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Hirarchical Multi-ferroic $FeBiO_3$ Nanoparticles Prepared by a Facile Solvothermal Method: Undergraduate Experiments for Inorganic Chemistry

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Abstract Wetting chemical method is a common method for the preparation of nano-materials, which are useful for experimental study by undergraduate students. Hierarchical multi-ferroic $FeBiO_3$ nanoparticles were prepared by a facile solvo-thermal method and adopted as dispersing materials for electrorheological (ER) fluids. The morphology of $FeBiO_3$ nanoparticles was characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The structure was characterized by X-ray powder diffraction. Moreover, the electrorheological (ER) behavior of $FeBiO_3$ nanoparticles was characterized using a rotational rheometer.

Keywords Multi-ferroic material, Bismuth ferrite, Electrorheological fluid, Solvothermal method, Hirarchical Structure

1. Introduction

Electrorheological (ER) fluids, acting as a type of smart material, exhibit a response to an applied external electric field where there occurs a rapidly reversible liquid to solid transition. An ER fluid is a two-phase suspension system typically composed of polarized particles dispersed in an insulating medium [1-3]. The ER effect, instantaneous and reversible changing in rheological properties of the fluids under the applied electric field, arises from the formation of chain-like or column-like structures between neighboring polarized particles along the direction of the applied electric field and results in a rapid transformation from a fluid-like state to a solid-like state [4-7]. Its response with and without an external electric field is shown as a schematic diagram as Figure 1. The application of multiferroic materials in electrorheological fluids is important but is seldom.

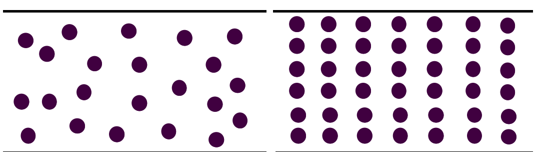

Figure 1. Schematic illustration of the particles change of an ER fluid before and after an external electric field is applied

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In recent years, much research interest has been drawn to bismuth ferrite ($BiFeO_3$, also commonly referred to as BFO in Materials Science), which is known to be the only multiferroic compound that exhibits simultaneous ferroelectric and G-type anti-ferromagnetic orders over a broad range above room temperature [8, 9]. $BiFeO_3$ is the only multiferroic material that retains its properties above room temperature with an anti-ferromagnetic Néel temperature TN = 370°C and a ferroelectric Curie temperature TC= 830°C [10, 11]. The Néel temperature, TN, is the temperature above which an anti-ferromagnetic material becomes paramagnetic—that is, the thermal energy becomes large enough to destroy the microscopic magnetic ordering within the material. The Curie temperature, TC, is the temperature at which certain materials lose their permanent magnetic properties, to be replaced by induced magnetism. $BiFeO_3$ is an inorganic chemical compound with a perovskite structure and an unusual compound mixture of bismuth, iron, and oxygen as shown as Figure 2.

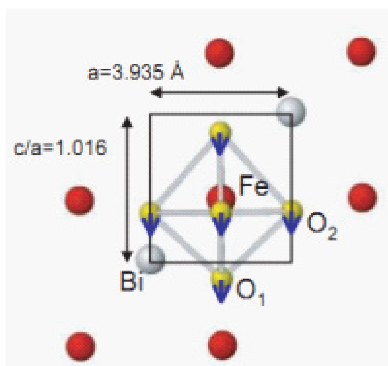

Figure 2. The structure of Bismuth ferrite

Several synthetic strategies have been developed for the formation of $BiFeO_3$, including solid-state, sol–gel, hydrothermal as well as microwave-assisted hydrothermal, self-combustion, and electro-spinning reactions. For example, $BiFeO_3$ can be obtained by a solid-state reaction as shown as follow:

$$Bi_2O_3+Fe_2O_3=2\ BiFeO_3 \quad (1)$$

Furthermore, $BiFeO_3$ can also be prepared by a simple solvothermal method, which is adopted in this study, as in the following reaction:

$$Bi(NO_3)_3+Fe(NO_3)_3=2\ BiFeO_3+6NO_2 \quad (2)$$

BFO can be used for the development of new high tech magnetic tapes, superconductivity, environmental engineering, enhancing spontaneous magnetization, etc. The work presented here aims at the development of an integrated research-education activity on the wetting method, because of its unique characteristics. In this study, a simple solvothermal method was used to synthesize nanostructured $BiFeO_3$ (BFO). In addition, the obtained BFO nanoparticles were characterized by X-ray diffraction analysis (XRD), transmission electron microscopy (TEM) and scanning electron microscopy (SEM), and their rheological properties were also studied via a rheometer. These characteristics could benefit undergraduate students by exposing them to several important instruments that are widely used in academic research and industrial work.

