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Bismuth titanate nanorods and their visible light photocatalytic properties

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ABSTRACT

Bismuth titanate nanorods have been prepared using a facile hydrothermal process without additives. The bismuth titanate products were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), high-resolution TEM (HRTEM) and UV–vis diffusion reflectance spectrum. XRD pattern shows that the bismuth titanate nanorods are composed of cubic $Bi_2Ti_2O_7$ phase. Electron microscopy images show that the length and diameter of the bismuth titanate nanorods are 50–200 nm and 2 μm, respectively. Hydrothermal temperature and reaction time play important roles on the formation and size of the bismuth titanate nanorods. UV–vis diffusion reflectance spectrum indicates that bismuth titanate nanorods have a band gap of 2.58 eV. The bismuth titanate nanorods exhibit good photocatalytic activities in the photocatalytic degradation of methylene blue (MB) and *Rhodamine B* (*RB*) under visible light irradiation. The bismuth titanate nanorods with cubic $Bi_2Ti_2O_7$ phase are a promising candidate as a visible light photocatalyst.

1. Introduction

Titanium dioxide is one of the most effective photocatalysts for the degradation of organic, inorganic pollutes and toxic materials under ultraviolet (UV) light irradiation. However, titanium dioxide belongs to a wide band gap semiconductor with the value of 3.02 eV for rutile and 3.18 eV for anatase [1]. It can absorb only 5% of sunlight in UV region limiting its practical applications. Sunlight consists of UV light with the value of less than 2%. Therefore, it is of important significance to explore new types of photocatalysts under visible light irradiation. Bismuth titanate with different phases, such as $Bi_{12}TiO_{20}$ [2,3], $Bi_4Ti_3O_{12}$ [4], $Bi_2Ti_2O_7$ [5] and $Bi_{20}TiO_{32}$ [6,7] have been widely studied as a class of promising photocatalysts which can degradate organic pollutes under visible light.

Low-dimensional titanate nanoscale materials may improve the photocatalytic properties for the degradation of organic pollutes owing to their special structure, morphology, size and spatial arrangement, quantum confinement effect and low dimensionality. Some efforts have been devoted to low-dimensional bismuth titanate nanoscale materials. For example, Lin et al. [8] reported the synthesis of bismuth titanate microspheres with $Bi_4Ti_3O_{12}$ phase by a simple hydrothermal process. The bismuth titanate microspheres exhibited good photocatalytic activities for the degradation of methyl orange (MO) under visible light irradiation. Bismuth titanate nanospheres, nanowires, microflowers and microspheres with $Bi_{12}TiO_{20}$ phase displayed high photocatalytic activities for the degradation of *Rhodamine B* under visible light irradiation in comparison with bulk bismuth titanate powders [9]. Bismuth titanate nanospheres with the diameter of 10–90 nm and perovskite $Bi_4Ti_3O_{12}$ phase showed high photocatalytic activities to degradate 10 ppm methyl orange in 4 h [10]. Bismuth titanate nanorods can inhibit the recombination of electron–hole pairs and enhance the photocatalytic activity for the degradation of organic pollutes due to their special one-dimensional nanostructure, size and high photocatalytic sensitivity in the visible region [11]. Bismuth titanate nanorods exhibited better photocatalytic activity for the degradation of *Rhodamine B* under visible light irradiation than commercial TiO_2 and bulk bismuth titanate powders. To date, bismuth titanate nanorods are rarely reported.

Hydrothermal method belongs to a facile process for synthesizing nanorods with different composition [12–14]. Therefore, it is of important significance to synthesize bismuth titanate nanorods by a facile hydrothermal process for researching the photocatalytic activities of organic pollutes, such as methylene blue (MB) and *Rhodamine B* (*RB*). MB and *RB* are important organic dye molecules originated from dyestuff manufactures, finishers and dyers which pollutes the environments [15]. It is important to remove MB and *RB* molecules by the photocatalytic process using bismuth

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titanate nanorods as the photocatalysts. In the paper, bismuth titanate nanorods have been synthesized by a facile hydrothermal process without any additives. The growth process of the bismuth titanate nanorods has been analyzed in detail by analyzing the roles of hydrothermal temperature and reaction time on the formation of the bismuth titanate nanorods. The photocatalytic properties of the bismuth titanate nanorods for the degradation of MB and *RB*, respectively under visible light irradiation have also been analyzed.

