Structural, photophysical and photocatalytic properties of new Bi$_2$SbVO$_7$ under visible light irradiation

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Bi$_2$SbVO$_7$ was prepared by solid-state reaction technique for the first time and the structural and photocatalytic properties of Bi$_2$SbVO$_7$ and Bi$_2$GaTaO$_7$ were investigated. The results showed that Bi$_2$SbVO$_7$ crystallized with the tetragonal crystal system by space group $I4/mmm$. In addition, the band gaps of Bi$_2$SbVO$_7$ and Bi$_2$GaTaO$_7$ were estimated to be 2.33 and 2.52 eV. The photocatalytic degradation of aqueous methylene blue (MB) dye over Bi$_2$SbVO$_7$ and Bi$_2$GaTaO$_7$ was investigated under visible light irradiation. Bi$_2$SbVO$_7$ showed higher catalytic activity compared with Bi$_2$GaTaO$_7$ for MB photocatalytic degradation under visible light irradiation. The photocatalytic MB degradation followed first-order reaction kinetics, the apparent first-order rate constant $k$ being 0.0262 and 0.0060 min$^{-1}$ with Bi$_2$SbVO$_7$ and Bi$_2$GaTaO$_7$, respectively. Complete removal of aqueous MB was realized after visible light irradiation for 210 min with Bi$_2$SbVO$_7$ as a catalyst. The reduction of the total organic carbon (TOC), the formation of inorganic products (SO$_4^{2-}$ and NO$_3^-$) and the evolution of CO$_2$ revealed complete removal of aqueous MB during the photocatalytic process by this novel photocatalyst.

1. Introduction

Semiconductor photocatalysts have attracted extensive attention from both academic and industrial organizations since the first manuscript of Honda and Fujishima in 1972, where electrochemical photolysis of water at a semiconductor electrode was reported. Recently, some photocatalysts with different structures have been prepared to investigate the effective utilization of solar energy. In particular, many scientific investigations on the photocatalytic degradation of aqueous organic contaminants have been reported. Methylene blue (MB) dye is often used as a probe contaminant to evaluate the activity of a photocatalyst owing to its high stability against degradation in the natural environment, both under ultraviolet light and under visible light. Within the context of visible light photodegradation of MB one may outline the work of Asahi et al. utilizing N-doped titanium dioxide, the work of Wang and Min utilizing nanocrystalline TiO$_2$/polymiline, and the work of Zhao et al. who used surface-fluorinated TiO$_2$.

Visible light photodegradation phenomena are not limited to titanium dioxide. In fact other oxides, and in particular mixed oxides such as A$_2$B$_2$O$_7$ compounds, are often considered to have photocatalytic properties. Of particular interest are vanadium oxide-based catalysts where the photocatalytic degradation of organic pollutants was as observed by Weckhuysen and Keller. In our previous work, we have found that Bi$_2$GaTaO$_7$ crystallizes with the pyrochlore-type structure, acts as a photocatalyst under ultraviolet light irradiation and seems to have potential for activity improvement upon modification of its structure. Along this line, it can be postulated that substitution of Ga$^{3+}$ by Sb$^{3+}$ and substitution of Ta$^{5+}$ by V$^{5+}$ in this compound may lead to an increase in carrier concentration; this may result in improved photocatalytic properties.

Bi$_2$SbVO$_7$ is a material that was never synthesized before. The similarity between the molecular composition of this material and other A$_2$B$_2$O$_7$ compounds suggests that this material may possess photocatalytic properties under visible light, similar to those of other members of the family. This contribution reports on the preparation and characterization of Bi$_2$SbVO$_7$ and Bi$_2$GaTaO$_7$. The structural, photophysical and photocatalytic properties of Bi$_2$SbVO$_7$ and Bi$_2$GaTaO$_7$ were investigated in detail. A comparison between the photocatalytic properties of Bi$_2$SbVO$_7$ and those of Bi$_2$GaTaO$_7$ was done in order to elucidate the structure–photocatalytic activity relationship in this newly synthesized material.