2. Experiment Description

2.1. Experimental Materials

$Fe(NO_3)_3$ (Beijing Chemicals, Beijing, China), $Bi(NO_3)_3$ (Sinopharm Chemical Reagent Corporation, Shanghai, Chian), cetyltrimethyl ammonium bromide (CTAB, Tianjin Bodi Chemical Co. Ltd., Tianjin, China), Ethanol glycol (EG, Laiyang Fine Chemical Factory, China), anhydrous methanol (Tianjin Fuyu Fine Chemical Co. Ltd., Tianjin, China) and silicone oil (Tian Jin Damao limited company, Tianjin, China) were purchased. All reagents were of analytical grade and used as received without further treatment.

2.2. Instruments and Characterization

The morphology of obtained BFO nanoparticles were observed by field emission scanning electron microscopy (FE-SEM, JEOL-670) and transmission electron microscopy (TEM, JEOL-2100). X-ray diffraction (XRD, Rigaku D/MAX-2500/PC) was performed to analyze the crystalline structure of as-prepared samples. The rheological properties of ER fluids were measured using a rotational rheometer (HAAKE Rheo Stress 6000, Thermo Scientific, Germany) equipped with a parallel-plate system (PPER35, 35 mm in plate diameter and 1 mm in gap width) and a WYZ-020 DC high-voltage generator (voltage: 0–5 kV, current: 0–1 mA) under a controlled shear rate (CSR) mode ranging from 1 to 500 s^{-1}.

2.3. Experimental Procedure

The hierarchical multi-ferroic $FeBiO_3$ nanoparticles were prepared by using a facial solvothermal route [12]. In a typical procedure, 20.2g $Fe(NO_3)_3$ and 24.25g $Bi(NO_3)_3$ were added into a 120mL EG solution together under vigorously stirring to obtain a homogeneous solution. Then 5g CTAB was added into 30mL EG, followed by stirring for another 30 min. Then the two prepared EG solutions were mixed together and stirred for about 1h. Subsequently, the clear solution was transferred into a 100mL Teflon-lined stainless-steel autoclave, which was sealed tightly and heated at 200°C for 12 h. After cooling down to room temperature naturally, the resulting white precipitate was harvested by centrifuging and washed with ethanol for 3 times, the $FeBiO_3$ products were collected and dried at 80°C overnight.

3. Results and Discussion

The crystalline structures of $FeBiO_3$ nanoparticles were analyzed using an X-ray diffractometer. As shown in Fig. 3, the pattern of Ti-containing precursor is to be readily indexed to perovskite (space group R_{3c}) $BiFeO_3$ (JCPDS Card No. 20-0169) and no peaks from other phase were detected, demonstrating that well-crystallized single phase $BiFeO_3$ can be obtained under the current synthesis conditions. These reflections correspond to crystal planes 2θ=22.490(101), 31.808(012), 39.509(021), 45.813(202), 51.376(113), 57.012(122), 67.087(220), 71.338(303), 76.082(312) (PDF#20-0169).

