

Article

The Structural, Photocatalytic Property Characterization and Enhanced Photocatalytic Activities of Novel Photocatalysts $\text{Bi}_2\text{GaSbO}_7$ and $\text{Bi}_2\text{InSbO}_7$ during Visible Light Irradiation

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Abstract: In order to develop original and efficient visible light response photocatalysts for degrading organic pollutants in wastewater, new photocatalysts $\text{Bi}_2\text{GaSbO}_7$ and $\text{Bi}_2\text{InSbO}_7$ were firstly synthesized by a solid-state reaction method and their chemical, physical and structural properties were characterized. $\text{Bi}_2\text{GaSbO}_7$ and $\text{Bi}_2\text{InSbO}_7$ were crystallized with a pyrochlore-type structure and the lattice parameter of $\text{Bi}_2\text{GaSbO}_7$ or $\text{Bi}_2\text{InSbO}_7$ was 10.356497 Å or 10.666031 Å. The band gap of $\text{Bi}_2\text{GaSbO}_7$ or $\text{Bi}_2\text{InSbO}_7$ was estimated to be 2.59 eV or 2.54 eV. Compared with nitrogen doped TiO_2 , $\text{Bi}_2\text{GaSbO}_7$ and $\text{Bi}_2\text{InSbO}_7$, both showed excellent photocatalytic activities for degrading methylene blue during visible light irradiation due to their narrower band gaps and higher crystallization perfection. $\text{Bi}_2\text{GaSbO}_7$ showed higher catalytic activity compared with $\text{Bi}_2\text{InSbO}_7$. The photocatalytic degradation of methylene blue followed by the first-order reaction kinetics and the first-order rate constant was 0.01470 min^{-1} , 0.00967 min^{-1} or 0.00259 min^{-1} with $\text{Bi}_2\text{GaSbO}_7$, $\text{Bi}_2\text{InSbO}_7$ or nitrogen doped TiO_2 as a catalyst. The evolution of CO_2 and the removal of total organic carbon were successfully measured and these results indicated continuous mineralization of methylene blue during the photocatalytic process. The possible degradation scheme and pathway of methylene blue was also analyzed. $\text{Bi}_2\text{GaSbO}_7$ and $\text{Bi}_2\text{InSbO}_7$ photocatalysts both had great potential to purify textile industry wastewater.

Keywords: photocatalysts; $\text{Bi}_2\text{GaSbO}_7$; $\text{Bi}_2\text{InSbO}_7$; methylene blue; photocatalytic degradation; visible light irradiation

1. Introduction

Dye contaminants from textile wastewater were difficult to treat for their high chroma, high chemical oxygen demand content and complicated ingredients. Some conventional methods including biodegradation [1–3], electrochemistry [3–6], adsorption [7–9], and flocculation–precipitation [10,11] had been exploited to degrade those dye contaminants, but there still existed a series of problems with them. Methylene blue (MB), usually adopted as dyestuff, was one of the most common dye contaminants.

Photocatalysis had gained great development since photocatalytic reaction was found in 1972 [12]. Photocatalytic degradation of the pollutants in wastewater entailed a chain of advantages including conserving energy and little secondary pollution; it had therefore gradually attracted more and

more attention in textile wastewater treatment. Metal oxides [13–24] and metal sulfides [21–33] were the most common semiconductor photocatalysts. Among metal oxides, anatase TiO_2 was investigated most repeatedly owing to its non-toxic property, excellent stability and low cost. However, with a wider band gap (3.2 eV), anatase TiO_2 only efficiently absorbed ultraviolet light which occupied only 5% of the solar energy, and thus failed to make good use of optical energy. In order to make the best use of visible light which occupied 43% of sunlight, developing visible light responsive photocatalysts was an inevitable tendency in the field of photocatalysis research, which could be embodied from abundant endeavors of previous scholars in realizing the degradation of the pollutants during visible light irradiation by the method of iron doping [34–36], forming heterojunction [37–42] or photosensitization [43–48]. Several years ago, Zou and Arakawa [49,50] found that two types of metal oxides, ABO_4 and $\text{A}_2\text{B}_2\text{O}_7$, had great potential for photocatalytic H_2 production during visible light irradiation. It was well known that minute changes in internal structure of the semiconductor photocatalysts would presumably promote the separation of photogenerated electrons and holes and thus improve photocatalytic activities. Zou et al. synthesized Bi_2MNbO_7 ($\text{M} = \text{Al}, \text{Ga}, \text{In}, \text{Y}$ or Fe) [51–53] which was one remarkable representative of the family of $\text{A}_2\text{B}_2\text{O}_7$ compounds with the $\text{A}^{3+}_2\text{B}^{4+}_2\text{O}_7$ pyrochlore structure by substituting B^{4+} sites in $\text{A}^{3+}_2\text{B}^{4+}_2\text{O}_7$ for M^{3+} ($\text{M}^{3+} = \text{Al}^{3+}, \text{Ga}^{3+}, \text{In}^{3+}$) and Nb^{5+} . Similarly, previous studies had reported Bi_2GaVO_7 [54] and Bi_2SbVO_7 [55] by element doping, which had realized visible-light photocatalytic degradation and H_2 production. Previous works indicated that the Ga^{3+} and In^{3+} ions could influence the band gap and the electronic structure of the compound photocatalysts, which was expected to cause the different photocatalytic activity [56,57].

As an important element with higher electron drift velocity and mobility, antimony (Sb) has been extensively studied as a good dopant candidate for enhancing the electron transfer rate of semiconductors [58]. Omid et al. [59] evaluated the photocatalytic activity of Sb-doped ZnO nanostructures ($0 \leq \text{mol fraction of Sb}^{3+} \text{ ions} \leq 0.15$) for the photodegradation of MB. In addition, the acquired results showed that doping the ZnO nanostructures with 0.03 mol fraction of Sb^{3+} ions increased the reaction rate by about three times, indicating that the decreasing recombination of charge carriers could enhance the photocatalytic activity. Al-Hamdi et al. [60] reported that Sb-doped dioxide (SnO_2) nanoparticles with different Sb concentrations (at % = 0, 2, 4 and 6), which was prepared by a sol-gel method, could degrade 12%, 45%, 71% and 97% of phenol in the mineralization process under UV irradiation for 120 min, which showed higher photocatalytic activity than the undoped SnO_2 catalyst. These previous reports have shown that moderate Sb doped on the photocatalysts could greatly enhance the photocatalytic activity.

In this paper, new photocatalysts, $\text{Bi}_2\text{GaSbO}_7$ and $\text{Bi}_2\text{InSbO}_7$, were synthesized by doping element Ga or In with a solid-state reaction method. Meanwhile, the structural properties of $\text{Bi}_2\text{GaSbO}_7$ and $\text{Bi}_2\text{InSbO}_7$ were also characterized and their photocatalytic activities were also examined in degrading MB solution compared with N-doped TiO_2 , which had achieved the visible light response.

2. Materials and Methods

2.1. Synthesis of $\text{Bi}_2\text{GaSbO}_7$, $\text{Bi}_2\text{InSbO}_7$ and N-doped TiO_2 Photocatalysts

New $\text{Bi}_2\text{GaSbO}_7$ and $\text{Bi}_2\text{InSbO}_7$ samples were firstly synthesized by a solid-state reaction method. Firstly, for the sake of the synthesis of $\text{Bi}_2\text{GaSbO}_7$, Bi_2O_3 , Ga_2O_3 and Sb_2O_5 with a purity of 99.99% (Sinopharm Group Chemical Reagent Co., Ltd., Shanghai, China) were obtained by an atomic ratio of 2:1:1 to serve as raw materials. All powders were dried at 200 °C for 4 h before synthesis. In order to synthesize $\text{Bi}_2\text{GaSbO}_7$, the precursors were fully mingled with each other, then pressed into small columns and put into an alumina crucible (Shenyang Crucible Co., Ltd., Shenyang, China). Eventually, calcination was performed at 1100 °C for 40 h in an electric furnace (KSL 1700X, Hefei Kejing Materials Technology Co., Ltd., Hefei, China). Accordingly, Bi_2O_3 , In_2O_3 and Sb_2O_5 with a purity of 99.99% (Sinopharm Group Chemical Reagent Co., Ltd., Shanghai, China) were obtained by an atomic ratio of 2:1:1 for the preparation of $\text{Bi}_2\text{InSbO}_7$. The synthesization procedure of $\text{Bi}_2\text{InSbO}_7$ was similar to

that of $\text{Bi}_2\text{GaSbO}_7$, just the calcination was performed at 1070 °C for 30 h during mixed powder in the alumina crucible. The preparation of N-doped TiO_2 was by the sol-gel method which was mentioned in our previous studies [61].