2. Experimental

The novel photocatalysts were synthesized by a solid-state reaction method. Sb$_2$O$_3$, Ga$_2$O$_3$, Bi$_2$O$_3$, V$_2$O$_5$ and Ta$_2$O$_5$ with...
purities of 99.99% (Sinopharm Group Chemical Reagent Co., Ltd, Shanghai, China) were used as starting materials. All powders were dried at 200 °C for 4 h before synthesis was performed. In order to synthesize Bi₂SbVO₇, the precursors were stoichiometrically mixed, then pressed into small columns and put into an alumina crucible (Shenyang Crucible Co., LTD, China). Finally, calcination was carried out at 750 °C for 46 h in an electric furnace (KSL 1700X, Hefei Kejing Materials Technology Co. Ltd, China). Similarly, Bi₂GaTaO₇ was prepared by calcination at 1100 °C for 52 h. The crystal structures of Bi₂SbVO₇ and Bi₂GaTaO₇ were analyzed by the powder X-ray diffraction method (D/MAX-RB, Rigaku Corporation, Japan) with Cu Kα radiation ($\lambda = 1.54056$ nm). The data were collected at 295 K with a step-scan procedure in the range of $2\theta = 5 – 100^\circ$. The step interval was 0.02° and the time per step was 1.2 s. The chemical composition of the compound was determined by scanning electron microscope-X-ray energy dispersion spectrum (SEM-EDS), LEO 1530VP, LEO Corporation, Germany) and X-ray fluorescence spectrometer (XFS, ARL-9800, ARL Corporation, Switzerland). The oxygen content, Bi³⁺ content and V⁵⁺ content of Bi₂SbVO₇ were determined by X-ray photoelectron spectroscopy (XPS, ESCALAB MK-2, VG Scientific Ltd., UK). The chemical composition within the depth profile of Bi₂SbVO₇ was examined by the argon ion denudation method when X-ray photoelectron spectroscopy was used. The optical absorption of Bi₂SbVO₇ and Bi₂GaTaO₇ was analyzed with a UV-visible spectrophotometer (Lambda 35, Perkin-Elmer Corporation, USA). The surface areas were measured by the Brunauer–Emmet–Teller (BET) method (MS-21, Quantachrome Instruments Corporation, USA) with N₂ adsorption at liquid nitrogen temperature. The particle sizes of the photocatalysts were measured by Malvern’s Mastersizer-2000 particle size analyzer (Malvern Instruments Ltd, United Kingdom).

The photocatalytic degradation of aqueous methylene blue (MB) (Tianjin Kermel Chemical Reagent Co., Ltd) was performed with 0.3 g Bi₂SbVO₇ or Bi₂GaTaO₇ powder suspended in 100 ml 0.0506 × 10⁻³ M methylene blue solution in a pyrex glass cell (Jiangsu Yancheng Huaou Industry, China). The photocatalytic reaction system consisted of a 300 W Xe arc lamp with the main emission wavelength at 436 nm (Nanjing JYZCPST CO., LTD), a magnetic stirrer and a cut-off filter ($\lambda > 400$ nm, Jiangsu Nantong JSOL Corporation, China). The Xe arc lamp was surrounded by a quartz jacket and was positioned within the inner part of a photoreactor quartz vessel (5.8 cm in diameter and 68 cm in length), through which a suspension of methylene blue and photocatalyst was circulated. An outer recycling water glass jacket maintained a near constant reaction temperature (22 °C), and the solution was continuously stirred and aerated. 2 ml aliquots were sampled at various time intervals. The incident photon flux $I_o$ measured by a radiometer (Model FZ-A, Photoelectric Instrument Factory Beijing Normal University, China) was determined to be $4.76 \times 10^{-6}$ Einstein L⁻¹ s⁻¹ under visible light irradiation (wavelength range of 400–700 nm), and $6.01 \times 10^{-6}$ Einstein L⁻¹ s⁻¹ under ultraviolet light irradiation. The incident photon flux on the photoreactor was varied by adjusting the distance between the photoreactor and the Xe arc lamp. No pH adjustment was done and the initial pH value was 7.0. The concentration of MB was determined based on the absorption at 664 nm as measured by a UV-Vis spectrophotometer (Lambda 40, Perkin-Elmer Corporation, USA). The inorganic products obtained from MB degradation were analyzed by ion chromatograph (DX-300, Dionex Corporation, USA). The identification of MB and its degradation intermediate products were performed by gas chromatograph-mass spectrometer (GC-MS) (HP 6890 Series Gas Chromatograph (ATM column, 20.3 m × 0.32 mm, ID of 0.25 μm) operating at 320 °C, connected to HP 5973 Mass Selective Detector, and to a Flame Ionization Detector with H₂ as the carrier gas. Intermediate products were measured by liquid chromatograph-mass spectrometer (LC-MS) (Thermo Quest LCQ Duo, USA, Beta Basic-C₁₈ HPLC column: 150 × 2.1 mm, ID of 5 μm, Finnigan, Thermo, USA). Here, 20 μL of post-photocatalysis solution was injected automatically into the LC-MS system. The eluent contained 60% methanol and 40% water, and the flow rate was 0.2 ml min⁻¹. MS conditions included of an electrospray ionization interface, a capillary temperature of 27 °C with a voltage of 19.00 V and 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 CO₂ was analyzed with an intersmat™ IGC120-MB gas chromatograph equipped with a porapack Q column (3 m in length and an inner diameter of 0.25 in.), connected to a catharometer detector. The total organic carbon (TOC) concentration was determined with a TOC analyzer (TOC-5000, Shimadzu Corporation, Japan). The photonic efficiency was calculated according to the following equation:55,56

