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Binary-phase TiO_2 modified Bi_2MoO_6 crystal for effective removal of antibiotics under visible light illumination



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ABSTRACT

A series of binary-phase TiO₂ modified Bi_2MoO_6 nanocrystals have been prepared via a solvothermal-calcination process. Trace TiO₂ modification can effectively enhance the visible light catalytic activity of Bi_2MoO_6 to remove the antibiotics in aqueous solution. The obtained TiO₂/Bi₂MoO₆ composites were investigated by some physicochemical techniques like XRD, N₂ adsorption, SEM, TEM, UV–vis DRS, Raman, XPS, PL and Photo-electrochemical measurement. The presence of TiO₂ nanoparticles (NPs) influenced the crystal growth of Bi_2MoO_6 , decreasing the crystal size of Bi_2MoO_6 and effectively promoting its specific surface area. Moreover, the conduction band of TiO₂ can serve as the electron transfer platform, which largely boosts the effective separation of photocarriers at TiO₂/Bi₂MoO₆ heterojunction interface. With optimal TiO₂ content (0.41 wt%), TiO₂/Bi₂MoO₆ exhibited the best photocatalytic performance for different antibiotics degradation, e.g. ciprofloxacin, tetracycline and oxytetracyline hydrochloride under visible light irradiation. Moreover, the mechanism for enhanced photocatalytic performance in ciprofloxacin degradation was illuminated.

1. Introduction

Antibiotics are the antibacterial drugs which can kill or inhibit the growth of bacteria. As a major discovery in medical development, antibiotics have made great contribution for human being. However, the discharged antibiotics are a grave threat to human health and aquatic life. The typical antibiotics include ciprofloxacin (CPFX) [1,2], tetracycline (TC) [3,4] and oxytetracyline hydrochloride (OTTCH) [5,6]. When antibiotics absorbed by the body, more than 90% are discharged into the environment by excretory. The discharged antibiotics further flow into water resources. Most of antibiotics cannot be biologically degraded or eliminated in common waste water treatment plants because of their high stability. Therefore, considerable efforts have been committed to developing various techniques for degradation of antibiotics, e.g. adsorption, microorganism decomposition and advanced oxidation technology [7–10]. In 1976, Carey et al. [11] first found that

nanosized TiO₂ powder can decompose polychlorinated biphenyls under ultraviolet light irradiation. Unfortunately, ultraviolet light only accounts for 3–5% of the whole solar energy [12]. In consideration of TiO₂ cannot utilize the sunlight effectively, the visible-light-driven photocatalysts are highly desired.

Recent years, the ternary bismuth oxides, e.g. $BiVO_4$, Bi_2WO_6 , and Bi_2MoO_6 have attracted much research interests due to their ideal band gap energy. Bi_2MoO_6 belongs to Aurivillius-related oxide with layer structure (the $[Bi_2O_2]^{2+}$ layers located in the middle between MoO_4^{2-} slabs [13,14]). This unique structure is conducive to the formation of an internal electric field, which benefits the effective separation of carriers.

However, bare Bi_2MoO_6 always displays low photocatalytic activity and it is hard to meet the practical requirement [15]. The construction of heterojunction is an effective method to enhance the transfer of photogenerated carriers and boost the photocatalytic activity. For

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example, in Bi2MoO6@Ag2MoO4 core-shell heterojunction, the separation efficiency of carriers is improved. In addition, surface plasmon resonance of Ag nanoparticles (NPs) at the interface between the Bi₂MoO₆ and Ag₂MoO₄ will enhance the transform of electrons from the CB of Bi2MoO6 [16]. Besides, Z-scheme BiOBr-Bi2MoO6 heterojunction possessed highly oxidation and reduction capability [17]. Moreover, a number of other Bi₂MoO₆-based composites were reported, e.g. Bi_2O_3 [18,19], CdS [20], α -Fe₂O₃ [21,22], g-C₃N₄ [23,24] and so on. Zhang et al. [25] first fabricated one-dimensional anatase TiO₂ nanofibers by electrospining technique, and then one-dimensional Bi₂MoO₆/TiO₂ hierarchical heterostructures were fabricated. The obtained Bi₂MoO₆/TiO₂ heterostructures exhibited high visible light photocatalytic performance for the decomposition of RhB under UV light and visible light illumination ($\lambda > 420$ nm). Tian et al. [26] employed anatase TiO₂ nanobelts as template to fabricate the 3D Bi₂MoO₆/TiO₂ heterostructures. Under UV and visible light irradiation, the Bi2MoO6/TiO2 composite exhibited high oxygen production. Li et al. [27] prepared flake-like Bi2MoO6 on anatase TiO2 nanofiber, and the produced composites showed the enhanced photocatalytic activity for the degradation of MB.

In this work, we developed a series of binary-phase TiO_2 modified Bi_2MoO_6 crystals by solvothermal-calcination method. The effects of TiO_2 on the texture, crystal, band structure, and optical property of the Bi_2MoO_6 were investigated. The outstanding photocatalytic performances over TiO_2/Bi_2MoO_6 composites for removing the antibiotics (tetracycline, ciprofloxacin, and oxytetracycline hydrochloride) in water were reported.

2. Experimental

2.1. Catalyst preparation

 $Bi(NO_3)_3$ - $5H_2O$ (99%), (NH₄)₆Mo₇O₂₄· $4H_2O$, ethylene glycol (EG), titanium trichloride (15% hydrochloric acid), cetyltrimethylammonium bromide (CTAB), n-pentanol, n-hexane, were analytical grade and purchased from Sinopharm Chemical Reagent Co. Ltd. China. Tetracycline (TC), ciprofloxacin (CPFX), and oxytetracycline hydrochloride (OTTCH) were purchased from Shanghai Macklin Biochemistry Technology Co., Ltd.

The synthesis of TiO₂ is in a W/O emulsion system. The detailed experimental procedure is from the literature [28]. Briefly, 5.8 g CTAB was dissolved in a mixture of 10 mL n-pentanol, 60 mL n-hexane and 10 mL H₂O. After stirring for 30 min, 0.8 mL titanium (III) chloride was added. The obtained microemulsion was poured into a 100 mL Teflon-lined stainless-steel autoclave and maintained at 200 °C for 6 h. After cooling down to room temperature, the resultant precipitation was centrifuged and washed with water, acetone and ethanol to remove surfactants. The collected sample was dried at 60 °C for 8 h.