2.2. Characterization

In our paper, we adopted the X-ray diffraction method (XRD, D/MAX-RB, Rigaku Corporation, Tokyo, Japan) with Cu K α radiation ($\lambda = 1.54056$ angstrom) to confirm the crystal structures of $\text{Bi}_2\text{GaSbO}_7$ and $\text{Bi}_2\text{InSbO}_7$. The patterns of $\text{Bi}_2\text{GaSbO}_7$ and $\text{Bi}_2\text{InSbO}_7$ were recorded at 295 K with a step-scan procedure in the range of $2\theta = 10^\circ\text{--}100^\circ$ (for $\text{Bi}_2\text{GaSbO}_7$) or $10^\circ\text{--}95^\circ$ (for $\text{Bi}_2\text{InSbO}_7$). The step interval was 0.02° and the time per step was 1 s. The transmission electron microscopy (TEM, Tecna F20 S-Twin, FEI Corporation, Hillsboro, OR, USA) was used to observe the surface state and structure of the photocatalysts. The Malvern's mastersize-2000 particle size analyzer (Malvern Instruments Ltd., Malvern, UK) was utilized to measure the particle size of the photocatalysts. We also utilized X-ray photoelectron spectroscopy (XPS, ESCALABMK-2, VG Scientific Ltd., London, UK) to determine the Bi^{3+} content, Ga^{3+} content, Sb^{5+} content, In^{3+} content and O^{2-} content of $\text{Bi}_2\text{GaSbO}_7$ and $\text{Bi}_2\text{InSbO}_7$. The chemical composition of $\text{Bi}_2\text{GaSbO}_7$ and $\text{Bi}_2\text{InSbO}_7$ was determined by scanning the electron microscope-X-ray energy dispersion spectrum (SEM-EDS, LEO 1530VP, LEO Corporation, Dresden, Germany). The surface areas of $\text{Bi}_2\text{GaSbO}_7$ and $\text{Bi}_2\text{InSbO}_7$ were measured by the Brunauer-Emmett-Teller (BET) method (MS-21, Quantachrome Instruments Corporation, Boynton Beach, FL, USA) with N_2 adsorption at liquid nitrogen temperature. Their diffuse reflectance spectrums were analyzed by a UV-visible spectrophotometer (Shimadzu UV-2550 UV-Visible spectrometer, Kyoto, Japan).

2.3. Photocatalytic Properties Test

MB ($\text{C}_{16}\text{H}_{18}\text{ClN}_3\text{S}$) (Tianjin Bodi Chemical Co., Ltd., Tianjin, China) served as our objective pollutant. The whole photocatalytic activity process was as follows: firstly, we prepared 300 mL MB aqueous solution in quartz tubes whose initial concentration was $0.025\text{ mmol}\cdot\text{L}^{-1}$ and initial PH value was 7.0. Then, 0.8 g photocatalyst powder of N-doped TiO_2 , $\text{Bi}_2\text{GaSbO}_7$ or $\text{Bi}_2\text{InSbO}_7$ was placed into every quartz tube, respectively. In order to ensure the establishment of an adsorption/desorption equilibrium among photocatalysts, the MB dye and atmospheric oxygen, above per solution was magnetically stirred in the dark for 45 min. In our paper, we employed a 500 W Xenon lamp ($\lambda > 420\text{ nm}$), which utilized a 420 nm cutoff filter as a visible-light source. The photoreaction was carried out in a photochemical reaction apparatus (Nanjing Xujiang Machine Plant, Nanjing, China). During visible light illumination, the MB dye pollution was stirred by a magnetic stirrer and the photocatalyst powder was kept suspended in the solution. The filtrate was subsequently measured by a Shimadzu UV-2450 UV-visible spectrometer (Kyoto, Japan) with the detecting wavelength at 665 nm. The identification of MB and the degradation intermediate products of MB were measured by a liquid chromatograph-mass spectrometer (LC-MS, Thermo Quest LCQ Duo, Silicon Valley, CA, USA, Beta Basic- C_{18} HPLC column: $150 \times 2.1\text{ mm}^2$, ID of 5 μm , Finnigan, Thermo, Silicon Valley, CA, USA). Here, post-photocatalysis solution (20 μL) was injected automatically into the LC-MS system. The eluent contained 60% methanol and 40% water, and the flow rate was $0.2\text{ mL}\cdot\text{min}^{-1}$. MS conditions included an electrospray ionization interface, a capillary temperature of 27 °C with a voltage of 19.00 V, a spray voltage of 5000 V and a constant sheath gas flow rate. The spectrum was acquired in the negative ion scan mode, sweeping the m/z range from 50 to 600. Evolution of CO_2 was analyzed with an intersmatTM IGC120-MB gas chromatograph (6890 N, Agilent Technologies, Palo Alto, CA, USA) equipped with a porapak Q column (3 m in length and with an inner diameter of 0.25 in.), which was connected to a catharometer detector. The total organic carbon (TOC) concentration was determined with a TOC analyzer (TOC-5000, Shimadzu Corporation, Kyoto, Japan). The photonic efficiency was calculated according to the following equation [62,63]:

$$\xi = R/I_0 \quad (1)$$

where ξ was the photonic efficiency (%), and R was the rate of MB degradation ($\text{mol}\cdot\text{L}^{-1}\cdot\text{s}^{-1}$), and I_0 was the incident photon flux ($\text{Einstein}\cdot\text{L}^{-1}\cdot\text{s}^{-1}$). The incident photon flux I_0 which was measured by a radiometer (Model FZ-A, Photoelectric Instrument Factory Beijing Normal University, Beijing, China) was determined to be $4.76 \times 10^6 \text{ Einstein}\cdot\text{L}^{-1}\cdot\text{s}^{-1}$ under visible light irradiation (wavelength range of 400–700 nm).

3. Results and Discussion

3.1. Characterization

Figure 1a,b shows the TEM images of $\text{Bi}_2\text{GaSbO}_7$ and $\text{Bi}_2\text{InSbO}_7$ with high magnification. We could observe from the images of $\text{Bi}_2\text{GaSbO}_7$ and $\text{Bi}_2\text{InSbO}_7$ that their particles presented a similar oblate spheroid appearance and that their distribution was relatively uniform. The average particle size of $\text{Bi}_2\text{GaSbO}_7$ approached 190 nm, which was smaller than that of $\text{Bi}_2\text{InSbO}_7$, whose average particle size approached 390 nm. We could observe from the BET results that the specific surface area of $\text{Bi}_2\text{GaSbO}_7$ approached $2.36 \text{ m}^2/\text{g}$, which was bigger than that of $\text{Bi}_2\text{InSbO}_7$, whose specific surface area approached $1.82 \text{ m}^2/\text{g}$. It was clear that the BET results were consistent with the TEM results, indicating that the samples with small average particle size would have a higher specific surface area. Figure 2a,b shows the SEM-EDS spectra taken from $\text{Bi}_2\text{GaSbO}_7$ and $\text{Bi}_2\text{InSbO}_7$. It could be seen from Figure 2a,b that the superfluous peaks did not exist in the spectra of $\text{Bi}_2\text{GaSbO}_7$ and $\text{Bi}_2\text{InSbO}_7$, meaning that $\text{Bi}_2\text{GaSbO}_7$ and $\text{Bi}_2\text{InSbO}_7$ crystals were both pure phase without impure elements.

