



Editor's Choice paper

Citric acid assisted solvothermal synthesis of BiFeO₃ microspheres with high visible-light photocatalytic activity

Yuning Huo*, Yi Jin, Ya Zhang

Department of Chemistry, Shanghai Normal University, 100 Guilin R., Shanghai 200234, PR China

ARTICLE INFO

Article history:

Received 1 April 2010

Received in revised form 29 July 2010

Accepted 7 August 2010

Available online 14 August 2010

Keywords:

BiFeO₃ photocatalyst

Solvothermal preparation

Citric acid

Visible light

Methylene blue (MB)

ABSTRACT

A novel BiFeO₃ photocatalyst in the shape of uniform microspheres has been synthesized by solvothermal process assisted with chelating effect of citric acid. The higher photoactivity of this catalyst than that of BiFeO₃ via solid-state reaction for methylene blue (MB) degradation under visible-light irradiation is owing to the high crystallization of perovskite-type BiFeO₃, high surface area with hollow structure, narrow band gap energy of 2.1 eV, and the promotion of separation of photo-induced electrons and holes. Additionally, no decrease of activity after being reused repetitively for five times is indicative of the high hydrothermal stability of BiFeO₃ particles without crystal phase transformation.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Due to the increasing environmental pollution in recent years, the degradation of organic pollutants has generated broad interest of photocatalysis for both scientific understanding and potential applications [1,2]. The TiO₂ photocatalyst is widely employed in the environmental cleaning by degrading organic pollutants and hydrogen production by splitting water, due to their excellent photochemical stability, low cost, and non-toxicity [3,4]. However, the large band gap energy (3.2 eV) of TiO₂ severely restricts its absorption in the visible-light region, although many efforts have been devoted to extend optical response of TiO₂ into visible-light region and to improve the quantum efficiency of photocatalysis by modifying TiO₂ with metals, non-metals, semiconductor oxides, and/or photo-sensitizers [5–8]. The development of novel non-titania semiconductors with strong absorbance for broad ranged visible lights represents a current trend in photocatalysis [9,10]. Bismuth-oxide-based photocatalysts are attractive materials [11–14], however, Bi₂O₃ shows deactivation due to formation of carbonate and this limitation is only partially solved via formation of nanocomposites. Bi-contained oxides often offer interesting optical properties for photocatalytic applications [15–17]. Recently, the perovskite-type BiFeO₃ photocatalyst (BFO) has attracted considerable attention owing to the narrow band-gap energy (2.1 eV) [18–21], and high chemical stability [17,22], in addition to acting as a well-known multiferric compound, which exhibiting a coexis-

tence of simultaneous ferroelectric and magnetic order parameters [23,24]. Various methods have been developed for the preparation of micrometer- and nanometer-sized BiFeO₃ crystallites, such as conventional solid-state reaction [25,26], co-precipitation [27], sol-gel process [28–30], and hydrothermal route [21,31–33]. However, in general, it is still inconvenient to prepare BiFeO₃ compounds without impurity phases due to the low stability of Bi atom in perovskite BiFeO₃ [34], and it is not easy to achieve the structure-controllable BiFeO₃ with high surface area [16,35]. Furthermore, the synthesis of BiFeO₃ sometimes is based on complex solution processes and involves toxic precursors [28,36]. Therefore, it is essential to develop an environmental-friendly method to obtain the pure BiFeO₃ photocatalyst with controllable structure. As we know, the solvothermal process has emerged as a powerful method for the fabrication of inorganic materials, because of their great synthetic flexibility and controlled growth of small-scale crystallites [37,38]. In this paper, we report a solvothermal synthesis route, which involves no toxicants and is carried out at lower temperature, to prepare pure BiFeO₃ crystals in the shape of uniform microspheres with high surface area. The correlation between controllable structure of BiFeO₃ and high photoactivity together with durability under visible-light irradiations is investigated.

