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Internal Polarization Modulation in Bi₂MoO₆ for Photocatalytic Performance Enhancement under Visible Light Illumination

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Abstract: A built-in electric field from their internal polarization inside polar photocatalysts could provide the driving force for photogenerated electrons and holes to move in opposite directions for better separation to improve their photocatalytic performance. In this study, we enhanced the photocatalytic performance of a polar photocatalyst of Bi2MoO6 by the precise control of its structure to increase its internal polarization. DFT calculation predicted that a shortened crystal lattice parameter b in Bi2MoO6 could induce a larger internal polarization, which was achieved by the modulation of the reaction solution pH in its solvent-thermal synthesis process. A series of Bi2MoO6 samples were created with the reaction solution pH of ~ 1, 4, and 8, respectively, and their crystal lattice parameter b was found to decrease gradually with the increase of the solution pH. Accordingly, these Bi₂MoO₆ samples demonstrated a gradually enhanced photocatalytic performance with the decrease of their crystal lattice parameter b as demonstrated by their photocatalytic degradation of sulfamethoxazole/phenol and disinfection of staphylococcus aureus bacteria under visible light illumination due to the improved photogenerated charge carrier separation. This study demonstrated a novel material design strategy to further enhance the photocatalytic performance of polar photocatalysts for a broad range of technical applications.

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Introduction

Since the discovery of photocatalytic water splitting on the TiO₂ photoanode in the 1972,^[1] semiconductor-based photocatalysis has been attracting significant research attentions due to its promising potentials in solar energy conversion and environment remediation.^[1-4] Despite the significant progresses achieved in the past decades, the current research on photocatalysis still could not meet the efficiency requirement for its industrial applications in renewable/clean energy technologies and the environment protections. The overall efficiency of a photocatalyst is determined by its light absorption, charge carrier separation, and surface reactions, while the charge carrier separation is generally believed to be the most important factor among them.^[5,6] Thus, the enhancement of the charge carrier separation efficiency is critical for the improvement of the overall efficiency of a photocatalyst. Various approaches had been developed for the enhancement of charge carrier separation efficiency in photocatalysts, including doping with transition metals,^[7,8] forming composite photocatalysts with matched band gap structures,^[9-11] noble metal modification,^[12-14] and crystal facet engineering.[5,15-17]

Recently, the introduction of a built-in electric field inside polar photocatalysts was proved effective for the improvement of their photocatalytic performances because the internal electric filed could provide the driving force for electrons and holes to move in opposite directions for their enhanced separation.^[18] Most research in polar photocatalysts is now focused on exploring polar semiconductors as novel photocatalysts, including GaN,^[19] ZnO.^[20,21] BaTiO₃,^[22,23] NaNbO₃,^[24] Sr₂(Ta,Nb)₂O₇,^[25] Cu₂(OH)PO₄,^[26] BiOCl,^[27] BiOF,^[28] BiOlO₃,^[29] Na₃VO₂B₆O₁₁,^[30] and Bi₇Fe₃Ti₃O₂₁,^[31] while fewer efforts had been made on the modulation of their internal polarization through the precise control of their structure to modulate their photocatalytic performances.

 Bi_2MoO_6 is one of the simplest members of the Aurivillius family, which is composed by $[Bi_2O_2]^{2+}$ layers sandwiched between MoO_4^{2-} slabs.^[32] The strong covalent bonding within these layers and the weak interlayer van der Waals interaction give rise to a highly anisotropic structure of Bi_2MoO_6 . It had been found that the internal electric field formed between the $[Bi_2O_2]^{2+}$ and MoO_4^{2-} layers in Bi_2MoO_6 could effectively separate photogenerated charge carriers,^[32-36] while the hybridization between its O 2*p* and Bi 6*s* states could narrow its band gap to enable the absorption of visible light. Thus, it had drawn research attentions as an efficient visible-light-activated photocatalyst for various applications.^[36-45] More interestingly, its layered structure with weak interlayer interaction could provide the potential to be modulated, which could subsequently change its internal polarization and open up an unexplored avenue to further enhance the photocatalytic performance of a polar photocatalyst.

Herein, we report the modulation of internal polarization in Bi₂MoO₆ by the precise control of its structure through both the theoretical and experimental approaches for the first time. Theoretical calculation based on density function theory (DFT) discovered that the internal polarization in Bi₂MoO₆ could be increased by shortening its crystal lattice parameter b. Subsequently, a simple, one-pot template-free solvent-thermal process was developed for the synthesis of Bi2MoO6 photocatalyst, and the addition of NaOH in the reaction solution was found to be effective to shorten its crystal lattice parameter b. With shortened crystal lattice parameter b, the Bi2MoO6 photocatalyst demonstrated improved photogenerated charge carrier separation efficiency due to its increased internal polarization as demonstrated by the powder second-harmonic generation (SHG) signal measurement, and subsequently possessed a largely enhanced photocatalytic performance as demonstrated in its photocatalytic degradation of organic pollutants and disinfection of staphylococcus aureus bacteria under visible light illumination.

Results and Discussion

Calculations of dipole moment variations with the change of lattice constant b

The polarity of a polar photocatalyst is critical for its separation of photogenerated charge carriers to enhance the photocatalytic performance, which could be quantitatively described by its dipole moment. With a larger dipole moment, the polar photocatalyst has a higher polarity for a better separation of photogenerated charge carriers. Figure 1a shows the schematic illustration of the crystal lattice structure of Bi2MoO6, and the direction of dipole moment was along the *b* axis from MoO_4^{2-} layer to [Bi₂O₂]²⁺ layer.^[33,46] Thus, the change of lattice parameter b should affect its dipole moment. Figure 1b shows the calculated dipole moments of the system with different lattice parameter b values. It was found that the dipole moment could slightly increase with the increase of lattice parameter b value when lattice a/c as well as the internal positions of the atoms were fixed (before relaxation). This result could be easily understood because in this case the distances between all atoms were changed uniformly and the effective distance between the centers of the positive charge and the negative charge will increase/decrease with the increase/decrease of the lattice parameter b value.