$$\varphi = R/I_o$$

where $\varphi$ is the photonic efficiency (%), $R$ is the rate of MB degradation (mol L⁻¹ s⁻¹), and $I_o$ is the incident photon flux (Einstein L⁻¹ s⁻¹).

3. Results and discussion

3A Characterization

Fig. 1 presents a SEM image of Bi₂SbVO₇, revealing elongated rectangular shapes, having 1–3 μm in length and 0.3–0.7 μm in the other dimensions. These shapes seem to be covered by smaller particles, having a typical dimension of 0.1–0.4 μm. Some of these smaller particles showed a cubic-like symmetry, while others had no specific shape. The SEM-EDS spectrum taken from the prepared Bi₂SbVO₇ indicated, as expected, the presence of bismuth, oxygen, vanadium and antimony. No other elements could be identified.

Fig. 2 presents the powder X-ray diffraction pattern of Bi₂SbVO₇ together with full-profile structure refinement of the collected data as obtained by the REITAN™ 57 program, which is based on Rietveld analysis. The result of the final refinement for Bi₂SbVO₇ indicated a good agreement between the observed and calculated intensities for a tetragonal crystal system having a $I4/mnm$ space group (O atoms were included in the model). The lattice parameters were found to be
\[ a = 3.9068(1), \quad b = 3.9068(1), \quad c = 15.4385(7) \, \text{Å} \]. All the diffraction peaks for Bi\(_2\)SbVO\(_7\) could be successfully indexed based on the lattice constant and above space group. The atomic coordinates and structural parameters of Bi\(_2\)SbVO\(_7\) are listed in Table 1. It is noteworthy that the measured peaks could not be matched with other crystals containing Bi, V, O, Sb such as Bi\(_3\).2Sb\(_0.8\)V\(_2\)O\(_{10}\), Bi\(_4\)Sb\(_0.8\)V\(_{1.2}\)O\(_{11}\), Bi\(_4\)Sb\(_{0.5}\)V\(_{1.5}\)O\(_{10.7}\), and Bi\(_{1.86}\)Sb\(_{0.09}\)V\(_{0.84}\)O\(_{5.02}\) described in ref. 58, 59 and 60. This suggests that our samples contained only one crystalline phase (Bi\(_2\)SbVO\(_7\)), although the presence of minute amounts of amorphous phase cannot be excluded.

The final refinement procedure was applied also to the homolog Bi\(_2\)GaTaO\(_7\) produced by the same technique. Here, the unweighted and weighted \( R \) factors were \( R_P = 9.27\% \) and \( R_{WP} = 14.22\% \), respectively, indicating a cubic, pyrochlore-type crystal structure, having \( Fd\bar{3}m \) space group (O atoms included in the model) and a lattice parameter of \( a = 10.4516(5) \, \text{Å} \).

Our X-ray diffraction results showed that Bi\(_2\)SbVO\(_7\) and Bi\(_2\)GaTaO\(_7\) crystallized in a different structure. The cubic system structure with space group \( Fd\bar{3}m \) for Bi\(_2\)GaTaO\(_7\) turned into a tetragonal system structure with space group \( I\bar{4}/mmm \) using Ta\(^{5+}\) being substituted by V\(^{5+}\) and Ga\(^{3+}\) being substituted by Sb\(^{3+}\). The outcome of refinements for Bi\(_2\)SbVO\(_7\) generated the unweighted \( R \) factors, \( R_P = 12.32\% \) with space group \( I\bar{4}/mmm \). Zou et al.\(^{15}\) refined the crystal structure of Bi\(_2\)InNbO\(_7\) and obtained a large \( R \) factor for Bi\(_2\)InNbO\(_7\), which was due to a slightly modified structure model for Bi\(_2\)InNbO\(_7\). Based on the high purity of the precursors that were used in this study and the EDS results that did not trace any other elements, it is unlikely that the observed space groups originated from the presence of impurities. Therefore, it is suggested that the slightly high \( R \) factors for Bi\(_2\)SbVO\(_7\) were due to a slightly modified structure model for Bi\(_2\)SbVO\(_7\). It should be emphasized that the defects or the disorder/order of a fraction of the atoms could result in the change of structures, including different bond-distance distributions, thermal displacement parameters and/or occupation factors for some of the atoms.