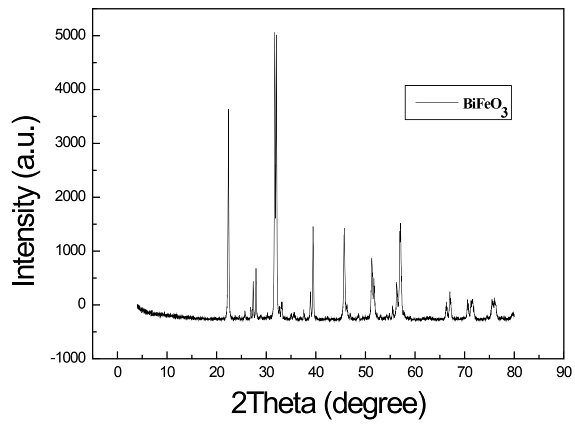

Figure 3. XRD pattern of as-synthesized $FeBiO_3$ sample

SEM was used to reveal the morphological characteristics of the synthesized particles. As shown in Fig. 4(a. b), the flower-like $FeBiO_3$ nanoparticles constructed with nanoplates in a radioactive manner were obtained with a high yield. Through the detailed observation from a high-magnification SEM image in Fig. 4b, it was clearly found that the $FeBiO_3$ nanosheets were successfully distributed on the surface. The thickness of assembled nanosheets is approximate 20 nm.

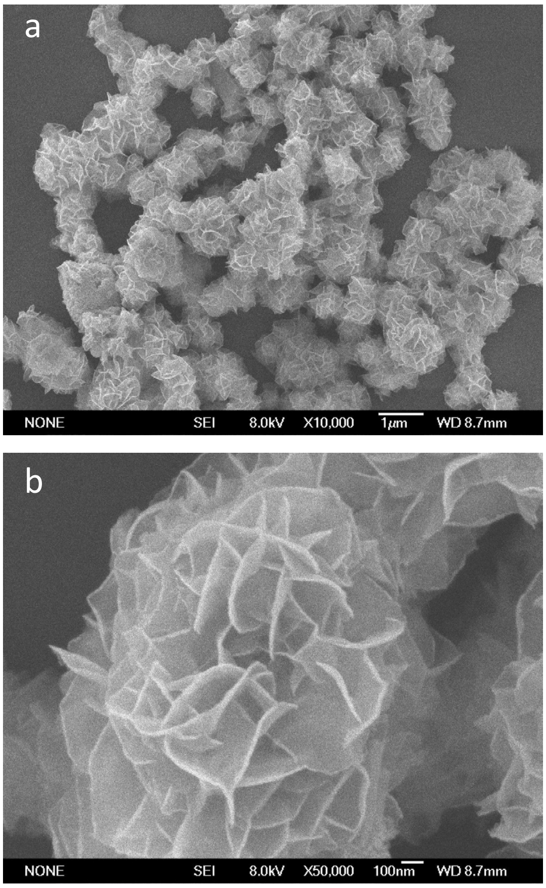

Figure 4. SEM images of as-prepared $FeBiO_3$

The $FeBiO_3$ nanoflower was further evaluated by TEM pictures. As shown in Fig. 5(a, b), the morphology of $FeBiO_3$ nanoparticles is flower-like, in accordance with the observation result of SEM images. Moreover, the sheets of nanoflower are found to be smooth and well-defined.

By using $BiFeO_3$ as an ER dispersed materials into silicone oil, obvious ER activity can be observed. To investigate the ER performance, $FeBiO_3$ a suspension of nanoparticles was prepared by dispersing the dried particles, respectively in silicone oil (10 wt%). The flow curve of $FeBiO_3$ nanoparticles based ER fluid was investigated by using a Controlled Shear Rate (CSR) mode under the absence and presence of an applied electric field. The shear stress curve as a function of shear rate for $FeBiO_3$ nanoparticles based ER fluid was plotted in Fig. 6. In the absence of an external electric filed, the shear stress was nearly proportional to shear rate in a log-log plot without yielding, which corresponds to the typical behavior of a Newtonian fluid. Notably, a dramatic increase of shear stress was observed in the low shear rate region under the influence of an applied external electric field with a yield stress, which behaves like a typical Bingham fluid [13-17]. As the strength electric field increases to 3 kV/mm, the enhancement of shear stress is more significant and the shear stress maintained a plateau in the low shear rate region. It is generally accepted that the occurrence of a plateau region can be ascribed to a balance between the electrostatic force generated from polarization between neighboring particles and the hydrodynamic force induced by mechanical shearing field. As introduced above, the particles polarized along the direction of the electric field and are formed into columnar structures as soon as the electric field was applied. Furthermore, the ER efficiency $e = (\tau_E - \tau_0)/\ \tau_0$ was also calculated, where τ is the shear stress, subscript E and 0 means with and without electric field, respectively). [18] The ER efficiency e for $FeBiO_3$ nanoparticles ER fluids at shear rate 0.1 s^{-1} is 58.6 under electric field strength E=3 kV/mm, respectively.

