Materials Today Communications 8 (2016) 134–138

Contents lists available at ScienceDirect

Materials Today Communications

journal homepage: www.elsevier.com/locate/mtcomm

Microwave hydrothermal synthesis of a new bismuth titanate compound

Ao Xia*, Guoqiang Tan, Huijun Ren

School of Materials Science and Technology, Shaanxi University of Science and Technology, Weiyang District, Xi'an 710021, China

ARTICLE INFO

Article history:
Received 18 February 2016
Received in revised form 31 May 2016
Accepted 18 July 2016
Available online 19 July 2016

Keywords:
Bismuth titanate compound
Photocatalyst
Microwave hydrothermal
Semiconducting materials

ABSTRACT

A new bismuth titanate compound was synthesized by microwave hydrothermal method, using $Bi(NO_3)_3{\cdot}5H_2O$ and $(NH_4)_2TiF_6$ as raw materials. The EDS result reveals that the new compound is composed of Bi, Ti, O and F elements. The XRD results indicate that increasing reaction temperature or prolonging reaction time is beneficial to the growth of the crystal. The SEM results show that the morphology of samples changes from sphere to irregular polyhedron with increase of reaction time. According to the UV–vis diffuse reflectance spectrum, the compound has a band gap of 2.76 eV. The photocatalytic performance of the sample synthesized at 180 °C for 10 min was evaluated by the decolorization of rhodamine B (RhB) under UV-light irradiation, and the result shows that the degradation rate of RhB is more than 90% after 60 min irradiation.

1. Introduction

As a semiconductor photocatalyst, TiO_2 has been widely applied in the degradation of organic, inorganic pollutes and toxic materials, because it possesses many advantages such as chemical stability, low cost, nontoxicity, and high photocatalytic activity [1,2]. However, due to its large band gap energy (3.2 eV), TiO_2 can exhibit the higher photocatalytic activity only under UV light irradiation. Therefore, many efforts have been made to develop photocatalysts with high activity under a wide range of visible light. Recently, much attention has been given to a series of visible light active bismuth-based photocatalysts, such as $BiVO_4$ [3], $BiFeO_3$ [4], Bi_2WO_6 [5], Bi_2MoO_6 [6] and bismuth titanate compounds. Many Bi^{3+}-containing compounds have been found to possess a narrow band gap and exhibit high visible light photocatalytic activity because of the hybridized O 2*p* and Bi $6s^2$ valence bands [7].

Bismuth titanate with different phases, such as $Bi_{12}TiO_{20}$ [8], $Bi_4Ti_3O_{12}$ [9], $Bi_2Ti_2O_7$ [10] and $Bi_{20}TiO_{32}$ [11] have been widely studied as a class of promising photocatalysts which can degradate organic pollutes under visible light. Among them, perovskite $Bi_4Ti_3O_{12}$ and sillenite $Bi_{12}TiO_{20}$ have received more attention for their higher photocatalytic ability in degrading organic pollutants. Different methods have been developed for the synthesis of different phases of bismuth titanate powders such as solid state reaction [12], microemulsion method [13], co-precipitation [14], mechanical synthesis [15], sol–gel routes [16], hydrothermal processing [17] and microwave hydrothermal processing [18]. Among these methods, microwave hydrothermal process has the features of quick response, high efficiency and energy-saving. Moreover, it is easy to control the crystallinity and morphology of powders synthesized by microwave hydrothermal method.

In our experiment, we aimed to synthesis $Bi_4Ti_3O_{12}$ powder via microwave hydrothermal method, using $Bi(NO_3)_3{\cdot}5H_2O$ and $(NH_4)_2TiF_6$ as raw materials. However, a new compound was obtained unexpectedly. The synthesis process is facile and rapid. In the paper, the constitution and the morphology of the new material have been characterized. Its photocatalytic properties for the degradation of rhodamine B (RhB) dye in aqueous solution under UV-light irradiation have also been analyzed.

2. Experimental

2.1. Synthesis

All chemicals were analytically pure grade and used directly without any purification. 0.693 g $Bi(NO_3)_3{\cdot}5H_2O$ and 0.212 g $(NH_4)_2TiF_6$ were dissolved respectively in 22 mL dilute nitric acid (the volume ratio 1:10 between nitric acid and distilled water) and 20 mL distilled water at room temperature. Mixing the two solutions, and 8 mL distilled water was added to adjust the volume of the mixture to 50 mL. After stirring for 30 min at room temperature, the precursor was transferred into 100 mL polytetrafluoroethylene (PTFE) autoclave. The autoclave was sealed and maintained at different temperature for different time, then cooled

* Corresponding author.
E-mail address: xiaao@sust.edu.cn (A. Xia).