However, to minimize the system energy, a relaxation will happen in the crystal lattice with the change of lattice parameter b value.^[33,47] Interestingly, an opposite trend was found after the relaxation when the lattice a/c and the atomic positions were free to relax. The dipole moment decreased with the increase of the lattice parameter b value (see Figure 1b). To figure out its origin, the atomic movements after the relaxation were studied. It was found that the deformation was nonuniform inside the deformed cell. Only oxygen atoms near Bi demonstrated

apparent movements when the strain was applied on lattice *b*, which should be attributed to the lower atomic density of $[Bi_2O_2]^{2+}$ layers compared to MOQ_4^{2-} layers. Thus, the atomic relaxation was mainly contributed by oxygen atoms near Bi. The directions of the oxygen atom movements were shown in Figure 1a when the lattice parameter *b* was compressed, while their movement directions would be reversed for a tensile strain (*b* increased). Thus, the calculation results of dipole moment variations with the change of lattice constant *b* suggested that the lattice parameter *b* value should be decreased for the increase of the polarity in Bi₂MOO₆ for a better separation of photogenerated charge carriers, which provide the guidance in the following synthesis of Bi₂MOO₆ photocatalysts for a better photocatalytic performance.



Figure 1. (a) The schematic illustration of the crystal lattice structure of Bi_2MOO_6 (Note, dashed circles show oxygen atoms with significant movements after the relaxation when the crystal lattice parameter *b* decreased). (b) The calculated dipole moments of the system with different lattice parameter *b* values before and after the relaxation, respectively (with the dipole moment of equilibrium state of Bi_2MOO_6 (*b*=16.31 Å) as the reference).

Synthesis of Bi₂MoO₆ photocatalysts with a series of crystal lattice parameter *b* values

A solvent-thermal process was used for the synthesis of Bi₂MoO₆ photocatalysts, in which C₂H₅OH and ethylene glycol (EG) served both as the reaction solvents and the complexing agents to control the release of Bi(III).[37] It had been demonstrated that hydroxyl groups in the reaction system could largely affect the hydrolysis and condensation reactions for the synthesis of metal oxide nanoparticles, [48-51] and the reaction solution pH could have an impact on the electrostatic interactions between reactants to modulate the crystal growth.^[44] Thus, the addition of NaOH was adopted to vary the reaction solution pH in our solvent-thermal synthesis of Bi2MoO6 photocatalysts to examine its effect on the obtained samples. When the reaction solution pH was over 8, it was found that phases other than Bi₂MoO₆ could occur. Thus, the highest reaction solution pH was limited at 8. By the addition of proper amounts of NaOH, the reaction solution pH was adjusted to 4 and 8 to obtain the BMO-4 and BMO-8 samples, respectively, while the BMO-1 sample was synthesized without the addition of NaOH in the reaction solution (pH \sim 1). It was found that 160 $^{\circ}$ C was the optimized solvent-thermal reaction temperature to



obtain samples with better photocatalytic performances, while the solvent-thermal reaction time was set at 20 h to avoid the occurrence of other phases besides Bi2MoO6 in the obtained product due to incomplete reaction. The product yields of the BMO-1, BMO-4 and BMO-8 samples were ~ 79%, 82%, and 87%, respectively. Figure 2a shows the XRD patterns of all three samples, which demonstrated that they had the same crystal structure type and their diffraction peaks all belonged to the pure Bi₂MoO₆ phase (JCPDS No. 21-0102). However, a slight shift towards the higher 20 direction of their corresponding diffraction peaks could be observed on these Bi2MoO6 sample with the increase of the reaction solution pH as demonstrated in Figure 2b with their (131) peaks as an examples at a higher magnification. This observation clearly suggested that the addition of NaOH in the reaction solution could affect the crystallization and growth of Bi₂MoO₆ in our synthesis approach. From the XRD analysis data, the crystal lattice parameters of these three Bi₂MoO₆ samples were obtained as shown in Table 1. which clearly demonstrated that their crystal lattice parameter b values gradually decreased from 16.3947 Å of the BMO-1 sample, to 16,2906 Å of the BMO-4 sample, and to 16,2415 Å of the BMO-8 sample, respectively. Thus, a simple and robust approach of the addition of NaOH in the reaction solution was found to be effective for the creation of Bi₂MoO₆ photocatalysts with shortened crystal lattice parameter b in our synthesis process, which could increase its internal polarization and subsequently enhance its photocatalytic performance as demonstrated in relevant sections followed.



Figure 2. (a) The XRD patterns of the BMO-1 sample, the BMO-4 sample and the BMO-8 sample. (b) The (131) peak of the BMO-8 sample at a higher magnification, compared with that of the BMO-1 sample and that of the BMO-4 sample.

Table 1. Th samples	e crystal lattice	e parameters o	of the Bi_2MoO_6	photocatalyst	
Sample	a (Å)	b (Å)	c (Å)	Vol (Å3)	
BMO-1	5.5330	16.3947	5.4924	498.23	
BMO-4	5.5290	16.2906	5.4879	494.30	
BMO-8	5.4900	16.2415	5.4810	488.71	

Characterization of Bi_2MoO_6 photocatalyst with a series of crystal lattice parameter *b* values

Figure 3a to Figure 3c show the bright field TEM observations of the BMO-1 sample, the BMO-4 sample, and the BMO-8 sample, respectively, which demonstrated their nano-sized features. The BMO-1 sample was composed of irregular nanoplates, the BMO-4 sample was composed of thicker nanoblocks, while the BMO-8 sample was composed of relatively large nanosheets close to the rectangular shape. The insert image in Figure 3c shows the selected area electron diffraction (SAED) pattern obtained from the black circular area on the nanosheet in the BMO-8 sample, which clearly demonstrated its single crystal feature. Figure 3d shows the high resolution TEM (HRTEM) image of the nanosheet in the BMO-8 sample marked by the black rectangular in Figure 3c, and the insert images in Figure 3d show the fast Fourier transformation (FFT) pattern and the magnified high resolution TEM image of the area marked by the white rectangular in Figure 3d, respectively. From the TEM analysis results, the basal plane of the nanosheet in the BMO-8 sample could be indexed as {010}, which was exactly perpendicular to the b axis of Bi2MoO6 (the dipole moment direction). Two side faces of the nanosheet in the BMO-8 sample could be indexed as {100} plane and {001} plane, respectively. BET analysis results demonstrated that the BET specific surface area of the BMO-1 sample was ~ 46.52 m²·g⁻¹, that of the BMO-4 sample was ~ 34.79 m²·g⁻¹, and that of the BMO-8 sample was ~ 15.77 m²·g⁻¹. The isoelectric point (IEP) values of the BMO-1, BMO-4, and BMO-8 samples were determined at ~ 3.8, 4.7, and 5.0, respectively (see Figure S1 in the supplementary information).

