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# Construction of $Bi_2Ti_2O_7/Bi_4Ti_3O_{12}$ composites with enhanced visible light photocatalytic activity

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ABSTRACT

Novel $Bi_2Ti_2O_7/B_4Ti_3O_{12}$ heterostructures have been synthesized via a facile and economical method. The as prepared B24 sample ($Bi_2Ti_2O_7/Bi_4Ti_3O_{12}$) with small crystal size exhibits enhanced visible light response and efficient separation of photogenerated carriers. Thus, compared with pure $Bi_2Ti_2O_7$ or $Bi_4Ti_3O_{12}$, $Bi_2Ti_2O_7/Bi_4Ti_3O_{12}$ composites show better performance in the photodegradation and mineralization of tetracycline hydrochloride (TC). According to experimental results, the possible photocatalytic mechanism has been proposed.



## 1. Introduction

Recently, visible-light-driven photocatalysis has stimulated considerable attention, as it shows great potential in solar energy conversion and environmental purification [1]. Among various photocatalysts, $Bi_4Ti_3O_{12}$, a typical aurivillius oxide semiconductor, has a lower optical band gap (Eg of 2.8 eV), compared to $TiO_2$ (Eg of 3.2 eV) [2]. It has been explored as a novel photocatalyst, owing to its unique crystal structure of alternating $(Bi_2O_2)^{2+}$ and perovskite $(Bi_2Ti_3O_{10})^{2-}$ layers, as well as the electronic structure consisting of a hybridized valence band at the Bi 6s and O 2p levels [3]. However, the same as $TiO_2$, single $Bi_4Ti_3O_{12}$ also has two main drawbacks which greatly hinder its further practical application: one is the relatively limited absorption of visible-light and the other is the rapid recombination of photogenerated electron-hole pairs [4].

To address these problems, coupling $Bi_4Ti_3O_{12}$ with a narrower-band-gap semiconductor may be an effective method to increase its photocatalytic property. It has been proved that the formation of heterojunctions with intimate interface can efficiently facilitate the separation of electron-hole pairs [5,6]. Thus, lots of work have be done to prepare novle-$Bi_4Ti_3O_{12}$-based composites, especially mixed crystal materials. Du et al. and Liu et al. reported $Bi_{12}TiO_{20}/Bi_4Ti_3O_{12}$ and Au@Fe-$Bi_4Ti_3O_{12}$ heterojunctions by solid-state reaction [7,8]. Zhao et al. and Shi et al. prepared $Bi_2Ti_2O_7/Bi_4Ti_3O_{12}$ nanofibers by electrospinning [9,10]. However, these methods demand high-level equipment and the products obtained show large crystal size, which will limit their practical application and photocatalytic performance. Very recently, Yu's group reported novel $Bi_2MoO_6$ nanocrystals with lattice shrinkage and decrease crystal size by $F^-$ doping [11]. Thus, It is necessary to design a facile way to prepare $Bi_4Ti_3O_{12}$-based composite with small crystal size.

In this work, novel $Bi_2Ti_2O_7/Bi_4Ti_3O_{12}$ mixed crystal materials have been prepared by a facile and economical method. The as-obtained heterostructures exhibit small crystal size and improved visible light absorption. Additionally, greatly reduced recombination ratio of photogenerated carriers can be observe by photoluminescence and photocurrents measurement. Compared with pure $Bi_2Ti_2O_7$ or $Bi_4Ti_3O_{12}$, $Bi_2Ti_2O_7/Bi_4Ti_3O_{12}$ composites show better performance in the photodegradation and mineralization of TC. It is anticipated that the repeatable and imitable method may open up an effective strategy to design other mixed crystal photocatalysts with distinguished performance.

## 2. Experimental

In a typical procedure, 0.5 ml $Ti(OBu)_4$, 0.5 ml diacetone and a certain amount of $Bi(NO_3)_3{\cdot}5H_2O$ were dissolved in 20 ml glacial acetic acid under vigorous stirring. The resulting transparent solution was transferred into an open petri dish and heated at 180 °C in the oven. After 30 min, the solvent has been evaporated and the precursor powder can be obtained. Finally, the precursor powder obtained was calcined at 650 °C for 2 h in air. Also, the

