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Surfactant-assisted hydrothermal preparation of submicrometer-sized two-dimensional $BiFeO_3$ plates and their photocatalytic activity

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Abstract 2-Dimensional bismuth ferrite ($BiFeO_3$) plates were hydrothermally synthesized starting from $Bi(NO_3)_3$ and $Fe(NO_3)_3$ in the presence of cetyltrimethylammonium bromide (CTAB) as a morphology directing template. The amount of CTAB was altered to study their effects on the final results. The average diameter and thickness of $BiFeO_3$ plates were about 1.3–2 μm and 200–300 nm. X-ray diffraction (XRD), scanning electron microscopy (SEM), UV–visible diffuse reflection spectrum (UV–vis DRS) were used to investigate the samples' crystallinity, purity, morphology, spectral features. Furthermore, the effect of the morphology on photocatalysis was also evaluated by photodecolorization of orange II under a blended-light mercury fluorescent lamp ($\lambda \geq 410$ nm). As a result, $BiFeO_3$ plates showed a much higher photocatalytic activity than bulk $BiFeO_3$ for photodecolorization of orange II, suggesting potential application in photocatalysis.

Introduction

Bismuth ferrite $BiFeO_3$ having Fe^{3+} is not only an interesting magnetic material but also a ferroelectric and antiferromagnet with a Néel temperature of 643 K [1]. Moreover, $BiFeO_3$ is a composite system of small band-gap metal oxides of Fe_2O_3 and Bi_2O_3, both of which have been used as visible light-driven photocatalyst [2, 3].

$BiFeO_3$ and its solid solution films with a pure ABO_3 structure were fabricated by many methods such as the pulsed-laser, the magnetic controlling sputtering technology on various substrates [4] and a solution evaporation method of tartrate precursor and ferrioxalate precursor route [5, 6]. During synthesis process, $BiFeO_3$ usually existed in multiphase due to the effect of the formation kinetics. How to prepare phase pure and nanosized $BiFeO_3$ with different morphologies is still an interesting research topic. Hydrothermal synthesis can be processed at lower temperature compared to solid phase synthesis and obtain phase pure at certain condition [7].

In the present work, uniform $BiFeO_3$ submicrometer plates with an rhombohedral structure were hydrothermally synthesized with the assistance of the surfactant CTAB. The effect of the morphology of the resultant $BiFeO_3$ on photocatalysis was also evaluated by photocatalytic decolorization of orange II under visible light irradiation.

Experimental section

Synthesis of the samples

All chemicals were analytical grade and used as received without further purification. In a typical procedure, CTAB was added into 0.15 mol/L stoichiometric amount of $Bi(NO_3)_3$ and $Fe(NO_3)_3$ aqueous solution and magnetically stirred until a homogeneous gel was formed. To control the shape of the products, the concentration of CTAB were adjusted to 0, 0.05, 0.1 mol/L. Subsequently, 0.006 mol $Fe(NO_3)_3$ and 6 g NaOH were added to the above solution under stirring. After further stirring for half an hour, the mixture was transferred into a Teflon-lined stainless autoclave and deionized water was added to 80% of the total

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volume. After that, the autoclave was heated at 180 °C for 24 h. Then the autoclave was cooled to room temperature naturally. The resulted samples were collected and washed with deionized water and ethanol and dried at 80 °C in air.

Characterization of the samples

Purity and crystallization of the as-prepared samples were characterized by powder X-ray diffraction (XRD) on a *D*/max –γA X-ray diffract meter at 40 kV and 200 mA with monochromatic CuK_α (λ = 1.5418Å) radiation. Diffraction patterns from powdered samples held on quartz zero background plates were obtained by θ–θ geometry. Morphologies of the prepared samples were further examined with scan electron microscopy (SEM) by a XL-30 electron microscope operated at an accelerating voltage of 20 kV. UV–vis diffuse reflectance spectra (DRS) of the samples were measured by using an UV-2401 (Shimadzu) UV–vis spectrophotometer.