2. Experiment

2.1. Catalyst preparation

All source chemicals (analytical grade) are purchased from Shanghai Chemical Regents Company and used without further purification. In a typical run of synthesis, 0.040 mol/L bismuth

* Corresponding author. Tel.: +86 21 64322642; fax: +86 21 64322272.
E-mail address: Huoyuning@shnu.edu.cn (Y. Huo).

nitrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$), iron nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) and citric acid with a molar ratio of 1:1:1 are added into the mixture solution of 10.0 mL glycerol and 30.0 mL ethanol. It has been found that $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ is very difficult to be dissolved without glycerol. After ultrasonic dispersion for 10 min, the mixed solution becomes clear and presents brownish red color. Then, the solution is poured into a 50.0 mL stainless-steel Teflon-lined autoclave for the solvothermal reaction with a filling capacity of 80%. After being sealed, the autoclave is heated up to a certain temperature and held for the desired time, and then is cooled to room temperature naturally. The products are filtered and washed with both distilled water and anhydrous ethanol several times, followed by being dried at 353 K for 12 h and being calcined at expected temperature for 4 h. The as-prepared samples are denoted as BFO-X-Y-Z, where X, Y and Z refer to the alcoholysis time in hours (X), alcoholysis temperature in K (Y) and calcination temperature in K (Z), respectively. For comparison, the BiFeO_3 prepared without citric acid under the same condition of BFO-24-433-773 is expressed as BFO-NCA, and the conventional BiFeO_3 is synthesized via solid-state reaction at 1073 K for 5 h [26] and denoted as BFO-SSR. The P25 TiO_2 is commercially available and used without further treatment.

2.2. Characterizations

The sample composition is determined by inductively coupled plasma (ICP, Varian VISTA-MPX). The catalyst structure is investigated by X-ray diffraction (XRD, Rigacu Dmax-3C, Cu Ka radiation). The grain size is calculated by using Scherrer equation based on the principal XRD peak. Surface morphology and particle size are observed through scanning electron microscopy (SEM, JEOL JSM-6380LV) and transmission electronic microscopy (TEM, JEM-2010). N_2 adsorption-desorption isotherms are measured on a Quantachrome NOVA 4000e at 77 K. The Brunauer-Emmett-Teller (BET) method is used to calculate the specific surface area (S_{BET}). The thermal stability is investigated by a thermogravimetric analyzer (DTG-60H, $10^\circ\text{C}/\text{min}$ heating rate). The light absorption ability is analyzed by UV-vis diffuse reflectance spectra (DRS, MC-2530).

2.3. Activity test

The photocatalytic degradation of methylene blue (MB) is carried out at 303 K in a self-designed 100 mL glassy reactor containing 0.050 g catalyst and 50.0 mL of 10.0 mg/L MB aqueous solution. The reaction system is stirred vigorously (>800 rpm) to eliminate diffusion effect on the reaction kinetics. Keeping the mixture for more than 1 h to reach adsorption equilibrium, the photocatalytic reaction is initiated by irradiating with a 500 W Xenon lamp (CHF-XM500, light intensity = $600 \text{ mW}/\text{cm}^2$) located at 18 cm above the solution. To make sure that the photocatalytic reaction is really driven by visible-light, all the UV lights with wavelength lower than 420 nm are removed by a glass filter (JB-420). Each run of the reactions is lasted for 4 h and the MB left in the solution is analyzed by a UV spectrophotometer (UV 7504/PC) at its characteristic wavelength ($\lambda = 665 \text{ nm}$) [39]. Little organic byproducts have been identified by HPLC-MS after the reaction for 4 h. Preliminary tests show that there is a good linear relationship between the light absorbance and the concentration of organic compounds. Meanwhile, experimental results also confirm that only less than 9.0% MB is adsorbed by catalysts after reaction for 4 h without light irradiation (Table 1), and only 6.0% MB is decomposed under light irradiation in the absence of catalysts, and thus could be neglected in comparison with the photocatalysis process. The reproducibility of the results is checked by repeating the experiments at least three times and is found to be within acceptable limits ($\pm 5\%$). The durability of catalyst is measured according to the following procedure. After each run of photocatalysis reactions, the photocatalyst