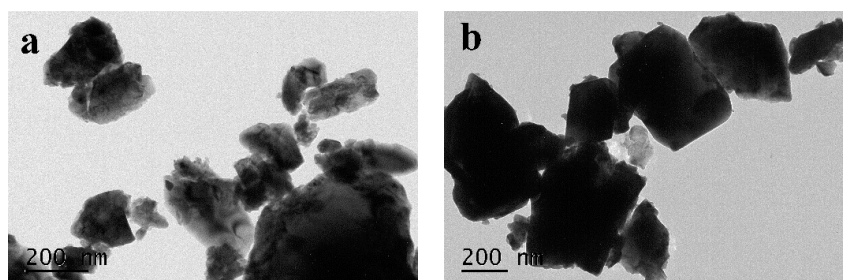


Figure 1. TEM images of (a) $\text{Bi}_2\text{GaSbO}_7$ and (b) $\text{Bi}_2\text{InSbO}_7$ with high magnification.

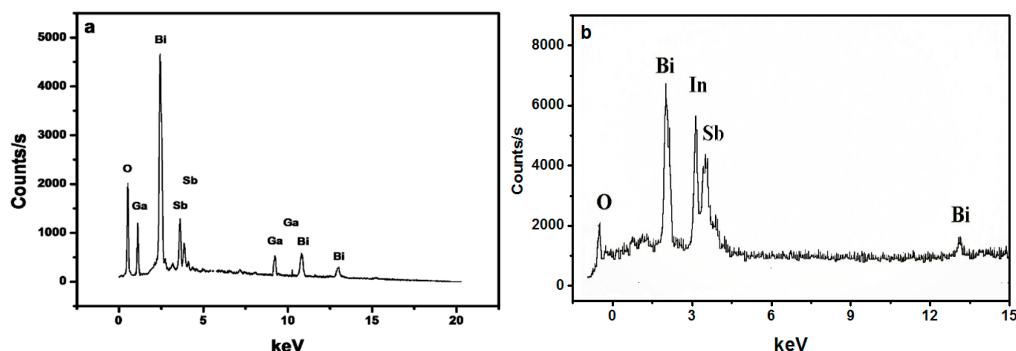


Figure 2. SEM-EDS spectra taken from (a) $\text{Bi}_2\text{GaSbO}_7$ and (b) $\text{Bi}_2\text{InSbO}_7$.

In this paper, X-ray photoelectron spectroscopy analysis techniques were utilized to reveal the surface chemical compositions and the valence states of various elements in $\text{Bi}_2\text{GaSbO}_7$ and $\text{Bi}_2\text{InSbO}_7$. The various elemental peaks which are corresponding to specific binding energies are given in Table 1. Analysis results of the full XPS spectra were as follows: the prepared $\text{Bi}_2\text{GaSbO}_7$ sample contained Bi, Ga, Sb and O elements. Similarly, the prepared $\text{Bi}_2\text{InSbO}_7$ sample contained Bi, In, Sb and O elements. These results also uncovered that $\text{Bi}_2\text{GaSbO}_7$ crystal or $\text{Bi}_2\text{InSbO}_7$ crystal were both at a high pure

phase. Moreover, the analysis results of the XPS spectra also manifested that the valence of Bi, Ga, Sb, In or O from $\text{Bi}_2\text{GaSbO}_7$ and $\text{Bi}_2\text{InSbO}_7$ was +3, +3, +5, +3 or −2, respectively. Eventually, according to our comprehensive XPS and SEM–EDS analyses, as for $\text{Bi}_2\text{GaSbO}_7$, the mean atomic ratio of Bi, Ga, Sb and O was 2.00:0.98:1.02:6.98. As for $\text{Bi}_2\text{InSbO}_7$, the mean atomic ratio of Bi, In, Sb and O was 2.00:0.99:1.01:6.99.

Table 1. Binding energies (BE) for key elements of $\text{Bi}_2\text{InSbO}_7$ and $\text{Bi}_2\text{GaSbO}_7$.

Compound	$\text{Bi}_{4f7/2}$ BE (eV)	$\text{Sb}_{3d5/2}$ BE (eV)	$\text{Ga}_{3d5/2}$ BE (eV)	$\text{In}_{3d5/2}$ BE (eV)	O_{1s} BE (eV)
$\text{Bi}_2\text{InSbO}_7$	159.70	531.20	—	444.60	530.85
$\text{Bi}_2\text{GaSbO}_7$	159.60	531.40	20.60	—	531.10

Figure 3 presents the X-ray powder diffraction patterns of $\text{Bi}_2\text{GaSbO}_7$ and $\text{Bi}_2\text{InSbO}_7$, respectively. We could judge from Figure 3 that $\text{Bi}_2\text{GaSbO}_7$ crystal or $\text{Bi}_2\text{InSbO}_7$ crystal was single phase. Figure 4a,b shows the Pawley refinement results of XRD data for $\text{Bi}_2\text{GaSbO}_7$ and $\text{Bi}_2\text{InSbO}_7$. The refined outcomes from Figure 4a,b displayed that the actual intensities of $\text{Bi}_2\text{GaSbO}_7$ or $\text{Bi}_2\text{InSbO}_7$ were both highly in accordance with the intensities of the pyrochlore-type structure with a cubic crystal system and a space group $Fd\bar{3}m$ (O atoms were included in the model), indicating that $\text{Bi}_2\text{GaSbO}_7$ and $\text{Bi}_2\text{InSbO}_7$ indeed formed the same crystal structure. The atomic coordinates and structural parameters of $\text{Bi}_2\text{GaSbO}_7$ and $\text{Bi}_2\text{InSbO}_7$ are listed in Tables 2 and 3, respectively. Above results showed that the lattice parameter a of $\text{Bi}_2\text{GaSbO}_7$ was 10.356497 Å, which was slightly lower than that of $\text{Bi}_2\text{InSbO}_7$ whose lattice parameter a was 10.666031 Å. From the SEM–EDS spectra and XPS spectra which were taken from $\text{Bi}_2\text{GaSbO}_7$ and $\text{Bi}_2\text{InSbO}_7$, we had known that $\text{Bi}_2\text{GaSbO}_7$ crystal or $\text{Bi}_2\text{InSbO}_7$ crystal was both pure phase. Therefore, excluding the effects of impurities, we could deduce that the difference between the lattice parameter a for $\text{Bi}_2\text{GaSbO}_7$ and $\text{Bi}_2\text{InSbO}_7$ was perhaps concerned with M ionic radii which belonged to Bi_2MSbO_7 . The reason was that the ionic radii of Ga^{3+} (0.62 Å) was minutely lower than that of In^{3+} (0.92 Å). Lastly, all the diffraction peaks (222), (400), (440), (622), (444), (800), (662), (840), (844) for $\text{Bi}_2\text{GaSbO}_7$ and $\text{Bi}_2\text{InSbO}_7$ were successfully indexed according to the lattice constant and above space group.

Figure 5 presents the diffuse reflection spectra of $\text{Bi}_2\text{GaSbO}_7$ and $\text{Bi}_2\text{InSbO}_7$, respectively. Compared with N-doped TiO_2 whose absorption edge was about 445 nm, the absorption spectrum of newly prepared photocatalyst $\text{Bi}_2\text{GaSbO}_7$ or $\text{Bi}_2\text{InSbO}_7$ was estimated to be 480 nm or 490 nm, respectively, implicating that they had sizable potential to realize visible light response. The maximum absorption wavelength of MB was detected by an ultraviolet spectrophotometer, while the diffuse reflection spectra of $\text{Bi}_2\text{GaSbO}_7$, $\text{Bi}_2\text{InSbO}_7$ or N-doped TiO_2 was detected by ultraviolet spectrophotometer with integrating sphere. In addition, the above two testing methods were totally different. Furthermore, the absorbance was obtained from the reflectance data and scattering should also be taken into consideration in data conversion from reflectance into absorbance, which was the reason why the ordinate of the diffuse reflection spectra in Figure 5 was absorbance.

