Synthesis of porous Bi$_4$Ti$_3$O$_{12}$ nanofibers by electrospinning and their enhanced visible-light-driven photocatalytic properties†

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Bi$_4$Ti$_3$O$_{12}$ nanofibers with diameters of 50–100 nm have been fabricated for the first time through a simple and economical technique of electrospinning combined with subsequent calcination. The as-formed Bi$_4$Ti$_3$O$_{12}$ nanofibers are porous and composed of inter-linked nanoparticles of 30–50 nm in size. They exhibit both enhanced visible-light-driven photocatalytic decomposition of rhodamine B (RhB) and favorable recycling capability. It is attributed to not only the macrostructure, such as the morphology, surface texture, and grain shape, but also the intrinsic structures of oxygen vacancies and surface adsorbed oxygen.

Introduction

Since the first report by Fujishima and Honda$^1$ on photoelectrochemical water splitting on a TiO$_2$ electrode in 1972, heterogeneous semiconductor photocatalysis has stimulated considerable interest because of wide applications such as decomposition of organic contaminants, production of clean hydrogen energy by splitting water, and CO$_2$ conversion to hydrocarbon fuel.$^{2,3}$ During the past four decades considerable effort has been made to achieve novel high-efficiency semiconductor photocatalysts via crystal growth, doping, and heterostructure design.$^{4–14}$ Generally, crystal growth is vital in controlling the phase, morphology, and size of photocatalysts, as well as their crystallinity and surface area, and therefore the surface atomic structures and states of the derived photocatalysts can be tailored.$^{6,8}$ So far, a variety of synthetic strategies have been developed to control the morphology of photocatalysts in the nanoscale, leading to large surface areas, abundant surface states, and enhanced photocatalytic performances.$^{15}$

One-dimensional (1D) semiconductor photocatalysts with high surface areas and porosities have aroused much attention.$^{16,17}$ As expected, those semiconductor photocatalysts with 1D nanostructures indeed exhibit enhanced photocatalytic activities.$^{17–19}$ Among various methods, electrospinning is the most convenient and direct technique that allows the fabrication of continuous fibers with diameters down to a few nanometers, and receives a great deal of attention for the low cost, versatility and ease of manufacturing.$^{20–22}$ Zhang et al.$^3$ reported that hollow mesoporous 1D TiO$_2$ nanofibers by electrospinning exhibit enhanced photocatalytic activity towards photo-degradation of rhodamine B (RhB). Liu and coworkers$^{23}$ demonstrated that the biocomponent TiO$_2$/SnO$_2$ nanofibers have an excellent photocatalytic activity over the degradation of organic pollutants. Electrospun Bi$_2$WO$_6$ nanofibrous mats exhibit enhanced photocatalytic activity in the decomposition of CH$_3$CHO and aqueous ammonia.$^{23}$

Bismuth titanate (Bi$_4$Ti$_3$O$_{12}$, BTO) belongs to a family of layered perovskite compounds.$^{24}$ It has been widely explored for optical displays, piezoelectrics, and optoelectronic devices.$^{25–27}$ The Aurivillius phases can be described as intergrowth structures composed of alternating layers of (Bi$_2$O$_2$)$_n$ blocks.$^{28,29}$ The three-layer member ($n = 3$) of the Aurivillius phase is Bi$_4$Ti$_3$O$_{12}$. The schematic structure of Bi$_4$Ti$_3$O$_{12}$ is shown in Fig. 1. More
recently, Bi₄Ti₃O₁₂ has been explored as a photocatalyst since the discovery of photocatalytic behavior in degradation of organic pollutants and water splitting. For instance, Bi₄Ti₃O₁₂ particulates prepared by decomposition of a chemical solution, nanosheets immobilized on the surface of electrosprun TiO₂ fibers, nanowires, and electrospun TiO₂ nanostructures by a hydrothermal method exhibit high photocatalytic activity towards photodegradation of organic pollutants. Chromium-doped Bi₄Ti₃O₁₂ by sol–gel and hydrothermal routes was used for photocatalytic production of H₂ under visible light irradiation. Here we develop a facile route of electrospinning to fabricate 1D porous Bi₄Ti₃O₁₂ nanofibers with diameters of 50–100 nm on a large scale. The as-formed nanofibers comprise numerous interlinked Bi₄Ti₃O₁₂ nanocrystals of 30–50 nm. To the best of our knowledge, this is the first report on nanostructured porous Bi₄Ti₃O₁₂ with well-defined 1D nanoarchitectures. More importantly, the resulting Bi₄Ti₃O₁₂ nanofibers exhibit high visible-light-driven photocatalytic activity by using RhB as a model organic compound.

