#### Accepted Manuscript

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PII:	S0926-860X(16)30339-8
DOI:	http://dx.doi.org/doi:10.1016/j.apcata.2016.06.025
Reference:	APCATA 15921
To appear in:	Applied Catalysis A: General
Received date:	15-12-2015
Revised date:	15-6-2016
Accepted date:	17-6-2016

Please cite this article as: Li Jinhai, Mengshu Han, Yang Guo, Fei Wang, Lingjun Meng, Danjun Mao, Shanshan Ding, Cheng Sun, Hydrothermal synthesis of novel flower-like BiVO4/Bi2Ti2O7 with superior photocatalytic activity toward tetracycline removal, Applied Catalysis A, General http://dx.doi.org/10.1016/j.apcata.2016.06.025

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## Hydrothermal synthesis of novel flower-like BiVO<sub>4</sub>/Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> with superior photocatalytic activity toward tetracycline removal

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#### **Graphical abstract**



#### Highlights

• A novel flower-like  $BiVO_4$  and  $BiVO_4/Bi_2Ti_2O_7$  heterojunction was firstly prepared via facile and green hydrothermal route.

•The novel BiVO<sub>4</sub>/Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> composites exhibit superior visible-light driven photocatalytic activity and recycling ability toward tetracycline removal.

•The photocatalytic mechanisms and removal pathways were studied deeply.

#### Abstract

A novel flower-like BiVO<sub>4</sub> and BiVO<sub>4</sub>/Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> heterojunction photocatalyst was firstly synthesized by surfactant-free hydrothermal route, which is very convenient, rapid, controllable and environmentally friendly. The crystal structures, chemical composition, morphology, optical and photo-catalytic property of the as-prepared samples were characterized by the techniques of XRD, XPS, SEM, HRTEM, BET, UV–vis DRS, and PL. The BiVO<sub>4</sub>/Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> heterojunction photocatalyst exhibited higher photocatalytic activity than pure BiVO<sub>4</sub> and Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> for the degradation of tetracycline (TC) under xenon lamp irradiation. The enhanced photocatalytic activities of BiVO<sub>4</sub>/Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> composites were either related to the particular structural features or the mass ratios of BiVO<sub>4</sub> and Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> in the composites. The possible photocatalytic mechanism of the BiVO<sub>4</sub>/Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> composite has been speculated by detecting reactive species based on free radicals trapping experiments. The preliminary removal pathways of tetracycline was proposed on the basis of the identified intermediates using LC-TOF/MS.

**Keywords:** BiVO<sub>4</sub>/Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>, Flower-like, Hydrothermal synthesis, Photocatalytic, Tetracycline

#### **1. Introduction**

To treat bacterial diseases in humans and to promote growth in animal and plant, large amounts of antibiotics are produced and consumed. Among various antibiotics, tetracyclines are one kind of the most important antibiotics, which are widely used for controlling disease and promoting growth due to their excellent efficacy. However, many antibiotics can be easily entered into the environment because of the poor absorption, low metabolism, abuse and overuse. Antibiotics in environment could cause lots of direct toxicities and potential risks (the effects include the development of super bacteria, direct or indirect toxicity to microorganism and possible risks to human beings) [1-4].

Over the past decades, antibiotic residues are increasingly found in the water environment and have attracted much attention. To eliminate these challenges, many studies were aimed to deal with antibiotic wastewater, such as physical adsorption, chemical reactions and biological degradation, etc. However, the efficiencies of these methods are usually very poor as the low concentrations and biochemical rate. Comparing with the traditional methods, photocatalytic technology is considered a very promising and effective method of revealing environmental pollutants due to high mineralization efficiency, no secondary pollution, low energy consumption and simple process. Often, semiconductor plays a very important role in the photocatalytic process. Among numerous semiconductor photocatalytic materials, BiVO<sub>4</sub> is one of the newly visible-light-driven photocatalyst owing to its moderate band gap (about 2.4 eV) [5, 6]. BiVO<sub>4</sub> has also been widely reported as photocatalyst for water splitting and the pollutants removal, and so on. However, the commercialization of BiVO<sub>4</sub> has been hindered by poor solar response efficiency. To overcome this obstacle, many efforts have been tried to improve the photocatalytic activity of semiconductor, such as element doping and semiconductor coupling, etc. It is well known that the building of heterojunction photocatalysts by coupling with semiconductors, which is beneficial to separate of charge carriers and to promote photocatalytic performance. Therefore, building of heterojunction is a relatively effective and common method of exploiting for synthesis of new high-efficiency photocatalysts. Furthermore, the physical and

chemical properties of most photocatalyst are also strongly dependent on structure, morphology and size. These properties of functional materials are closely related to the synthetic methodologies and preparation conditions. Therefore, selecting an appropriate method to control preparation of photocatalyst has been paid more and more attention. Among various morphologies, flower-like architectures are made of many nanoparticles, which have been given considerable attention due to numerous advantages in photocatalysts, promoting solar light absorption, providing abundant exposed interfacial active area and enhancing the separation of photo-generated charge carriers [7-9].

Recently, synthesized BiVO<sub>4</sub> based heterojunction photocatalysts has aroused significant scientific interest. A lots of BiVO<sub>4</sub> based heterojunction photocatalysts were reported, such as BiVO<sub>4</sub>/g-C<sub>3</sub>N<sub>4</sub>, BiVO<sub>4</sub>/SnO<sub>2</sub>/WO<sub>3</sub>, BiVO<sub>4</sub>-TiO<sub>2</sub> [10-12], etc. However, BiVO<sub>4</sub>/Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> composite has not been explored. Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> has been confirmed the photocalalytic activity for water splitting and pollutants removal. However, there are a few practical problems when using Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> photocatalysts, such as low catalytic activity and difficult to recycle after the reaction [13, 14], and so on. These problems could be resolved by constructing the heterojunction of BiVO<sub>4</sub>/Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>.