2. Experimental details

All raw materials were AR grade and used without any treatment. High pure bismuth acetate ($C_6H_9BiO_6$, AR grade) and titanium butoxide ($C_{16}H_{36}O_4Ti$, AR grade) were purchased from Aladdin Reagent Co., Ltd. of PR China. In a typical procedure, 0.45 g bismuth acetate and 0.4 g titanium butoxide were dissolved in 60 mL deionized water, respectively under vigorous stirring. Then, the mixture was placed in a 100 mL autoclave with a Teflon liner. The autoclave was maintained at 80–180 °C for different reaction time. Subsequently the autoclave was cooled naturally in air. The obtained grey precipitates were filtered, washed with deionized water for several times and dried at 60 °C in air. Finally, grey bismuth titanate powders were obtained.

The products were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), high-resolution TEM (HRTEM) and UV diffusion reflectance spectrum. XRD pattern was carried out on a Bruker AXS D8 X-ray diffractometer equipped with a graphite monochromatized Cu Kα radiation (λ = 1.5406 Å). The samples were scanned at a scanning rate of 0.05°/s in 2θ range of 20–80°. SEM observation was performed using JEOL JSM-6490LV SEM with a 15 kV accelerating voltage. TEM and HRTEM samples were prepared by putting several drops of solution with bismuth titanate nanorods onto a standard copper grid with a porous carbon film after the nanorods samples were dispersed into distilled water and treated for about 10 min using supersonic wave apparatus. TEM and HRTEM observations were performed using JEOL JEM-2100 TEM operating with 1.9 Å point-to-point resolution operating with a 200 kV accelerating voltage with a GATAN digital photography system. The UV–vis diffusion reflectance spectrum of the bismuth titanate nanorods was obtained using a UV3600 UV–vis spectrometer (Shimadzu International Co., Ltd. of Japan) and a thermo Electron Corporation with a reflectance diffuse accessory.

The photocatalytic degradation of MB and *RB* was employed to evaluate the photocatalytic activities of the bismuth titanate nanorods. The photocatalytic reaction was performed in the OCRS-IV photocatalytic system which was purchased from Kaifeng Hongxing Technology Co., Ltd. of Henan province of PR China. MB and *RB* were AR grade, purchased from Aladdin Reagent Co., Ltd. of PR China and used without further treatment. The photocatalytic experiments were conducted after solar visible light irradiation. The photocatalytic reaction was carried out with 2.5–20 mg bismuth titanate nanorods suspended in 10 ml MB and *RB* solution with the concentration of 10 mg L^{-1}, respectively in a quartz glass cell. Before visible light irradiation, the suspensions were magnetically stirred and maintained in the dark for 30 min to ensure the adsorption and desorption equilibrium between bismuth titanate nanorods and organic pollutants. Then the solution mixture was exposed to visible light irradiation under magnetic stirring. All experiments were carried out at room temperature in air. The MB and *RB* solution was separated from bismuth titanate nanorods by filter unit, respectively. The obtained solution was analyzed by UV756 UV–visible spectrometer (Shanghai Youke Instrument Co., Ltd. of PR China) to record the intensity of the maximum band in the UV–vis absorption spectra. The absorption was converted to the concentration of MB and *RB*, respectively referring to a standard curve showing a linear behavior between the concentration of organic molecules and the intensity of the absorption peak at maximum band.