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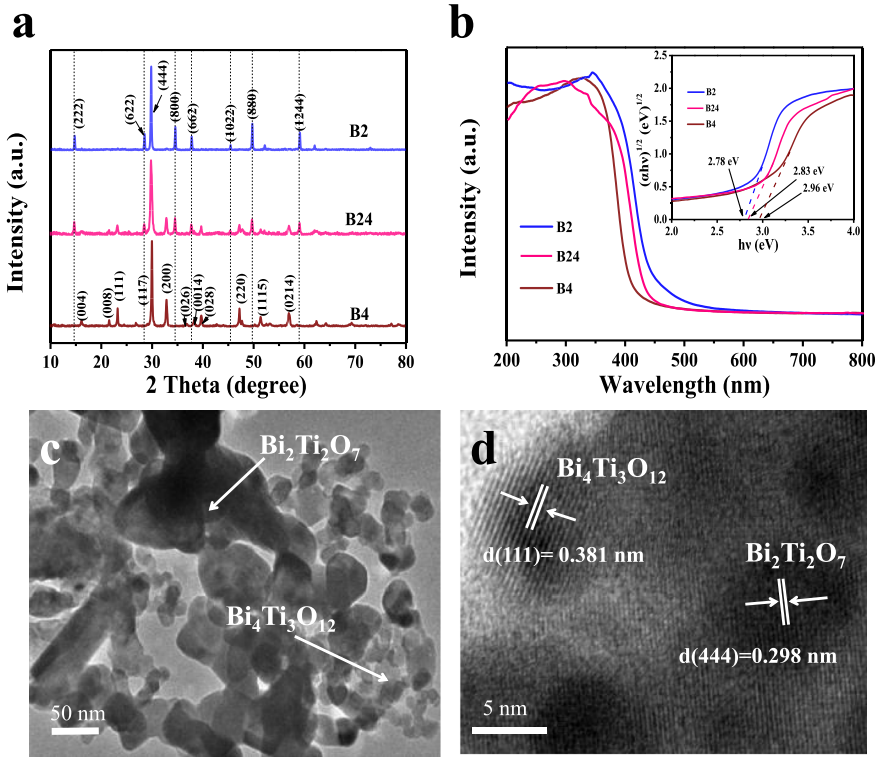


**Fig. 1.** (a) XRD patterns and (b) UV–vis diffuse reflectance spectra of the as-prepared B2, B24 and B4 samples. (c) TEM image and (d) HRTEM image of the B24 sample. (inset) plot of $(\alpha hv)^{1/2}$ for the band gap energy of B2, B4 and B24 samples.

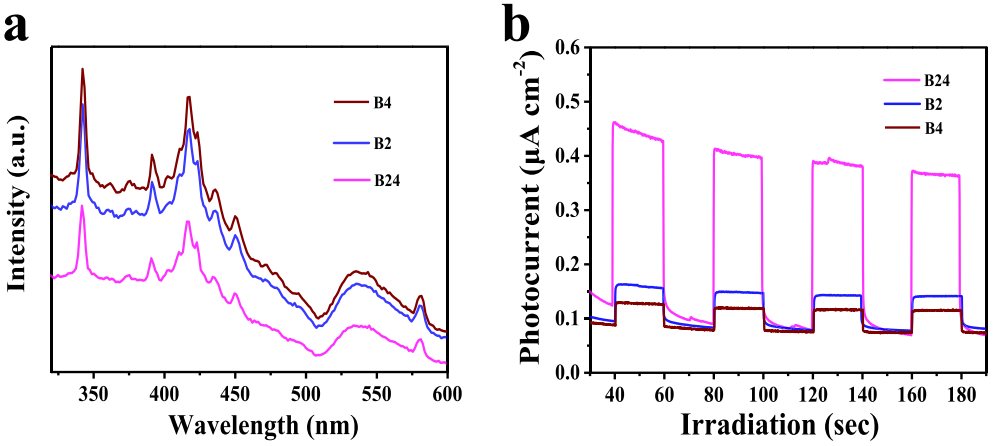


**Fig. 2.** (a) PL spectra and (b) transient photocurrent response of B2, B4 and B24 samples.

corresponding samples obtained from different amounts of Bi $(NO_3)_3{\cdot}5H_2O$ (0.6 g, 0.9 g and 1.1 g) were respectively labeled as B2 (pure $Bi_2Ti_2O_7$), B24 ($Bi_2Ti_2O_7/Bi_4Ti_3O_{12}$ composites) and B4 (pure $Bi_4Ti_3O_{12}$).

The details of characterization, photoelectrochemical measurements and photocatalytic activity measurements are shown in Supporting Information.

## 3. Results and discussion

The crystal structure and phase composition of the pure and composite systems were examined by XRD. Fig. 1a shows the XRD curves of the B2, B24 and B4 samples. For the B2 sample, the main distinctive peaks could match well with pyrochlore $Bi_2Ti_2O_7$ (JCPDS card No. 32-0118) [8]. Also, in curve of B4, the observed diffraction peaks could be perfectly indexed to the corresponding planes of perovskite $Bi_4Ti_3O_{12}$ (JCPDS card No. 21-1272) [9]. For B24, all the peaks can be assigned to $Bi_2Ti_2O_7$ or $Bi_4Ti_3O_{12}$ and no extra peaks are found, which indicate no impurity in the heterojunction systems.

UV–vis DRS was performed to study the light absorption properties of the as-prepared samples and the results are shown in Fig. 1b. Compared with pure B2, B24 exhibits an obvious red shift, indicating the enhanced visible light absorption. The well matched energy level and abundant heterogeneous structure may account for this enlarged absorption, which could possibly lead to the better photocatalytic performance [12]. The band gaps of the samples