In this work, a novel flower-like BiVO<sub>4</sub> and BiVO<sub>4</sub>/Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> composite catalyst were firstly successfully prepared by a facile and controllable hydrothermal method. The structures, morphologies, optical absorption properties, of as-prepared BiVO<sub>4</sub> and BiVO<sub>4</sub>/Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> were carefully studied by relevant tests. The results of tetracycline removal were investigated under sunlight driven showed that BiVO<sub>4</sub>/Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> heterogeneous catalysts exhibited excellent photocatalytic activity. Moreover, the possible activity photocatalytic mechanism and removal pathways of tetracycline have been investigated and proposed in detail.

#### 2. Experimental

#### 2.1. Reagents

Bismuth nitrate pentahydrate (Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O, AR), trisodium tetraoxovanadate dodecahydrate (Na<sub>3</sub>VO<sub>4</sub>·12H<sub>2</sub>O, CP), tetrabutyl titanate (C<sub>16</sub>H<sub>36</sub>O<sub>4</sub>Ti, CP) and ethanol

absolute ( $C_2H_5OH$ , AR) were purchased from Sinopharm Chemical Reagent Co., Ltd. (SCRC, Shanghai, China). All reagents were used without any further purification.

2.2. Preparation

2.2.1 Synthesis of flower-like BiVO<sub>4</sub>

In a typical experiment, 60 mg Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O was dissolved in 40 mL distilled water; after sonication for 5 min, 100 mg Na<sub>3</sub>VO<sub>4</sub>·12H<sub>2</sub>O was added into. The suspension was transferred to a sealed Teflon autoclave and was heated at 160°C for 12 h [15, 16]. Then, the autoclave was cooled to room temperature, and the precipitation was washed with distilled water and ethanol absolute for three times, respectively. Subsequently the precipitation was dried in an oven at 60 °C for 3 h.

2.2.2 Synthesis of flower-like BiVO<sub>4</sub>/Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>

The fabrication process of flower-like BiVO<sub>4</sub>/Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> via a template method, which was described in Fig. 3 (Growth process of as-prepared samples). Firstly, the flower-like BiVO<sub>4</sub> (0.1g) was dispersed into 40 mL deionized water by sonication for 5 min. Then, a certain amount of Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O and C<sub>16</sub>H<sub>36</sub>O<sub>4</sub>Ti were added into the supernatant solution. During the process, Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> particles were produced and loaded on the petals of BiVO<sub>4</sub>. A series of BiVO<sub>4</sub>/Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> samples were obtained by changed the mass ratio of BiVO<sub>4</sub> and Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> (2:1, 4:1, 8:1), and the pure Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> was prepared by the same method except for addition of BiVO<sub>4</sub>, for the purpose of comparison [17, 18].

#### 2.3 Characterization

The crystalline structures of as-prepared samples were determined by powder X-ray diffraction (XRD) using XRD-6000 X-ray diffractometer (Shimadzu). The chemical compositions was and determined by X-ray photoelectron spectroscopy (XPS) on a PHI 5000 Versa Probe spectrometer (ULVAC-PHI, Japan). The morphology characteristics of the samples were observed by a scanning electron microscope (SEM, QUANTA FEG 250), the energy dispersive X-ray spectroscopy (EDS). The chemical mapping was performanced on an energy dispersive X-ray spectroscopy (EDS) detector, the transmission electron microscopy (TEM) and high-resolution

transmission electron microscopy (HRTEM) were taken over a JEM-200CX instrument. The Brunauer–Emmett–Teller (BET) surface area of the samples was determined by nitrogen adsorption on a BET ASAP 2020 Micrometrics instrument. Both UV–Vis diffuse reflectance spectra (UV-Vis/DRS) and photoluminescence spectra (PL) were recorded to illustrate the optical properties of the samples by UV-Visible spetrometry (UV-3600) and Fluorescence Spectrometry (Horiba HJY FM-4P-TCSPC).

#### 2.4 Photocatalysis

The photocatalytic activities of as-prepared samples were evaluated by the photocatalytic degradation of tetracycline in aqueous solution under sunlight irradiation. In a typical process, 50 mg catalyst was added to 50 mL of 10 mg  $L^{-1}$ tetracycline solution. The suspension mixture was stirred in the dark for 30 min to ensure the establishment of an adsorption-desorption equilibrium between catalyst particles and tetracycline molecules before illumination. Then the suspension solution was irradiated by the light originated from a 500W Xe lamp. During the reaction processes, the suspension mixture was stirred continuously. At given time (10 min) intervals of light irradiation, about 3 mL sample solution was collected, centrifuged and then analyzed in the subsequent research. Meanwhile, the cyclic degradation tests were implemented to investigate the stability and reusability of catalyst. Furthermore, the active species of photocatalytic reactivity were detected by the trapping experiments. Ammonium oxalate (AO), isopropanol (IPA) and benzoquinone (BQ) were served as the scavengers to scavenge the reactivity of superoxide  $(\bullet O_2)$  radical anions, photogenerated holes (h<sup>+</sup>) and hydroxyl (•OH) radicals, respectively. The procedures of trapping experiment were similar to the degradation experiment. The scavengers introduced separately into the aqueous tetracycline solution before addition of the photocatalyst.