The XPS spectra of Bi\(_2\)SbVO\(_7\) and its precursors Sb\(_2\)O\(_3\), V\(_2\)O\(_5\) and Bi\(_2\)O\(_3\) were measured. The various elemental peaks corresponding to specific binding energies are given in Table 2. The results for Bi\(_2\)SbVO\(_7\) showed that the V 2p\(_{3/2}\) binding energy changed from 517.70 to 516.75 eV, the Bi 4f\(_{7/2}\) binding energy changed from 159.80 to 158.80 eV and the Sb 3d\(_{3/2}\) binding energy changed from 539.50 to 539.70 eV after Bi\(_2\)SbVO\(_7\) was produced from its precursors. The results further suggest that the oxidation state of Bi, Sb, V, and O ions are +3, +3, +5 and +1/2, respectively. The average atomic ratios for Bi: Sb: V: O, based on averaging our XPS, SEM-EDS and XFS results gave values of 2.00: 0.99: 1.01: 6.97, respectively. Hence, it could be deduced that the resulting material was of high purity under our preparation conditions. Table 2 also presents the XPS measurements taken with Bi\(_2\)GaTaO\(_7\) and its precursors Ga\(_2\)O\(_3\), Ta\(_2\)O\(_5\) and Bi\(_2\)O\(_3\). As shown in the Table, the Ga 2p\(_{3/2}\) binding energy changed from 1116.90 to 1117.85 eV, the Bi 4f\(_{7/2}\) binding energy changed from 159.80 to 158.70 eV, and that of Ta 4f\(_{7/2}\) changed from 26.90 to 25.35 eV once Bi\(_2\)GaTaO\(_7\) was produced, indicating the formation of a new phase.

It is noteworthy that neither shoulders nor widening of any of the Bi\(_2\)SbVO\(_7\) and Bi\(_2\)GaTaO\(_7\) XPS peaks were observed, suggesting (albeit not proving) the absence of any other phases.

Fig. 3 presents the absorption spectra of Bi\(_2\)SbVO\(_7\) and Bi\(_2\)GaTaO\(_7\). In contrast to the well-known TiO\(_2\) whose absorption edge is at less than 380 nm, the newly synthesized absorption edge of Bi\(_2\)SbVO\(_7\) was found to be at 518 nm, i.e. at the visible region of the spectrum. Likewise, the absorption

![Fig. 1 SEM image of Bi\(_2\)SbVO\(_7\).](image1)

![Fig. 2 X-Ray powder diffraction patterns and Rietveld refinement of Bi\(_2\)SbVO\(_7\) prepared by a solid-state reaction method at 750 °C. A difference (observed – calculated) profile is shown beneath. The tick marks represent reflection positions.](image2)

![Table 1 Structural parameters of Bi\(_2\)SbVO\(_7\) prepared by solid-state reaction method](table1)
edge of Bi$_2$GaTaO$_7$ was found to be also in the visible region (475 nm). It is noteworthy that the apparent absorption (defined hereby as 1-transmission) cannot take into consideration reflection and scattering. As a consequence, the apparent absorbance at sub-bandgap wavelengths (550 to 800 nm for Bi$_2$SbVO$_7$, and 560 to 800 nm for Bi$_2$GaTaO$_7$) was higher than zero.

For a crystalline semiconductor, the optical absorption near the band edge followed the equation:

\[ a(hn) = A\left(\frac{hn}{E_g}\right)^n. \]

Here, $A$, $a$, $E_g$, and $n$ are the proportionality constant, absorption coefficient, band gap and light frequency respectively. Within this equation, $n$ determines the character of the transition in a semiconductor. $E_g$ and $n$ can be calculated by the following steps: (i) plotting $\ln(a(hn))$ versus $\ln(hn/E_g)$ assuming an approximate value of $E_g$; (ii) deducing the value of $n$ based on the slope in this graph; (iii) refining the value of $E_g$ by plotting $(a(hn))^{1/n}$ versus $hn$ and extrapolating the plot to $(a(hn))^{1/n} = 0$. Based on the above-mentioned method, the value of $E_g$ for Bi$_2$SbVO$_7$ and Bi$_2$GaTaO$_7$ was calculated to be 2.33 and 2.52 eV, respectively, while the $n$ values were calculated to be 0.52 and 0.59, respectively, indicating that the optical transition for these oxides was directly allowed.