Bi₂MoO₆ and TiO₂/Bi₂MoO₆ samples were prepared via a solvothermal- calcination process [29]. 1.94 g Bi(NO₃)₃·5H₂O was dissolved in 70 mL EG under sonication. Under magnetically stirring, 0.35 g (NH₄)₆Mo₇O₂₄·4H₂O was added to above solution. 20 mg TiO₂ was dispersed in 40 mL EG under ultrasound irradiation. Then desired volume (0, 6, 10, 15 and 20 mL) of TiO₂ suspension solution was added in above-mentioned solution and the pH value of the solution was adjusted to 7. After stirring for 30 min, the solution was placed in a Teflon-lined stainless autoclave and maintained at 160 °C for 10 h. The obtained product was centrifugal collection. After washing three times by water and ethanol, the obtained samples were dried at 60 °C for 10 h. Finally, the power was placed in a muffle furnace and calcined at 400 °C for 2 h. The final samples were denoted as TiO₂(x wt%)/Bi₂MoO₆ (x = 0, 0.16, 0.27, 0.41, 0.55). The content of TiO₂ in TiO₂/Bi₂MoO₆ composite was obtained by adding the volume of TiO₂ suspension.



Fig. 1. XRD patterns of the prepared $\rm TiO_2,\,Bi_2MoO_6$ and $\rm TiO_2/Bi_2MoO_6$ samples.

2.2. Characterization

Powder X-ray diffraction data were recorded at a scanning rate of 0.05°/s using a Bruker D8-advance X-ray diffractometer at 40 kV and 40 mA for Cu K α radiation ($\lambda = 0.15418$ nm). The Brunauer-Emmett-Teller (BET) surface areas of the sample were obtained from N2 adsorption/desorption isotherms determined at liquid nitrogen temperature on an automatic analyzer (Micromeritics, ASAP 2010). The samples were outgassed for 2 h under vacuum at 180 °C prior to adsorption. Scanning electron microscopy (SEM) of sample was measured on FLA650 F microscope (the FEI Company). Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were recorded on a Tecnai 20 FEG microscope. UV-vis diffuse reflectance spectra (DRS) were measured using a UV-vis spectrophotometer (UV-2600, Shimadzu). Fourier transform infrared (FT-IR) spectra were recorded with a Nicolet 5700 FT-IR spectrometer. The surface composition was determined by X-ray photoelectron spectroscopy (XPS) using a PHI Quantum 2000 XPS system with a monochromatic Al Ka source and a charge neutralizer. All the binding energies were referenced to the C1s peak at 284.8 eV of the surface adventitious carbon. The photoluminescence (PL) emission spectra of the samples were recorded on a fluorescence spectrometer (Hitachi F-4500, Japan). Photocurrent and electrochemical impedance spectroscopy measurements were carried out on an electrochemical workstation with three-electrode (CHI-660E, China). 0.1 M Na₂SO₄ solution was used as electrolyte solution. Saturated Ag/AgCl and platinum wires were utilized as reference electrodes and the counter electrode, respectively. The working electrode is the sample films coated on indium tin oxide (ITO) conducting glass. The homogeneous mixtures of 1 mL ethanol and 10 mg samples were coated over ITO and dried at 100 °C for 5 h. A 300 W xenon lamp was utilized as the excitation light source.

2.3. Degradation of organic pollutants

The photodegradation experiments were operated in a photochemical reactor. The simulated organic pollutants are CPFX, TC, and OTTCH in an aqueous solution, respectively. The visible light source was a 350 W Xe lamp (XuJiang electromechanical XPA-7) with a UV Cut-off filter (UVCUT420). Briefly, 30 mg catalyst was added into CPFX (50 mL, 10 mg/L), TC (50 mL, 20 mg/L), OTTCH (50 mL, 20 mg/L) solutions, respectively. The suspensions were magnetically stirred in the dark for 40 min to reach adsorption-desorption equilibrium before turning on the light. ~3 mL suspension was sampled and centrifuged at given time intervals to measure the changes of the pollutants



Fig. 2. SEM images of the typical samples. (a) Bi_2MoO_6 ; (b) $TiO_2(0.41 \text{ wt\%})/Bi_2MoO_6$.



Fig. 3. (a) TEM, (b) and (c) HR-TEM images of TiO₂(0.41 wt%)/Bi₂MoO₆; (d)The EDX spectrum of TiO₂(0.41 wt%)/Bi₂MoO₆.

concentration during light irradiation. The concentration of the antibiotics was measured with a UV–vis spectrophotometer at their maximum absorption wavelength (270 nm for CPFX, 358 nm for TC, 355 nm for OTTCH). The degradation rate was calculated according to the following equation: Degradation rate (%) = $(1-C_t/C_0)*100\% = (1-A_t/A_0)*100\%$

Where C_0 and C_t represent the concentrations of target pollutant at irradiation times 0 and t, respectively; A_t and A_0 are the corresponding values for target pollutant absorbance.



Fig. 4. N_2 adsorption-desorption isotherms and Barret-Joyner-Halenda (BJH) pore size distribution plots (inset) of the Bi_2MoO_6 and $TiO_2(0.41\,wt\,\%)/Bi_2MoO_6.$

Table 1Specific surface area of samples.

Sample	$S_{BET}(m^2/g)$
$\begin{array}{l} Bi_2 MoO_6 \\ TiO_2 (0.16 \ wt\%)/Bi_2 MoO_6 \\ TiO_2 (0.27 \ wt\%)/Bi_2 MoO_6 \\ TiO_2 (0.41 \ wt\%)/Bi_2 MoO_6 \\ TiO_2 (0.55 \ wt\%)/Bi_2 MoO_6 \end{array}$	11.3 16.5 17.6 17.7 20.6



Fig. 5. Raman spectra of Bi_2MoO_6 and $TiO_2(0.41 \text{ wt\%})/Bi_2MoO_6$; Magnification spectrum of $TiO_2(0.41 \text{ wt\%})/Bi_2MoO_6$ in the range of 118 $^{\sim}$ 169 cm⁻¹ (inset).