#### 2.5 Analysis

The concentration of tetracycline in the solution was preliminarily determined by UV–Vis spectroscopy (UV–Vis 750, PerkinElmer) ,then was monitored accurately by

an Agilent 1200 high performance liquid chromatography (HPLC) with the UV–Vis spectrophotometer 2450 and a 4.6 mm×250 mm Zorbax Eclipse XDB-C18 at 25 °C. The maximum absorption wavelength of tetracycline was 357 nm which was determined by scanning from 200 to 800 nm using a PerkinElmer UV–Vis 750 spectrophotometer. The mobile phase was mixture of methanol-water (30:70, v/v, 2‰ formic acid containing in water) with a flow rate of 1 mL min<sup>-1</sup>. The removal rate for tetracycline was calculated using the formula of  $(C_0 - C)/C_0 \times 100\%$ , where the C is the concentration of tetracycline at a given irradiated time and the C<sub>0</sub> means the initial concentration [19-25]. Meanwhile, the mineralization of tetracycline was monitored by determining the total organic carbon (TOC) by means of a TOC analyser (1030D, OI).

To analyze the degradation pathway of tetracycline with photocatalysis, the intermediates were monitored by liquid chromatography-time-of-flight mass spectrometry (LC-TOF/MS, API 4000 Triple TOF 5600 LCQ Advantage MAX) with electrospray ionization (ESI) source and a Beta Basic-C18 column (150 mm  $\times$  2.1 mm). The mixture of methanol-water (30:70, v/v, 2‰ formic acid containing in water) was used as mobile phase with a flow rate of 1 mL min<sup>-1</sup>. The injection volume was 20µl, the vaporizer temperatures were 300°C, the spectra was scanned in mass range from 50 to 600 m/z with the positive ion mode [19-25].

#### 3. Results and discussion

#### 3.1 Characterizations

#### 3.1.1 Crystal structures

The XRD pattern of as-prepared samples (Fig. 1a) reveal that the diffraction peaks of pure BiVO<sub>4</sub> (as-prepared at 160 °C for 12 h) are in good agreement with the standard values of monoclinic BiVO<sub>4</sub> (JCPDS No. 14-0668). The strongest diffraction peak located at 20 value of 28°, which can be indexed to the (121) plane of monoclinic BiVO<sub>4</sub> [26, 27]. The grazing incidence of the diffraction patterns for as-prepared pure Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> sample demonstrates that the synthesized Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> diffraction peaks were well matched to the standard values of Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> (JCPDS No. 32-0118). The highest diffraction peak located at 20 value of 30°, which can be indexed to the (444) plane

[28, 29]. The pattern of synthesized  $BiVO_4/Bi_2Ti_2O_7$  composite samples indicate the characteristic diffraction peaks of both  $BiVO_4$  and  $Bi_2Ti_2O_7$  crystalline phases. It shows that the  $BiVO_4/Bi_2Ti_2O_7$  composite was prepared successfully.

3.1.2 Chemical composition

The results of XPS (Fig. 1b) analysis provided another insight into the chemical composition of the as-prepared BiVO<sub>4</sub>/Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> composite. The survey spectra of the BiVO<sub>4</sub>/Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> sample indicate a carbon peak at a binding energy of about 284.9–285.9 eV, which is derived from the carbon tape used for fixing sample and from atmospheric  $CO_2$  adsorbing on the sample surface [10, 11]. The two strong peaks are observed at approximately 465.8 eV and 458.3 eV, which are ascribed to the Ti  $2p_{3/2}$  and Ti  $2p_{1/2}$  binding energies, respectively [12, 13]. The dominant peak of O1s locates at 530 eV [14]. The peaks of 164.7 eV and 159.4 eV were attributed by Bi  $4f_{5/2}$  and Bi  $4f_{7/2}$ , which correspond to Bi<sup>3+</sup> [15, 16]. The two peaks at binding energies of 524.2 eV and 517.0 eV are the signals of V  $2p_{1/2}$  and V  $2p_{3/2}$ , which correspond to the V<sup>5+</sup> [17-18]. These XPS detected signals reveal that BiVO<sub>4</sub>/Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> composite containing these four elements and support the XRD results. In addition, no other impurity peaks have been identified in the survey spectra, which suggests the high purity of the obtained BiVO<sub>4</sub>/Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> composite. Furthermore, the SEM-EDS figure (Fig. 2a) and SEM-EDS mapping (Fig. 2b) confirmed that BiVO<sub>4</sub>/Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> composite possesses the elements of O, V, Bi and Ti. The highest peak in (Fig. 2a) is the background peak of aluminum foil for fixed sample. Meanwhile, the SEM-EDS mappings (Fig. 2b) indicate that the corresponding elements are uniformly distributed in BiVO<sub>4</sub>/Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> composite.

Fig. 1 (a) XRD patterns of as-prepared samples and (b) XPS figure of  $BiVO_4/Bi_2Ti_2O_7$  (4:1)

Fig. 2 (a) SEM-EDS of  $BiVO_4/Bi_2Ti_2O_7$  (4:1) and (b) SEM-EDS mapping of  $BiVO_4/Bi_2Ti_2O_7$  (4:1)

3.1.3 Morphology characteristics

The SEM image Fig. 3a (SEM figure of  $BiVO_4$ ) shows that the as-prepared  $BiVO_4$  consists of uniform flower-like morphology. It is also observed that the flower-like

microspheres of BiVO<sub>4</sub> are composed of numerous, thin, densely packed "nanosheet petals". The irregular Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> nanoparticles are revealed in Fig. 3a (SEM figure of Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>). Meanwhile, Fig. 3a (SEM figure of BiVO<sub>4</sub>/Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>) intuitively indicates that the nanoparticles of Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> were gathered on the surface of "petals" BiVO<sub>4</sub> under hydrothermal condition. This result is also confirmed by the results of BET determination (Fig. 3b), the BET surface area of the BiVO<sub>4</sub>/Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> composite sample was calculated to be  $46m^2 \text{ g}^{-1}$ , which is much larger than the surface area of the as-prepared flower-like BiVO<sub>4</sub> (16 m<sup>2</sup> g<sup>-1</sup>), and is less than the surface area of the as-prepared Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> nanoparticles (78 m<sup>2</sup> g<sup>-1</sup>).