### 3B Photocatalytic activity

In general, the process for photocatalysis by semiconductors begins with the direct absorption of supra-bandgap photons and the generation of electron–hole pairs in the semiconductor particles. This is followed by diffusion of the charge carriers to the surface of the particle. Changes in the UV-Vis spectrum of methylene blue (MB) upon exposure to visible light ($\lambda > 400$ nm) in the presence of Bi$_2$SbVO$_7$ or Bi$_2$GaTaO$_7$ are presented in Fig. 4A and B, respectively. The measurements were performed under oxygen-saturation conditions ([O$_2$]$_{sat} = 1.02 \times 10^{-3}$ M). As presented in the Figure a reduction in typical MB peaks at 664 and 613 nm is clearly noticed. A complete disappearance of the absorption signal, indicating a complete color change from deep blue into colorless solution was obtained with Bi$_2$SbVO$_7$ within less than 200 min. Here, the initial rate of MB degradation was about $4.22 \times 10^{-6}$ mol s$^{-1}$ m$^{-3}$ and the initial photonic efficiency was estimated to be 0.117% ($\lambda = 420$ nm) for Bi$_2$SbVO$_7$. In addition, the photodegradation conversion of MB was 94.2% after visible light irradiation for 120 min with Bi$_2$SbVO$_7$ as a catalyst. For comparison, MB photodegradation measured by us with fluorinated titanium dioxide made according to the scheme published by ref. 53 yielded, under the same experimental conditions, no more than 75% of removal.

The kinetics of MB degradation under visible light irradiation was deduced based on the spectral changes and is presented in Fig. 5, which depicts the kinetics not only with Bi$_2$SbVO$_7$ and Bi$_2$GaTaO$_7$ but also with TiO$_2$. As expected, reduction in MB signal in the presence of TiO$_2$ was exactly the same as that of the control measurements, taken in the absence of a photocatalyst. In contrast, fast degradation was observed with the two A$_2$B$_2$O$_7$ compounds.

The first-order nature of the photocatalytic degradation kinetics with the two A$_2$B$_2$O$_7$ compounds is clearly demonstrated in Fig. 6, which presents a linear correlation ($R^2 > 0.99$) between $\ln(C/C_0)$ and the irradiation time for the

### Table 2

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Bi$_{47/2}$ BE/eV</th>
<th>Sb$_{43/2}$ BE/eV</th>
<th>V$_{43/2}$ BE/eV</th>
<th>Ga$_{4d}$ BE/eV</th>
<th>Ga$_{2p3/2}$ BE/eV</th>
<th>Ta$_{4d7/2}$ BE/eV</th>
<th>O$_{1s}$ BE/eV</th>
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<tr>
<td>Bi$_2$SbVO$_7$</td>
<td>158.80</td>
<td>539.70</td>
<td>516.75</td>
<td>18.95</td>
<td>1117.85</td>
<td>25.35</td>
<td>529.95</td>
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<tr>
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<td>517.70</td>
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<td>1116.90</td>
<td>26.90</td>
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<td>20.20</td>
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Photocatalytic MB degradation at the presence of Bi$_2$SbVO$_7$ or Bi$_2$GaTaO$_7$. Here, $C$ represents the MB concentration at time $t$ and $C_0$ represents the initial MB concentration. The apparent first-order rate constant $k$ was estimated as $0.0262$ min$^{-1}/C_0$ with Bi$_2$SbVO$_7$ and $0.0060$ min$^{-1}/C_0$ with Bi$_2$GaTaO$_7$, indicating that Bi$_2$SbVO$_7$ is more suitable than Bi$_2$GaTaO$_7$ for the photocatalytic degradation of MB under visible light irradiation.

