Preparation and Characterization of BiFeO$_3$ Nanosystems as Visible Light Driven Photo-degradation of Organic Compounds

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ABSTRACT

BiFeO$_3$ (BFO) nanopowders were synthesized at relatively low temperatures via a self combustion method with the aid of citric acid as the fuel. The effect of different fuel concentration, calcinations temperature and duration is performed. The resultant BFO nanopowders are characterized in terms of their structural, morphological and optical properties. The synthesized BFO nanopowders are of very high purity without any secondary phases and exhibited a good absorption in the visible-light regime, which resulted in the efficient photocatalytic activity for decomposition of organic compounds.

1 INTRODUCTION

The use of renewable or low energy sources for the degradation of organic pollutants has generated broad interest in both scientific research and potential applications in recent years. Research on semiconductor photocatalysis came sharply into focus after the discovery that TiO$_2$ photochemical electrodes could split water using ultraviolet light [1]. Following that, the photocatalytic oxidation of organic contaminants using TiO$_2$-based semiconductors as a photocatalyst has been extensively investigated due to their excellent photochemical stability, high-efficiency, low cost, and non-toxicity. However, the photo-efficiency of TiO$_2$ is severely limited by its large band gap (3.2 eV), and the associated restriction of the absorption in the visible-light region. Only 4% of terrestrial radiation is suitable for the photoexcitation of TiO$_2$ [2]. This renders the overall process impractical.

Perovskite – type BiFeO$_3$ (BFO) materials have attracted much interest due to their multiferroic properties at room temperature [3,4]. In particular, BFO thin films have been investigated intensively in their various applications, including capacitors [5], nonvolatile memory [6], and magnetoelectric devices [7]. In addition to these electronic applications, the photocatalytic properties of BFO powders under visible-light illumination have also been reported recently [8]. Although the photocatalytic activity of BFO powders under visible light is ascribed mainly to a small band-gap energy, attempts to elucidate other factors, such as their weak ferromagnetic properties, are still being made [9]. Despite the fact that some work in this area has been undertaken, various research avenues such as synthesis, characterization, and the effects of magnetic fields remain to be explored.

BFO powders have been prepared using a variety of synthetic methods, such as sol-gel techniques [10], combustion [11], and hydrothermal processes [12]. From the perspective of synthesis, it is important to obtain pure materials using temperatures as low as possible. This point may be especially important for BFO materials because some secondary phases such as Bi$_2$Fe$_2$O$_7$, Bi$_2$O$_3$Fe$_2$O$_7$ and Bi$_2$Fe$_2$O$_7$ are usually formed during the synthesis [13,14]. In this study, pure BFO nanopowders were synthesized at very low temperatures via a self combustion method and follow by calcinations with the use of citric acid as fuel, and the absorptions property of the resultant BFO nanopowder were evaluated.

2 EXPERIMENTAL

2.1 Chemicals and materials

A commercially available reagents grade Bismuth Nitrate Pentahydrate (Bi(NO$_3$)$_3$·5H$_2$O) and Iron Nitrate Nonahydrate (Fe(NO$_3$)$_3$·9H$_2$O) (purity > 99%, International Laboratory) are used as raw materials. Nitric acid (HNO$_3$) with 70% concentration and De-Ionised (DI) water with resistivity of 18.3 MΩ were used to dissolve the salts raw materials above. All the chemicals and materials mentioned were used as purchased without further purification.

2.2 BFO nanopowders synthesis technique

Bismuth Nitrate Pentahydrate (Bi(NO$_3$)$_3$·5H$_2$O) and Iron Nitrate Nonahydrate (Fe(NO$_3$)$_3$·9H$_2$O) were used in stoichiometric proportions of 1:1 molar ratio to create 0.2 M solution. A solution containing of 0.2 mol of nitric acid (HNO$_3$) (25ml of 70% HNO$_3$) is mixed with 25 ml of DI water. Bismuth Nitrate Pentahydrate (Bi(NO$_3$)$_3$·5H$_2$O) salts were dissolved in the nitric acid solution mentioned earlier and Iron Nitrate Nonahydrate (Fe(NO$_3$)$_3$·9H$_2$O) were just
dissolved in the DI water only. Once dissolved, both Bismuth and Iron solutions were mixed together and citric acid with molar ration of Citric/Metal of 1:1 was added into the Bi-Fe ionic solution and stirred until complete dissolution. The Bi-Fe with citric acid solution were then heated up to 250°C until the solution dried and follow by auto ignition of the combustion and formed dark brownish flakes and left heated for another half hour. The dark brownish flakes were calcined in the furnace at varying temperatures of 450°C, 550°C, 650°C for 6 hours and varying soaking timing at 450°C of 6, 9, 12 and 24 hours and to evaluate the phase evolution of the BFO powders.

The calcined BFO powders were in the form of small flakes aggregates, and the calcined powder were then subjected to high energy planetary ball milling process at 400 RPM rotational speed for ½ hour to breakdown the agglomerated BFO nanopowders to obtained fine powders.