Fig. 3 SEM figures (a) and BET figures (b) of as-prepared samples

The TEM image of BiVO<sub>4</sub>/Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> Fig. 4a (TEM figure of BiVO<sub>4</sub>/Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>) further indicates that the flower-like BiVO<sub>4</sub>/Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> composite was successfully synthesized. BiVO<sub>4</sub>/Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> has a diameter of about 800 nm and ultrathin wall thickness of a few nanometers. The HRTEM image Fig.4a (HRTEM figure of BiVO<sub>4</sub>/Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>) clearly shows that the flower-like BiVO<sub>4</sub> possesses fine crystallinity and well agrees with the size and shape of BiVO<sub>4</sub> observed by SEM figures. One of lattice spacing was calculated to be 0.312 nm, corresponding to the (121) planes of monoclinic BiVO<sub>4</sub> [26-27], and another lattice spacing was calculated to be 0.298 nm, corresponding to the (444) planes of Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> [28-29].

#### 3.1.4 Growth process

Generally, various nanoparticle morphologies can be obtained by adding the surfactants during the synthesis process. However, in the present work, the uniform flower-like microspherical morphology of BiVO<sub>4</sub> and BiVO<sub>4</sub>/Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> was prepared without addition of any surfactants. As well-known that the absence of surfactants, the geometrical or individual building components of a material may be regarded as a route for the formation of flower-like morphology by a self-assembly process [30-33]. Based on the above, the growth process BiVO<sub>4</sub> and BiVO<sub>4</sub>/Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> could be approximately deduced and schematically represented in Fig. 4b. The BiVO<sub>4</sub> nanospecies were generated immediately when Bi<sup>3+</sup> and VO<sub>4</sub><sup>3-</sup> were collided under the hydrothermal reaction conditions. Subsequently, these BiVO<sub>4</sub> particles tend to

gather to reduce their surface energies, forming the BiVO<sub>4</sub> nanosheet. With the temperature increasing, the petal-like morphology of BiVO<sub>4</sub> starts to grow from the nanospecies, the single petal-like nanosheet petals can be clearly observed in the SEM and TEM figures. Then, the continuous hydrothermal reaction could lead to the self-assembly of these petals into the uniform flower-like morphology of BiVO<sub>4</sub>. In the process of BiVO<sub>4</sub>/Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> synthesized, the newly generating nanoparticles of Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> were loaded on the petals of BiVO<sub>4</sub> and formed the heterojunction of BiVO<sub>4</sub>/Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> by using flower-like BiVO<sub>4</sub> template.

Fig. 4 (a) TEM figures of  $BiVO_4/Bi_2Ti_2O_7$  (4:1) and (b) growth process of as-prepared samples

#### 3.1.5 Optical properties

The optical properties of the photogenerated electron-hole pairs are recognized as the key factors determining the catalytic activity of photocatalysts. Herein, the optical properties of as-prepared samples were studied by a UV-Vis/DRS and PL. The diffuse reflectance UV-vis spectra (UV-vis DRS) of the samples were recorded on an UV-visible spetrometry (UV-3600) in the wavelength range of 200-800 nm with BaSO<sub>4</sub> powders as the reference. The results of UV-Vis/DRS were showed in Fig. 5a. It indicates that the absorption spectrum of BiVO<sub>4</sub>/Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> composite photocatalyst lies between the ones of BiVO<sub>4</sub> and Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>, which could be attributed to the heterojunction effect in BiVO<sub>4</sub>/Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> composite. Usually, these data can also be converted to the band gap (Eg) to measure light absorption ability of a photocatalyst. The optical absorption near band edge can be evaluated by the equation  $(\alpha hv) = A(hv)$ - Eg)<sup>1/2</sup>, where  $\alpha$ , h, A, v, and Eg are the absorption coefficient, Planck's constant, constant, light frequency and band gap, respectively [10-18]. According to this equation, the band gap of as-prepared samples were calculated and showed in the insert of Fig. 5a (insert the figures of DRS). The band gap of BiVO<sub>4</sub>/Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> composite photocatalyst is 2.75 eV, which is larger than that of flower-like BiVO<sub>4</sub> (2.4 ev) and less than that of Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> (2.9 eV). Thus it can be seen that the light utilization efficiency could be promoted by building BiVO<sub>4</sub>/Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> heterojunction. Furthermore, the charge transfer efficiency can be observed by PL spectrum, the PL

spectrum is mainly photogenerated electron-hole pairs when semiconductor being irradiated by light, and the lower emission often reveals the higher separation efficiency of the charge carriers. The PL spectra of as-prepared samples (Fig. 5b) show that a strong emission peak of pure Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> centered at about 370 nm was observed, the maximum emission peak of BiVO<sub>4</sub> located at approximately 430 nm presents in the spectra, and the lowest emission peak belongs to BiVO<sub>4</sub>/Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>. It indicates that the BiVO<sub>4</sub>/Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> composite has the highest separation efficiency of photogenerated electron-hole pairs. Therefore, the optical properties of UV–Vis/DRS and PL implied that the photocatalytic activity of BiVO<sub>4</sub>/Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> heterojunction could be enhanced.