**Experimental**

**Material synthesis**

Bi(NO₃)₃·5H₂O, Bi₂O₃, tetrabutyltitanate (TBT), and N,N-dimethylformamide (DMF) were of analytical grade, and were supplied from Shanghai Sinopharm Chemical Reagent Co. Ltd., China. Poly(vinylpyrrolidone) (PVP, Mₙ ≈ 1 300 000) was obtained from Aladdin Chemical Co., Ltd. P25 (a commercial nanocrystalline TiO₂ that consists of ca. 80% anatase and 20% rutile; BET area ca. 50.0 m² g⁻¹) was purchased from Degussa. All the chemicals were used as received without further purification. In a typical procedure, the precursor solution for electrospinning was prepared by dissolving Bi(NO₃)₃·5H₂O (1.55 g) and TBT (0.82 g) in DMF (20 mL) at room temperature according to the stoichiometric composition. After stirring for 30 min, 2.5 g of PVP was added into the mixture. The mixture of Bi(NO₃)₃·TBT–PVP was stirred overnight, and a yellow and transparent precursor solution was obtained. This precursor solution was delivered into a plastic syringe equipped with a 20-gauge stainless steel needle. The feeding rate was 1.5 mL h⁻¹ monitored by a syringe pump. The metallic needle clamped with an electrode was connected to a variable high-voltage power supply, and a collector of an aluminum foil was placed 12 cm away from the tip of the needle. As a high voltage of 15 kV was applied, the Bi(NO₃)₃·TBT–PVP composite nanofibers were formed. The scheme of the electrospinning process is shown in Fig. 1. The as-collected electrospun fibers were dried at 80 °C in air for 6 h. Subsequently, the composite fibers were calcined at different temperatures (400, 500, 600, 700 and 800 °C) in air for 30 min at a heating rate of 2 °C min⁻¹. The as-prepared samples are denoted as BTO-EF4 (400 °C), BTO-EF5 (500 °C), BTO-EF6 (600 °C), BTO-EF7 (700 °C), and BTO-EF8 (800 °C), respectively.

For comparison, BTO crystallites were prepared by both a sol–gel method and a traditional solid-state reaction (SSR). For the sol–gel method, the same precursor solution of Bi(NO₃)₃·TBT–PVP was dried at 80 °C in air for 12 h and then calcined at 600 °C for 30 min. This sample is denoted as BTO-SG. For the SSR reaction, powdered Bi₂O₃ and P25 with appropriate stoichiometric amounts were used as the starting materials. They were mixed in acetone and ball-milled (200 rpm) for 8 h. Then, the mixed slurry was dried and calcined at different temperatures of 600, 700, and 800 °C for 2 h. These samples are denoted as BTO-SR6, BTO-SR7 and BTO-SR8 correspondingly.

**Materials characterization**

X-Ray diffraction (XRD) analysis was performed by the Rigaku D/MAX-RB diffractometer using filtered Cu Kα radiation. The full diffraction patterns of the products were taken in the 2θ range from 10° to 80° at a step model with a step size 0.02°. The average grain size of the samples was estimated using the Scherrer formula. The morphology of the samples was characterized using a field emission scanning electron microscope (FESEM, SIRON200, Holland; accelerating voltage: 10 kV). Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were recorded by a JEOL JEM-2100F microscope. X-Ray photoelectron spectroscopy (XPS) measurements were carried out on a VG MultiLab 2000 system with a monochromatic Al Kα X-ray source (ThermoVG Scientific). Infrared spectra were recorded using a Bruker VERTEX 70 FT-IR spectrometer. The thermogravimetric (TG) analysis and differential thermal analysis (DTA) were performed with a PerkinElmer Diamond TG/DTA apparatus. TG and DTA were carried out simultaneously at a heating rate of 10 °C min⁻¹ in a flowing air. UV-vis diffuse reflectance spectra were recorded on a SHIMADZU UV-2550 spectrophotometer with an integrating sphere, and BaSO₄ was used as the reference. The Brunauer–Emmett–Teller (BET) surface area was determined by nitrogen sorption using a Micromeritics ASAP 2020 analyzer.