Photocatalytic test

Photocatalytic activities of the $BiFeO_3$ extra fine plates were evaluated by degradation of orange II under irradiation of a 450 W blended-light mercury fluorescent lamp ($\lambda \geq 410$ nm). Photodegradation of orange II was carried out at atmospheric pressure using air as oxidant in the photoreactor. In a typical experiment, a 100 mL of orange II solution (concentration: 10 mg/L) was placed in the photoreactor under vigorously stirring. Prior to irradiation, the catalyst was immerged into the solution in dark for 30 min to ensure adsorption/desorption equilibrium, then the solution was irradiated. In order to monitor the dye concentration in the solution, a little amount of reaction solution (ca. 3 mL) for UV-spectroscopy analysis was taken from the photoreactor at appropriate time intervals.

Results and discussion

Chemical structure

The XRD patterns of the synthesized samples are shown in Fig. 1. The diffraction pattern of sample 1 ($BiFeO_3$ made without CTAB) agreed well and were indexed to $BiFeO_3$ with JCPDS card No. 20-0169. This result indicated that the present hydrothermal conditions are favorable for the formation of $BiFeO_3$ with a rhombohedral structure. However, the presence of trace impurity phases, such as $Bi_{25}FeO_{40}$, $Bi_2Fe_4O_9$ (product of high base concentration) appearing with diffraction peaks at 2θ of 28.09° and 28.89° was detected [7].

The effect of CTAB on the $BiFeO_3$ crystallization was demonstrated through the changes of the XRD patterns. At 0.05 mol/L CTAB concentration, the pattern of diffraction peaks (sample 2) was as same as that obtained in the blank experiment (sample 1), meaning that at a lower CTAB concentration the presence of CTAB unaffected the chemical structure of the resultant $BiFeO_3$. As increasing the concentration of CTAB up to 0.1 mol/L, rhombohedral structured $BiFeO_3$ was also synthesized, but other phases was also detected with diffraction peaks appearing at 2θ of 32.98° and 35.52°. Thus, $BiFeO_3$ can be synthesized in the presence of CTAB with a concentration of less than 0.1 mol/L. The effect of CTAB on the morphology of the resultant $BiFeO_3$ was discussed in other section.

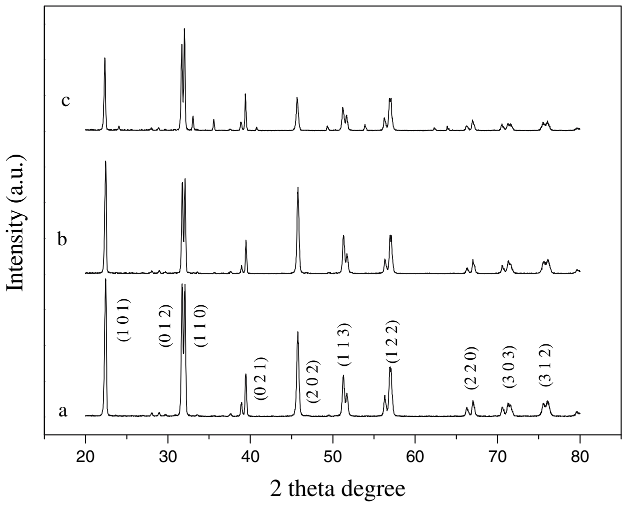

Fig. 1 X-ray diffraction patterns of different samples. (**a**)–(**c**) Represents hydrothermally synthesized $BiFeO_3$ with the presence of 0, 0.05, 0.1 mol/L CTAB, respectively

Band gap of the $BiFeO_3$ samples

Optical absorption of $BiFeO_3$ samples were measured by using an UV–vis spectrometer. Figure 2 showed a typical

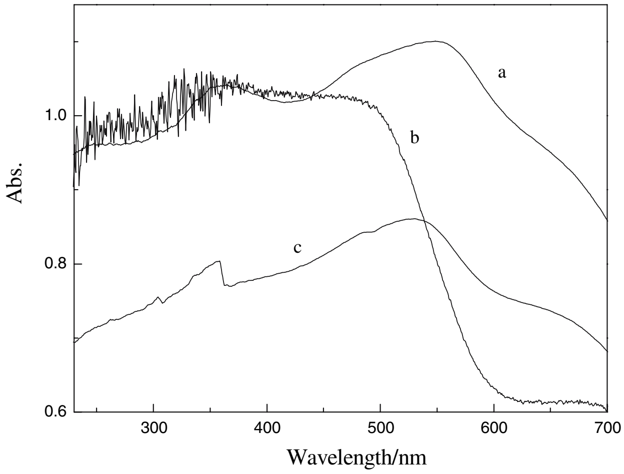

Fig. 2 UV–vis diffuse reflection spectra of $BiFeO_3$. (**a**)–(**c**) Represents $BiFeO_3$ samples made with 0.05 mol/L, 0 mol/L, 0.1 mol/L CTAB