The chemical compositions and element valence states in these Bi₂MoO₆ photocatalyst samples were investigated by Xray photoelectron spectroscopy (XPS). Figure 4a shows their XPS survey spectra, which demonstrated clearly the existence of Bi, Mo, and O in all of them. Due to the widespread presence of carbon in the environment, C 1s peak could also be observed in their XPS survey spectra. Elemental analysis was conducted on these samples, which demonstrated that the carbon contents in the BMO-1, BMO-4, and BMO-8 samples were ~ 0.3000 wt%, 0.2436 wt%, and 0.2412 wt%, respectively. Such a low carbon content should have minimum effect on their photocatalytic performance. Figure 4b to 4d show their high resolution XPS scans over Bi 4f, Mo 3d, and O 1s peaks, respectively, which demonstrated that they had very similar XPS spectra for all the three elements. For Bi 4f spectrum (Figure 4b), the two XPS peaks at 158.8 and 164.2 eV could be assigned to Bi3+ 4f7/2 and Bi³⁺ 4f_{5/2}, respectively. For Mo 3*d* spectrum (Figure 4c), the two XPS peaks at 232.2 and 235.3 eV could be assigned to Mo⁶⁺ $3d_{5/2}$ and Mo⁶⁺ $3d_{3/2}$, respectively.^[38,50] For O 1s spectrum (Figure 4d), the wide and asymmetric peak could be fitted into the combination of two peaks with the peak positions at 529.79 and 530.65 eV, which are related to Bi-O and Mo-O, respectively.^[52] This observation was in accordance with the XRD and TEM analysis results, suggesting that the BMO-1 sample, the BMO-4 sample and the BMO-8 sample had the same chemical composition as Bi₂MoO₆.

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Figure 3. (a) to (c) The bright field TEM observations of the BMO-1 sample, the BMO-4 sample, and the BMO-8 sample, respectively (Note, the insert image in Figure 3c shows the selected area electron diffraction (SAED) pattern obtained from the black circular area on the nanosheet in the BMO-8 sample). (d) The high resolution TEM (HRTEM) image of the nanosheet in the BMO-8 sample marked by the black rectangular in Figure 3c (Note, the insert images in Figure 3d show the fast Fourier transformation (FFT) pattern and the magnified high resolution TEM image of the area marked by the white rectangular in Figure 3d, respectively).



Figure 4. (a) XPS survey spectra of the BMO-8 sample, compared with that of the BMO-1 sample and that of the BMO-4 sample. (b) to (d) The high resolution XPS scans over Bi 4f, Mo 3d, and O 1s peaks of both samples, respectively.

Optical properties and energy band structures of Bi_2MoO_6 photocatalyst with a series of crystal lattice parameter *b* values

The optical properties of these three samples were examined by measuring their UV-vis diffuse reflectance spectra, and their light absorbance spectra could be approximated by the KubelkaMunk function.^[53,54] Figure 5a shows their light absorbance spectra compared with that of Degussa P25 TiO₂ nanoparticles, and the insert image in Figure 5a shows their band gap values determined by the construction of Tauc Plots $((F(R)^*hv)n vs. hv)$ from their light absorbance data.^[53] Degussa P25 TiO₂ nanoparticles demonstrated a characteristic adsorption stopping edge at ~ 400 nm, while all these BMO samples demonstrated a strong light absorbance from the UV light region into the visible light region, which was consistent with their yellow color appearance. For all three BMO samples, their light absorbance spectra had the steep shape with fundamental absorbance stopping edges into the visible light region (~ 500 nm), which indicated that its visible light absorption was arisen from the band-gap transition.^[37] Among them, the BMO-1 sample had the best visible light absorbance, while the BMO-8 sample had the lowest visible light absorbance. From their Tauc Plots, their band gaps were determined at ~ 3.03 eV for Degussa P25 TiO2 nanoparticles, ~ 2.74 eV for the BMO-1 sample, ~ 2.78 eV for the BMO-4 sample, and ~ 2.85 eV for the BMO-8 sample, respectively.

Mott-Schottky analysis was carried out to determine the conduction band (CB) minimums of our samples. From the M-S Plots (Figure 5b), the flat band potentials of our samples (vs. Ag/AgCI) were determined at ~ -0.22 V (BMO-1), -0.27 V (BMO-4), and -0.32 V (BMO-8), respectively. It is generally known that E (Ag/AgCI) is 0.2224 V (vs. NHE, Normal Hydrogen Electrode), and the bottom of the conduction band of an n-type semiconductor is 0.2 V more negative than its flat band potential.^[55,56] Thus, the conduction band (CB) minimums of our samples (vs. NHE) could be determined at ~ -0.20 V (BMO-1), -0.25 V (BMO-4), and -0.30 V (BMO-8), respectively. With the band gap values determined from their Tauc Plots, the valence band (VB) maximums of our samples (vs. NHE) could be determined at ~ 2.54 V (BMO-1), 2.53 V (BMO-4), and 2.55 V (BMO-8), respectively. Thus, their energy band structures could be constructed as demonstrated in Figure 5c, which demonstrated that their conduction band potentials were all more negative than the one-electron reduction potential of O₂ (-0.05 V vs NHE). VB-XPS measurements were also conducted on our samples (see Figure S2 in the supplementary information), which demonstrated that their relative positions of VB maximum edges were very close. This observation was in accordance with their energy band structures determined by their Mott-Schottky Plots and Tauc Plots.

Polarity measurements of Bi_2MoO_6 photocatalyst with a series of crystal lattice parameter *b* values

To demonstrate the increase of polarity in Bi_2MoO_6 by decreasing the lattice *b* experimentally, powder secondharmonic generation (SHG) signals of our BMO samples irradiated by a Nd:YAG laser (λ at 1064 nm) were measured, and the results were shown in Figure 6a. The noncentrosymmetric polar crystal structure of Bi_2MoO_6 could generate a non-linear optical (NLO) property, and a larger NLO response could indicate a larger polarity.^[57] Figure 6a clearly

demonstrated that the NLO response of our samples followed the ranking of the BMO-1 sample < the BMO-4 sample < the BMO-8 sample, although they had the same crystal structure and chemical composition. This experimental result clearly suggested that the polarity in Bi_2MOO_6 increased with the decrease of the lattice *b*, which was in accordance with the DFT calculation result.



Figure 5. (a) The light absorbance of the BMO-8 sample, compared with that of the BMO-1 sample, that of the BMO-4 sample, and that of Degussa P25 TiO_2 nanoparticles (Note, the insert image in Figure 5a shows their band gap values determined by the construction of Tauc Plots ($(F(R)^*hv)n vs. hv)$ from their light absorbance data). (b) The Mott-Schottky Plots of the BMO-8 sample, compared with that of the BMO-1 sample and that of the BMO-8 sample. (c) The energy band structures of the BMO-1, BMO-4, and BMO-8 samples, respectively.