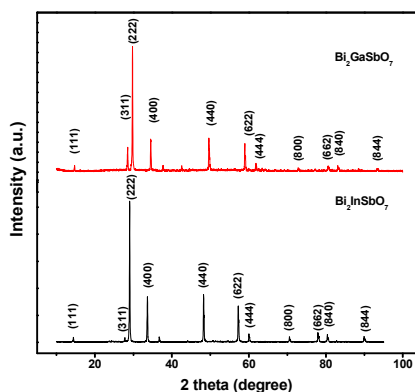


Figure 3. X-ray powder diffraction patterns of $\text{Bi}_2\text{GaSbO}_7$ and $\text{Bi}_2\text{InSbO}_7$.

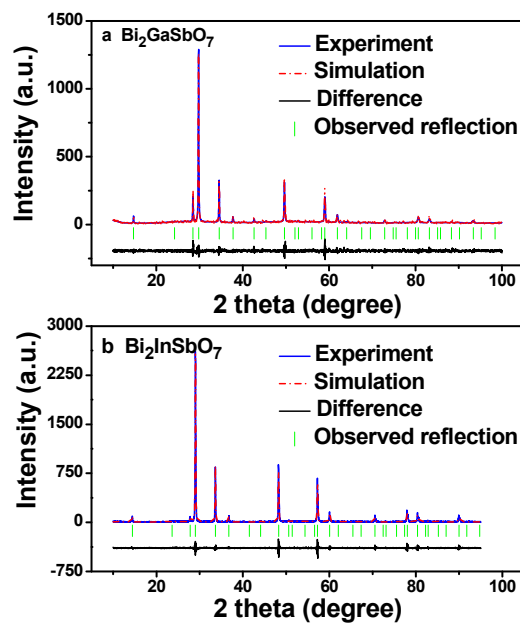


Figure 4. The Pawley refinement results of XRD data for (a) $\text{Bi}_2\text{GaSbO}_7$ and (b) $\text{Bi}_2\text{InSbO}_7$.

Table 2. Structural parameters of $\text{Bi}_2\text{GaSbO}_7$ prepared by the solid state reaction method.

Atom	x	y	z	Occupation Factor
Bi	0.00000	0.00000	0.00000	1.0
Ga	0.50000	0.50000	0.50000	0.5
Sb	0.50000	0.50000	0.50000	0.5
O(1)	−0.18500	0.12500	0.12500	1.0
O(2)	0.12500	0.12500	0.12500	1.0

Table 3. Structural parameters of $\text{Bi}_2\text{InSbO}_7$ prepared by the solid state reaction method.

Atom	x	y	z	Occupation Factor
Bi	0.00000	0.00000	0.00000	1.0
In	0.50000	0.50000	0.50000	0.5
Sb	0.50000	0.50000	0.50000	0.5
O(1)	−0.16500	0.12500	0.12500	1.0
O(2)	0.12500	0.12500	0.12500	1.0

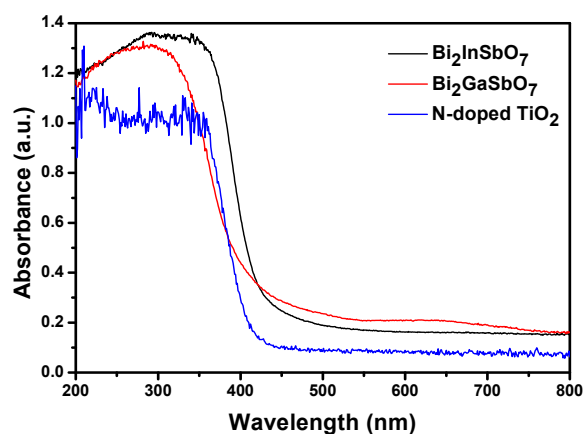


Figure 5. Diffuse reflection spectra of $\text{Bi}_2\text{GaSbO}_7$, $\text{Bi}_2\text{InSbO}_7$ and N-doped TiO_2 .

We realized that absorbance could not be proportional to 1-transmission, thus the absorbance was calculated using the Kubelka–Munk transformation method in our experiment. For a crystalline semiconductor compound, the optical absorption near the band edge followed the equation [64,65]:

$$\alpha h\nu = A \times (h\nu - E_g)^n \quad (2)$$

Here, A , α , E_g and ν denoted proportional constant, absorption coefficient, band gap and light frequency, respectively. In this equation, n determined the character of the transition in a semiconductor compound. E_g and n could be calculated by the following steps: (i) plotting $\ln(\alpha h\nu)$ versus $\ln(h\nu - E_g)$ assuming an approximate value of E_g ; (ii) deducing the value of n according to the slope in this graph; (iii) refining the value of E_g by plotting $(\alpha h\nu)^{1/n}$ versus $h\nu$ and extrapolating the plot to $(\alpha h\nu)^{1/n} = 0$. According to this method, we first estimated that the value of n for $\text{Bi}_2\text{GaSbO}_7$ or $\text{Bi}_2\text{InSbO}_7$ was 2, indicating that the optical transition for $\text{Bi}_2\text{GaSbO}_7$ or $\text{Bi}_2\text{InSbO}_7$ is indirectly allowed. Figure 6 presents the plot of $(\alpha h\nu)^{1/2}$ versus $h\nu$ for $\text{Bi}_2\text{GaSbO}_7$ and $\text{Bi}_2\text{InSbO}_7$. It could be found that the value of E_g for $\text{Bi}_2\text{GaSbO}_7$, $\text{Bi}_2\text{InSbO}_7$ or N-doped TiO_2 was calculated to be 2.59 eV, 2.54 eV or 2.78 eV.

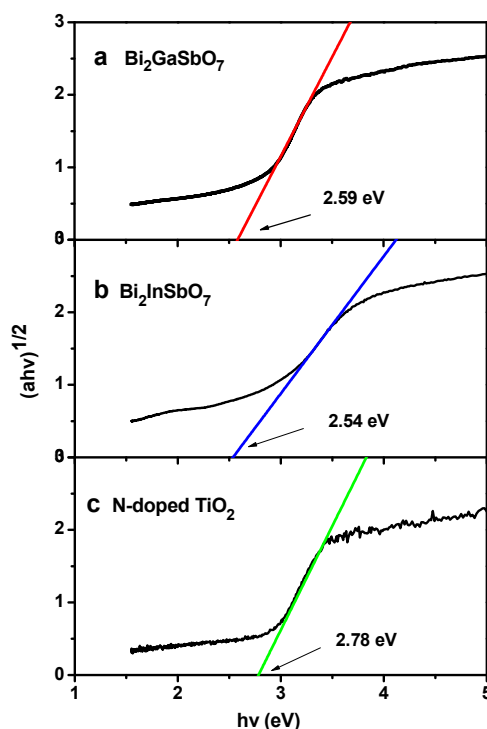


Figure 6. Plot of $(\alpha h\nu)^{1/2}$ versus $h\nu$ for (a) $\text{Bi}_2\text{GaSbO}_7$; (b) $\text{Bi}_2\text{InSbO}_7$ and (c) N-doped TiO_2 .