3. Results and discussion

3.1. Crystal properties

The crystal structure of the samples was analyzed by XRD and the obtained XRD patterns were displayed in Fig. 1(a). The pattern shows that the diffraction peaks at 2θ of 28.3°, 32.5°, 47.3° and 55.5° are

assigned to the crystal plane of (131), (200), (260) and (133) for orthorhombic Bi₂MoO₆ (JCPDS No. 76-2388), respectively. For the patterns of TiO₂, some typical diffraction peaks at $2\theta = 27.4^{\circ}$, 36.0° , 41.2° and 54.2° can be observed, which are ascribed to the (110), (101), (111) and (211) crystal facets of rutile TiO₂ (JCPDS No. 76-0318), respectively. Other typical diffraction peaks at $2\theta = 25.3^{\circ}$, 37.9° and 48.1° are assigned to the crystal planes of (101), (004) and (200) for anatase TiO₂ (JCPDS No. 21-1272), respectively. However, no diffraction peak for TiO₂ component in TiO₂/Bi₂MoO₆ was detected, which could be caused by the low content of TiO₂.

3.2. Morphologic structure

SEM and TEM are applied to analyze the morphology of the pure Bi_2MoO_6 and $TiO_2(0.41 \text{ wt\%})/Bi_2MoO_6$. As shown in Fig. 2, Bi_2MoO_6 and $TiO_2(0.41 \text{ wt\%})/Bi_2MoO_6$ are composed of sheets or particles with irregular morphology. In Fig. 2(a), some nanochips were observed in Bi_2MoO_6 sample and the inset displays a single disk with the thickness of ~40 nm. In Fig. 2(b), for the $TiO_2(0.41 \text{ wt\%})/Bi_2MoO_6$, the size of Bi_2MoO_6 slightly decreased after the introduction of TiO_2 .

Fig. 3(a) and (b) show the TEM and HRTEM images recorded from $TiO_2(0.41 \text{ wt\%})/Bi_2MoO_6$. Fig. 3(a) reveals that the morphology of $TiO_2(0.41 \text{ wt\%})/Bi_2MoO_6$ is irregular and the diameter of the Bi_2MoO_6 particle is about 20 nm. Fig. 3(b) reveals the lattice fringes of 0.315 nm and 0.326 nm deemed to the (131) and (041) planes of Bi_2MoO_6 (JCPDS No. 76-2388), respectively. The lattice of 0.325 nm was ascribed to the (110) plane of rutile TiO_2 (JCPDS No. 76-0318) and the lattice of 0.351 nm was indexed to the (101) plane of anatase TiO_2 (JCPDS No. 21-1272). The presence of different phase planes further proved that three phases of Bi_2MOO_6 , anatase and rutile TiO_2 coexist in the composite. The interface between the different phases could facilitate the transfer of charges in the bulk phase [30]. Fig. 3(c) shows that the rutile TiO_2 diameters are about ~12.4 nm and the anatase TiO_2 appears short rod-like morphology, with the diameter and length of 6.1 nm and 19.1 nm, respectively.

The EDX spectrum of $TiO_2(0.41 \text{ wt\%})/Bi_2MoO_6$ is shown in Fig. 3(d). Obviously, there are Bi, Mo, O, Ti and Cu elements. The Bi, Mo and O elements come from Bi_2MoO_6 , and Ti element comes from TiO_2 , while Cu element was attributed to the tested copper net.

3.3. Texture properties

The pore-size distributions (inset) and N₂ adsorption-desorption isotherms of the Bi₂MoO₆ and TiO₂(0.41 wt%)/Bi₂MoO₆ are shown in Fig. 4. According to the classification of Brunauer-Deming-Deming-Teller (BDDT) in IUPAC, the isotherms of the two samples can be classified as type-IV, which indicates the characteristic of mesoporous materials [30,31]. The hysteresis loops at relative pressure (P/P₀) range between 0.6 and 1.0 can be classified as type H3, associated with slitlike pores [32,33]. The pore-size distributions (inset in Fig. 4) of the samples are broad (from 2 to 70 nm), further indicating the presence of mesopores and macropores. TiO₂(0.41 wt%)/Bi₂MoO₆ has a larger dV/ dlogD than Bi₂MoO₆, indicating a high probability of mesoporous distribution. Table 1 gives the specific surface area of all samples. The result displays that the specific surface area of Bi₂MoO₆ increased with the increase of TiO₂ content. The reason could be that the introduction of TiO₂ decreased the particle size of Bi₂MoO₆.

3.4. Raman analysis

Raman spectra of TiO₂, Bi₂MoO₆ and TiO₂(0.41 wt%)/Bi₂MoO₆ are shown in Fig. 5. The spectra show a Raman vibraton in the range of 200–1000 cm⁻¹. The Raman band of TiO₂ lines at 143, 445, and 607 cm⁻¹ are in agreement with the data observed in the spectra of a rutile phase [34–36]. The other two bands at 512 and 634 cm⁻¹ are observed in the spectra of anatase phase [37,38]. The Raman peaks of



Fig. 6. XPS spectra of TiO₂(0.41 wt%)/Bi₂MoO₆ sample. (a) Survey spectrum; (b) Bi 4f; (c) Mo 3d; (d) O 1s; (e) Ti 2p & Bi 4d.

Bi₂MoO₆ above 600 cm⁻¹ can be assigned to the stretching modes of Mo-O bands [39]. The presence of modes below 400 cm⁻¹ can be attributed to both Bi-O stretches and lattice modes [40]. Comparing to the Raman peaks of TiO₂ in the range from 118⁻¹69 cm⁻¹, the peak of 146 cm⁻¹ can be seen, indicating the existence of TiO₂. The remaining peaks of TiO₂ disappear because of weak peaks or low content. In addition, TiO₂(0.41 wt%)/Bi₂MoO₆ and Bi₂MoO₆ have a similar Raman vibraton in the range of 200–1000 cm⁻¹.