As expected, Bi$_2$SbVO$_7$ serves as a photocatalyst not only under visible light irradiation but also under ultraviolet light irradiation (Fig. 7). The results reflect a complete color change from deep blue to colorless (i.e. to a MB concentration in the order of 0 M) within 60 min of ultraviolet light irradiation. The initial rate of MB degradation was about $1.39 \times 10^{-5}$ mol s$^{-1}$ m$^{-3}$ and the initial photonic efficiency was estimated to be 0.231%. Hence, based on the fact that the same amounts (by weight) were used, it can be concluded that within the experimental conditions of this measurement the photocatalytic properties of Bi$_2$SbVO$_7$ in degrading MB under ultraviolet light irradiation were not only better than those of Bi$_2$GaTaO$_7$ but in fact were found to be similar to those of titanium dioxide, known to be the photocatalyst of choice under ultraviolet light irradiation.

The photodegradation intermediates of MB in our experiment were identified as azure B, azure A, azure C, N,N-dimethyl-p-phenylenediamine, thionine, phenothiazine, benzenesulfonic acid, phenol and aniline. Based on the intermediate products found in this work, a possible photocatalytic degradation pathway for MB is proposed in Fig. 8. This pathway is similar, but not identical, to the one proposed by Houas et al. for the photodegradation of MB under ultraviolet light irradiation using TiO$_2$ as the photocatalyst.

The methyl groups were converted to smaller organic species and ultimately were mineralized together with other organic groups to form inorganic products (CO$_2$ and water). The CO$_2$ yield during the photocatalytic degradation of MB with Bi$_2$SbVO$_7$ or Bi$_2$GaTaO$_7$ under ultraviolet light irradiation. The results show that the CO$_2$ yield increased gradually with increasing reaction time with both photocatalysts. The CO$_2$ production rate with Bi$_2$SbVO$_7$ was higher than the CO$_2$ yield with Bi$_2$GaTaO$_7$, in line with the absorption curves (Fig. 3) of the two photocatalysts. For example, the CO$_2$ production following visible light irradiation for 200 min was 0.08042 mmol with Bi$_2$SbVO$_7$ and 0.05689 mmol with Bi$_2$GaTaO$_7$.

Total organic carbon (TOC) measurements (Fig. 10) revealed total disappearance of organic carbon within 210 min of exposure of a solution containing Bi$_2$SbVO$_7$. This was not the case with Bi$_2$GaTaO$_7$, where the mineralization after 210 min of exposure was approximately 70%. The turnover numbers (the ratio between total amount of gas evolved and catalyst that was used) after 24 h of reaction time under visible light irradiation was calculated to be (under the experimental
conditions) more than 1.32 and 1.05 for Bi$_2$SbVO$_7$ and Bi$_2$GaTaO$_7$, respectively. The turnover number in terms of reacted electrons relative to the amount of Bi$_2$SbVO$_7$ reached 1 after 18 h of reaction time. This turnover number is enough to prove that the reaction occurred catalytically. The reaction stopped when the light was turned off in this experiment, showing the obvious light response.

Other inorganic ions such as NH$_4^+$, NO$_3^-$ and SO$_4^{2-}$ were formed in parallel as the end products of nitrogen and sulfur atoms existing in MB. Monitoring the presence of ions in the

![Fig. 8](image_url)  
**Fig. 8** Suggested photocatalytic degradation pathway scheme for MB under visible light irradiation in the presence of Bi$_2$SbVO$_7$ and Bi$_2$GaTaO$_7$.

![Fig. 9](image_url)  
**Fig. 9** CO$_2$ production kinetics during the photocatalytic degradation of MB with Bi$_2$SbVO$_7$ (filled circles) and Bi$_2$GaTaO$_7$ (empty stars) under visible light irradiation.

![Fig. 10](image_url)  
**Fig. 10** Disappearance of total organic carbon (TOC) during the visible light photocatalytic degradation of MB with Bi$_2$SbVO$_7$ (filled circles) and Bi$_2$GaTaO$_7$ (empty stars).
solution revealed that at the end of the process (200 min exposure time) the SO₄²⁻ ion concentration was as high as 0.0424 × 10⁻³ M, indicating that 83.8% of sulfur from MB was converted into sulfate ions. In parallel, the NO₃⁻ ion concentration at that point was found to be 0.1516 × 10⁻³ M. The sulfur was first hydrolytically removed, and subsequently was oxidized and transformed into SO₄²⁻. At the same time, nitrogen atoms in the −3 oxidation state produced NH₄⁺ cations that subsequently were oxidized into NO₃⁻ ions. Fig. 11 presents the kinetics of NO₃⁻ and SO₄²⁻ production with the two photocatalysts. As expected, the formation kinetics with Bi₂SbVO₇ was significantly faster than that of Bi₂GaTaO₇. For example, the amount of SO₄²⁻ ions released into the solution was lower than that expected from stoichiometry. One possible reason can be a loss of sulfur-containing volatile compounds such as SO₂. A second possible explanation is a partially irreversible adsorption of some SO₄²⁻ ions on the surface of the photocatalyst as already observed by Lachheb et al. for titanium dioxide. Regardless whether the sulfate ions were adsorbed irreversibly on the surface or not, it is important to stress that no evidence for restrained photocatalytic activity was noticed. In contrast to the sulfate ions, the amount of nitrate ions at the end of the process was found to follow the expected stoichiometric ratio of three.