3.2. Photocatalytic Properties of $\text{Bi}_2\text{GaSbO}_7$ and $\text{Bi}_2\text{InSbO}_7$ Photocatalysts

From the UV-vis spectra of $\text{Bi}_2\text{GaSbO}_7$ and $\text{Bi}_2\text{InSbO}_7$, we had analyzed that both of the novel photocatalysts sent a strong absorption signal in the visible light region. Therefore, we expected that they could have the potential to degrade organic pollutants under visible light irradiation. In order to evaluate their visible light photocatalytic degradation capabilities, we listed N-doped TiO_2 as a referential photocatalyst. Figure 7a presents the kinetics of MB degradation with $\text{Bi}_2\text{GaSbO}_7$, $\text{Bi}_2\text{InSbO}_7$, N-doped TiO_2 as well as in the absence of a photocatalyst under visible light irradiation (>420 nm). Consistent with our expectations, as time went by, the color of the MB solution gradually shallowed and the concentration of MB gradually declined in our measurements in the absence of a photocatalyst. After visible light irradiation for 400 min, the removal rate of MB was estimated to be 99.75%, 98.95%, 59.92% or 40.6% with $\text{Bi}_2\text{GaSbO}_7$, $\text{Bi}_2\text{InSbO}_7$, N-doped TiO_2 as catalyst, as well as in the absence of a photocatalyst, respectively. The sharp decrease in the concentration of MB under visible light irradiation from 0 to 120 min was mainly due to the adsorption of MB on the surface of

$\text{Bi}_2\text{GaSbO}_7$, $\text{Bi}_2\text{InSbO}_7$ or N-doped TiO_2 as a photocatalyst [66]. In the meantime, the photocatalytic degradation of MB with $\text{Bi}_2\text{GaSbO}_7$, $\text{Bi}_2\text{InSbO}_7$ or N-doped TiO_2 as a catalyst also played a significant role compared with the absence of a photocatalyst under visible light irradiation in this sharp decrease. In addition, the slower speed of MB degradation by using $\text{Bi}_2\text{GaSbO}_7$, $\text{Bi}_2\text{InSbO}_7$ or N-doped TiO_2 as a photocatalyst during the later reaction process could be the result of as-prepared samples surface blocking by adsorbed MB degradation byproducts [67]. Moreover, the photocatalytic degradation rate of MB was $1.039 \times 10^{-9} \text{ mol}\cdot\text{L}^{-1}\cdot\text{s}^{-1}$, $1.031 \times 10^{-9} \text{ mol}\cdot\text{L}^{-1}\cdot\text{s}^{-1}$ or $0.624 \times 10^{-9} \text{ mol}\cdot\text{L}^{-1}\cdot\text{s}^{-1}$ with $\text{Bi}_2\text{GaSbO}_7$, $\text{Bi}_2\text{InSbO}_7$ or N-doped TiO_2 as a catalyst during 400 min of visible light irradiation, respectively. The self-degradation rate of MB was $0.422 \times 10^{-9} \text{ mol}\cdot\text{L}^{-1}\cdot\text{s}^{-1}$ without a catalyst. Furthermore, the photonic efficiency was estimated to be 0.0218% ($\lambda = 420 \text{ nm}$), 0.0217% ($\lambda = 420 \text{ nm}$) or 0.0131% ($\lambda = 420 \text{ nm}$) with $\text{Bi}_2\text{GaSbO}_7$, $\text{Bi}_2\text{InSbO}_7$ or N-doped TiO_2 as a catalyst, indicating that the sufficient use of a large number of photons could lead to the production of a large number of electron/hole pairs which were responsible for the photocatalytic degradation reaction directly and/or indirectly [68]. According to above results, it was apparent that $\text{Bi}_2\text{GaSbO}_7$ and $\text{Bi}_2\text{InSbO}_7$ harvested the highest photocatalytic degradation rate and photonic efficiency compared with N-doped TiO_2 for degrading MB. The decolored MB solution and the decrease of MB concentration reflected from Figure 7a might ascribe to the destruction of chromophore and the thorough degradation of the whole MB molecular [69]. We have verified our conjecture by detecting the mount variation of TOC and CO_2 during MB degradation.

Figure 7b presents the UV-vis spectral changes during the photodegradation of MB with $\text{Bi}_2\text{GaSbO}_7$ as a photocatalyst. Noticeably, we could observe a subtle blue shift in the maximum absorbance of MB in the spectral changes by using $\text{Bi}_2\text{GaSbO}_7$ as a photocatalyst under visible light irradiation, indicating the rather facile cleavage of the whole conjugated chromophore structure [70]. This blue shift in the maximum absorbance of MB also proved the existence of some photodegradation intermediate products of MB during the photocatalytic degradation of MB under visible light irradiation in the presence of $\text{Bi}_2\text{GaSbO}_7$.

Figure 8 shows the change of TOC for the photocatalytic degradation of MB during visible light irradiation with $\text{Bi}_2\text{GaSbO}_7$, $\text{Bi}_2\text{InSbO}_7$ or N-doped TiO_2 as a photocatalyst, which is consistent with the tendency shown in Figure 7. The gradual decrease of TOC represented the gradual disappearance of organic carbon when the MB solution which contained $\text{Bi}_2\text{GaSbO}_7$, $\text{Bi}_2\text{InSbO}_7$ or N-doped TiO_2 was exposed under visible light irradiation and the removal rate of TOC was 98.23%, 96.42% or 58.08% with $\text{Bi}_2\text{GaSbO}_7$, $\text{Bi}_2\text{InSbO}_7$ or N-doped TiO_2 as a catalyst after visible light irradiation for 400 min. In addition, the reactions stopped when the light was turned off in this experiment, which showed the obvious light response, suggesting that MB had been converted to other kinds of byproducts and the organic carbon in the MB had not been decomposed to CO_2 [71].

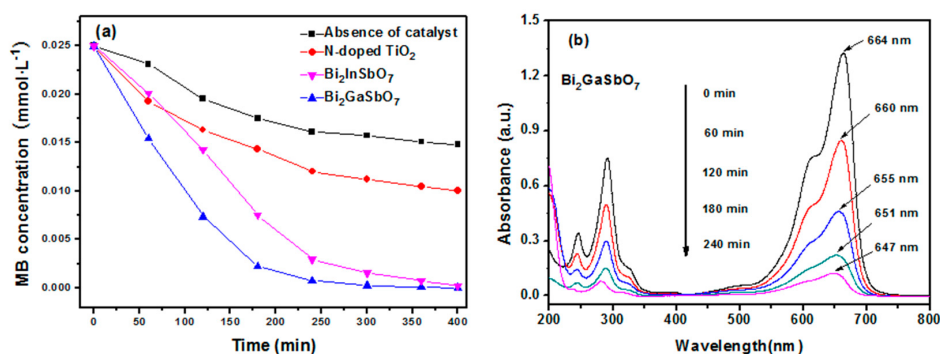


Figure 7. (a) Photocatalytic degradation of methylene blue under visible light irradiation in the presence of $\text{Bi}_2\text{GaSbO}_7$, $\text{Bi}_2\text{InSbO}_7$, N-doped TiO_2 as well as in the absence of a photocatalyst; (b) Temporal UV-vis absorption spectral changes during the photocatalytic degradation of MB (0.025 mmol/L, pH = 7) in aqueous $\text{Bi}_2\text{GaSbO}_7$ suspensions.

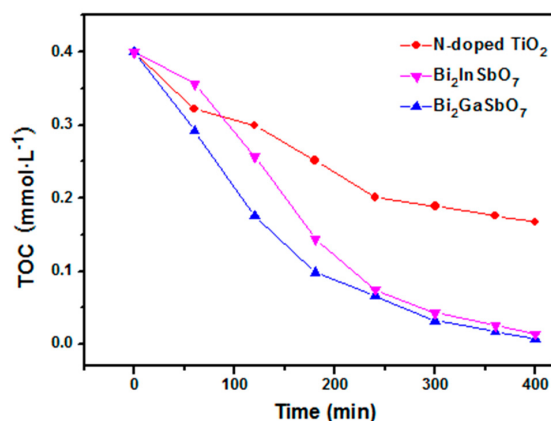


Figure 8. Disappearance of the total organic carbon (TOC) during the photocatalytic degradation of methylene blue with Bi₂GaSbO₇, Bi₂InSbO₇ or N-doped TiO₂ as a catalyst under visible light irradiation.