**Fig. 5** DRS figure (a) and PL figure (b) of as-prepared samples (the insert shows a plot of  $(Ahu)^2$  vs. energy hu)

3.2 Photocatalytic activity

According to the formula of  $(C_0 - C)/C_0 \times 100\%$  and analytical concentration of tetracycline during the process of photocatalytic experiments, the removal rates of tetracycline were calculated and summarized in Fig. 6a. Further, the kinetics of the photocatalytic degradation of tetracycline were studied. It was been reported that degradation of tetracycline followed pseudo first order kinetics [34-35]. According to the following equation, the Ln ( $C_0/C_t$ ) values are obtained and graphically presented in Fig. 6b.

$$\operatorname{Ln}\left(\mathrm{C}_{0}/\mathrm{C}\right) = k_{app} \cdot t \tag{1}$$

Where  $C_0$  is initial concentration of tetracycline, and C is the concentration of tetracycline at a given time 't'. Fig. 6b clearly showed that the experimental data were consistent with the pseudo first order kinetics model. The results also suggested that reducing the concentration of tetracycline the  $k_{app}$  values increase in the photocatalytic reaction system. Therefore, the low initial concentration of tetracycline is found to be efficient.

The result of the blank test (without the photocatalyst) revealed that the tetracycline molecule was very stable in the aqueous solution. Because the photodegradation of the tetracycline was very slowly. The removal rate of pure  $BiVO_4$  (53%) and pure

Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>(60%) were lower than that of BiVO<sub>4</sub>/Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> composites. Furthermore, to examine practical value of BiVO<sub>4</sub>/Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>, the comparative experiment with TiO<sub>2</sub> was carried out, and the removal rate of TiO<sub>2</sub> was about 30%. It indicated that the photoactivity of TiO<sub>2</sub> was lower than that of BiVO<sub>4</sub>/Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> composites. It showed that the as-synthesized BiVO<sub>4</sub>/Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> photocatalysts can efficientlyenhance the photocatalytic activity in compared with the pure BiVO<sub>4</sub> and pure Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>. Meanwhile, the mass ratio of BiVO<sub>4</sub> and Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> in the composite plays an important role for improving the photocatalytic activity of BiVO<sub>4</sub>/Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> compound catalyst. With increasing the mass ratio of BiVO<sub>4</sub>, the photocatalytic activities first increase and then decrease. While the mass ratio of BiVO<sub>4</sub> and Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> is 4:1 in the composite, BiVO<sub>4</sub>/Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> catalyst demonstrates the highest photocatalytic activities for degradation tetracycline. The removal rate approximated 98% after 60 min irradiation under sunlight. It maybe that the suitable mass ratio of BiVO<sub>4</sub> and Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> could be conducive to form the more heterojunctions in BiVO<sub>4</sub>/Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> composite. The heterojunctions can efficiently facilitate charge separation, delay the recombination of photogenerated electron-hole pairs and broad the scope of visible light response. However, with increasing BiVO<sub>4</sub> or Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> could lead some particles of BiVO<sub>4</sub> or Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> couldn't be contacted closely. Hence, the less heterojunctions were constituted effectively and the photocatalytic activity were also reduced. Furthermore, the significantly enhanced photocatalytic activity of flower-like BiVO<sub>4</sub>/Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> composite could also be attributed to the physical properties such as the synergic effect of heterogeneous structure between BiVO<sub>4</sub> and Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>, morphology effect, crystal size, BET surface area, and so on. In particular, the large (diameter of about 800 nm) and ultrathin petals wall with a few nanometer thickness could be more beneficial to promote light absorption and the separation of photogenerated electron-hole pairs.

Usually, it is highly desirable to completely degrade or mineralize pollutants. However, many pollutants can't be completely degraded or mineralized in most of pollution treatment process, and high degradation rate doesn't mean high mineralization rate. To investigate the effective removal rate of tetracycline, the TOC

disappearance was examined during the photocatalytic degradation experiments. It showed that the TOC value of tetracycline decreased from 3.38 mg/L to 1.05 mg/L, and the corresponding mineralization rate was approximately 70% for the  $BiVO_4/Bi_2Ti_2O_7$  (4:1) under the experimental conditions. It suggested that most of tetracycline molecules could be completely mineralized in the photocatalytic process.

To study the stability of heterojunction photocatalyst, the circulation experiments of the as-synthesized  $BiVO_4/Bi_2Ti_2O_7$  (4:1) sample were invetisgated and the results were presented in Fig. 6c. It showed that the photocatalytic activity of the  $BiVO_4/Bi_2Ti_2O_7$  (4:1) sample had no apparent deactivation after three successive recycles for the degradation of tetracycline under visible light irradiation, which revealed that the as-synthesized  $BiVO_4/Bi_2Ti_2O_7$  heterojunction photocatalyst possessed high stability for the practical application. Moreover, the XRD pattern and SEM figure of the  $BiVO_4/Bi_2Ti_2O_7$  (4:1) sample were also been researched after 3th run cycle (Fig. 6d). They clearly indicated that the phase and structure of the  $BiVO_4/Bi_2Ti_2O_7$  sample was not been unchanged, which revealed that the  $BiVO_4/Bi_2Ti_2O_7$  sample was very stable.