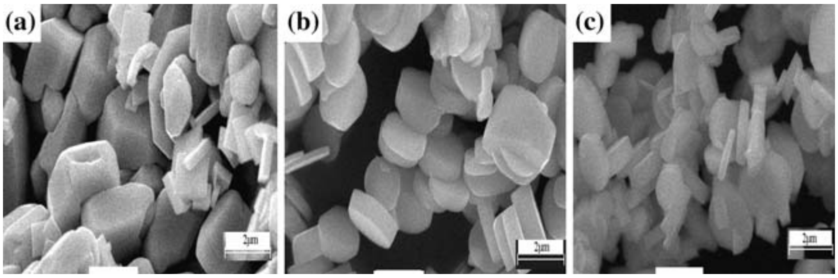

Fig. 3 SEM images of $BiFeO_3$ prepared by hydrothermal synthesis in the presence of 0, 0.05, 0.1 mol/L CTAB, respectively

diffuse reflection spectra of $BiFeO_3$ samples. The step shape of the spectra indicated that the visible light absorption was not due to the transition from the impurity level but was due to the band-gap transition [8]. The band gap was estimated to be 2.1 eV, which is in agreement with previously reported value [9]. $BiFeO_3$ samples made with CTAB exhibited a very broad absorption and the absorption edge red shift compared with $BiFeO_3$ made without CTAB, showing more potential of visible light usage.

Morphologies of the $BiFeO_3$ samples

Surface morphologies of the $BiFeO_3$ synthesized by hydrothermal process were characterized by SEM. In the absence of CTAB, the irregularly shaped $BiFeO_3$ particles were obtained, and the average particle size was about 2 μm. However, the presence of CTAB in the synthesis significantly improved the uniformity of resultant $BiFeO_3$ morphology, being beneficial to the formation of uniform plates. As shown in Fig. 3b, a low concentration of CTAB (0.05 mol/L) led to the formation of plate-structured $BiFeO_3$ with a average diameter and thickness of ca. 2 μm and 300 nm, respectively. As the concentration of CTAB increased to 0.1 mol/L, the resultant $BiFeO_3$ had an average diameter and thickness of ca. 1.3 μm and 200 nm, respectively. With increasing the concentration of CTAB, the particle size was decreased except that the uniformity of the resultant particle was improved. Thus, it can be concluded that uniform $BiFeO_3$ extra fine plates were able to be hydrothermally synthesized with the assistance of the CTAB surfactant. The surfactant would form lamellar plates at a certain concentration, and the bismuth and iron species were intercalated between the lamellar structures. Under hydrothermal conditions, the $BiFeO_3$ would form bismuth iron extra fine plates with a high aspect ratio.

Photodecoloration of orange II

A representative temporal evolution of the spectral changes taking place during the photodecoloration of orange II catalyzed by $BiFeO_3$ (prepared with 0.05 mol/L CTAB) is displayed in Fig. 4. Orange II showed a major absorption band at 484 nm corresponding to the big conjugate structure of benzene ring and naphthalene ring rounded by –N = N–, which is color development group in visible region. In the photodecoloration process, the major absorption band (484 nm) decreased gradually with elapsing of time. The apparent decrease of the absorption band at 484 nm indicated that $BiFeO_3$ had initiated photodegradation and made the azo band break and decolorize.

It is clear that TiO_2 is inactive under visible light illumination (Fig. 5), as reported by Asahi et al. [10]. Under illumination without $BiFeO_3$, the decolorization efficiency could reach 5% within 90 min. About 14.2% of orange II

