



# Enhanced photocatalytic performance over Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> nanosheets with controllable size and exposed {001} facets for Rhodamine B degradation



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## ABSTRACT

Single-crystalline Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> nanosheets with rectangular shape and exposed {001} facets were successfully synthesized via a sol-gel hydrothermal process for the first time. Their average side lengths were around 100 and 150 nm, respectively, and thickness ~20 nm. As a result, the Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> nanosheets reached as high as 79.2% of photodegradation efficiency of Rhodamine B (6 ppm of initial concentration) under 90 min of sunlight irradiation, which was ~3 times that of conventionally calcined Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub>. The synthesized nanosheet catalyst also exhibited high reusability for the photodegradation reaction due to the chemical stability of its single crystalline structure. Moreover, photodegradation efficiency of the Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> nanosheets increased as decreasing Rhodamine B concentrations in the range of 6–20 ppm or pH values in the range of 3.1–11.2. Addition of 0.1 M SO<sub>4</sub><sup>2-</sup> to reaction solution increased almost 6% of photodegradation efficiency of Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> nanosheets under 90 min of illumination. These results demonstrate the superiority of the novel synthesis technique for preparing bismuth titanate photocatalyst. The much-enhanced photocatalytic performance of Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> nanosheets is attributed to their increased active surface sites, efficient separation and transfer of photogenerated charge carriers and greatly suppressed recombination rate of e<sup>-</sup>/h<sup>+</sup> pairs, arising from their large specific surface area, small particle size, single crystallinity, and specific exposed facets.

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## 1. Introduction

Recently, visible light driven photocatalysis has attracted increasing attention because of its applicability in taking advantage of sunlight to eliminate environmental pollutants [1–4]. TiO<sub>2</sub> is one of the most widely investigated photocatalysts due to its high activity, low cost, and availability. Yet its large band gap (~3.2 eV) greatly decreases efficient absorption of solar light and restricts practical application in visible light driven catalysis reactions [5]. Chemical modification of TiO<sub>2</sub> is a viable approach to adjust the wide band gap, allowing the active photocatalysts to work in visible light region [6,7].

Bismuth titanate (Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub>) is a very attractive candidate as highly active photocatalyst due to its unique crystal and electron

structures. As a member of Aurivillius family compounds, Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> has a layered perovskite structure built up by [Bi<sub>2</sub>O<sub>2</sub>]<sup>2+</sup> fluorite-type and [Bi<sub>2</sub>Ti<sub>3</sub>O<sub>10</sub>]<sup>2-</sup> perovskite-type layers. The [Bi<sub>2</sub>Ti<sub>3</sub>O<sub>10</sub>]<sup>2-</sup> layer is composed of three TiO<sub>6</sub> octahedral layers with Bi<sup>3+</sup> at an A-site, which are sandwiched between the [Bi<sub>2</sub>O<sub>2</sub>]<sup>2+</sup> layers along c-axis [8,9]. Theoretical first-principle calculation suggests that the band structure of Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> is composed of Ti 3d and Bi 6p orbitals for conduction band and hybridization between O 2p and Bi 6s orbitals for valence band. In addition, interaction between Bi and O atoms, integrating the Bi 6s and 6p states in the valence band and the conduction band, should promote the generation and separation of photoexcited electron–hole pairs and thus, narrow its band gap [10]. Subsequently, several visible light sensitive Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> photocatalysts have been developed. For example, Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> nanofibers [11], particulates [12–14], platelets [15], and films [16] have been reported as visible light driven photocatalysts for either energy development or degradation of organic pollutants.