Fig. 6 (a) results of photocatalytic activity, (b) the kinetics of photocatalytic degradation, (c) results of cycling experiments, (d) XRD patterns of cycling  $BiVO_4/Bi_2Ti_2O_7$ (4:1) and SEM figure of cycling  $BiVO_4/Bi_2Ti_2O_7$ (4:1)

#### 3.3 Photocatalytic mechanism

It is well known that the photocatalytic activity of a heterojunction photocatalyst is directly related to its energy band structure and the fate of the photoinduced electron-hole pairs, and the photocatalytic removal of pollutants occurs mainly through the involvement of the active species (such as  $h^+$ , •OH, and •O<sub>2</sub><sup>-</sup>). To investigate the photocatalytic reaction mechanism of the BiVO<sub>4</sub>/Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> heterojunction, the energy band structure of BiVO<sub>4</sub>/Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> and the trapping experiments of the active species were studied. According to the references [10-18], the conduction band of BiVO<sub>4</sub> and Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> are 0.31 eV and -0.24 eV, respectively. And the valence band of BiVO<sub>4</sub> and Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> are 2.78 eV and 2.66eV, respectively. Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> has more negative CB and VB than BiVO<sub>4</sub>, which could result in transfer of

photoinduced electron-hole pairs under light irradiation, and the electron hole recombination could also be successfully impeded.

Meanwhile, the trapping experiments of active species involved in the photocatalytic reaction and the enhanced catalytic activity of  $BiVO_4/Bi_2Ti_2O_7$  were invested. The effects of different scavengers on the removal efficiency of tetracycline were shown in Fig. 7a. The results indicated that the removal ratio of tetracycline was significantly decreased to approximate 60%, 30%, 40% after the addition of IPA, BQ, and AO, respectively. Comparing with 98% in the absence of the scavengers, these results reveal that the main reactive species of h<sup>+</sup>, •OH, and •O<sub>2</sub><sup>-</sup> participated in the photocatalytic degradation processes, and h<sup>+</sup> and •O<sub>2</sub><sup>-</sup> radicals play more important role in the photocatalytic degradation reaction.

Furthermore, the photoelectrochemical characterization was conducted on a CHI760E electrochemical workstation (Shanghai, China) with a standard three-electrode system. The prepared samples were loaded onto ITO electrode (1cm\*2cm squares) and served as the working electrode. The counter and reference electrodes were Pt plate and Ag/AgCl electrode and 0.2 M Na<sub>2</sub>SO<sub>4</sub> was used as electrolyte. A 500 W xenon lamp was used to provide light source. The photocurrent was recorded and shown in Fig. 7b. It indicate that the BiVO<sub>4</sub>/Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> (4:1) heterojunction exhibited a higher transient photocurrent density (about 0.6–1.1  $\mu$ A/cm<sup>2</sup>) than that of pure BiVO<sub>4</sub> and Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>, which suggested that the separation efficiency of photogenerated electrons and holes was significantly enhanced at heterojunction interface.

Based on the obtained results and the above discussion, the probable mechanism diagram for the photocatalytic removal of tetracycline using  $BiVO_4/Bi_2Ti_2O_7$  heterojunction under sunlight irradiation maybe proposed and described in Fig. 7c. Under the light illumination, the electrons (e<sup>-</sup>) in the CB of  $Bi_2Ti_2O_7$  are excited and transferred to the CB of  $BiVO_4$ , and the generated holes in the VB of  $BiVO_4$  are synchronously excited and transferred to the VB of  $Bi_2Ti_2O_7$ . Then the electrons in the CB of  $BiVO_4$  could be trapped by surface chemisorbed  $O_2$  to generate  $\cdot O_2^{-}$ . Meanwhile, the h<sup>+</sup> in VB of  $Bi_2Ti_2O_7$  can directly oxidize the organic compounds or react with surface-adsorbed H<sub>2</sub>O to produce  $\cdot OH$ . Therefore, the photogenerated

charge carriers are effectively separated by heterojunction between  $BiVO_4$  and  $Bi_2Ti_2O_7$ , and the photocatalytic activity is also improved.

**Fig. 7** (a) results of active species detection, (b) The photocurrent responses of as-prepared samples for each switch-on/off event under sunlight irradiation and (c) possible photocatalytic mechanism

3.4 Removal pathways

To identify the degradation products generated during the photocatalytic process and deduce degradation pathways, the degradation intermediates of tetracycline were monitored by LC-TOF/MS. In the reaction process of BiVO<sub>4</sub>/Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> heterojunction photocatalysis of tetracycline, numerous intermediates produced are presented in Table 1. Based on these results and previous studies [19-25], the proposed removal pathways were speculated in Fig. 8.

Table 1 The identified intermediate products of tetracycline degradation by using LC-TOF/MS

No.	[M + H]+ measured	Molecular formula	Chemical structure (symbol in Fig. 8)
TC	445	$C_{22}H_{24}N_{2}O_{8} \\$	TC
1 <sup>st</sup>	461	$C_{22}H_{25}N_2O_9$	p (1)
2 <sup>nd</sup>	434	$C_{20}H_{22}N_2O_9$	p (2)
3 <sup>rd</sup>	393	$C_{19}H_{23}NO_8$	p (3)
4 <sup>th</sup>	375	$C_{19}H_{21}NO_7$	p (4)
5 <sup>th</sup>	208	$C_{11}H_{12}O_4$	p (5)
6 <sup>th</sup>	171	C <sub>8</sub> H <sub>13</sub> NO <sub>3</sub>	p (6)
7 <sup>th</sup>	416	$C_{20}H_{20}N_{2}O_{8} \\$	p (7)
8 <sup>th</sup>	402	$C_{20}H_{20}NO_8$	p (8)
9 <sup>th</sup>	357	$C_{19}H_{17}O_7$	p (9)
$10^{\text{th}}$	191	$C_{11}H_{11}O_3$	p (10)
11 <sup>th</sup>	172	$C_8H_{12}O_4$	p (11)