Figure 9 shows the amount of variation of CO₂ produced during the photocatalytic degradation of MB by using Bi₂GaSbO₇, Bi₂InSbO₇ or N-doped TiO₂ as a photocatalyst under visible light irradiation. It could be distinctly seen from Figure 9 that the amount of CO₂ gradually augmented along the light irradiation time and increased less during the last 100 min when much TOC was eliminated according to the results of Figure 8. In addition, after visible light irradiation of 400 min, the CO₂ production of 0.11711 mmol or 0.11512 mmol with Bi₂GaSbO₇ or Bi₂InSbO₇ as a catalyst was higher than that of 0.06875 mmol with N-doped TiO₂ as a catalyst. In addition, the amount of CO₂ production was nearly equivalent to that of the removed TOC; at the same time, the amount of CO₂ production or the removed TOC was slightly lower than the amount of reduced MB by using different catalysts with respect to the C element equilibrium, which indicated that MB was mainly degraded into some inorganic products including CO₂ and eventually H₂O.

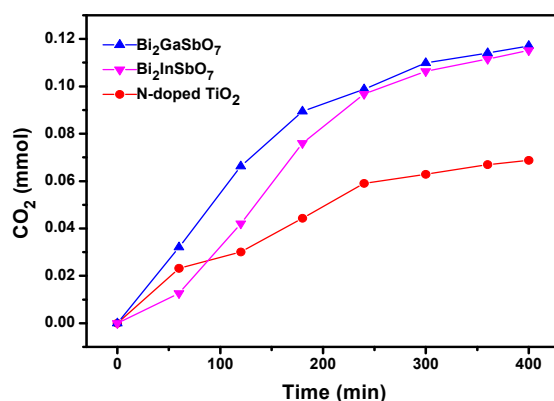


Figure 9. CO₂ production kinetics during the photocatalytic degradation of methylene blue with Bi₂GaSbO₇, Bi₂InSbO₇ or N-doped TiO₂ as a catalyst under visible light irradiation.

Figure 10 presents the first order nature of the photocatalytic degradation kinetics with Bi₂GaSbO₇, Bi₂InSbO₇ or N-doped TiO₂ as a catalyst, which exhibits a linear correlation between $\ln(C/C_0)$ or $\ln(TOC/TOC_0)$ and the irradiation time for the photocatalytic degradation of MB under visible light irradiation by using the aforementioned catalysts. The pseudo-first-order kinetic curves of MB photodegradation were plotted to quantitatively compare the degradation rate of MB [72]. In the above expression, C and TOC represented the MB concentration and the total organic carbon concentration at time t , respectively. Likewise, C_0 and TOC_0 represented the initial concentration of MB and the initial total organic carbon concentration, respectively. By a linear fit for the relationship between

$\ln(C/C_0)$ and the irradiation time, the first-order rate constant k_C was estimated to be 0.01470 min^{-1} with $\text{Bi}_2\text{GaSbO}_7$ as a catalyst, 0.00967 min^{-1} with $\text{Bi}_2\text{InSbO}_7$ as a catalyst or 0.00259 min^{-1} with N-doped TiO_2 as a catalyst, which distinctly showed that $\text{Bi}_2\text{GaSbO}_7$ and $\text{Bi}_2\text{InSbO}_7$, with the highest and the second highest value of k_C , respectively, exhibited more excellent visible light photocatalytic activities for degrading MB compared with N-doped TiO_2 . Similarly, by a linear fit for the relationship between $\ln(\text{TOC}/\text{TOC}_0)$ and the irradiation time, the first-order rate constant k_{TOC} was estimated to be 0.00881 min^{-1} with $\text{Bi}_2\text{GaSbO}_7$ as a catalyst, 0.00745 min^{-1} with $\text{Bi}_2\text{InSbO}_7$ as a catalyst or 0.00239 min^{-1} with N-doped TiO_2 as a catalyst. The difference between k_C and k_{TOC} reflected that there might be some photodegradation intermediate products of MB which were produced during the photocatalytic degradation of MB under visible light irradiation.

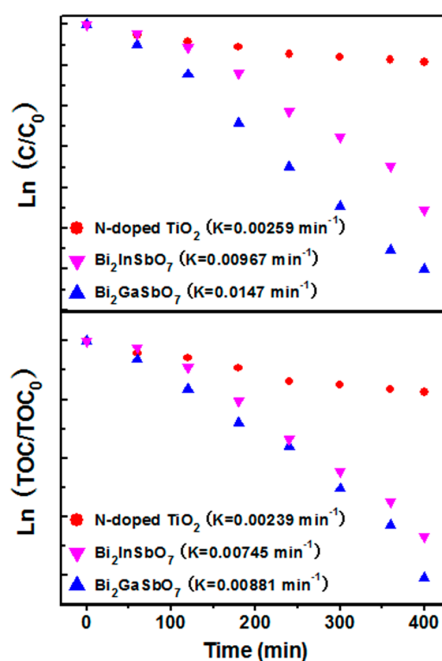


Figure 10. Observed first-order kinetic plots for the photocatalytic degradation of methylene blue with $\text{Bi}_2\text{GaSbO}_7$, $\text{Bi}_2\text{InSbO}_7$ or N-doped TiO_2 as a catalyst under visible light irradiation.

Figure 11 presents the photocatalytic degradation rate of phenol under visible light irradiation in the presence of $\text{Bi}_2\text{GaSbO}_7$, $\text{Bi}_2\text{InSbO}_7$ or N-doped TiO_2 as a photocatalyst with respect to time. It could be seen from Figure 11 that improved activity was obtained when colorless phenol was selected as a contaminant model with $\text{Bi}_2\text{GaSbO}_7$ or $\text{Bi}_2\text{InSbO}_7$ as a photocatalyst in comparison with the N-doped TiO_2 . The photocatalytic degradation efficiency of phenol by using $\text{Bi}_2\text{GaSbO}_7$, $\text{Bi}_2\text{InSbO}_7$ or N-doped TiO_2 as a photocatalyst under visible light irradiation after 400 min was estimated to be 75.00%, 69.76% or 47.08%, respectively, indicating that $\text{Bi}_2\text{GaSbO}_7$ or $\text{Bi}_2\text{InSbO}_7$ itself had photocatalytic activity and that the photodegradation process of MB by using $\text{Bi}_2\text{GaSbO}_7$ or $\text{Bi}_2\text{InSbO}_7$ as a photocatalyst was not mainly due to the photosensitive effect [73]. Moreover, we could observe that the photodegradation efficiency or apparent rate constant of phenol or MB in the presence of $\text{Bi}_2\text{GaSbO}_7$ or $\text{Bi}_2\text{InSbO}_7$ was much higher than that in the presence of N-doped TiO_2 , meaning that the visible-light photocatalytic activity of $\text{Bi}_2\text{GaSbO}_7$ or $\text{Bi}_2\text{InSbO}_7$ was higher than that of N-doped TiO_2 .

The specific surface area of $\text{Bi}_2\text{GaSbO}_7$ or $\text{Bi}_2\text{InSbO}_7$ was measured to be $2.36 \text{ m}^2 \cdot \text{g}^{-1}$ or $1.82 \text{ m}^2 \cdot \text{g}^{-1}$, which was much smaller than that of N-doped TiO_2 , whose specific surface area was $45.53 \text{ m}^2 \cdot \text{g}^{-1}$. Generally speaking, a larger specific surface area would facilitate higher photocatalytic activities at the same experimental condition [74,75]. However, according to preceding results and discussions, $\text{Bi}_2\text{GaSbO}_7$ and $\text{Bi}_2\text{InSbO}_7$ showed higher activities than N-doped TiO_2 for degrading MB

during visible light irradiation, which sufficiently highlighted the excellent photocatalytic properties of $\text{Bi}_2\text{GaSbO}_7$ and $\text{Bi}_2\text{InSbO}_7$, and the above results might ascribe to two explanations. Firstly, as already mentioned, the calculated band gap for $\text{Bi}_2\text{GaSbO}_7$, $\text{Bi}_2\text{InSbO}_7$ or N-doped TiO_2 was 2.59 eV, 2.54 eV or 2.78 eV. Apparently, $\text{Bi}_2\text{GaSbO}_7$ or $\text{Bi}_2\text{InSbO}_7$ possessed a narrower band gap than N-doped TiO_2 , meaning that $\text{Bi}_2\text{GaSbO}_7$ or $\text{Bi}_2\text{InSbO}_7$ could utilize more visible light energy than N-doped TiO_2 [76,77]. Secondly, according to the XRD results of $\text{Bi}_2\text{GaSbO}_7$ and $\text{Bi}_2\text{InSbO}_7$, we could find that $\text{Bi}_2\text{GaSbO}_7$ and $\text{Bi}_2\text{InSbO}_7$ were both obtained with high crystallization perfection, which might more efficiently inhibit the recombination of photoinduced electrons and holes than N-doped TiO_2 .