Figure 6. (a) The second harmonic generation (SHG) responses of the BMO-1, BMO-4, and BMO-8 samples, respectively. (b) The photocurrent responses of the BMO-1, BMO-4, and BMO-8 samples under illumination in the applied potential range between 0.2 V to 1.0 V versus Ag/AgCl, respectively. (c) The electrochemical impedance spectra of the BMO-1, BMO-4, and BMO-8 samples under illumination, respectively (Note, the insert image in Figure 6c shows the equivalent circuit used to fit the spectra). (d) The IPCE spectra of the BMO-1, BMO-4, and BMO-8 samples, respectively.

Photoelectrochemical (PEC) measurements of Bi_2MoO_6 photocatalysts with a series of crystal lattice parameter *b* values

A better light absorbance, however, could not directly suggest a better photocatalytic activity because photogenerated charge carriers may be lost due to their recombination and could not produce radicals. Thus, the detection of charge carriers that transferred to the surface of the photocatalyst could provide a more accurate estimation of its photocatalystic response. As a powerful tool for investigating the photogenerated charge carrier separation and transfer behavior, the photoelectrochemical (PEC) measurement were conducted on these three samples, respectively, and the results were shown in Figure 6b and 6c.

Figure 6b compares the photocurrent responses of these samples under illumination. Under applied potential between 0.2 V to 1.0 V versus Ag/AgCl, the dark current of all these three samples remained a very low level. When the illumination was on, they all exhibited obvious photocurrent densities. Although the visible light absorbance of the BMO-1 sample was higher than that of the BMO-4 sample and the visible light absorbance of the BMO-8 sample (see Figure 6a), their photocurrent densities obviously had the opposite ranking. The photocurrent density of the BMO-8 sample was ~ 4 times as that of the BMO-1 sample, while the photocurrent density of the BMO-8 sample.

Figure 6c compares the electrochemical impedance spectra (EIS) of these samples under illumination, which clearly demonstrated that the BMO-8 sample had the smallest diameter of the Nyquist circular radius among them and the BMO-4 sample had a smaller diameter of the Nyquist circular radius than the BMO-1 sample. The arc radius on the EIS Nyquist plot could reveal reaction rate occurring at the surface of the electrodes. A smaller arc radius indicated a more effective separation of photogenerated carriers and faster interfacial charge transfer to the electron acceptor or donor.^[46] To better understand the EIS measurement results, the EIS data were fitted to the equivalent circuit as demonstrated in Figure 6c. Rs is the series resistance which depends on the external circuit dynamics, C_{dl} is the space charge capacitance in the semiconducting layer, and R_{ct} is the charge-transfer resistance. The C_{dl} values of the BMO-1, BMO-4, and the BMO-8 samples were 3.87 $\mu F,$ 9.271 $\mu F,$ and 30.26 $\mu F,$ respectively, while their \textit{R}_{ct} values were 94.7 kΩ, 30.16 kΩ, and 10.6 kΩ, respectively. A smaller R_{ct} value and a larger C_{dl} value could suggest an improved charge transport characteristics.^[58,59] Thus, the BMO-8 sample had the best charge transfer efficiency among these samples.

Figure S3 in the supplementary information compares the surface photovoltage (SPV) spectra of the BMO-1 sample and the BMO-8 sample. It clearly demonstrated that the surface photovoltage of the BMO-8 sample was much stronger than that of the BMO-1 sample, which suggested that the BMO-8 sample had a largely enhanced charge separation efficiency than that of the BMO-1 sample. This observation was consistent with the

photocurrent responses and the electrochemical impedance spectra of these samples.

These observations indicated that the photogenerated charge carrier separation efficiencies of these Bi_2MoO_6 photocatalysts were different, which could be attributed to their different internal polarizations from their different crystal lattice parameter *b* values. With their gradually decreased crystal lattice parameter *b* values, their photogenerated charge carrier separation efficiencies increased as predicted by the DFT calculation results of dipole moment variations with the change of crystal lattice constant *b* and the SHG measurement results. Thus, a better photocatalytic performance should be expected with the ranking of the BMO-1 sample < the BMO-4 sample < the BMO-8 sample when their crystal lattice constant *b* gradually decreased.

Incident photon to current efficiency (IPCE) spectra of Bi_2MoO_6 photocatalysts with a series of crystal lattice parameter *b* values

The incident photon to current efficiency (IPCE) spectra measurements were conducted on our BMO samples to provide a comparison of standard quantum efficiencies of these samples. and the result was shown in Figure 6d. As expected, the IPCE values of these samples followed the ranking of the BMO-1 sample < the BMO-4 sample < the BMO-8 sample in the whole visible light region, although their visible light adsorption capabilities followed the ranking of the BMO-8 sample < the BMO-4 sample < the BMO-1 sample. It is well known that IPCE is mainly affected by the light harvesting efficiency, charge separation and collection yields.^[60,61] Thus, these results further suggested that the BMO-8 sample had an improved charge separation and collection yield, which was in good agreement with its polarity increase from the decrease of the lattice b and subsequent better PEC measurement results. Thus, the BMO-8 sample should have the best photocatalytic performance among these BMO samples.

Photocatalytic degradation of SMX under visible light illumination

photocatalytic performances of these The Bi₂MoO₆ photocatalysts with a series of crystal lattice parameter b values were first demonstrated by their degradation of organic pollutants under visible light illumination. As a widely used veterinary medicine, SMX has been identified in surface water due of its low biodegradability as an emerging pollutant, which could cause environmental pollution and increase antibiotic resistance in human.^[62-64] Unlike colorful organic dyes, SMX does not absorb visible light, which could exclude the potential photosensitization effect from organic dyes on the evaluation of the photocatalytic activity under visible light illumination. Figure 7a summaries the residue SMX concentrations vs. treatment time under visible light illumination by the P25 TiO₂ nanoparticle, the BMO-1 sample, the BMO-4 sample, and the BMO-8 sample, respectively. At the solution pH of ~ 6.5, both SMX and these

BMO photocatalysts were negatively charged. Thus, its adsorptions onto these BMO photocatalysts were not favored due to the electrostatic repulsion between them, and the adsorption effect was not obvious. Due to the co-existence of anatase and rutile phases in P25 TiO2 nanoparticle, it demonstrated a moderate photocatalytic degradation effect on SMX under visible light illumination. After 40 min treatment, the residue SMX concentration was still ~ 90%. The BMO-1 demonstrated a better photocatalytic degradation effect on SMX under visible light illumination than P25 TiO₂ nanoparticle. After 40 min treatment, the residue SMX concentration dropped to ~ 70%. When its crystal lattice parameter b was shortened by the increase of the reaction solution pH from ~ 1 to ~ 4, the BMO-4 sample demonstrated a better photocatalytic degradation effect on SMX than the BMO-1 sample under visible light illumination. After 40 min treatment, the residue SMX concentration dropped to ~ 50%. As expected, the BMO-8 sample with the shortest crystal lattice parameter b demonstrated the best photocatalytic degradation effect on SMX under visible light illumination among these three Bi₂MoO₆ photocatalysts. After 40 min treatment, the residue SMX concentration largely dropped to just ~ 25%.