It could be observed that the peak with m/z of 445 was identified, which was regarded as the tetracycline molecule. Meanwhile, a lot of extra peaks appeared along with the

degradation of tetracycline (such as m/z = 461, 434, 393, 375, 208, 171, 416, 402, 357,191, 172). Combining with these detection results and the literature [19-25], the degradation removal process could be proposed as two main pathways. The first pathway showed that the intermediates (p1) with the m/z of 461 was caused from a cycloaddition of •OH locating the C11a-C12 double-bond, and the maximum adsorption band of tetracycline at the 357 nm would be disappeared by this effect. With continuous irradiation and attack of the active species (such as  $\cdot OH$ ,  $\cdot O_2^-$ , and  $h^+$ ), tetracycline molecules and the intermediates were broken down into secondary degradation products with lower molecular weight. The compound (p2) with m/z of 434 was produced by losing of two methyls from the tertiary amine; the product (p3) with m/z of 394 was dissociated off a formamid. The intermediate product (p4) m/z of 375 was removal of a hydroxyl from p3. Further degraded products with m/z of 172 and 209 (p5 and p6) resulted from the breaking of the C5a–C6 bond and C11a–C12 bond of p4. The second pathway should be considered as the two methyls locating at the tertiary amine from the tetracycline molecules were left firstly and produced the m/z of 416 (p7). Following, the amino connecting with the C5 was removed with m/zof 402 (p8), then a formamid was abandoned with m/z of 358 (p9). Two additional ions at m/z 191 and 173 (p10 and p11) were obtained due to broking of the C5a-C6 bond and C11a–C12 bond.

Thus, it can be seen that tetracycline had been gradually disintegrated, and the relevant degradation intermediates were produced and then decomposed, finally these substances were converted into  $CO_2$ ,  $H_2O$ ,  $NH_4^+$  and the other degradation products. In the removal process, these intermediate products mainly stemmed from tetracycline degradation after losses of some groups from the ring or wreck of bridge ring, and the positions were vulnerable to be attacked by the active species often locating at the oxhydryl, methyl, third amine, formamid and the band of C5a–C6 and C11a–C12, etc. However, the photocatalytic removal of tetracycline is a very complex process, and about which further studies should be carried out.

Fig. 8 The proposed pathways for removal of tetracycline

#### 4. Conclusion

A novel flower-like BiVO<sub>4</sub> was firstly synthesized by a facile surfactant-free hydrothermal process, and a novel flower-like BiVO<sub>4</sub>/Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> heterojunction photocatalyst was successfully prepared by the template method. The growth process of flower-like BiVO4 and BiVO4/Bi2Ti2O7 composite could be considered to be a self-assembly process. The optical properties of DRS and PL indicate that the as-synthesized BiVO<sub>4</sub>/Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> heterojunction catalyst sample can enhance photoresponse and exhibit an excellent separation ability of photogenerated electron-hole pairs. The as-synthesized BiVO<sub>4</sub>/Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> heterojunction exposed a superior photocatalytic efficiency and stability for removal of tetracycline in aqueous solution. The improvement in photocatalytic activity displayed by flower-like BiVO<sub>4</sub>/Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> composite catalyst could be attributed to the heterojunction structure, morphology effect, crystal size, BET surface area, and so on. The results of free radicals trapping experiments reveal that  $h^+$  and  $\bullet O_2^-$  radicals play more important role. The LC-TOF/MS analysis showed that the degradation intermediates of tetracycline mainly stemmed from tetracycline degradation after losses of some groups from the ring or wreck of bridge ring. This work will not only contribute to the shape control about synthesis of uniform BiVO<sub>4</sub> hierarchical structures and excellent BiVO<sub>4</sub> composite heterojunction photocatalyst, but also offer a valuable insights into purifying polluted water resources and environmental governance.

#### Acknowledgements

This work was supported by the National Natural Science Foundation of China (No. 21307103), the funds of Southwest University (No. XDJK2010E002), the Institute of Circular Economy of Bijie and Guizhou University (No. ZK005), the Guizhou Provincial Science and Technology Supporting Program (No. LKB [2013] 08, No. LH [2014] 7518), the Guizhou Provincial Education Department Supporting Program (No. KY [2015] 406), the National Natural Science Foundation of China (No. 21307103).

#### Reference

[1] P. Wang, P.S. Yap, T.T. Lim, Appl. Catal. A 399 (2011) 252–261.

[2] C.V. Gómez-Pacheco, M. Sánchez-Polo, J. Rivera-Utrilla, J. López-Penalver,

Chem. Eng. J. 178 (2011) 115-121.

[3] Z. Cetecioglu, B. Ince, M. Gros, S. Rodriguez-Mozaz, D. Barceló, D. Orhon, O. Ince, Water Res. 47 (2013) 2959-2969.

[4] A. L. Giraldo, G.A. Penuela, R.A. Torres-Palma, N. J. Pino, R. A. Palominos, H.

D. Mansilla, Water Res. 44 (2010) 5158-5167.

- [5] Z. Zhang, W. Wang, M. Shang, W. Yin, Catal. Commun. 11 (2010) 982-986.
- [6] C. Karunakaran, S. Kalaivani, P. Vinayagamoorthy, Mater. Lett. 122 (2014) 21-24.
- [7] Z. Wang, K. Xie, L. Zhao, B. S. Zhang, Chem. Commun. 51 (2015) 2437-2439.
- [8] Y. Qiu, G. Xu, Q. Kuang, S. Sun, S. Yang, Nano Res. 5 (2012) 826-832.
- [9] N. S. Chaudhari, A. P. Bhirud, R. S. Sonawane, L. K. Nikam, S. S. Warule, V.H.

Rane, B. B. Kale, Green Chem. 13 (2011) 2500-2506.

[10] L. Zhang, J. S. Hu, C. L. Pan, X. H. Huang, C. M. Hou, Rsc Advances 5 (2015)78457-78467.