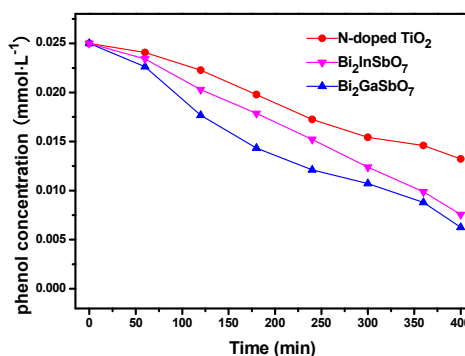


Figure 11. Photocatalytic degradation of phenol under visible light irradiation in the presence of $\text{Bi}_2\text{GaSbO}_7$, $\text{Bi}_2\text{InSbO}_7$ or N-doped TiO_2 as a photocatalyst.

Meanwhile, the photocatalytic degradation rate and photonic efficiency of $\text{Bi}_2\text{GaSbO}_7$ were slightly higher than that of $\text{Bi}_2\text{InSbO}_7$. There were perhaps two probable reasons to explain it. As we all know, the greater mobility of the photoinduced electrons and holes indicated the greater chance that the photoinduced electrons and holes would reach the reactive sites of the catalyst surface, which would bring higher photocatalytic activities. As we previously mentioned, the lattice parameter $a = 10.356497 \text{ \AA}$ for $\text{Bi}_2\text{GaSbO}_7$ was lower than the lattice parameter $a = 10.666031 \text{ \AA}$ for $\text{Bi}_2\text{InSbO}_7$. Generally speaking, the smaller the ionic radius was, the smaller the size of the particles could be; and the lower the lattice parameter was, the larger the specific surface area could be, which could increase more reactive sites on the photocatalyst surface and absorb more reactive species to improve the photocatalytic activities [78]. In addition, according to previous luminescent studies, the closer the M–O–M bond angle was to 180° , the more delocalized the excited state was [79]. As a result, the charge carriers could move easily in the matrix. In this experiment, for $\text{Bi}_2\text{GaSbO}_7$, the Ga–O–Ga bond angle was 131.302° ; accordingly, for $\text{Bi}_2\text{InSbO}_7$, the In–O–In bond angle was 128.640° . Obviously, the bond angle of the Ga–O–Ga bond angle of $\text{Bi}_2\text{GaSbO}_7$ was larger than the bond angle of $\text{Bi}_2\text{InSbO}_7$, which induced that $\text{Bi}_2\text{GaSbO}_7$ exhibited higher photocatalytic activity than $\text{Bi}_2\text{InSbO}_7$.

3.3. Photocatalytic Degradation Pathway of MB with $\text{Bi}_2\text{GaSbO}_7$ and $\text{Bi}_2\text{InSbO}_7$ as Photocatalysts

The photodegradation intermediate products of MB in our experiment were identified as azure A, azure C, thionine, phenothiazine, leucomethylene blue, *N,N*-dimethyl-*p*-phenylenediamine, benzenesulfonic acid, phenol and aniline. There generated holes h^+ , $\cdot\text{O}_2^-$ and $\cdot\text{OH}$ radicals, as oxidative agents in the photocatalytic reactions. According to previous studies [80,81], the photodegradation of MB might occur by demethylation. Besides, there were also reports [82] which pointed out that $\cdot\text{OH}$ radicals would first attack $\text{C} = \text{S}^+ = \text{C}$ functional group bonds to open the central aromatic ring which contained both heteroatoms S and N. Therefore, according to previous studies and our test results, a possible photocatalytic degradation pathway for MB was proposed. Figure 12 shows the suggested photocatalytic degradation pathway scheme for MB under visible light irradiation with $\text{Bi}_2\text{GaSbO}_7$ or $\text{Bi}_2\text{InSbO}_7$ as a catalyst. The MB molecule was converted to small organic species, which were subsequently mineralized into inorganic products such as SO_4^{2-} ions, NO_3^- ions, CO_2 and ultimately water.

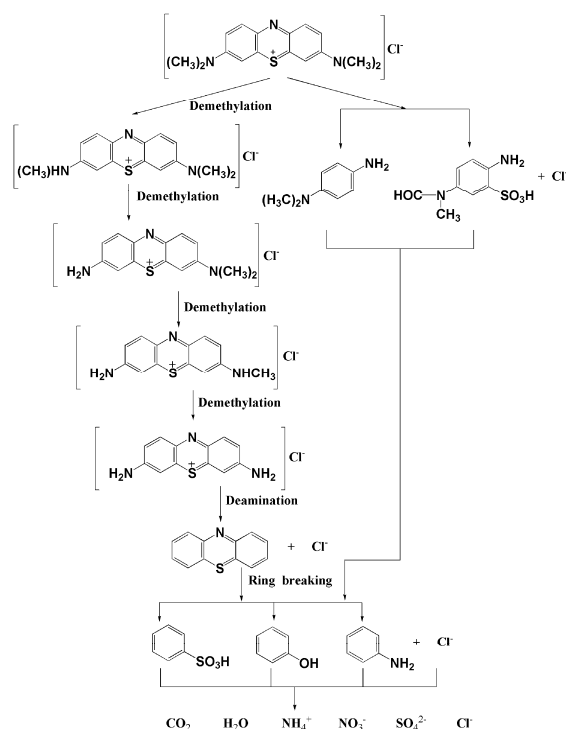


Figure 12. Suggested photocatalytic degradation pathway scheme for methylene blue under visible light irradiation in the presence of $\text{Bi}_2\text{GaSbO}_7$ or $\text{Bi}_2\text{InSbO}_7$.

3.4. Photocatalytic Degradation Mechanism

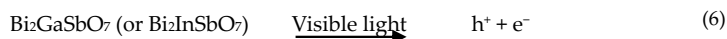
Figure 13 presents the action spectra of MB degradation with $\text{Bi}_2\text{GaSbO}_7$ or $\text{Bi}_2\text{InSbO}_7$ as a catalyst under visible light irradiation. A clear photonic efficiency (0.00964% for $\text{Bi}_2\text{GaSbO}_7$ and 0.00942% for $\text{Bi}_2\text{InSbO}_7$ at their respective maximal point) at wavelengths which corresponded to sub- E_g energies of the photocatalysts (λ from 480 to 700 nm for $\text{Bi}_2\text{GaSbO}_7$ and λ from 490 to 700 nm for $\text{Bi}_2\text{InSbO}_7$) was observed. The existence of photonic efficiency at this region revealed that the photons were not absorbed by the photocatalysts. Enlightened by the correlation between the low-energy action spectrum and the absorption spectrum of MB, we speculated that any photodegradation which results at wavelengths above 480 nm, should be attributed to photosensitization effect by the dye MB itself (Scheme 1). According to the photosensitization scheme, MB which was adsorbed on $\text{Bi}_2\text{GaSbO}_7$ or $\text{Bi}_2\text{InSbO}_7$ was excited by visible light irradiation. Subsequently, an electron was injected from the excited MB to the conduction band of $\text{Bi}_2\text{GaSbO}_7$ or $\text{Bi}_2\text{InSbO}_7$ where the electron was scavenged by molecular oxygen. This explained the results which were gained with $\text{Bi}_2\text{GaSbO}_7$ or $\text{Bi}_2\text{InSbO}_7$ as a catalyst under visible light irradiation, where the catalyst could serve to reduce recombination of photoinduced electrons and photoinduced holes by scavenging of electrons.