Raman spectra of Bi_2MoO_6 gives a very strong band at 796 cm⁻¹ along with two shoulder bands at 713 cm⁻¹ and 845 cm⁻¹, and the strong band at 796 cm⁻¹ is presumably A_{1g} mode, corresponding to Mo-O stretching modes of the distorted MoO₆ octahedral [41]. Compared to pure Bi_2MoO_6 , the characteristic peaks about Bi_2MoO_6 in the TiO₂(0.41 wt%)/Bi₂MoO₆ have an obvious shift. The peaks of the stretching modes of Mo-O bands at 713, 796 and 845 cm⁻¹ were shifted to 731, 814 and 863 cm⁻¹, respectively. The relationship between Raman stretching frequency and bond length was found to follow a

simple exponential form [42]:

$$R_{\rm Mo-O} = 0.48239 \,\ln(32895/\nu) \tag{1}$$

Where ν is the Raman stretching frequency in wavenumbers and *R* is the metal-oxygen bond length in angstroms [43]. The results show that the lower frequency of Raman stretching band corresponds to the longer bond length. A calculation of the Mo-O bond length for Bi₂MoO₆ based on the expression suggests that one of the Mo-O (apical) bond length (796 cm⁻¹) decreased from 1.7952 Å to 1.7838 Å in the TiO₂(0.41 wt %)/Bi₂MoO₆ composite. The gradual decrease in the bond length of the Mo-O distance suggested the strong chemical interaction between Bi₂MoO₆ and TiO₂.

3.5. XPS analysis

The element composition and chemical state of $TiO_2(0.41 \text{ wt } \%)/Bi_2MoO_6$ were analyzed by XPS. Fig. 6(a) shows the XPS survey



Fig. 7. UV–vis absorption spectra; The curves of $(ahv)^2$ versus hv of the prepared Bi₂MoO₆ and TiO₂/Bi₂MoO₆ samples (inset).



Fig. 8. PL spectra of Bi₂MoO₆ and TiO₂/Bi₂MoO₆.

spectrum of Bi 4f, Mo 3d, Ti 2p and O 1s in TiO₂(0.41 wt%)/Bi₂MoO₆. The C 1s peak is the element carbon from XPS instrument. Fig. 6(b) gives two strong peaks at 164.6 and 159.3 eV corresponding to Bi $4f_{5/2}$ and Bi $4f_{7/2}$, respectively [44]. In Fig. 6(c), the peaks around 235.5 and

232.4 eV can be ascribed to Mo $3d_{5/2}$ and Mo $3d_{7/2}$ of MoO₄²⁻, respectively [45]. Fig. 6(d) shows the O1 s peak with band energy at 529.8 eV. This peak can be fitted into three peaks around 529.63, 530.24 and 531.68 eV, corresponding to the Bi-O, Mo-O and Ti-O bonds [46,47], respectively. This result confirmed the existence of TiO₂ over the surface of Bi₂MoO₆. Fig. 6(e) implies an overlap XPS spectra over Ti 2*p* and Bi 4*d*. The peak at 464.15 eV is for Ti 2*p*_{1/2} [48,49]; the peak at 459.35 eV (2*p*_{3/2}) is for anatase TiO₂ and 458.5 eV (2*p*_{3/2}) is for rutile TiO₂ [50]. The peak at 465.85 eV is for Bi 4*d* [47].

3.6. Light absorption

The UV–vis diffuse spectra of Bi₂MoO₆ and TiO₂/Bi₂MoO₆ composites are presented in Fig. 7. Compared with bare Bi₂MoO₆, TiO₂/Bi₂MoO₆ composites show almost the same absorption edge (Fig. 7) at about 480 nm, indicating they have similar light absorption in the visible region. Besides, the light absorption of the composite samples in the UV region slightly strengthened. Fig. 7 provides the band gap energies for the present series of catalysts, which was determined with Tauc's law from the intercept of a straight line fitted through the rise of the function $[F(R_a)hv]^2$ plotted versus hv, where $F(R_a)$ is a Kubelka-Munk function and hv is the energy of the incident photon [47,15]. The approximate band gap energies are ~2.59 eV for Bi₂MoO₆ and 2.60–2.68 eV for TiO₂/Bi₂MoO₆, respectively.

3.7. Charge separation analysis

The photocatalytic activity of a semiconductor material is intimately associated with the charge carrier density, bulk charge separation, movement on the surface of material and interfacial transfer of photogenerated charges. The PL spectra of Bi₂MoO₆ and TiO₂/ Bi₂MoO₆ composites are displayed in Fig. 8. The fluorescence intensity at 470 nm was monitored upon excitation at 350 nm. The PL spectra of TiO₂(0.41 wt%)/Bi₂MoO₆ gives the lowest intensity, indicating the lowest recombination rate of charge carrier [51]. TiO₂/Bi₂MoO₆ has the low recombination rate of charge carrier compared to Bi₂MoO₆. It could be attributed to the TiO₂/Bi₂MoO₆ interface which could transfer the photoelectron, thus improving the separation of charge carries.

Photo-electrochemical measurements are used to explore the interface charge separation efficiency. Fig. 9(a) presents the photocurrent responses of Bi₂MoO₆ and TiO₂/Bi₂MoO₆. Generally, a high photocurrent density demonstrates a high separation of photo-induce electron and hole [52]. Obviously, the photocurrent density increased in the order of Bi₂MoO₆ < TiO₂(0.16 wt%)/Bi₂MoO₆ < TiO₂(0.27 wt%)/Bi₂MoO₆ < TiO₂(0.41 wt%) /Bi₂MoO₆. This conclusion is consistent with PL results.



Fig. 9. Photo-electrochemical measurements of the prepared samples. (a) Transient photocurrent responses; (b) Nyguist plots of electrochemical impedance spectroscopy.



Fig. 10. (a) Absorption ability evaluation of the as-prepared samples for CPFX under dark condition; (b)Photocatalytic degradation CPFX curves; (c) Changes of UV–Vis spectra as a function of time; First-order kinetic plots (d) and rate constants (e) of CPFX degradation in the presence of the samples.