A first-order exponential decay of SMX concentration was observed for all these four photocatalysts, which could be fitted to Eq. (1):

$$\ln(C/C_0) = -kt \tag{1}$$

where C is the residue SMX concentration, t is the visible light illumination time, and k is the decay rate constant that could be used to compare the photocatalytic SMX degradation efficiency of different samples. The decay rate constant k of the BMO-8 sample on SMX was determined at ~ 0.0502 min⁻¹, which was ~ 2.8 times, ~ 3.6 times, and ~ 13 times as that of the BMO-4 sample (0.0178 min⁻¹), the BMO-1 sample (0.0140 min⁻¹), and P25 TiO₂ nanoparticle (0.0038 min⁻¹), respectively. Although they had the same Bi₂MoO₆ crystal structure and composition, the photocatalytic SMX degradation performance ranking of these Bi₂MoO₆ samples followed the sequence as the BMO-8 sample > the BMO-4 sample > the BMO-1 sample, opposite to their visible light absorbance ranking and BET specific area ranking. This observation was in accordance to their photogenerated charge carrier separation efficiency ranking result and IPCE ranking result, which could be attributed to their gradually increased internal polarization as we shortened its crystal lattice parameter *b* in the material design and synthesis. The apparent quantum efficiency is an important parameter to demonstrate the performance of a photocatalyst in heterogeneous photocatalysis,[65-67] which could be defined as Eq. (2):

$$\varphi_x = -\left(d[C]/dt\right)/(d[hv]_{inc}/dt) \tag{2}$$

where d[C]/dt is the change rate of the pollutant concentration, and $d[hv]_{inc}/dt$ is the total light illumination power striking the sample. The apparent quantum efficiencies of these samples on the photocatalytic degradation of SMX under visible light illumination could be determined as Eq. (3):

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$$\varphi_{\rm x} = {\rm kC_0} {\rm e}^{-{\rm kt}} / ({\rm d}[{\rm hv}]_{\rm inc} / {\rm dt}) \tag{3}$$

which was dependent on the treatment time t. In our photocatalytic organic degradation experimental setup. $d[hv]_{inc}/dt$ is a constant of 76.34 J/min. Thus, the initial apparent quantum efficiencies $(t \rightarrow 0)$ of the BMO-1 sample, the BMO-4 sample, and the BMO-8 sample on the photocatalytic degradation of SMX under visible light illumination could be determined at ~ 4.58×10⁻³ ppm/J, 5.83×10⁻³ ppm/J, and 1.65×10⁻ ² ppm/J, respectively, while that of P25 TiO₂ nanoparticle was only ~ 1.24×10^{-3} ppm/J. After being normalized by their specific surface areas to exclude the surface area factor in the comparison, the initial apparent quantum efficiencies of these BMO samples with the same surface area on the photocatalytic degradation of SMX under visible light illumination could be determined at ~ 9.8×10^{-5} ppm·g/(J·m²), 1.67×10^{-4} ppm·g/(J·m²), and 1.05×10^{-3} ppm·g/(J·m²), respectively, which further confirmed the largely enhanced photocatalytic degradation effect on SMX by the BMO-8 sample with the enhanced internal polarization from its shortened crystal lattice parameter b.



Figure 7. (a) The residue SMX concentrations vs. treatment time under visible light illumination by the P25 TiO₂ nanoparticle, the BMO-1 sample, the BMO-4 sample, and the BMO-8 sample, respectively. (b) The residue phenol concentrations (in C/C_0 form) vs. treatment time under visible light illumination by the P25 TiO₂ nanoparticle, the BMO-1 sample, the BMO-4 sample, and the BMO-8 sample, respectively. (c) The survival ratio of *S. aureus* by the treatment of the BMO-1 sample, the BMO-4 sample, and the BMO-1 sample, the BMO-4 sample under visible light illumination, respectively, compared with that without the presence of photocatalyst under visible light illumination.

Photocatalytic degradation of phenol under visible light illumination

Phenol is one of the widely-distributed organic pollutants in wastewater from industrial activities, which could cause damages to both the environment and human beings due to its bio-recalcitrance and acute toxicity.^[68,69] As a colorless organics, phenol also does not absorb visible light, which could exclude the potential photosensitization effect from organic dyes and

serve as a model organic pollutant for the evaluation of the photocatalytic activity under visible light illumination. Figure 7b summaries the residue phenol concentrations (in C/C_0 form) vs. treatment time under visible light illumination by the P25 TiO2 nanoparticle, the BMO-1 sample, the BMO-4 sample, and the BMO-8 sample, respectively. At the solution pH of ~ 6.5, both phenol and these BMO photocatalysts were negatively charged. Thus, its adsorptions onto these BMO photocatalysts were not favored due to the electrostatic repulsion between them, and the adsorption effect was not obvious. After 120 min treatment with the P25 TiO₂ nanoparticle, the residue phenol concentration was still ~ 90%. All the Bi₂MoO₆ photocatalysts demonstrated better photocatalytic degradation performances on phenol than the P25 TiO₂ nanoparticle under visible light illumination. The BMO-1 and BMO-4 samples demonstrated a better photocatalytic degradation effect on phenol than P25 TiO₂ nanoparticle. After 120 min treatment under visible light illumination, the residue phenol concentration dropped to ~ 80% for the BMO-1 sample. ~ 70% for the BMO-4 sample, and ~ 60% for the BMO-8 sample, respectively. A zero-order decay of phenol concentration was observed for all these four photocatalysts, which could be fitted to Eq. (4):

$$C/C_0 = -kt \tag{4}$$

where *C* is the residue phenol concentration, *t* is the visible light illumination time, and *k* is the decay rate constant that could be used to compare the photocatalytic phenol degradation efficiency of different samples. The decay rate constant k of the BMO-8 sample on phenol was determined at 0.0032 min⁻¹, which was ~ 1.4 times, ~ 2.3 times and ~ 6 times as that of the BMO-4 sample (0.0023 min⁻¹), the BMO-1 sample (0.0014 min⁻¹) and the P25 TiO₂ nanoparticle (0.00053 min⁻¹), respectively. The apparent quantum efficiencies of these samples on the photocatalytic degradation of phenol under visible light illumination could be determined as Eq. (5):