**Activity evaluation**

The photochemical reactor was a self-made cylindrical glass vessel with a water-cooling jacket. Photocatalytic activities of the as-prepared samples were evaluated by the degradation of RhB as a model organic compound under visible light irradiation of a 500 W Xe lamp with a 420 nm cut-off filter at ambient temperature. The irradiation distance between the lamp and the sample was 12 cm. The photocatalyst (80 mg) was dispersed uniformly into the reactor containing 80 mL of RhB solution (6 ppm). Before irradiation, the suspension was stirred for 30 min and kept in the dark until ensuring an adsorption–desorption equilibrium. At a certain time interval, 3 mL of the reaction solution was taken, centrifuged, and measured on a UV-vis spectrometer at a maximum absorption wavelength of 554 nm.

**Results and discussion**

The crystallization and morphology of Bi₄Ti₃O₁₂ are influenced by many factors, which should also be sensitive to the reaction temperature, starting materials, synthesis methods and so on. Fig. 2a shows the FESEM images of the as-spun...
Bi(NO$_3$)$_3$–TBT–PVP nanofibers. Clearly, the surface of these nanofibers is very smooth, and they have diameters of about 100–300 nm. Fig. 2b–f display the FESEM images for the products that were obtained by annealing the as-spun Bi(NO$_3$)$_3$–TBT–PVP nanofibers at 400, 500, 600, 700, and 800 °C, respectively. Obviously, the as-formed nanofibers exhibit shrinkage with increasing the calcination temperature, resulting from the decomposition of PVP, TBT and Bi(NO$_3$)$_3$. Also, the surface of these nanofibers tends to be rougher when the calcination temperature was raised from 400, 500 to 600 °C. Typically, the nanofibers with diameters of 50–100 nm were obtained at 600 °C. If the annealing temperature was continuously increased to 700 °C, the fibrous architecture collapsed into numerous rod-like particles. However, the morphology of the nanofibers disappeared at 800 °C, and transformed completely into nanoplates with an average thickness of about 50 nm. In addition, these nanoplates aggregate and stack in disorder.

The XRD results of the products obtained by annealing the as-spun Bi(NO$_3$)$_3$–TBT–PVP nanofibers at different temperatures are shown in Fig. 3. There is no typical diffraction peak for the sample of BTO-EF4, in addition to a wide bump centered at 30.0°. As the annealing temperature was increased to 500 °C, most of the diffraction peaks can be attributed to orthorhombic Bi$_4$Ti$_3$O$_{12}$ (JCPDS 35-0795). Also, there exist some impurities including Bi$_2$Ti$_2$O$_7$ and Bi$_2$O$_3$, probably arising from the metastable phase during the formation of Bi$_4$Ti$_3$O$_{12}$. It is noted that the diffraction peaks for the impurities disappear completely in the sample of BTO-EF6. Also, the intensity of the XRD patterns for BTO-EF7 (700 °C) and BTO-EF8 (800 °C) is much enhanced, owing to the improved crystallinity and the enlarged sizes. Considering the crystal phase, morphology and microstructure of the as-prepared samples, we conclude that the optimal temperature for annealing the Bi(NO$_3$)$_3$–TBT–PVP nanofibers should be 600 °C. It is also confirmed that all the organic substances in the Bi(NO$_3$)$_3$–TBT–PVP nanofibers could be removed at 600 °C for 30 min by TG analysis (Fig. S1†) and FTIR spectra (Fig. S2†).

TEM and HRTEM images provide further insight into the microstructure of the products. Fig. 4a displays the representative TEM images of the BTO-EF6 product, indicating the typical fiber morphology. The Bi$_4$Ti$_3$O$_{12}$ nanofibers comprise linked nanoparticles with sizes of about 30–50 nm. It is well known that the particle size is a crucial factor in the dynamics of electron–hole recombination processes and generally, a decrease in particle size could be expected to lead to a higher efficiency in photocatalysis. Also, the nanoporous structural configuration is clearly observed along the nanofibers. The nanoporous architecture is very beneficial in catalyst design since it can facilitate the molecular transport of reactants and products. Fig. 4b shows the HRTEM image at the edge of an individual Bi$_4$Ti$_3$O$_{12}$ nanofiber. This HRTEM image supports the claim of crystallinity for the Bi$_4$Ti$_3$O$_{12}$ nanofiber. The periodic fringe spacing of ~3.8 Å corresponds to interplanar spacing between the [111] planes of Bi$_4$Ti$_3$O$_{12}$, which agrees well with the XRD result.
The surface composition and chemical state of the composite nanofibers were analyzed by XPS. The binding energies obtained from the XPS analysis were corrected for specimen charging by referencing the C1s line to 284.5 eV. The survey XPS spectrum (Fig. 5a) for the BTO-EF6 product reveals that the nanofibers are composed of Bi, Ti, and O. Fig. 5b shows the high-resolution XPS spectrum of Bi 4f of the BTO-EF6, 159.1 eV for 4f5/2 and 164.5 eV for 4f7/2, whereas the 4f7/2 and 4f5/2 peaks of metallic bismuth locate at 156.8 and 162.2 eV, respectively. The chemical shift of the Bi 4f doublet with respect to metallic Bi is 2.3 eV, which is less than the typical value of 3.1 eV between Bi2O3 and metallic Bi. It suggests the existence of bismuth in the (+3 – x) valence state (i.e., Bi suboxides), generated due to a deficiency in oxygen and an enhanced concentration of oxygen vacancies in the vicinity of bismuth cations, which are more likely inside the Bi2O2 layer. The oxygen vacancy has been proven to have a crucial role in the electronic structures and physical properties of oxide materials.