Electrochemical impedance spectra (EIS) were used to analyze the charge transfer and the recombination behaviors of the prepared sample. Fig. 9(b) shows the Nyquist plots of Bi_2MoO_6 and TiO_2/Bi_2MoO_6 composites. The arc radius of TiO_2/Bi_2MoO_6 is smaller than that of Bi_2MoO_6 and $TiO_2(0.41 \text{ wt}\%)/Bi_2MoO_6$ displays the smallest arc radius, witnessing the highest efficiency of charge transfer on the surface of TiO_2/Bi_2MoO_6 . The results of PL, photocurrent and EIS test confirmed that the TiO_2/Bi_2MoO_6 photocatalyst has efficient charge transfer and a low recombination rate of photo-generated electrons and holes.

3.8. Photocatalytic activity

The phtocatalytic activity of the samples was tested by the degradation of CPFX, TC and OTTCH under visible-light ($\lambda \ge 420$ nm) irradiation. The adsorption capability of the samples for CPFX were shown in Fig. 10(a). Obviously, the adsorption capability of the composites increases with the increase of TiO₂ content. The increase of adsorption is due to the introduction of TiO₂, which reduced the particle size and increase the specific surface area. As shown in Fig. 10(b), blank test confirmed that CPFX cannot destroyed without the catalyst



Fig. 11. Photocatalytic degradation of OTTCH (a) and TC (b) over Bi₂MoO₆ and TiO₂/Bi₂MoO₆ samples.



Fig. 12. Photogenerated carrier trapping in the system of photodegradation of CPFX over $TiO_2(0.41 \text{ wt\%})/Bi_2MoO_6$.

under visible light irradiation. TiO_2/Bi_2MoO_6 composites exhibited significantly activity than bare Bi_2MoO_6 , indicating the photocatalytic activity of Bi_2MoO_6 enhanced with the TiO_2 introduced.

The degradation rate of CPFX is 54% over pure Bi_2MoO_6 . The corresponding degradation rates are 77%, 82%, 88% and 84% for

 $TiO_2(0.16 \text{ wt\%})/Bi_2MoO_6$, $TiO_2(0.27 \text{ wt\%})/Bi_2MoO_6$, $TiO_2(0.41 \text{ wt\%})/Bi_2MoO_6$ and $TiO_2(0.55 \text{ wt\%})/Bi_2MoO_6$, respectively. The time-dependent UV-vis spectral of CPFX was presented in Fig. 10(c). The intensity of characteristic peak decreased with the increasing of irradiation time and no other peaks appeared. Moreover, the kinetics of the degradation reaction was investigated by applying the Langmuir-Hinshelwood (L-H) model [53,54]. After fitting, the plots of $ln(C_0/C_t)$ versus light irradiation time were found to be linear as displayed in Fig. 10(d), suggesting the reaction followed the pseudo-first-order model.

The apparent reaction rate constants (*k*) were displayed in Fig. 10(e). The reaction rate constants for different samples appear as following order: $TiO_2(0.41 \text{ wt\%})/Bi_2MoO_6 > TiO_2(0.55 \text{ wt\%})/Bi_2MoO_6 > TiO_2(0.27 \text{ wt\%})/Bi_2MoO_6 > TiO_2(0.16 \text{ wt\%})/Bi_2MoO_6 > Bi_2MoO_6$. The reaction rate constant of $TiO_2(0.41 \text{ wt\%})/Bi_2MoO_6$ is about 2.65 times of the pure Bi_2MoO_6 .

In addition to the degradation of CPFX, catalysts were also used to eliminate the antibiotic TC and OTTCH. Fig. 11(a) and (b) shows the concentration variation of OTTCH and TC during the reaction process. Obviously, the decomposition of OTTCH and TC without catalyst can be neglected. In Fig. 11(a), the OTTCH degradation rate over TiO₂(0.41 wt %)/Bi₂MoO₆(77.6%) is much higher than that of Bi₂MoO₆(49.8%). A similar phenomenon was observed for TC degradation in Fig. 11(b).

In order to monitor the reactive radicals involved in reaction, three quenchers, nitrogen (N_2) , triethanolamine (TEOA, 1 mM) and tertbutyl



Fig. 13. The suggested photocatalytic degradation mechanism of organic pollutants over TiO₂/Bi₂MoO₆ system.

alcohol (TBA, 1 mM) were utilized as the scavengers of $'O_2^-$, h^+ and 'OH, respectively [55,56]. In Fig. 12, the trapping experiments indicated that with the addition of N₂ and TBA, the activity decreased slightly. In contrast, the presence of trace TEOA caused a higher decrease in the degradation of CPFX. Therefore, photo-induced holes are the main active species for pollutant degradation over TiO₂/Bi₂MoO₆ system, while the 'O₂⁻ and 'OH are not the main active species for CPFX degradation in this system.

Furthermore, the potentials of CB and VB for TiO_2 and Bi_2MoO_6 were calculated by the following empirical formulas:

$$E_{VB} = X \cdot E^e + 0.5E_g \tag{2}$$

$$E_{CB} = E_{VB} - E_g \tag{3}$$

Where E_{VB} and E_{CB} are the valence band (VB) edge potential and the conduction band (CB) edge potential, respectively; *X* is the absolute electro negativity of the semiconductor and reflects the absolute electro negativity of constituent atoms; E^e is the energy of free electrons on the hydrogen scale (the value of E^e is 4.5 eV); E_g is the band gap energy of the semiconductor [57]. The band gap energy of Bi₂MoO₆ was ~2.59 eV. Herein, the *X* value for Bi₂MoO₆ is ~5.54 eV [26]. By application the constants into the respective formulas, the bottom of CB and the top of VB of Bi₂MoO₆ were calculated to be ~ -0.255 eV and ~2.335 eV, respectively. The *X* value for TiO₂ is 5.89 eV [58]; the band gap of rutile and anatase TiO₂ are 3.02 eV and 3.23 eV separately [59]. Accordingly, the top of the VB and the bottom of the CB of rutile TiO₂ were obtained as ~ -0.12 eV and ~2.90 eV, respectively, and the anatase TiO₂ were calculated to ~ -0.225 eV and ~3.005 eV, correspondingly.