$$\varphi_x = kC_0/(d[hv]_{inc}/dt)$$
 (5)

which was independent on the treatment time t due to the zero order decay behavior. Thus, the apparent quantum efficiencies of the BMO-1 sample, the BMO-4 sample, and the BMO-8 sample on the photocatalytic degradation of phenol under visible light illumination could be determined at ~ 1.83×10⁻⁴ ppm/J, 3.01×10^{-4} ppm/J, and 4.19×10^{-4} ppm/J, respectively, while that of P25 TiO₂ nanoparticle was only ~ 6.94×10^{-5} ppm/J. After being normalized by their specific surface areas to exclude the surface area factor in the comparison, the initial apparent quantum efficiencies of these BMO samples with the same surface area on the photocatalytic degradation of phenol under visible light illumination could be determined at ~ 4.83×10^{-5} ppm·g/(J·m²), 8.65×10⁻⁵ ppm⋅g/(J⋅m²), and 2.66×10⁻⁴ $ppm \cdot g/(J \cdot m^2),$ respectively, which further confirmed the largely enhanced photocatalytic degradation effect on phenol by the BMO-8 sample with the enhanced internal polarization from its shortened crystal lattice parameter b.

Photocatalytic disinfection of *staphylococcus aureus* bacteria under visible light illumination

The superior photocatalytic performance of the BMO-8 sample was further demonstrated by its photocatalytic disinfection of S. aureus cells, which is a commonly found pathogenic coccus in hospitals that could cause nonspecific infection and nosocomial infection.^[70] The photocatalytic disinfection experiment was conducted by exposing the cells suspended in the buffer solution with the photocatalyst under visible light illumination for varying time intervals. Figure 7c shows the survival ratio of S. aureus by the treatment of the BMO-1 sample, the BMO-4 sample, and the BMO-8 sample under visible light illumination, respectively, compared with that without the presence of photocatalyst under visible light illumination. Without the presence of photocatalyst, no obvious vitality loss was observed on S. aureus cells under visible light illumination. The BMO-1 sample demonstrated a moderate photocatalytic disinfection effect on S. aureus cells under visible light illumination. After 120 min treatment, the survival ratio of S. aureus cells dropped to ~ 85%. The BMO-4 sample demonstrated a better photocatalytic disinfection effect on S. aureus cells than the BMO-1 sample under visible light illumination. After 120 min treatment, the survival ratio of S. aureus cells dropped to ~ 43%. As expected, the BMO-8 sample demonstrated the best photocatalytic disinfection effect on S. aureus cells under visible light illumination. The survival ratio of S. aureus cells continuously decreased with the increase of the treatment time. After 120 min treatment, the survival ratio of S. aureus cells treated by the BMO-8 sample largely dropped to less than 16%, which was more than 5 times lower than that treated by the BMO-1 sample. A zero-order decay of the survival ratio of S. aureus cells was observed, which could be fitted to Eq. (6):

$$N_t/N_0 = -kt \tag{6}$$

where N_0 and N_t are the numbers of colony forming units at the initial and each following time interval, respectively, *t* is the visible light illumination time, and *k* is the decay rate constant that could be used to compare the photocatalytic efficiency of different samples. The decay rate constant *k* of the BMO-8 sample on S. aureus cells was determined at 0.007 min⁻¹, which was ~ 1.25 times and ~ 5.6 times as that of the BMO-4 sample (0.0056 min⁻¹) and the BMO-1 sample (0.00125 min⁻¹). The apparent quantum efficiencies of these samples on the photocatalytic disinfection of *S. aureus* cells under visible light illumination could be determined as Eq. (7):

$$\varphi_x = kN_0/(d[hv]_{inc}/dt)$$
(7)

which was also independent on the treatment time *t* due to the zero order decay behavior. In our photocatalytic disinfection experimental setup, $d[hv]_{inc}/dt$ is a constant of 53.01 J/min. Thus, the apparent quantum efficiencies of the BMO-1 sample, the BMO-4 sample, and the BMO-8 sample on the photocatalytic disinfection of *S. aureus* cells under visible light illumination could be determined at ~ 236 (cfu/mL)/J, 1056 (cfu/mL)/J, and

1320 (cfu/mL)/J, respectively. After being normalized by their specific surface areas to exclude the surface area factor in the comparison, the initial apparent quantum efficiencies of these samples with the same surface area on the photocatalytic disinfection of *S. aureus* cells under visible light illumination could be determined at ~ 3.5 (cfu/mL)·g/(J·m²), 21 (cfu/mL)·g/(J·m²), and 58 (cfu/mL)·g/(J·m²), respectively, which further confirmed the largely enhanced photocatalytic disinfection effect on *S. aureus* cells by the BMO-8 sample with the enhanced internal polarization from its shortened crystal lattice parameter *b*.

Main reactive oxygen species for the photocatalytic activity of Bi_2MoO_6 photocatalyst with shortened crystal lattice parameter *b* under visible light illumination

Under proper illumination, various reactive oxygen species (ROSs) could be produced by photocatalysts, and the determination of main ROSs involved in the photocatalytic process is critical for the understanding of its working mechanism. Thus, radical scavengers of Benzoquinone (P-BQ), NaBrO₃, isopropanol (IPA), and ammonium oxalate were used in radical trapping experiments for superoxide $(\cdot O_2)$, electrons (e), hydroxyl radicals (·OH), and holes (h⁺), respectively, to examine if their existence could affect the photocatalytic degradation of SMX by the BMO-8 sample. Figure 8 shows the residue SMX concentrations vs. treatment time under visible light illumination by the BMO-8 sample with different radical scavengers, respectively. The results demonstrated that the addition of NaBrO₃ or IPA had no effect on the photocatalytic degradation of SMX by the BMO-8 sample, while the addition of P-BQ or ammonium oxalate largely inhibited the photocatalytic degradation of SMX by the BMO-8 sample. Thus, the dominant ROSs involved in the photocatalytic SMX degradation by the BMO-8 sample were $\cdot O_2^-$ and h^+ . This observation was consistent with its energy band structure of the BMO-8 sample (Figure 5c). Due to its more negative conduction band potential than the one-electron reduction potential of O₂, photogenerated electrons could readily react with O_2 to produce $\cdot O_2$, while photogenerated holes reacted directly with SMX.