For comparison, we have prepared Bi4Ti3O12 crystallites by a conventional sol-gel process and a solid-state reaction. It should be noted that pure orthorhombic Bi4Ti3O12 could not be obtained at 600 and 700 °C by the solid-state reaction method. The XRD patterns for the BTO-SG (calcined at 600 °C) and BTO-SR8 (calcined at 800 °C) products are shown in Fig. 6a. All the diffraction peaks can be perfectly indexed to the orthorhombic phase of Bi4Ti3O12 (JCPDS 35-0795). The crystallite sizes determined from the FWHM of the most intensive diffraction peaks (171, 020, 111) using the Scherrer equation are listed in Table 1. The XRD patterns for the BTO-SG (calcined at 600 °C) and BTO-SR8 (calcined at 800 °C) products are shown in Fig. 6a. All the diffraction peaks can be perfectly indexed to the orthorhombic phase of Bi4Ti3O12 (JCPDS 35-0795). The crystallite sizes determined from the FWHM of the most intensive diffraction peaks (171, 020, 111) using the Scherrer equation are listed in Table 1. The XRD patterns for the BTO-SG (calcined at 600 °C) and BTO-SR8 (calcined at 800 °C) products are shown in Fig. 6a. All the diffraction peaks can be perfectly indexed to the orthorhombic phase of Bi4Ti3O12 (JCPDS 35-0795). The crystallite sizes determined from the FWHM of the most intensive diffraction peaks (171, 020, 111) using the Scherrer equation are listed in Table 1. The XRD patterns for the BTO-SG (calcined at 600 °C) and BTO-SR8 (calcined at 800 °C) products are shown in Fig. 6a. All the diffraction peaks can be perfectly indexed to the orthorhombic phase of Bi4Ti3O12 (JCPDS 35-0795). The crystallite sizes determined from the FWHM of the most intensive diffraction peaks (171, 020, 111) using the Scherrer equation are listed in Table 1. The XRD patterns for the BTO-SG (calcined at 600 °C) and BTO-SR8 (calcined at 800 °C) products are shown in Fig. 6a. All the diffraction peaks can be perfectly indexed to the orthorhombic phase of Bi4Ti3O12 (JCPDS 35-0795). The crystallite sizes determined from the FWHM of the most intensive diffraction peaks (171, 020, 111) using the Scherrer equation are listed in Table 1.

Fig. 5a shows the typical high-resolution XPS spectrum of Bi nanofibers. The Bi 4d spectra of metallic Bi and Bi2O3 show the binding energies of 156.8 and 162.2 eV, respectively. The chemical shift of the Bi 4d doublet with respect to metallic Bi is 2.3 eV, which is less than the typical value of 3.1 eV between Bi2O3 and metallic Bi. It suggests the existence of bismuth in the (+3 – x) valence state (i.e., Bi suboxides), generated due to a deficiency in oxygen and an enhanced concentration of oxygen vacancies in the vicinity of bismuth cations, which are more likely inside the Bi2O2 layer. The oxygen vacancy has been proven to have a crucial role in the electronic structures and physical properties of oxide materials. The oxygen vacancy serving as electron traps can enhance the efficiency of visible light absorption.

Fig. 6 shows the typical FESEM images of the as-prepared BTO-SG and BTO-SR8. The BTO-SG product exhibits small and thin plate morphology with sizes of about 20–100 nm (Fig. 6b). The micrograph of the BTO-SR8 (Fig. 6c) illustrates the presence of randomly distributed piles of thick plates of the crystallites of about 80 nm in thickness.