Based on the above discussion, a possible photocatalytic reaction mechanism of $\text{TiO}_2/\text{Bi}_2\text{MoO}_6$ was proposed and presented in Fig. 13. Under visible light irradiation, only the Bi_2MoO_6 can be excited. Because the E_{CB} of Bi_2MoO_6 (-0.255 eV) is more negative than TiO_2 (rutile TiO_2 (-0.12 eV) and anatase TiO_2 (-0.225 eV)). Thus, the excited electrons migrate from Bi_2MoO_6 to TiO_2 , which benefits the effective separation of electrons and holes.

4. Conclusions

In summary, the binary-phase TiO₂ modified Bi₂MoO₆ heterostructures have been successfully prepared by solvothermal-calcination method. The TiO₂/Bi₂MoO₆ composites showed superior photocatalytic activity for the photodegradation of CPFX, TC and OTTCH under visible-light irradiation. The heterojunction composite with optimal TiO₂ content (0.41 wt%) exhibited the excellent photocatalytic activity. The reasons for the enhanced activity are as following. On the one hand, the introduction of TiO₂ increases the surface area, thus enhancing antibiotics capture. On the other hand, the formation of TiO₂/ Bi₂MoO₆ heterojunction effectively promotes the separation of photogenerated electron-hole pairs. Moreover, the radical trapping experiment confirmed that holes mainly accounted for the ciprofloxacin degradation.

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References

- [1] X. Van Doorslaer, K. Demeestere, P.M. Heynderickx, H. Van Langenhove, J. Dewulf, UV-A and UV-C induced photolytic and photocatalytic degradation of aqueous ciprofloxacin and moxifloxacin: reaction kinetics and role of adsorption, Appl. Catal. B 101 (2011) 540–547.
- [2] Y. Zhao, X. Liang, Y. Wang, H. Shi, E. Liu, J. Fan, X. Hu, Degradation and removal of ceftriaxone sodium in aquatic environment with Bi₂WO₆/g-C₃N₄ photocatalyst, J. Colloid Interface Sci. 523 (2018) 7–17.
- [3] J. Niu, S. Ding, L. Zhang, J. Zhao, C. Feng, Visible-light-mediated Sr-Bi₂O₃photocatalysis of tetracycline: kinetics, mechanisms and toxicity assessment, Chemosphere 93 (2013) 1–8.
- [4] Z. Xie, Y. Feng, F. Wang, D. Chen, Q. Zhang, Y. Zeng, W. Lv, G. Liu, Construction of carbon dots modified MoO₃/g-C₃N₄ Z-scheme photocatalyst with enhanced visiblelight photocatalytic activity for the degradation of tetracycline, Appl. Catal. B 229 (2018) 96–104.
- [5] X.J. Wen, C.G. Niu, L. Zhang, G.M. Zeng, Fabrication of SnO₂ nanopaticles/BiOI n-p heterostructure for wider spectrum visible-light photocatalytic degradation of antibiotic oxytetracycline hydrochloride, ACS Sustain. Chem. Eng. 5 (2017) 5134-5147.
- [6] P. Raizada, B. Priya, P. Thakur, P. Singh, Notes solar light induced photodegradation of oxytetracyline using Zr doped TiO₂/CaO based nanocomposite, Indian J. Chem. 55 (2016) 803–809.
- [7] F.A. El-Gohary, S.I. Abou-Elela, H.I. Aly, Evaluation of biological technologies for wastewater treatment in the pharmaceutical industry, Water Sci. Technol. 32 (1995) 13–20.
- [8] Y. Zhuang, F. Yu, J. Ma, J. Chen, Graphene as a template and structural scaffold for the synthesis of a 3D porous bio-adsorbent to remove antibiotics from water, RSC Adv. 5 (2015) 27964–27969.
- [9] S. Esplugas, D.M. Bila, L.G.T. Krause, M. Dezotti, Ozonation and advanced oxidation technologies to remove endocrine disrupting chemicals (EDCs) and pharmaceuticals and personal care products (PPCPs) in water effluents, J. Hazard. Mater. 149 (2007) 631–642.
- [10] M.J.G. Galán, M.S. Díaz-Cruz, D. Barceló, Removal of sulfonamide antibiotics upon conventional activated sludge and advanced membrane bioreactor treatment, Anal. Bioanal. Chem. 404 (2012) 1505–1515.
- [11] J.H. Carey, J. Lawrence, H.M. Tosine, Photodechlorination of PCB's in the presence of titanium dioxide in aqueous suspensions, Bull. Environ. Contam. Toxicol. 16 (1976) 697–701.
- [12] N.L. Wu, M.S. Lee, Enhanced TiO₂ photocatalysis by Cu in hydrogen production from aqueous methanol solution, Int. J. Hydrogen Energy 29 (2004) 1601–1605.
- [13] H. Li, J. Liu, W. Hou, N. Du, R. Zhang, X. Tao, Synthesis and characterization of g-C₃N₄/Bi₂MoO₆ heterojunctions with enhanced visible light photocatalytic activity, Appl. Catal. B 160 (2014) 89–97.
- [14] B. Zhang, J. Li, Y. Gao, R. Chong, Z. Wang, L. Guo, X. Zhang, C. Li, To boost photocatalytic activity in selective oxidation of alcohols on ultrathin Bi₂MoO₆ nanoplates with Pt nanoparticles as cocatalyst, J. Catal. 345 (2017) 96–103.
- [15] J. Long, S. Wang, H. Chang, B. Zhao, B. Liu, Y. Zhou, W. Huang, Bi₂MoO₆ nanobelts for crystal facet-enhanced photocatalysis, Small 10 (2014) 2791–2795.
- [16] Z. Wang, Y. Huo, J. Zhang, C. Lu, K. Dai, C. Liang, G. Zhu, Facile preparation of twodimensional Bi₂MoO₆@Ag₂MoO₄ core-shell composite with enhanced visible light photocatalytic activity, J. Alloys Compd. 729 (2017) 100–108.
- [17] S. Wang, X. Yang, X. Zhang, X. Ding, Z. Yang, K. Dai, H. Chen, A plate-on-plate sandwiched Z-scheme heterojunction photocatalyst: BiOBr-Bi₂MoO₆ with enhanced photocatalytic performance, Appl. Surf. Sci. 391 (2017) 194–201.
 [18] Y.S. Xu, Z.J. Zhang, W.D. Zhang, Facile preparation of heterostructured Bi₂O₃/
- [18] Y.S. Xu, Z.J. Zhang, W.D. Zhang, Facile preparation of heterostructured Bi₂O₃/ Bi₂MoO₆ hollow microspheres with enhanced visible-light-driven photocatalytic and antimicrobial activity, Mater. Res. Bull. 48 (2013) 1420–1427.
- [19] J. Ma, L.Z. Zhang, Y.H. Wang, S.L. Lei, X.B. Luo, S.H. Chen, G.S. Zeng, J.P. Zou, S.L. Luo, C.T. Au, Mechanism of 2,4-dinitrophenol photocatalytic degradation by ζ-Bi₂O₃/Bi₂MoO₆ composites under solar and visible light irradiation, Chem. Eng. J. 251 (2014) 371–380.
- [20] Y. Feng, X. Yan, C. Liu, Y. Hong, L. Zhu, M. Zhou, W. Shi, Hydrothermal synthesis of CdS/Bi₂MoO₆ heterojunction photocatalysts with excellent visible- light- driven photocatalytic performance, Appl. Surf. Sci. 353 (2015) 87–94.
- [21] J. Zhao, Q. Lu, M. Wei, C. Wang, Synthesis of one-dimensional α-Fe₂O₃/Bi₂MoO₆ heterostructures by electrospinning process with enhanced photocatalytic activity, J. Alloys Compd. 646 (2015) 417–424.
- [22] J. Hao, Q. Lu, Q. Wang, Q. Ma, α-Fe₂O₃ nanoparticles on Bi₂MoO₆ nanofibers: onedimensional heterostructures synergistic system with enhanced photocatalytic activity, Superlattices Microstruct. 91 (2016) 148–157.
- [23] J. Li, Y. Yin, E. Liu, Y. Ma, J. Wan, J. Fan, X. Hu, In situ growing Bi₂MoO₆ on g-C₃N₄ nanosheets with enhanced photocatalytic hydrogen evolution and disinfection of bacteria under visible light irradiation, J. Hazard. Mater. 321 (2017) 183–192.
- [24] W. Chen, G.R. Duan, T.Y. Liu, S.M. Chen, X.H. Liu, Fabrication of Bi₂MoO₆ nanoplates hybridized with g-C₃N₄ nanosheets as highly efficient visible light responsive heterojunction photocatalysts for rhodamine B degradation, Mater. Sci. Semiconductor Process. 35 (2015) 45–54.
- [25] M. Zhang, C. Shao, J. Mu, Z. Zhang, Z. Guo, P. Zhang, Y. Liu, One-dimensional Bi₂MoO₆/TiO₂ hierarchical heterostructures with enhanced photocatalytic activity, CrystEngComm 14 (2012) 605–612.
- [26] J. Tian, P. Hao, N. Wei, H. Cui, H. Liu, 3D Bi₂MoO₆ nanosheet/TiO₂ nanobelt heterostructure: enhanced photocatalytic activities and photoelectochemistry performance, ACS Catal. 5 (2015) 4530–4536.
- [27] H. Li, T. Zhang, C. Pan, C. Pu, Y. Hu, X. Hu, E. Liu, J. Fan, Self-assembled Bi₂MoO₆/