Performance of photocatalysts strongly relies on their sizes, crystallinities, morphologies, and exposed facets [17–22]. For instance, single phase metal oxides are found to be more stable

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and active in visible light driven photocatalysis reactions [17–19]. Pore and small  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  nanofibers exhibit enhanced photodegradation performance of Rhodamine B (RhB) and favorable recycling stability under visible light irradiation [20]. Bae and Ohno reported that synthesized  $\text{TiO}_2$  particles with specific exposed crystal faces show higher photocatalytic activity for degradation of acetaldehyde and toluene than commercial  $\text{TiO}_2$  particles [23].  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  platelets with both micro scale size and exposed  $\{001\}$  facets show higher photodegradation activity of methylene blue than commercial  $\text{TiO}_2$  [15]. In addition, N-doped  $\text{Na}_2\text{Ti}_6\text{O}_{13}@\text{TiO}_2$  core-shell nanobelts with exposed  $\{101\}$  anatase facets display high stability and enhanced catalytic activity for photodegradation of methylene blue under visible light irradiation [4].

Synthesis methods of chemical materials play a vital role in obtaining desired size, morphology, and surface microstructure of products for potential photocatalytic applications [20–22]. Conventionally,  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  powders are synthesized by solid state reaction of  $\text{Bi}_2\text{O}_3$  and  $\text{TiO}_2$  [12,17], which often results in volatilization of  $\text{Bi}_2\text{O}_3$  and reduces their compositional homogeneity due to high calcination temperature ( $\geq 800^\circ\text{C}$ ). Several alternative routes, such as chemical solution decomposition [13], sol-gel reaction [24], electrospinning [20], citrate-gel method [25], coprecipitation processes [26], and polymeric precursor method [27], have been developed to obtain  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  with different nanostructures and sizes. Very recently,  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  nanosheets with controllable size and specific exposed facets are prepared via a molten salt synthesis method [28]. Still, these methods require an additional calcination process at temperature of  $>400^\circ\text{C}$ , which is far from low cost and may result in agglomeration, inhomogeneous particle size and Bi composition volatilization of products. Therefore, it is of fundamental significance to explore additional synthetic techniques to prepare highly photocatalytic active  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  under more moderate reaction conditions.

As a novel method to prepare desired oxide powders under mild reaction temperatures, sol-gel hydrothermal technique has combined the advantages of both sol-gel synthesis and hydrothermal processing, e.g., high degree of crystallinity, well-controlled morphology, and narrow particle size distribution for the synthesized products [29]. In this work, the process was adopted as a new route to produce single crystal  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  nanosheets with predominantly abundant exposed  $\{001\}$  facets under the hydrothermal temperature as low as  $160^\circ\text{C}$ . The process has advantages of simplicity, template and surfactant free, and energy-saving. More importantly, the as-prepared  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  nanosheets exhibit highly visible-light-driven photocatalytic activity and favorable stability.

## 2. Experimental

### 2.1. Catalyst preparation

$\text{Bi}_4\text{Ti}_3\text{O}_{12}$  nanosheets were prepared via sol-gel synthesis and subsequent hydrothermal processing. First, according to the composition of  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ , solutions A and B were obtained by dissolving 0.02 mol  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  in 15 ml acetic acid and 0.15 mol  $\text{Ti}(\text{C}_4\text{H}_9\text{O})_4$  in 15 ml ethylene glycol monomethylether under stirring at room temperature, respectively. All reagents were of analytical grade. Solution B was slowly added into solution A dropwise, and the mixture was vigorously stirred for 2 h, resulting in a homogeneous sol. The sol was stabilized when its concentration was adjusted to 0.1 M by adding 10 ml acetic acid and 10 ml ethylene glycol monomethylether, before being heated to  $80^\circ\text{C}$  for 24 h to produce dry gel. The gel was added to 75 ml of a 3 M NaOH solution to form suspension, followed by pouring into a Teflon-lined stainless steel autoclave (volume of 100 ml) with filling capacity of 80% and being subject to hydrothermal treatment at  $160^\circ\text{C}$  for

16 h unless otherwise stated. Finally, the synthesized product was cooled down, filtered, washed with distilled water, and dried at room temperature. For comparison,  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  powders were also prepared via conventional solid-state reaction between  $\text{TiO}_2$  and  $\text{Bi}_2\text{O}_3$  at  $800^\circ\text{C}$  for 3 h, as reported elsewhere [17].