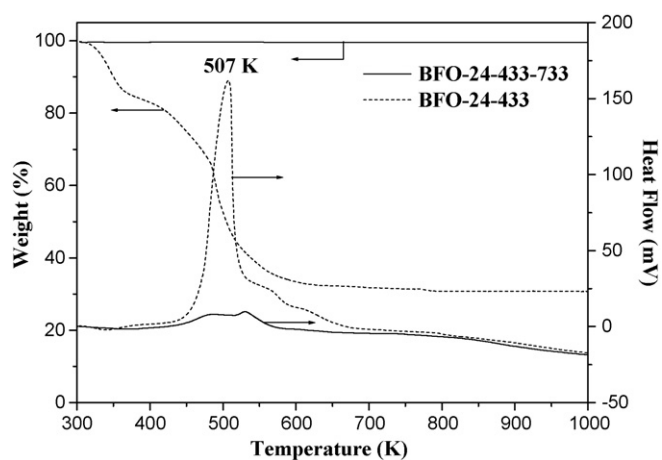


Fig. 1. TG-DTA curves of BFO-24-433 and BFO-24-433-773 samples.

is separated from aqueous solution by centrifugation, washed with distilled water for three times and dried at 373 K for 12 h. Then, each recycling test is conducted under the same conditions for 4 h and the MB degradation yield is determined to show the change of activity.

3. Results and discussion

The TG-DTA curves in Fig. 1 reveal that BFO-24-433 sample exhibits an exothermic peak around 507 K with weight loss around 30%, while the BFO-24-433-773 displays no significant weight loss and exothermic peaks, suggesting the complete removal of organic residues after the calcination. According to the ICP results, the Bi/Fe molar ratio in BFO-24-433-773 determines the formation of BiFeO_3 . XRD patterns in Fig. 2 further demonstrate that both BFO-24-433-773 and BFO-SSR have the typical perovskite-type BiFeO_3 with R3c rhombohedral structure (JCPDS 86-1518), as shown in Scheme 1 [32,40], and no other crystal phases can be observed in the diffraction patterns. However, based on the Scherrer equation ($D = K\lambda/\beta \cos \theta$), the BFO-24-433-773 has much smaller crystallite size than BFO-SSR (see Table 1). It could be attributed that the rate of crystal nucleation is greater than that of crystal growth during the solvothermal process, and thus leads to smaller crystal size and lower aspect ratio of the crystal than those resulted from fast crystal growth under solid-state reaction at high temperature [32]. Accordingly, the BFO-24-433-773 reveals much higher S_{BET} than

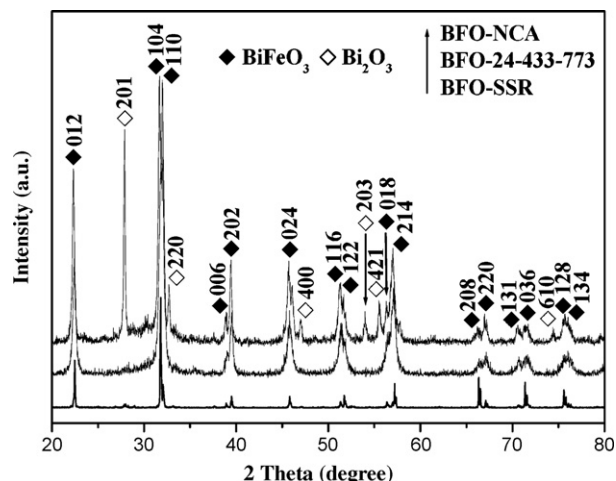


Fig. 2. XRD patterns of BiFeO_3 samples synthesized via with different routes.

Download English Version:

<https://daneshyari.com/en/article/66444>

Download Persian Version:

<https://daneshyari.com/article/66444>

[Daneshyari.com](https://daneshyari.com)