



Shape-controlled preparation of bismuth ferrite by hydrothermal method and their visible-light degradation properties



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ABSTRACT

Bismuth ferrite (BiFeO₃) has been prepared by hydrothermal method using Fe(NO₃)₃·9H₂O and Bi(NO₃)₃·5H₂O as the starting materials. The single-phase cube-like BiFeO₃ materials with defined morphologies were successfully synthesized by controlling the experimental parameters. Effects of reaction time, KOH concentration and organic dispersant on the BiFeO₃ particle morphology, size and property were systematically investigated. The prepared BiFeO₃ particles present tunable absorption characters by controlling the particle size and morphology. The prepared samples can degrade methyl orange (MO) under visible light (>420 nm). Cubic BiFeO₃ particles with a size of ca.1.4 μm could be synthesized by using PVP as the dispersant, which shows the highest activity of MO photo-degradation. The photocatalytic mechanism is proposed and active components are further convinced by EPR analysis.

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1. Introduction

As the fast development of industry and economy, environment pollution and energy depletion become unavoidable problem for human being. A variety of organic compounds from dyeing industry may pollute the water since they are often hard to be degraded owing to their complex structures and specific ring atoms [1,2]. The wastewater treatment is more and more important for pollution control and sustainable development. In comparison with conventional wastewater treatment, semiconductor photocatalysis is an advanced and environmentally friendly treatment which directly degrades organic compound into CO₂ and H₂O by using solar light as the power source.

BiFeO₃ (BFO) is an attractive material because of its fascinating applications in novel electronic device, which shows ferroelectric and antiferromagnetic properties at room temperature and has

high phase transition temperatures (magnetic transition temperature, defined as *Neel* temperature, $T_N = 350\text{--}380\text{ }^\circ\text{C}$ [3,4] and ferroelectric phase transition temperature, defined as *Curie* temperature, $T_C = 820\text{--}850\text{ }^\circ\text{C}$ [5,6]). Recently, BiFeO₃ has attracted significant attentions for solar applications such as photo-degradation of organic pollutants and H₂ generation from water splitting due to its narrow band gap and the bulk photovoltaic effect [7,8]. Comparing with conventional TiO₂ photocatalysts, BiFeO₃ has a narrower band gap of ca.2.1 eV which promotes the photocatalytic activity under visible light. This is particularly important since more than 40% of the total solar energy is visible light; on the contrary, the UV light responding TiO₂-based photocatalysts only occupies ca. 4% [8].

There are various methods including sol–gel method [7,9], hydrothermal method [10], microwave hydrothermal method, solid state reaction [11,12], rapid liquid-phase sintering [13], pulsed laser deposition [14], electro-spinning [15], magnetron sputtering [16] and other methods [17,18] have been employed to obtain BiFeO₃ particles with destined size and morphology. However, there are still some obstacles have to be solved before the application of BiFeO₃ material. The main problem is the appearance of impurity

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phases (such as $\text{Bi}_{25}\text{FeO}_{40}$, $\text{Bi}_2\text{Fe}_4\text{O}_9$, and $\text{Bi}_{36}\text{Fe}_{24}\text{O}_{57}$) during preparation which may influence the practical performances [12,19–21]. Three reasons have been attributed to the appearance of impurity. One is the evaporation of Bi component during the preparation due to the low decomposition temperature of bismuth salts. The other is the altered chemical valence of Fe ion in an oxygen-deficient atmosphere [22]. Thirdly, the synthesis of perovskite BiFeO_3 is difficult in thermodynamics [23]. Therefore, the synthesis of pure-phase BiFeO_3 material is still the focus of research.

Hydrothermal method has also been used to synthesize BiFeO_3 particles [24–29]. Comparing with the indispensably high calcination temperature in sol–gel process, e.g. 600 °C, the hydrothermal method can directly synthesize BFO at a relatively low temperature. It offers an opportunity to better control the purity, morphology and size of BiFeO_3 material. However, impurity, particle size and shape control are the remanent challenges that have to be solved in the synthesis of BiFeO_3 by the hydrothermal method. The influence of experiment parameters such as reaction time, mineralizer (KOH) concentration and organic dispersant on the controllable synthesis of BiFeO_3 is still not clear. Additionally, the shape-related performance, especially the photocatalytic activity under visible light irradiation, is necessary to be clarified.

In this study, we report the synthesis of single-phase BiFeO_3 particles with destined morphologies by a facile hydrothermal method under different experimental conditions. Effects of reaction time, KOH concentration and dispersants on the morphology and size of BiFeO_3 particle were systematically investigated. The photocatalytic performance of synthesized BiFeO_3 has been investigated and methyl orange (MO), a typically stable organic contaminant, could be degraded under visible light (wavelength >420 nm). The catalytic performance is found to have a close relationship with the specific shape and the mechanism has also been proposed.