The stability and reusability of Bi_2MoO_6 photocatalyst with shortened crystal lattice parameter *b*

The stability and reusability of a photocatalyst is critical for its potential applications in environmental remediation practice. Figure 9a shows the photocatalytic degradation of SMX by the BMO-8 sample under visible light illumination for five runs. After each run, the photocatalyst was collected, washed, dried, and then reused in the photocatalytic degradation of SMX for the next run. In general, the BMO-8 sample demonstrated similar photocatalytic degradation behavior on SMX under visible light illumination for the five runs, and no obvious reduction of the photocatalytic degradation efficiency was observed. Figure 9b shows the XRD patterns of the BMO-8 sample before and after the photocatalytic SMX degradation experiment for five runs, respectively, which clearly demonstrated that the two XRD patterns were identical. Figure S4 in the supplementary information shows the TEM image of the BMO-8 sample after the photocatalytic SMX degradation experiment for five runs. which clearly demonstrated that its nanosheet morphology was not changed. Thus, the recycle photocatalytic degradation experiment, the XRD analysis results, and the TEM observations suggested that the BMO-8 sample had a good stability and reusability, which was beneficial for its potential applications.



Figure 9. (a) The photocatalytic degradation of SMX by the BMO-8 sample under visible light illumination for five runs. (b) The XRD patterns of the BMO-8 sample before and after the photocatalytic SMX degradation experiment for five runs, respectively.

Conclusions

In summary, a novel approach was developed to enhance the photocatalytic performance of a polar photocatalyst of Bi_2MoO_6 by the precise control of its structure to increase its internal polarization. From the DFT calculation results, Bi_2MoO_6 with a shortened crystal lattice parameter *b* could have a larger internal polarization, which was beneficial for a better photogenerated charge carrier separation efficiency to enhance its photocatalytic performance. A simple and robust approach of the addition of NaOH in the reaction solution was found to be effective for the creation of Bi_2MoO_6 photocatalyst with shortened crystal lattice parameter *b* in its solvent-thermal synthesis process. With the decrease of crystal lattice parameter *b*, the Bi_2MoO_6 photocatalyst demonstrated a gradually enhanced photocatalytic performance in both the photocatalytic degradation of organic pollutants and disinfection of *staphylococcus aureus* bacteria

under visible light illumination. This observation could be attributed to its increased internal polarization with the decrease of crystal lattice parameter *b*, which subsequently improved photogenerated charge carrier separation efficiency as verified in the photoelectrochemical measurement results. This study demonstrated an unexplored strategy for the design and synthesis of polar photocatalysts to enhance their photocatalytic performance, which may have the potential for a broad range of technical applications.

Experimental Section

Calculation methods

All the calculations were performed in the framework of Density Functional Theory as implemented in Vienna ab initio simulation package (VASP).^[71,72] Exchange-correlation potential was described by generalized gradient approximation (GGA-PBE).^[46] The plane-wave cutoff energy was set as 400 eV, and a k-point mesh of 9x 3x 9 was used for the unit cell. Van der Waals (vdW) interactions^[73] were considered in the structure optimization, leading to the lattice parameters (a = 5.52 Å, b = 16.31 Å, and c = 5.50 Å) in much better agreement with the experimental data than that in the absence of vdW corrections.^[34,47,74] The structural optimization stopped when the forces on the atoms were smaller than 0.01 eV/ Å. The effects of lattice parameter b on the dipole moments of the system were evaluated by the following steps. A tensile/compression strain was firstly applied in the b direction. Then, the supercell including the internal positions of the atoms was allowed for a full relaxation, and the dipole moments of the deformed structures were calculated both before and after the relaxation.

Chemicals and materials

Ethylene glycol (EG, 98%, Aladdin Industrial Corporation Co. Ltd., Shanghai, P. R. China) and ethyl alcohol (EtOH, 99.7%, Beijing Yili Fine Chemicals Co. Ltd., Beijing, P. R. China) were used as the solvents in solvent-thermal process. Sodium molybdate the dihvdrate (Na2MoO4·2H2O, 99%, Sinopharm Chemical Reagent Co., Ltd., Shanghai, P. R. China) and bismuth nitrate pentahydrate (Bi(NO₃)₃·5H₂O, 99%, Sinopharm Chemical Reagent Co., Ltd., Shanghai, P. R. China) were used as the Mo and Bi sources in the synthesis of Bi₂MoO₆. respectively. Commercially available Degussa P25 TiO2 nanoparticles (Evonik Industries, Germany) were used for the comparison, Sodium hydroxide (NaOH, 96%, Sinopharm Chemical Reagent Co., Ltd., Shanghai, P. R. China) was used to modulate the reaction solution pH. Deionized (DI) water was obtained from a water purification system (Sichuan Wortel Water Treatment Equipment Co., Ltd, Chengdu, P. R. China) with resistivity higher than 18 MΩ·cm. Sulfamethoxazole (SMX, 98%, Aladdin Industrial Corporation Co. Ltd., Shanghai, P. R. China), Phenol (C₆H₆O, 99.5%, Aladdin Industrial Corporation Co. Ltd., Shanghai, P. R. China) were used as the target organic pollutants in photocatalytic degradation experiments. All chemicals were of analytically pure grade and used without further purification. Bnzoquinone (BQ, 98%, Sinopharm Chemical Reagent Co., Ltd. Shanghai, P. R. China), sodium bromate (NaBrO₃, 99,7%, Sinopharm Chemical Reagent Co., Ltd., Shanghai, P. R. China), isopropanol (IPA, 99.7%, Sinopharm Chemical Reagent Co., Ltd. Shanghai, P. R. China), and ammonium oxalate (C2H8N2O4·H2O, 99.5%, Sinopharm Chemical Reagent Co., Ltd., Shanghai, P. R. China) were

used as radical scavengers in the photocatalytic SMX degradation experiments.

Synthesis of Bi₂MoO₆ photocatalysts

In a typical process, 6 mmoL Bi(NO₃)₃·5H₂O (2.91 g) and 3 mmoL Na₂MoO₄·2H₂O (0.726 g) were dissolved in 10 mL ethylene glycol (EG) under magnetic stirring, respectively, and they were then mixed together. Proper amount of NaOH (0 g, 0.24 g, and 0.57 g, respectively) was dissolved in 40 mL ethanol (0 M, 0.16 M, or 0.37 M, respectively), and it was slowly added into the above mixture solution to adjust the solution pH to ~ 1, 4, and 8, respectively. After being further stirred for 10 min, the mixture solution was transferred into a 100 mL teflon-lined stainless steel autoclave. The solvent-thermal process was conducted at 160 °C for 20 h, and the autoclave was then cooled to room temperature naturally. After the reaction, the precipitate was filtered, washed with ethanol several times, and then dried at 80 °C in air for 12 h to obtain the desired Bi₂MoO₆ photocatalyst. The samples were named as BMO-1, BMO-4, and BMO-8, respectively, according to their different reaction solution pH values.