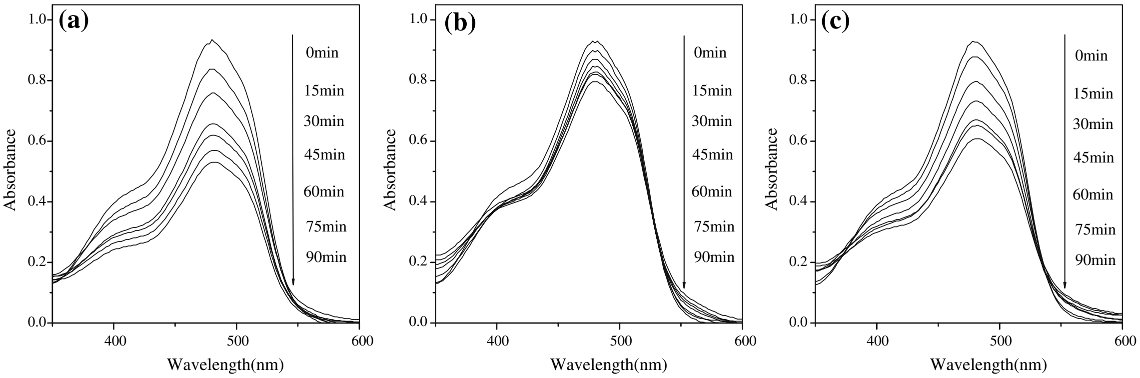

Fig. 4 Absorbance changes of orange II under photocatalytic process with 50 mg different catalyst added into 100 mL of 10 mg/L orange II solution. (**a**) $BiFeO_3$ prepared with 0.05 mol/L CTAB, (**b**) $BiFeO_3$ prepared without CTAB (some figure has been overlain), (**c**) $BiFeO_3$ prepared with 0.1 mol/L CTAB

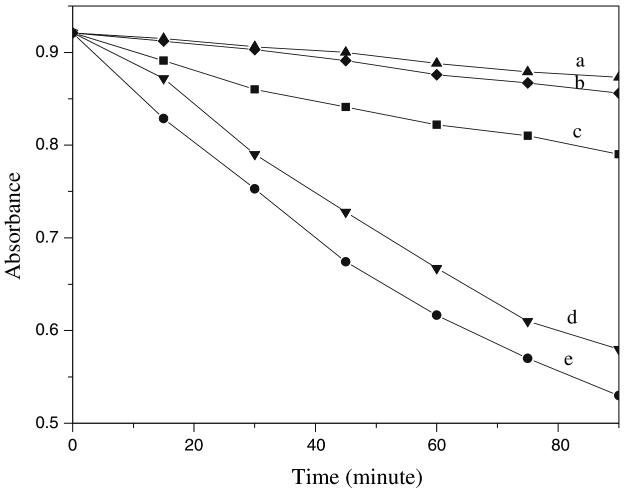

Fig. 5 Photodecolorization of orange II in the presence of different samples. (**a**)–(**e**) Represents blank experiment, TiO_2, experiment with $BiFeO_3$ synthesized hydrothermally with the presence of 0, 0.1, 0.05 mol/L CTAB, respectively

was decolorized with $BiFeO_3$ obtained without CTAB, While 42.5% of orange II was decolorized with 0.05 mol/L CTAB and 37% with 0.1 mol/L CTAB. The photocatalytic decolorization activities of the synthesized $BiFeO_3$ with or without CTAB were also illustrated in Fig. 5. $BiFeO_3$ synthesized with 0.05 mol/L CTAB showed higher activity than that synthesized in the absence of CTAB. This observation might be explained due to the regular structure and micro dimension of the resultant $BiFeO_3$. However, although $BiFeO_3$ synthesized with 0.1 mol/L CTAB had smaller particle size, but showed lower activity as compared to that obtained with 0.05 mol/L CTAB, indicating that the impurity affected the photocatalytic activity as certified by the XRD analysis.

It is well known that $BiFeO_3$ belong to the structure of perovskite-type. In the process of synthesis, because of the deviation of the mole ratio of Bi/Fe from chemical stoichiometric proportion, they lost the metal atoms at the crank points of the cells and produced metal vacancies. To maintain the charge balance, oxygen vacancies should form resulting in the increase of oxygen absorbed. The densities of reactive $OH^{\cdot}$ become higher when oxygen absorbed is increased, which facilitates the photocatalytic reaction [11].

Conclusion

In summary, $BiFeO_3$ was successfully synthesized by hydrothermal synthesis. The uniform $BiFeO_3$ extra fine plates with an rhombohedral structure was made with the assistance of the surfactant CTAB. Extra fine plates of $BiFeO_3$ showed a much higher photocatalytic activity than bulk sample for photodecoloration of orange II under visible irradiation, suggesting potential application in photocatalysis.

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