 TiO_2 nanofiber heterojunction film with enhanced photocatalytic activities, Appl. Surf. Sci. 391 (2017) 303–310.

- [28] R. Mo, Z. Lei, K. Sun, D. Rooney, Facile synthesis of anatase TiO₂ quantum-dot/ graphene-nanosheet composites with enhanced electrochemical performance for lithium-ion batteries, Adv. Mater. 26 (2014) 2084–2088.
- [29] C. Yu, Z. Wu, R. Liu, D.D. Dionysiou, K. Yang, C. Wang, H. Liu, Novel fluorinated Bi₂MoO₆ nanocrystals for efficient photocatalytic removal of water organic pollutants under different light source illumination, Appl. Catal. B 209 (2017) 1–11.
- [30] C. Yu, W. Zhou, C.Y. Jimmy, H. Liu, L. Wei, Design and fabrication of heterojunction photocatalysts for energy conversion and pollutant degradation, Chin. J. Catal. 35 (2014) 1609–1618.
- [31] Q. Xiang, J. Yu, M. Jaroniec, Preparation and enhanced visible-light photocatalytic H₂-production activity of graphene/C₃N₄ composites, J. Phys. Chem. C 115 (2011) 7355–7363.
- [32] K.S. Sing, Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity (Recommendations 1984), Pure Appl. Chem. 57 (1985) 603–619.
- [33] R. Liu, Z. Wu, J. Tian, C. Yu, S. Li, K. Yang, X. Liu, M. Liu, The excellent dyephotosensitized degradation performance over hierarchical BiOCI nanostructures fabricated via a facile microwave-hydrothermal process, New J. Chem. 42 (2018) 137–149.
- [34] T. Hirata, M. Kitajima, K.G. Nakamura, E. Asari, Infrared and Raman spectra of solid solutions Ti_{1-x}Zr_xO₂ (x < 0.1), J. Phys. Chem. Solids 55 (1994) 349–355.</p>
- [35] M.S.P. Francisco, V.R. Mastelaro, Inhibition of the anatase-rutile phase transformation with addition of CeO₂ to CuO-TiO₂ system: Raman spectroscopy, X-ray diffraction, and textural studies, Chem. Mater. 14 (2002) 2514–2518.
- [36] M. Ocana, J.V. Garcia-Ramos, C.J. Serna, Low-temperature nucleation of rutile observed by Raman spectroscopy during crystallization of TiO₂, J. Am. Ceram. Soc. 75 (1992) 2010–2012.
- [37] C.Y. Xu, P.X. Zhang, L. Yan, Blue shift of Raman peak from coated TiO₂ nanoparticles, J. Raman Spectrosc. 32 (2001) 862–865.
- [38] T. Ohsaka, F. Izumi, Y. Fujiki, Raman spectrum of anatase TiO₂, J. Raman Spectrosc. 7 (1978) 321–324.
- [39] Y. Hong, J. Zhang, F. Huang, J. Zhang, X. Wang, Z. Wu, L. Zhang, J. Yu, Enhanced visible light photocatalytic hydrogen production activity of CuS/ZnS nanoflower spheres, J. Mater. Chem. A 3 (26) (2015) 13913–13919.
- [40] G. Tian, Y. Chen, J. Zhou, C. Tian, R. Li, C. Wang, H. Fu, In situ growth of Bi₂MoO₆ on reduced graphene oxide nanosheets for improved visible-light photocatalytic activity, CrystEngComm 16 (2014) 842–849.
- [41] R. Murugan, Investigation on ionic conductivity and Raman spectra of γ-Bi₂MoO₆, Physica B 352 (2004) 227–232.
- [42] F. Zhou, R. Shi, Y. Zhu, Significant enhancement of the visible photocatalytic degradation performances of γ-Bi₂MoO₆ nanoplate by graphene hybridization, J. Mol. Catal. A: Chem. 340 (2011) 77–82.
- [43] F.D. Hardcastle, I.E. Wachs, Molecular structure of molybdenum oxide in bismuth molybdates by Raman spectroscopy, J. Phys. Chem. 95 (1991) 10763–10772.
- [44] Q. Jay, X. Wang, X. Zhao, J. Hong, Q. Zhang, R. Xu, Z. Chen, Enhanced visible light hydrogen production via a multiple heterojunction structure with defect-engineered g-C₃N₄ and two-phase anatase/brookite TiO₂, J. Catal. 342 (2016) 55–62.
- [45] X.B. Zhang, L. Zhang, J.S. Hu, X.H. Huang, Facile hydrothermal synthesis and