Characterization of Bi₂MoO₆ photocatalysts

The crystal structures of samples were obtained by X-ray diffraction (XRD) on a D/MAX-2004 X-ray powder diffractometer (Rigaku Corporation, Japan) with Cu K α (λ =1.54178 Å) radiation at 56 kV and 182 mA. The scanning step width was 0.02⁰ in 2 theta and the sampling time was 4 s per step. The morphologies of samples were observed by TEM observations conducted on a JEOL 2100 TEM (JEOL Ltd., Japan) operated at 200 kV with the point-to-point resolution of 0.28 nm. TEM samples were prepared by dispersing a thin film of these powder samples on Cu grids. Brunauer-Emmett-Teller (BET) measurement was conducted by N₂ adsorption-desorption isotherm with an Autosorb-1 Series Surface Area and Pore Size Analyzers (TriStar II 3020, Micromeritics Instrument Corporation, USA). Isoelectric point (IEP) values of these samples were measured on a Nano-ZS90 Zetasizer (Malvern, UK). X-ray photoelectron spectroscopy (XPS) measurements were conducted on an ESCALAB 250 X-ray photoelectron spectrometer (Thermo Fisher Scientific Inc., Waltham, USA.) with an AI K anode (1486.6 eV photon energy, 300 W). Elemental analysis was performed on an EA: CHONS elemental analyser (Thermo Flash 2000, USA) to determine the mass fractions of carbon in these samples. The UV-vis spectra of samples were measured on a UV-2550 spectrophotometer (Shimadzu Corporation, Japan). Mott-Schottky analysis was carried out at a dc potential range from -0.6 V to +0.7 V vs Ag/AgCl electrode as the reference electrode with the ac potential frequency of 2 kHz and an amplitude of ac potential of 50 mV in the dark on a CHI 660D electrochemical workstation (Shanghai Chenhua Instrument Ltd., P. R. China). Powder second-harmonic generation (SHG) signals of these BMO samples were measured according to the Kurtz-Perry method.^[75] The measurements were performed with a Q-switched Nd:YAG laser at the wavelength of 1064 nm using KDP as the reference sample. Since the powder SHG efficiencies depended strongly on particle size, polycrystalline samples were ground into the same particle size range. Photoelectrochemical (PEC) measurements were conducted in a conventional three-electrode configuration in 0.2 M Na₂SO₄ solution with platinum as the counter electrode and Ag/AgCl electrode as the reference electrode on the CHI 660D electrochemical workstation.[76] Electrochemical impedance spectra (EIS) of these samples were

measured under illumination at 0 V versus Ag/AgCl electrode as the reference electrode with the frequency range of 0.01 Hz to 50 Hz on the CHI 660D electrochemical workstation. The incident photon to current efficiency spectra (IPCE) measurements were conducted on our samples by using a QEX10 solar cell quantum efficiency measurement system (QEX10, PV Measurements, USA).

Photocatalytic degradation of sulfamethoxazole (SMX) and phenol under visible light illumination

The photocatalytic activities of Bi₂MoO₆ photocatalysts were evaluated firstly by the degradation of model organic pollutants of sulfamethoxazole (SMX) and phenol under visible light irradiation, respectively. In a typical experiment, 50 mL of SMX solution (25 ppm) or 50 mL of phenol solution (10 ppm) was added into a 100 mL beaker (radius at 3 cm), and 0.05 g of photocatalyst sample was dispersed then dispersed into the organic pollutant solution. A 300 W xenon lamp (PLS-SXE300, Beijing Perfect Light Technology Co., Ltd., Beijing, P. R. China) was used as the light source, which had two glass filters to provide zero light intensity below 400 nm and over 700 nm. The light intensity striking the solution was at 45 mW/cm² as measured by a FZ-A optical radiometer (Photoelectric Instrument Factory of Beijing Norman University, P. R. China). Prior to irradiation, the suspension was kept in the dark under stirring for 30 min to ensure the establishment of the adsorption/desorption equilibrium. At given time intervals, 3 mL aliquots were collected from the suspension and immediately centrifuged at 9700 rpm for 5 min to separate photocatalysts, and the light absorption of the clear solution was measured by the UV-2550 spectrophotometer. For the recycle performance tests, the recovered photocatalysts after the SMX degradation experiment were washed by de-ionized water and dried in a vacuum oven for 10 h before being used for the next run. All analyses were in triplicate.

Photocatalytic disinfection of staphylococcus aureus (S. aureus) bacteria under visible light illumination

Wild-type S. aureus (CMCC (B) 26003, China national standard material network, P. R. China) were used for the photocatalytic disinfection experiments. After overnight culture, cells were diluted to a cell suspension (ca.107 cfu/mL) in 0.9% NaCl solution prior to the use for photocatalytic disinfection experiments. All solid or liquid materials had been autoclaved for 30 min at 121 $^{\rm 0}{\rm C}$ before use, and the same visible light source was used as in the photocatalytic degradation experiments. In the photocatalytic disinfection of S. aureus bacteria experiment, aliquot of 10 mL S. aureus cell suspension was pipetted onto a sterile 50 x 10 mm petri dish with the photocatalytst sample, which was first spin coated at the bottom of the dish. A fixed concentration of ~ 1.0 mg photocatalyst/mL S. aureus suspension was used. At regular time intervals, 100 µL of aliquots of the treated cell suspensions were withdrawn in sequence. After appropriate dilutions in 0.9% NaCl solution, aliquot of 100 µL was spread onto an agar medium plate and incubated at 37 °C for 24 h. The number of viable cells in terms of colony-forming units was counted. Analyses were in triplicate, and control runs were carried out each time under the same experiment conditions except for the nonexistence of photocatalysts.

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Keywords: Bi₂MoO₆ • polar photocatalysts • internal polarization modulation • charge carrier separation • visible light

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FULL PAPER

The crystal lattice parameter *b* of Bi_2MoO_6 is modulated by adjusting the solution pH in its solvent-thermal synthesis to control its internal polarization. Both DFT calculation and powder SHG signal measurement show that Bi_2MoO_6 with a shortened crystal lattice parameter *b* has a larger internal polarization, beneficial for a better photogenerated charge carrier separation efficiency to enhance its photocatalytic performance.



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Internal Polarization Modulation in Bi₂MoO₆ for Photocatalytic Performance Enhancement under Visible Light Illumination