[11] S. Balachandran, N. Prakash, K. Thirumalai, M. Muruganandham, M. Sillanp, M. Swaminathan, Ind. Eng. Chem. Res. 53 (2014) 8346-8356.

[12-Ti] F. E. Oropeza, I. J. Villar-Garcia, R. G. Palgrave, D. J. Payne, Journal of Materials Chemistry A 2 (2014) 18241-18245.

[13-Ti] D. Hou, X. Hu, P. Hu, W. Zhang, M. Zhang, Y. Huang, Nanoscale 5 (2013) 9764-9772.

- [14] H. Shi, H. Tan, W. Zhu, Z. Sun, Y. Ma, E. Wang, Journal of Materials Chemistry A 3 (2015) 6586-6591.
- [15] J. Zhang, H. Cui, B. Wang, C. Li, J. Zhai, Q. Li, Applied Surface Science 300 (2014) 51-57.
- [16] A. Zhang, J. Zhang, Applied Surface Science 256 (2010) 3224-3227.

[17] S. Gu, W. Li, F. Wang, S. Wang, H. Zhou, H. Li, Applied CatalysisB-Environmental 170 (2015) 186-194.

[18] M. Long, W. Cai, J. Cai, B. Zhou, X. Chai, Y. Wu, Journal of Physical Chemistry B 110 (2006) 20211-20216.

[19] X.D. Zhu, Y.J. Wang, R.J. Sun, D.M. Zhou, Chemosphere 92 (2013) 925-932.

[20] S.L. Tang, A.M. Li, C.Z Wang, Adv. Mater. 239-242 (2011) 1888-1891.

[21] Z. Lu, P. Huo, Y. Luo, X. Liu, D. Wu, X. Gao, C. Li, Y. Yan, J. Mol. Catal. A: Chem. 378 (2013) 91-98.

[22] J. Wu, H. Zhang, N. Oturan, Y. Wang, L. Chen, M.A. Oturan, Chemosphere 87(2012) 614-620.

[23] Y.C. Fu, L. Peng, Q.R. Zeng, Y. Yang, H.J. Song, J.H. Shao, S.Y. Liu, J.D. Gu, Chem. Eng. J. 270 (2015) 631-640.

[24] H.W. Wang, D.Y. Zhang, S.Y. Mou, W.J. Song, F.A. Al-Misned , M.G. Mortuza,X.L. Pan, Chemosphere 136 (2015) 102-110.

[25] M.D. Cazes, M.P. Belleville, E. Petit, M. Llorca, S.R.Mozaz, J.D. Gunzburg, D. Barcelo, J.S. Marcano, Catal. Today 236 (2014) 146-152.

[26] J. Li, W. Zhao, Y. Guo, Z. Wei, M. Han, H. He, S. Yang, C. Sun, Appl. Surf. Sci. 351 (2015) 270-279.

[27] L.W. Zhang, C.Y. Lin, Small 10 (2014) 3970-3978.

[28] Z.Y. Zhang, C.Y. Jiang, P. Du, Y.P. Wang, Ceram. Int. 41 (2015) 3932-3939.

- [29] J.H. Yi, X.J. Yuan, H.J. Wang, H. Yu, F. Peng, Materials & Design 86 (2015) 152-155.
- [30] M. Muruganandham, G.J. Lee, J.J. Wu, I. Levchuk, M. Sillanpaa, Mater. Lett. 98 (2013) 86-89.

[31] Y. Sun, Y. Xie, C. Wu, S. Zhang, S. Jiang, Nano Res. 3 (2010) 620-631.

[32] Y. Li, Z.H. Sun, S.M. Zhu, Y.L. Liao, Z.X. Chen, D. Zhang, Carbon 94 (2015)599-606.

[33] X. Xing, Y. Ma, J. Li, G. Fan, H. Ding, X. Ma, L. Yang, G. Xi, CrystEngComm 16 (2014) 10218-10226.

[34] C. Lalhriatpuia, D. Tiwari, A. Tiwari, S.M. Lee, Chemical Engineering Journal 281 (2015) 782-792.

[35] D. Tiwari, C. Lalhriatpuia, Lalhmunsiama, S.M. Lee, S.H. Kong, Applied Surface Science 353 (2015) 275-283.

**Figure captions** 



Fig. 1 (a) XRD patterns of as-prepared samples and (b) XPS figure of  $BiVO_4/Bi_2Ti_2O_7~(4{:}1)$ 



Fig. 2 (a) SEM-EDS of  $BiVO_4/Bi_2Ti_2O_7$  (4:1) and (b) SEM-EDS mapping of  $BiVO_4/Bi_2Ti_2O_7$  (4:1)



Fig. 3 SEM figures (a) and BET figures (b) of as-prepared samples



Fig. 4 (a) TEM figures of  $BiVO_4/Bi_2Ti_2O_7\,(4{:}1)$  and (b) growth process of as-prepared samples



**Fig. 5** DRS figure (a, the insert shows a plot of  $(Ahu)^2$  vs energy hu) and PL figure (b) of as-prepared samples



Fig. 6 (a) results of photocatalytic activity, (b) the kinetics of photocatalytic degradation,

(c) results of cycling experiments, (d) XRD patterns of cycling  $BiVO_4/Bi_2Ti_2O_7$  (4:1) and SEM figure of cycling  $BiVO_4/Bi_2Ti_2O_7$  (4:1)



**Fig. 7** (a) results of active species detection, (b) The photocurrent responses of as-prepared samples for each switch-on/off event under sunlight irradiation and (c) possible photocatalytic mechanism



Fig. 8 The proposed pathways for removal of tetracycline