3. Results and discussion

The structure of the bismuth titanate nanorods has been researched by analyzing the XRD pattern of the bismuth titanate nanorods obtained from 180 °C for 24 h (Fig. 1). By indexing the JCPDS cards (PDF cards, No. 32-0118), the diffraction peaks can be indexed to cubic $Bi_2Ti_2O_7$ phase. The strong and sharp diffraction peaks show a good crystallinity of the bismuth titanate nanorods. The cubic $Bi_2Ti_2O_7$ phase is same to that of the bismuth vanadate nanorods synthesized by the hydrothermal process using bismuth nitrate and titanium isopropoxide as the raw materials by adjusting the pH value [5]. However, the cubic $Bi_2Ti_2O_7$ phase is totally different from the $Bi_{12}TiO_{20}$, $Bi_4Ti_3O_{12}$ and $Bi_{20}TiO_{32}$ phases of the bismuth titanate with different morphologies synthesized by other methods [1–6].

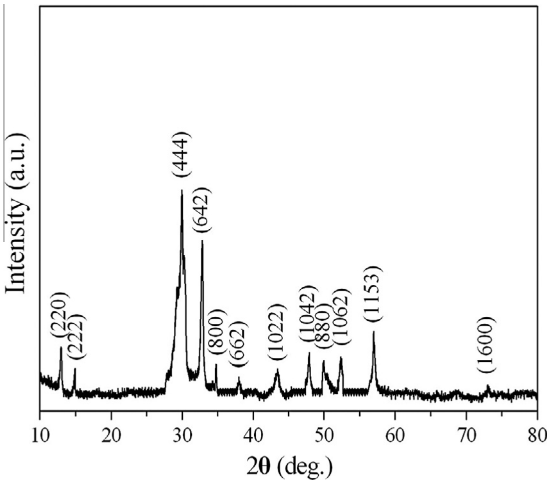

Fig. 1. XRD pattern of the bismuth titanate nanorods.

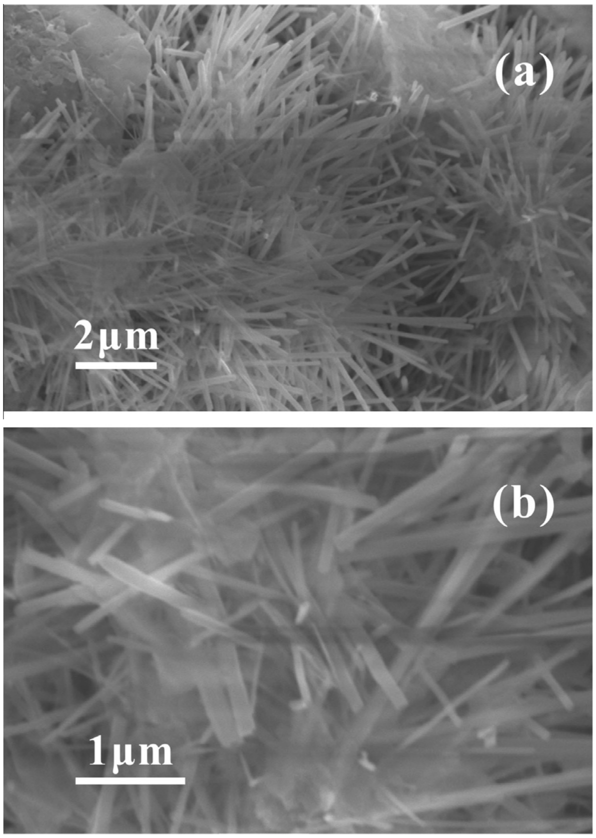

Fig. 2. SEM images of the bismuth titanate nanorods with different magnifications.

Fig. 2 shows the SEM image of the sample synthesized from 180 °C for 24 h. It can be observed that the products are composed of rod-shaped morphology (Fig. 2a). The SEM image with higher magnification (Fig. 2b) indicates that the diameter and length of the bismuth titanate nanorods are about 50–200 nm and 2 μm, respectively. The diameter is uniform throughout the nanorods. No other nanostructures are observed from the products showing that the products consist of high pure bismuth titanate nanorods.

The morphology and microstructure of the bismuth titanate nanorods are also observed by TEM. Fig. 3a shows typical TEM image of the bismuth titanate nanorods. The morphology is similar