http://dx.doi.org/10.1016/j.mtcomm.2016.07.003
2352-4928/

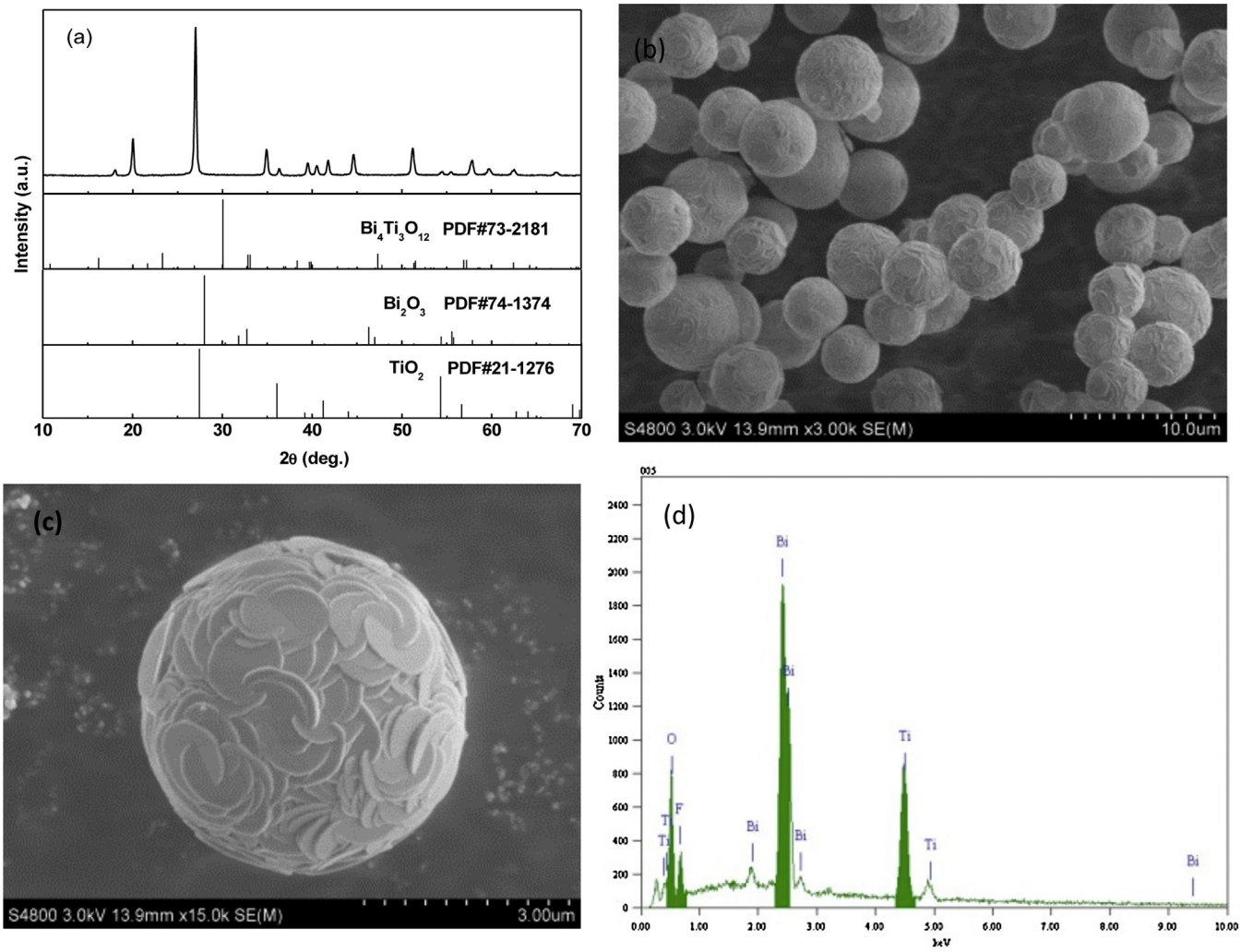

Fig. 1. (a) XRD pattern. (b, c) SEM images and (d) EDX spectrum of as-prepared sample.

to room temperature naturally. The precipitates were collected and washed with distilled water and absolute ethanol for three times, respectively. Finally, the products were dried at 90 °C for 12 h.

2.2. Characterization

XRD analysis was performed on an X-ray diffractometer (D/max-2200X, Rigaku, Japan) with Cu Kα radiation (λ = 0.15418 nm). The morphology was examined by a field emission scanning electron microscopy (FE-SEM, S4800, Hitachi), equipped with an energy-dispersive X-ray (EDX) analysis system. The photoabsorption performance was measured by an UV–vis diffuse reflectance spectroscope (UV-2550, Shimadzu, Japan).

2.3. Photocatalytic test

0.05 g photocatalyst was added into 50 mL RhB solution (5 mg/L) and the solution was stirred for 30 min in darkness before illumination to ensure the adsorption-desorption equilibrium. Then the suspension was exposed to UV irradiation (300 W mercury lamp) under magnetic stirring. At given time intervals, 5 mL of the suspension was taken out and centrifuged to remove the photocatalyst particles. The concentration of RhB was determined by a UV–vis spectrophotometer (Model SP-756p) by monitoring its characteristic absorption at 554 nm.

3. Results and discussion

Fig. 1a shows the XRD pattern of the sample synthesized at 180 °C for 10 min. It can be seen that all the XRD peaks are clear and sharp which indicates the sample crystallizes well. However, the XRD pattern is not in agreement with any one of the known standard cards including $Bi_4Ti_3O_{12}$ (PDF#73-2181), Bi_2O_3 (PDF#74-1374) and TiO_2 (PDF#73-2181) shown in Fig. 1a. By analyzing the XRD pattern, it is also found that the sample is not a mixture of two or various compounds containing the elements bismuth and/or titanium. So we inferred that the sample should be a new compound with distinctive composition and structure.

Fig. 1b and c show the typical FE-SEM images of the as-prepared sample. As shown in Fig. 1b, the sample is spherical shape with the diameter of 2–6 μm. From Fig. 1c, it can be seen that the spherical particle is assembled from numerous nano-flakes which crisscross together with thickness of about 80 nm and diameter of about 1 μm.

The chemical composition of the sample was determined by the EDX technique. As shown in Fig. 1d, the EDX spectrum displays that the sample contains Bi, Ti, O and F elements. According to Atom% of each element presented in Table 1, it could be calculated that the molar ratio of Bi, Ti, O and F elements corresponds to 3:6:14:5. Based on above analysis, we deduced the sample could be a new bismuth titanate compound doped by fluorine (signed as BTOF).

The experiments were repeated at different temperature for different time to synthesize the new compound. Fig. 2 shows the