Fig. 7 shows nitrogen adsorption–desorption isotherms of BTO-EF6 and the corresponding pore size distribution curves of BTO-EF6, BTO-SG, and BTO-SR8. It can be seen that the isotherm of the BTO-EF6 was of type IV (BDDT classification) with a hysteresis loop observed in the range of (0.6–1.0) P/P0. As listed in Table 1, the specific surface areas of the samples, calculated by the multipoint Brunauer–Emmett–Teller (BET) method, are 12.8 m2 g−1 for BTO-EF6, 10.06 m2 g−1 for BTO-SG, and 1.09 m2 g−1 for BTO-SR8. The pore size distribution of BTO-EF6, BTO-SG, and BTO-SR8 calculated from the desorption branch of the nitrogen isotherm by the BJH (Barrett–Joyner–Halenda) method (inset in Fig. 7) shows a relative wide range with some mesopores and macropores for the BTO-EF6, BTO-SG and no obvious pores for BTO-SR8. The result shows that BTO-EF6 contained more large macropores than BTO-SG, which come from the holes formed among nanofibers. Whereas, the mesopores may be attributed to the holes in the porous nanofibers. This also confirms the result of SEM and TEM analysis.

Fig. 5 (a) Survey XPS spectrum of the Bi4Ti3O12 nanofibers. High-resolution XPS spectra of (b) Bi 4d, Ti 2p, (c) Bi 4f, and (d) O 1s.

Fig. 6 (a) XRD patterns of BTO-SG by the sol–gel method and BTO-SR8 by the solid-state reaction. FESEM images of (b) BTO-SG and (c) BTO-SR8.
BTO-EF6 has relatively larger BET surface area, resulting from its fibrous architecture, which contributes to the harvesting of visible light and enhanced photocatalytic properties.

The UV-visible diffuse reflectance spectra in the wavelength range of 200–800 nm for the BTO products are shown in Fig. 8. The absorbance spectra reveal that there are some differences in the absorption edges among the samples, probably resulting from the different conditions of the crystal growth of these samples. The morphology, size, and defects that affect the surface atomic structure of a photocatalyst play an important role in the surface states and photocatalytic activity. The theoretical first-principle calculation suggests that the band structure of Bi$_4$Ti$_3$O$_{12}$ is composed of Ti 3d and Bi 6p orbits for the conduction band, and the hybridization between O 2p and Bi 6s orbits for the valence band. In addition, the 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 the photexcited electron–hole pairs and thus inspiringly enhance the photocatalytic activity of Bi$_4$Ti$_3$O$_{12}$. The band gap values were calculated using the UV-vis absorption spectra according to the following equation:

\[ a\nu = A(h\nu - E_g)^{n/2} \]  

where \( \alpha \), \( h\nu \), \( A \) and \( E_g \) signify the absorption coefficient, photon energy, proportionality constant and band gap, respectively. In the case that the fundamental absorption of Bi$_4$Ti$_3$O$_{12}$ possesses an indirect transition between bands, then \( n = 4 \). The energy of the band gap is calculated by extrapolating a straight line to the abscissa axis. The inset of Fig. 8 shows the plot of the \( (a\nu h\nu)^{1/2} \) versus \( E_g \). The band gaps of the BTO products are estimated to be 2.82 eV for BTO-EF6, 2.81 eV for BTO-EF7, 2.91 eV for BTO-EF8, 2.93 eV for BTO-SG, and 2.93 eV for BTO-SR8. The difference in band gap may result from the crystal phase of the Aurivillius structure that depends intensively on the temperature and experimental conditions. Thus, the UV-vis absorption spectra show that the optical properties of these BTO samples are relevant to the size, shape, and surface structure, which is consistent with the previous work.