As mentioned before, the photocatalytic efficiency with Bi₂GaTaO₇ was inferior to that with Bi₂SbVO₇. For example, within 200 min of exposure to the visible light, the MB concentration decreased only from 0.051 × 10⁻³ M to 0.015 × 10⁻³ M and the initial rate of MB degradation was no more than 2.97 × 10⁻⁶ mol s⁻¹ m⁻³. The initial photonic efficiency was estimated to be 0.062% (λ = 420 nm) for Bi₂GaTaO₇. At the same time, a SO₄²⁻ ion concentration of 0.031 × 10⁻³ M and a NO₃⁻ ion concentration of 0.107 × 10⁻³ M were detected in the solution, indicating that 87.0% of the MB sulfur was turned into sulfate ions.

The photocatalytic performance of the two A₂B₂O₇ compounds and in particular the new compound Bi₂SbVO₇, under both ultraviolet light irradiation and visible light irradiation is remarkable. This superior quality can be even more appreciated if one considers the fact that the specific surface area of these compounds is by far smaller than that of titanium dioxide. Here, BET isotherm measurements of the two compounds gave a specific surface area of 1.11 m² g⁻¹ and 1.23 m² g⁻¹ for Bi₂SbVO₇ and Bi₂GaTaO₇, respectively, which is almost 40 times smaller than that of TiO₂, measured to be 46.24 m² g⁻¹.

As depicted in Fig. 5, some decrease in the MB visible light absorbance signal was obtained under visible light irradiation even in the absence of a photocatalyst. Here, the initial rate of MB degradation was estimated as 1.22 × 10⁻⁶ mol s⁻¹ m⁻³ and the photonic efficiency averaged after 200 min of exposure was 0.026% (λ = 420 nm). Similar results were obtained in the presence of titanium dioxide, demonstrating the well-known fact that titanium dioxide is practically inactive under visible light irradiation. It is suggested that the observed disappearance of MB in the absence of a photocatalyst, and in the presence of TiO₂ was due to direct dye-sensitization, similar to the observation of Zhao et al. regarding alizarin red and X3B dyes. For the case of MB, it was evidenced that this sensitization process does not go beyond the first step, since no SO₄²⁻ ions could be detected at the end of the exposure time.

Fig. 12 shows the action spectra of MB degradation in the presence of Bi₂SbVO₇ and Bi₂GaTaO₇ under visible light irradiation. A clear photonic efficiency (0.063% at its maximal point) at wavelengths which correspond to sub-Eg energies of the photocatalysts (λ from 518 to 700 nm) is observed for the two. The existence of photonic efficiency at energies where no photons are absorbed by the photocatalysts, and in particular the correlation between the low-energy action spectrum and the absorption spectrum of MB, clearly demonstrate that any photodegradation at wavelengths above 518 nm should be attributed to photosensitization by the dye itself (Scheme 1).
According to this mechanism, MB adsorbed on Bi$_2$SbVO$_7$ is excited by visible light irradiation. An electron is then injected from the excited MB to the conduction band of Bi$_2$SbVO$_7$ where the electron is scavenged by molecular oxygen. A similar scheme (Scheme 2) serves to explain the results obtained with titanium dioxide under visible light, where the TiO$_2$ may serve at most to reduce recombination via the scavenging of electrons.\(^{65}\)

The situation is different below 500 nm, where the photonic efficiency correlates well with the absorption spectra of the two photocatalysts. This evidently shows that the mechanism responsible for the photodegradation of MB goes through the band gap excitation of the two A$_2$B$_2$O$_7$ compounds. Although detailed experiments on the effect of oxygen and water on the degradation scheme were not performed, it is sensible to assume that the mechanism in the first steps is similar to the one observed for titanium dioxide under supra-band gap irradiation, namely (Scheme 3):