### 2.2. Characterization

Crystalline structures of powders were examined using an X-ray diffractometer (XRD, D/Max-3C, Rigaku Co.) with Ni-filtered  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) in  $\theta$ - $2\theta$  scan mode, run at 40 kV and 30 mA. The  $2\theta$  range and step scan rate were  $13$ – $60^\circ$  and  $0.01^\circ/\text{s}$ , respectively.

Infrared spectra of samples were collected by a Nicolet-Nexus 670 FTIR spectrometer with the scan range of  $450$ – $4000 \text{ cm}^{-1}$  at a resolution of  $4 \text{ cm}^{-1}$ . The sample was prepared by the KBr pellet method, with around 1:50 ratio of sample and KBr.

Morphology of sample was observed by a scanning electron microscopy (SEM, LEO 1530 VP, Leo Ltd.) with accelerating voltage of 20 kV, and its composition was examined using energy dispersive spectroscopy (EDS) attached to the SEM. High resolution transmission electron microscopy (HRTEM) of the synthesized products was carried out on a JEOL-2011 instrument with accelerating voltage of 200 kV. The samples were prepared by dispersing  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  powders in anhydrous ethanol with sonication, and dripping on carbon-coated Cu grids.

Specific surface area of samples was measured using the multipoint Brunauer-Emmett-Teller (BET) method ( $\text{N}_2$  desorption) at liquid nitrogen temperature (Quantachrome 1900 Corporate Drive). All samples were degassed at  $100^\circ\text{C}$  for 4 h before measurements.

The chemical states of samples were determined using an X-ray photoelectron spectrometer (XPS Axis Ultra DCD, UK) with a monochromatic  $\text{Mg K}\alpha$  X-ray source. All binding energies were referenced to the C 1s peak at 284.8 eV of the adventitious surface carbon.

The diffuse reflection spectra of the  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  nanosheets were analyzed using a UV-vis spectrophotometer (Model lambda 35, PerkinElmer) with an integrating sphere in the range of 250–800 nm, and  $\text{BaSO}_4$  was used as the reference.

Zeta potential values of sample were measured using a Zetaplus meter (Brookhaven Instruments, Holtsville, NJ) in the pH range of 1.0–12.0. The sample was prepared by adding  $\sim 3$  mg of  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  powder to 50 ml DI water, followed by ultrasonic treatment for 15 min to create a suspension. The pH value of the resulting suspension was adjusted using 0.1 M HCl or NaOH.

Photoluminescence (PL) spectra of sample were recorded using a PerkinElmer LS55 fluorescence spectrometer with the excitation wavelength of 320 nm at room temperature. The sample was pressed into a thin disk and fixed on a quartz cell.

Electrochemical experiments were conducted using a CHI 660 electrochemical workstation (CH Instruments, Inc., Austin, USA) with frequencies between  $1 \times 10^{-5}$  and 100 kHz and a potential of 0.17 V at room temperature. All electrochemical measurements were based on a three-electrode system with a  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  electrode (see below for preparation) as the working electrode, a Ag/AgCl (3 M KCl) electrode as the reference electrode and a platinum wire as the auxiliary electrode. 0.1 M KCl and 0.1 M  $\text{K}_3[\text{Fe}(\text{CN})_6]/\text{K}_4[\text{Fe}(\text{CN})_6]$  in a 1:1 mixture were used as the detecting electrolyte. A 300 W Xe lamp held at 10 cm from the quartz cell with a 420 nm UV filter was used as the visible-light source. The  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  electrodes were prepared as follow: First, 5 mg of  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  nanosheets were added to 0.5 ml solution containing 0.15 ml of pure ethyl alcohol ( $\text{CH}_3\text{CH}_2\text{OH}$ ) and 0.35 ml of 5% Nafion DE 520 solution (EW is 1000, DuPont). The mixture was then ultrasonically dispersed for 20 min. Finally, 0.1 ml of the well-dispersed  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  slurry were cast onto

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