Scheme 1. The photosensitization effect by the dye MB.

The situation was different below 480 nm, where the photonic efficiency correlated well with the absorption spectra of $\text{Bi}_2\text{GaSbO}_7$ or $\text{Bi}_2\text{InSbO}_7$. This result evidently indicated that the mechanism

was the photodegradation of MB by the band gap excitation of $\text{Bi}_2\text{GaSbO}_7$ or $\text{Bi}_2\text{InSbO}_7$. As already mentioned, holes of h^+ , $\cdot\text{O}_2^-$ and $\text{OH}\cdot$ radicals served as oxidative agents in the photocatalytic reactions. Although the detailed experiments about the effect of oxygen and water on the degradation mechanism of MB were not performed, it was sensible to assume that the mechanism in the first step was similar to the observed mechanism for $\text{Bi}_2\text{GaSbO}_7$ or $\text{Bi}_2\text{InSbO}_7$ under supra-bandgap irradiation, and the production scheme of oxidative radicals commonly was shown below (Scheme 2).



Scheme 2. The production scheme of oxidative radicals with $\text{Bi}_2\text{GaSbO}_7$ or $\text{Bi}_2\text{InSbO}_7$ as catalyst.

Figure 14 shows the suggested band structures of $\text{Bi}_2\text{GaSbO}_7$ and $\text{Bi}_2\text{InSbO}_7$. The positions and width of the conduction band (CB) and the valence band (VB) were studied by calculating the electronic band structure of $\text{Bi}_2\text{GaSbO}_7$ or $\text{Bi}_2\text{InSbO}_7$ with the plane-wave-based density functional method. The band structure calculations of $\text{Bi}_2\text{GaSbO}_7$ and $\text{Bi}_2\text{InSbO}_7$ were carried out with the program of Cambridge serial total energy package (CASTEP) and first-principles simulation. It could be seen from Figure 14 that the conduction band of $\text{Bi}_2\text{GaSbO}_7$ was composed of Ga 4p and Sb 5p orbital component, meanwhile, the valence band of $\text{Bi}_2\text{GaSbO}_7$ was composed of a small dominant O 2p and Bi 6s orbital component. Similarly, the conduction band of $\text{Bi}_2\text{InSbO}_7$ was composed of In 5p and Sb 5p orbital component. In addition, the valence band of $\text{Bi}_2\text{InSbO}_7$ was composed of a small dominant O 2p and Bi 6s orbital component. Direct absorption of photons by $\text{Bi}_2\text{GaSbO}_7$ or $\text{Bi}_2\text{InSbO}_7$ could produce electron–hole pairs within the catalyst, indicating that the larger energy than the band gap of $\text{Bi}_2\text{GaSbO}_7$ or $\text{Bi}_2\text{InSbO}_7$ was necessary for decomposing MB by the photocatalysis method.

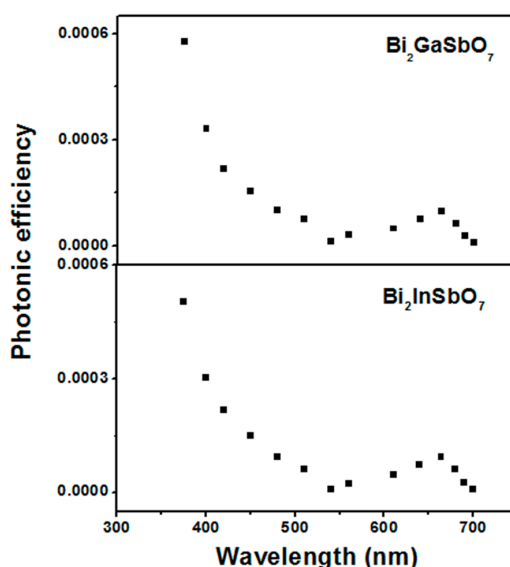


Figure 13. Action spectra of methylene blue degradation with $\text{Bi}_2\text{GaSbO}_7$ or $\text{Bi}_2\text{InSbO}_7$ as a catalyst under visible light irradiation.

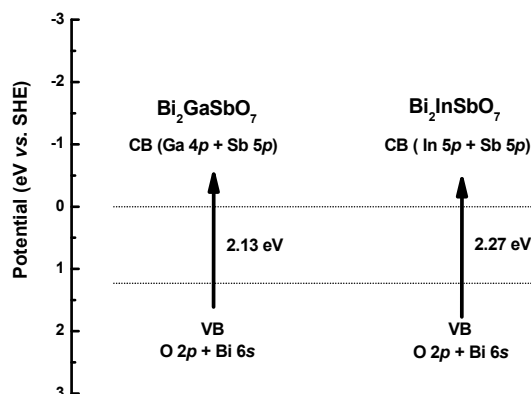


Figure 14. Suggested band structures of $\text{Bi}_2\text{GaSbO}_7$ and $\text{Bi}_2\text{InSbO}_7$.

4. Conclusions

New photocatalysts $\text{Bi}_2\text{GaSbO}_7$ and $\text{Bi}_2\text{InSbO}_7$ were firstly prepared by the solid-state reaction method. The structural properties and optical absorption properties of $\text{Bi}_2\text{GaSbO}_7$ and $\text{Bi}_2\text{InSbO}_7$ were characterized by some material characterization methods, the photocatalytic properties of $\text{Bi}_2\text{GaSbO}_7$ and $\text{Bi}_2\text{InSbO}_7$ were also verified in comparison with N-doped TiO_2 . XRD results indicated that $\text{Bi}_2\text{GaSbO}_7$ and $\text{Bi}_2\text{InSbO}_7$ crystallized with the pyrochlore-type structure, cubic crystal system and space group $Fd3m$. The lattice parameter a for $\text{Bi}_2\text{GaSbO}_7$ or $\text{Bi}_2\text{InSbO}_7$ was $a = 10.356497 \text{ \AA}$ or $a = 10.666031 \text{ \AA}$. According to the results from the UV-vis absorption spectra of $\text{Bi}_2\text{GaSbO}_7$ and $\text{Bi}_2\text{InSbO}_7$, the band gap of $\text{Bi}_2\text{GaSbO}_7$ or $\text{Bi}_2\text{InSbO}_7$ was estimated to be about 2.59 eV or 2.54 eV, indicating that $\text{Bi}_2\text{GaSbO}_7$ and $\text{Bi}_2\text{InSbO}_7$ showed a strong optical absorption in the visible light region ($\lambda > 420 \text{ nm}$). Photocatalytic degradation of aqueous MB was realized under visible light irradiation in the presence of $\text{Bi}_2\text{GaSbO}_7$ or $\text{Bi}_2\text{InSbO}_7$ accompanied with the formation of final products such as CO_2 and water. The complete removal of organic carbon from MB was obtained as indicated from TOC and CO_2 yield measurements with $\text{Bi}_2\text{GaSbO}_7$ or $\text{Bi}_2\text{InSbO}_7$ as a catalyst under visible light irradiation. Compared with N-doped TiO_2 , $\text{Bi}_2\text{GaSbO}_7$ and $\text{Bi}_2\text{InSbO}_7$ exhibited higher photocatalytic activities for MB degradation under visible light irradiation. Consequently, according to the above analyses, $\text{Bi}_2\text{GaSbO}_7$ and $\text{Bi}_2\text{InSbO}_7$ both had great potential to degrade MB in textile industry wastewater. In addition, $\text{Bi}_2\text{GaSbO}_7$ exhibited slightly higher photocatalytic activities for the degradation of MB than $\text{Bi}_2\text{InSbO}_7$.

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Author Contributions: Jingfei Luan were involved with all aspects of the study including conceiving, designing, data interpretation and writing the manuscript. Yue Shen, Yanyan Li and Yaron Paz performed the experiments and analyzed data. Jingfei Luan, Yue Shen and Yanyan Li wrote the paper. All authors read and approved the manuscript.

Conflicts of Interest: The authors declare no conflict of interest.

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