The photocatalytic activity of the prepared samples under visible light illumination (\( \lambda > 420 \) nm) was determined using RhB as the model pollutant. The typical temporal evolution of the spectra during the RhB adsorption and photodecomposition over BTO-EF6 is shown in Fig. S3. The RhB solution shows a major absorption band at 554 nm. In the presence of BTO-EF6, the absorbance decreased by ca. 30% before irradiation. Also, the BTO-EF6, BTO-EF7 and BTO-EF8 samples can adsorb RhB molecules in the dark much more efficiently than that of the BTO-SG and BTO-SR8 samples (Fig. 9a), possibly arising from the larger BET surface area and the unique architecture of electrospun nanofibers, which is of benefit to the enhanced photocatalytic properties. Fig. 9a shows the change in RhB concentration over the photocatalytic degradation reaction under visible light irradiation. Clearly, the exposure of RhB to visible light does not stimulate obvious self-photodegradation that could be negligible in comparison to the photodegradation of the BTO samples. After the adsorption–desorption equilibrium, the BTO-EF6 sample shows a considerably higher photocatalytic activity. Also, the photocatalytic efficiency reaches 89% after 240 min, which is also higher than that of the BTO-EF8 and BTO-EF7 samples. In contrast, the photodegradation efficiency of RhB by BTO-SG and BTO-SR8 just reaches 34% and 67% after illumination for 240 min, respectively. It is worth noting that the Bi$_4$Ti$_3$O$_{12}$ photocatalysts prepared by electrospinning exhibit enhanced activities compared to the products obtained by the sol–gel or the SSR method. Among the electrospun Bi$_4$Ti$_3$O$_{12}$ photocatalysts, the enhanced activity of BTO-EF6 may be attributed to more defects in Bi$_4$Ti$_3$O$_{12}$ (e.g., oxygen vacancies) that improve the absorption efficiency of visible light.
light. However, the concentration of oxygen vacancies in Bi$_4$Ti$_3$O$_12$ decreases when the treating temperature increases.\cite{46} This also brings about the difference in the band gap leading to the different photocatalytic behavior. The BTO-EF6 sample possesses more oxygen vacancies and a slightly narrower band gap. Thus, more carries can be generated and the photocatalytic activity of BTO-EF6 can be enhanced.

The photodegradation reaction can be described by first-order kinetics with respect to the concentration of the organic compound. The time-dependent decomposition of RhB follows the first-order kinetics, $\ln(C_t/C_0) = kt$, where $t$ is the irradiation time and $k$ is the rate constant.\cite{47} The calculated curves of $k$ for the reaction in the presence of BTO-EF6, BTO-SG and BTO-SR8 are 0.00878, 0.00449, and 0.00167 min$^{-1}$, respectively, as shown in Fig. 9b, suggesting favorable photocatalytic performance of BTO-EF6 nanofibers. As well known, many factors can affect the photocatalytic efficiency including surface area and crystallinity and so on, while the synthesis method plays an important role in the morphology and microstructure of the products. The larger surface area of the photocatalyst could provide more reaction sites, which is in favor of the activity. In this regard, the unique porous and fibrous nature of BTO-EF6 benefits the exposure to the visible light, and provides more active sites in contrast to the BTO-EF7 and BTO-EF8 samples.

![Fig. 9](image_url) (a) Degradation profiles of RhB over different samples where $C$ is the concentration of the RhB, $C_0$ is the initial concentration of the RhB after adsorption–desorption equilibrium. (b) Kinetic linear simulation curves of RhB photocatalytic degradation with the products BTO-EF6, BTO-SG, and BTO-SR8.

![Fig. 10](image_url) (a) Cycling runs of photocatalytic degradation of RhB in aqueous BTO-EF6 dispersions under visible light irradiation. The catalyst was annealed at 400 °C for 30 min after the fifth cycle.
of photoexcited electron–hole pairs. The electron is first trapped by oxygen vacancies on the surface to form OH radicals and super oxide radicals O$_2^-$, resulting in the enhancement of photocatalytic activities.$^{41}$

(3) The nanofibrous morphology. The porous nanofibrous architecture with high surface area contributes to not only more active sites but also more efficient transfer of the photogenerated charges. Moreover, the nanosized particles that are the “building blocks” in the Bi$_4$Ti$_3$O$_12$ nanofibers make for diminishing the electron–hole recombination because of the reduced diffusion distance of photogenerated charges from the inside of particles to the outside surface. The smaller the particle is, the more surface atoms there are, which is highly preferable for harvesting visible light.$^2$

Conclusions

Bi$_4$Ti$_3$O$_12$ nanofibers with diameters of 50–100 nm have been successfully fabricated for the first time through the electrospinning method. The porous nanofibrous architecture with high surface area and a relatively narrowed band gap shows the highest photocatalytic activity for photodecomposition of RhB under visible light irradiation. A favorable recycling capability is obtained as well, indicating that electrospun nanofibrous Bi$_4$Ti$_3$O$_12$ is a promising candidate for visible light photocatalytic applications. This work provides a facile and economical strategy to fabricate Bi$_4$Ti$_3$O$_12$ nanofibers on a large scale. Also, we believe that this route can be extended to prepare other hierarchically nanostructured Aurivillius oxides for photocatalytic and optoelectronic applications.

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Notes and references


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