Nat. Mater., 2011,10(12):911-921