2.3 BFO nanopowders characterization

The synthesized BFO nanopowders size and morphology was characterized using FESEM (JEOL-JSM7500F). XRD patterns were obtained using PANalytical X’Pert Pro MPD advanced powder X-ray diffractometer (using Cu Kα = 1.54056 Å radiation) with scanning range of 2 theta from 20° to 70°. The absorption optical property of the resultant BFO nanopowders was characterized using Perkin Elmer model Lambda 950 UV-Vis-NIR spectrophotometer with integrating sphere. BFO nanopowders were spread thinly on the surface of quartz glass with the help of ethanol to prepare samples for absorption testing.

3 RESULTS AND DISCUSSION

The synthesized BFO nanopowders X-Ray Diffraction patterns at varying parameters are shown below:

Figure 1(a) presents the XRD pattern of the BFO nanopowders calcined at 450°C for 6 hours duration, and it was revealed that under this condition, there are Bi₂O₃ and Fe₂O₃ phases exist as shown by the circled and square box area respectively in figure 1(a). As the soaking duration increased to 9 hours as shown by figure 1(b), the Bi₂O₃ phase started to disappear and some Fe₂O₃ phases still existed. At figure 1(c) and 1(d) where soaking time were 12 hours and 24 hours at respectively, it is revealed that the BFO nanopowders obtained are highly crystallized and of high purity and exhibit a single-phase perovskite structure according to JCPDS card no. 71-2494. Non-perovskite phases such as Bi₂Fe4O9 and Bi₂O₃/Fe₂O₃ are not detected in XRD spectra. The obvious peak-splitting shows that the nanoparticles are rhombohedral, consistent with the structure of BFO ceramics.[8 from D01: 10.1002/adma.200602377].

Another experiment carried out for BFO nanopowder synthesis was calcination at different temperature to see the effect of varying calcinations temperature on the phases of the BFO nanopowders obtained. From figure 2 where BFO brownish flakes after self combustion process, they were subjected to different calcinations temperature of 450°C, 550°C and 650°C for 6 hours duration, it is revealed that the BFO phases were gradually vanished as the calcinations temperature increases from 450°C to 650°C.

Also, it is observed that as the calcination temperature increased, the resultant BFO materials is go towards more complete oxide systems as the peaks of Bi₂O₃ and Fe₂O₃ became more obvious as shown by the square box area in the figure 2. 6 hours of calcination soaking time at different calcinations temperature was enough to see the evolution of resultant BFO nanopowders phase instead of longer calcinations time such as 24 hours which is the optimum synthesis parameter.

The synthesized BFO nanopowders microstructure of optimum synthesized conditions (calcinations at 450°C for 24 hours) was characterized by FESEM and shown as follows:
As a feasible potential application of BFO nanopowders in photocatalytic degradation activity of organic compounds, the absorption characteristics of the BFO nanopowders were investigated using UV–Vis spectroscopy. As can be seen in Fig. 4, the absorption spectrum shows absorption peaks at 480 nm and 530 nm wavelength, suggesting that BFO nanopowders can absorb remarkable amounts of visible light.

In figure 5 shows the optical band gap of the BFO nanopowders calculated using Tauc’s relationship formula of \( a(h\nu) = A(h\nu-E_g)^n \) and \( n \) is \( \frac{1}{2} \) since BFO is a direct bandgap semiconductor. To obtain optical band gap (\( E_g \)) value, a curve of \( (a(h\nu)) \) are plotted against \( (h\nu) \) and extrapolation of the linear region of the graph intersecting \( x \)-axis at 0 value gives the value of the optical band gap, \( E_g \). The calculated value from the absorption spectrum is 1.9 eV, which is smaller band gap value with that of another report [8] and smaller than the BFO thin film of 2.5 eV as reported at other report [15]. The smaller band gap of BFO nanoparticles indicates a possibility of utilizing more visible light for photocatalysis.

**4 CONCLUSION**

The Bismuth Ferric Oxide perovskite structure nanopowders is successfully synthesized via self combustion method and its process parameters have been optimized to obtain high purity, high crystalline BFO nanopowders. From the micrograph study, the synthesized BFO nanopowders were confirmed obtained in the nanoscale size.

The resultant nanopowders optical property shown obvious absorption peaks at around 480 nm and 530 nm wavelength, hence the synthesized BFO nanopowders could be potentially used as photocatalytic agent at visible light range. The estimated optical band gap calculated using Tauc’s relationship is 1.9 eV, confirming the potential applications of the synthesized BFO nanopowders as photocatalyst under visible light region for degradation of organic compounds pollutants as smaller band gap indicates a possibility of utilizing more visible light for photocatalysis. Future works following this work would be photocatalytic activity evaluation of the synthesized BFO powder on Rhodamine

**Fig. 3.** FESEM micrograph of synthesized BFO nanopowder at (a) 10,000X magnifications, and (b) 25,000X magnifications

It was observed that the resultant BFO nanopowders are in spherical shape and ultra fine size with observed estimated size in the range of around 100 nm. Some nanowires morphology are observed as well, but it is of minority content as indicated by a circled area in figure 3(b). The BFO nanopowders are in agglomerated form, and further efforts need to break down the agglomerations such as using sonication to obtained better dispersed nanoparticles.

**Fig. 4.** UV-Vis absorption spectroscopy of BFO nanopowders

**Fig. 5.** Optical band gap value determination using Tauc’s relationship formula of the synthesized BFO nanopowders
Blue dyes which is commonly used dyes in the textile industry.

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6 REFERENCES