Previous luminescence studies have shown that the closer the M–O–M bond angle is to 180°, the more delocalized is the excited state,\(^{66}\) and the more easily the charge carriers can move in the matrix. The mobility of the photoinduced electrons and holes influences the photocatalytic activity since high diffusivity increases the probability that the photo-generated electrons and holes will reach reactive sites on the catalyst surface. In this experiment, the Sb–O–V bond angle was nearly 180° and the photocatalytic activities of Bi$_2$SbVO$_7$ was accordingly higher. The crystal structures of Bi$_2$SbVO$_7$ and Bi$_2$GaTaO$_7$ were different, and their electronic structures were also considered to be different. For Bi$_2$SbVO$_7$, V was a 3d-block metal element, and for Bi$_2$GaTaO$_7$, Ta was a 5d-block metal element, indicating that the photocatalytic activity might be affected by not only the crystal structure but also the electronic structure of the photocatalysts. Based on above analysis, the difference of photocatalytic degradation of MB between Bi$_2$SbVO$_7$ and Bi$_2$GaTaO$_7$ can be attributed mainly to the difference in their crystalline and electronic structure.

Fig. 13 shows the suggested band structures of Bi$_2$SbVO$_7$ and Bi$_2$GaTaO$_7$. Recently, the electronic structures of InMO$_4$ (M = V, Nb and Ta) and BiVO$_4$ were reported by Oshikiri et al. based on first principles calculations.\(^{67}\) The conduction bands of the InMO$_4$ (M = V, Nb and Ta) photocatalysts were mainly composed of a dominant d orbital component from V 3d, Nb 4d and Ta 5d orbitals, respectively. The valence bands of the BiVO$_4$ photocatalyst were composed of a small Bi 6s orbital component and a dominant O 2p orbital component. The band structures of Bi$_2$SbVO$_7$ and Bi$_2$GaTaO$_7$ should be similar to InMO$_4$ (M = V, Nb and Ta) and BiVO$_4$. Therefore, we concluded that the conduction band of Bi$_2$SbVO$_7$ was composed of V 3d and Sb 5p and the valence band of Bi$_2$SbVO$_7$ was composed of a small Bi 6s orbital component and a dominant O 2p orbital component. Similarly, the conduction band of Bi$_2$GaTaO$_7$ was composed of Ta 5d, Ga 4p and Ga 4s. The valence band of Bi$_2$GaTaO$_7$ was composed of a small Bi 6s orbital component and a dominant O 2p orbital component. Direct absorption of photons by Bi$_2$SbVO$_7$ could produce electron–hole pairs in the catalyst, indicating that the larger energy than the band gap was necessary for decomposing MB by photocatalysis.

The presented results indicate that Bi$_2$SbVO$_7$/(visible light) photocatalysis might be regarded as a method for practical treatment of diluted colored waste water. Our Bi$_2$SbVO$_7$/(visible light) photocatalysis system could be utilized for decolorization, purification and detoxification in textile industries and printing and dyeing industries in semi-arid countries. We designed the Bi$_2$SbVO$_7$/(visible light) photocatalysis system without demanding chemical reagents or using high pressure of oxygen or heating. The decolorized and detoxified water were submitted to our new system for treatment and the results showed that the Bi$_2$SbVO$_7$/(visible light) photocatalysis system might provide a valuable treatment for purifying and reusing colored aqueous effluents.
4. Conclusions

Bi$_2$SbVO$_7$ was prepared by a solid-state reaction method for the first time. The structural, optical absorption and visible light photocatalytic properties of this material were studied and compared with that of Bi$_2$GaTaO$_7$. XRD results indicated that the Bi$_2$SbVO$_7$ crystallized with the tetragonal crystal space group $I4/mmm$. The lattice parameters of Bi$_2$SbVO$_7$ were found to be $a = 3.9068(1)$, $b = 3.9068(1)$, $c = 15.4385(7)$ Angstroms. The band gaps of Bi$_2$SbVO$_7$ and Bi$_2$GaTaO$_7$ were estimated to be about 2.33 and 2.52 eV such that Bi$_2$SbVO$_7$ showed a strong optical absorption in the visible light region ($\lambda > 400$ nm). The photocatalytic decomposition of aqueous solutions of methylene blue was observed under visible light irradiation in the presence of Bi$_2$SbVO$_7$ accompanied with the formation of end products such as carbon dioxide, sulfate ions and nitrate ions. Complete removal of carbon was obtained as indicated from TOC measurements. Hence it can be concluded that Bi$_2$SbVO$_7$/visible light system may be regarded as an effective way for the removal of carbon was obtained as indicated from TOC measurements.

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References