2. Experimental

2.1. Preparation of BiFeO_3 powders

$\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and KOH were supplied by Sinopharm Chemical Reagent Co., Ltd. Polyvinylpyrrolidone (PVP) and polyethylene glycol (PEG 4000) were purchased from Aladdin industrial corporation; while cetrimonium bromide (CTAB) was supplied by Tianjin Yongda chemical reagent Co., Ltd. All the reagents were in A.R. grade and used without any purification.

BiFeO_3 powders were synthesized by hydrothermal method under different conditions. $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in stoichiometric proportions (1:1 M ratio) were dissolved in 10 mL distilled water under mechanical stirring. KOH solution was slowly dropped into the above solution to coprecipitate Bi^{3+} and Fe^{3+} ions and the mixture was mechanically stirred for 2 h. The final alkali concentrations and reaction times were systematically adjusted. Then, the dispersants such as PVP, CTAB or PEG 4000 were added to the above solution with 1 h stirring, respectively. Finally, the brown suspension was transferred into 100 mL Teflon vessel with a 70% volume filling degree. The temperature was increased to 200 °C and kept for 5 h. After naturally cooling down to room temperature, the products were washed several times with distilled water and alcohol, respectively.

2.2. Characterization

XRD patterns of the prepared BiFeO_3 particles were acquired on Bruker Axs D2 PHASER diffractometer using $\text{Cu-K}\alpha$ radiation as the source. SEM images were observed on Hitachi SU 8010 instrument.

UV–vis spectra were measured on a Shimadzu UV-3600 spectrophotometer under integrating sphere mode. The EPR spectra were measured on a Bruker A300 EPR spectrometer at room temperature. The parameters for the EPR analysis were set as below: power, 20.20 mW; microwave frequency, 9.85 GHz; center field, 3516 G; sweep width, 200 G; modulation frequency, 100 kHz.

2.3. Measurement of photocatalytic performance

The photocatalytic activity of the BiFeO_3 particles for degradation of MO was evaluated at the natural pH value under irradiation of a 300 W Xe lamp with a 420 nm cut-off filter. 0.30 g prepared catalyst was added into 5 mg L^{-1} MO solution to make a catalyst concentration of 30 mg L^{-1} . Xe lamp was switched off before the achievement of adsorption/desorption balance. A small quantity of the solution was taken at an interval of 0.5 or 1 h to test the concentration of MO. The concentration was determined by measuring the value of band around 464 nm using a UV–vis spectrophotometer. The catalyst particles were separated from the solution by 10 min centrifugation at 9000 rpm min^{-1} before the absorption measurement.

3. Results and discussions

Fig. 1 shows the XRD patterns of the BFO particles synthesized under varied conditions. Fig. 1a is the patterns of powders synthesized with different reaction time at a fixed KOH concentration of 7 M. Diffraction bands from $\text{Bi}_{25}\text{FeO}_{40}$ (JCPDS # 46-0416) are observed when the reaction time is 2.5 h and no signals from perovskite-phase BiFeO_3 appeared. However, single-phase BiFeO_3 could be achieved at a longer reaction time of 3 h. No signals from impure phases are observed in the XRD patterns and all the diffraction peaks can be signed to the rhombohedral structure of BiFeO_3 (space group: $R3m$, JCPDS # 20-0169). All the synthesized samples can be single-phase BiFeO_3 when the reaction time is longer than 3 h. Fig. 1b shows the patterns of samples synthesized at 200 °C for 5 h with different KOH concentrations. It is obvious that single-phase BiFeO_3 without any impurity can also be acquired at a low KOH concentration of 2 M. From the above analyses, it can be reasonably concluded that the reaction time is important for synthesizing single-phase BiFeO_3 and the minimum reaction time for achieving single-phase BiFeO_3 is 3 h; on the contrary, the concentration of KOH has no obvious influence on the formation of BFO which could be synthesized in a wide range of 2–7 M.

Fig. 1c, d and e shows the XRD patterns of the BFO particles synthesized with different dispersants at 200 °C for 5 h. Fig. 1c is the patterns of powders synthesized with different concentrations of PVP. It is obvious that single-phase BiFeO_3 can be acquired at different concentrations of PVP. However, the relative intensity of BFO diffraction bands increases with the increase of PVP amount which indicates that PVP may accelerate the crystallinity. Fig. 1d is the patterns of powders synthesized with different concentrations of CTAB. BiFeO_3 could be formed with the concentration of CTAB in the range of 1–3.3 wt%. Fig. 1e is the patterns of powders synthesized with different concentrations of PEG. As shown, pure-phase BiFeO_3 particles can also be achieved with different concentrations of PEG. On the contrary, the relative intensity of BFO synthesized by CTAB or PEG does not change with the increase of dispersant which suggests that CTAB or PEG may not promote the crystallinity.

Fig. 2 shows SEM images of BiFeO_3 particles prepared with different concentrations of KOH at 200 °C for 5 h. The product synthesized at 2 M KOH concentration is composed of submicron BiFeO_3 particles with particle size of ca. 3.0 μm (Fig. 2a). Order edges are also observed although the whole particle shape is

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