improved photocatalytic activities of ${\rm Zn}^{2+}$ doped ${\rm Bi}_2{\rm MoO}_6$ nanosheets, RSC Adv. 6 (2016) 32349–32357.

- [46] J. Cai, J. Huang, Y. Lai, 3D Au-decorated Bi₂MoO₆ nanosheet/TiO₂ nanotube array heterostructure with enhanced UV and visible-light photocatalytic activity, J. Mater. Chem. A 5 (2017) 16412–16421.
- [47] J. Li, X. Liu, Z. Sun, L. Pan, Novel Bi₂MoO₆/TiO₂ heterostructure microspheres for degradation of benzene series compound under visible light irradiation, J. Colloid Interface Sci. 463 (2016) 145–153.
- [48] L. Artiglia, D. Lazzari, S. Agnoli, G.A. Rizzi, G. Granozzi, Searching for the formation of Ti-B bonds in B-doped TiO₂-rutile, J. Phys. Chem. C 117 (2013) 13163–13172.
- [49] D. Wei, Y. Zhou, D. Jia, Y. Wang, Formation of CaTiO₃/TiO₂ composite coating on titanium alloy for biomedical applications, J. Biomed. Mater. Res. B 84 (2008) 444–451.
- [50] D.O. Scanlon, C.W. Dunnill, J. Buckeridge, S.A. Shevlin, A.J. Logsdail, S.M. Woodley, C.R.A. Catlow, M.J. Powell, R.G. Palgrave, L.P. Parkin, G.W. Watson, T.W. Keal, P. Sherwood, G.W. Watson, T.W. Keal, P. Sherwood, A. Walsh, A.A. Sokol, Band alignment of rutile and anatase TiO₂, Nat. Mater. 12 (2013) 798–801.
- [51] C. Zeng, Y. Hu, Y. Guo, T. Zhang, F. Dong, Y. Zhang, H. Huang, Facile in situ self-sacrifice approach to ternary hierarchical architecture Ag/AgX (X = Cl, Br, I)/ AgIO₃ distinctively promoting visible-light photocatalysis with composition -dependent mechanism, ACS Sustain. Chem. Eng. 4 (2016) 3305–3315.
- [52] Z. Yang, J. Yan, J. Lian, H. Xu, X. She, H. Li, g-C₃N₄/TiO₂ nanocomposites for degradation of ciprofloxacin under visible light irradiation, ChemistrySelect 1 (2016) 5679–5685.
- [53] M.R. Hoffmann, S.T. Martin, W. Choi, D.W. Bahnemann, Environmental applications of semiconductor photocatalysis, Chem. Rev. 95 (1995) 69–96.
- [54] Z. Liu, J. Tian, D. Zeng, C. Yu, L. Zhu, W. Huang, K. Yang, D. Li, A facile microwavehydrothermal method to fabricate B doped ZnWO₄ nanorods with high crystalline and highly efficient photocatalytic activity, Mater. Res. Bull. 94 (2017) 298–306.
- [55] N. Tian, Y. Zhang, H. Huang, Y. He, Y. Guo, Influences of Gd substitution on the crystal structure and visible-light-driven photocatalytic performance of Bi₂WO₆, J. Phys. Chem. C 118 (2014) 15640–15648.
- [56] H. Yu, B. Huang, H. Wang, X. Yuan, L. Jiang, Z. Wu, J. Zhang, G. Zeng, Facile construction of novel direct solid-state Z-scheme AgI/BiOBr photocatalysts for highly effective removal of ciprofloxacin under visible light exposure: mineralization efficiency and mechanisms, J. Colloid Interface Sci. 522 (2018) 82–94.
- [57] H.W. Huang, L.Y. Liu, Y.H. Zhang, N. Tian, One pot hydrothermal synthesis of a novel BiVO₄/Bi₂MoO₆, heterojunction photocatalyst with enhanced visible- light -driven photocatalytic activity for rhodamine B degradation and photocurrent generation, J. Alloys Compd. 619 (2015) 807–811.
- [58] Y. Hu, D. Li, Y. Zheng, W. Chen, Y. He, Y. Shao, X. Fu, G. Xiao, BiVO₄/TiO₂, nanocrystalline heterostructure: a wide spectrum responsive photocatalyst towards the highly efficient decomposition of gaseous benzene, Appl. Catal. B 104 (2011) 30–36.
- [59] K. Kabra, R. Chaudhary, R.L. Sawhney, Treatment of hazardous organic and inorganic compounds through aqueous-phase photocatalysis: a review, Ind. Eng. Chem. Res. 43 (2004) 7683–7696.