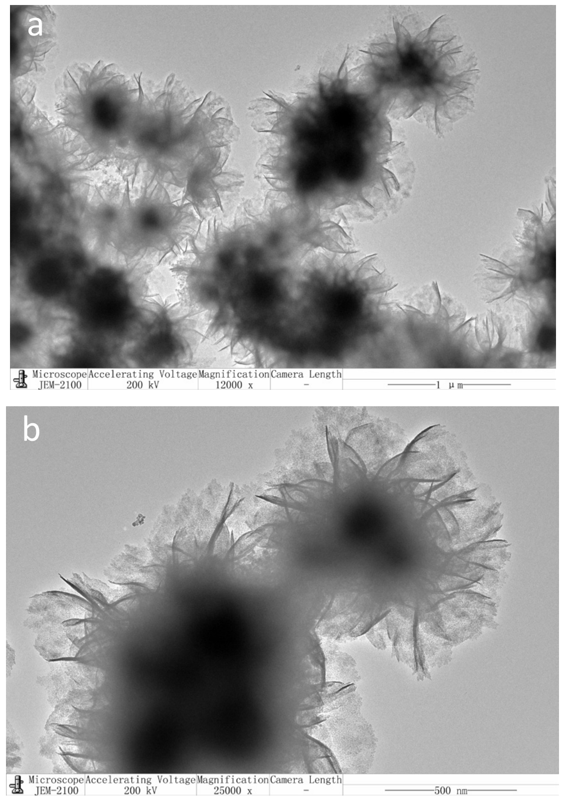

Figure 5. TEM images of $FeBiO_3$ nanoparticles

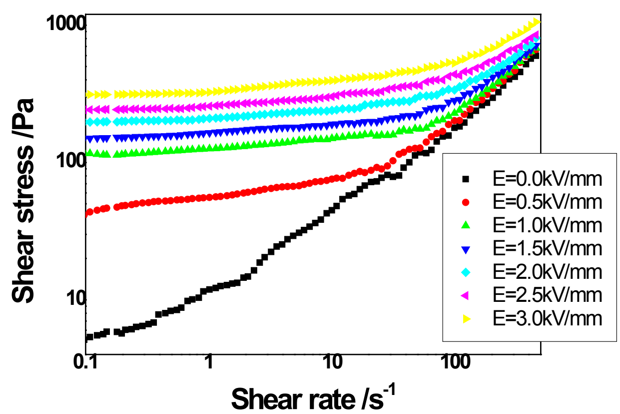

Figure 6. Flow curves of shear stress as a function of shear rate for $FeBiO_3$ nanoparticles the suspensions

Solvothermal method, as an important one of wetting chemical method, is useful to prepare nanoparticles with different shapes and sizes. In materials science there is also an emphasis on developing and using knowledge to understand how the properties of materials can be controllably designed by varying their compositions and structures. Materials utilization was totally a selection process, that is, deciding from a given, rather limited set of materials the one that was the best suited for an application by virtue of its characteristic. Thus, the interrelationship between processing, structure, properties, and performance is shown as following diagram:

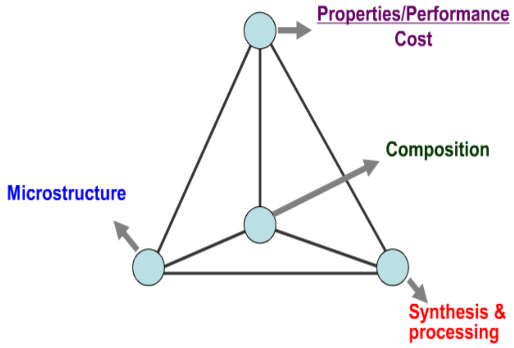

Figure 7. Schematic diagram of Material Four Element Tetrahedron

In summary, the $FeBiO_3$ nanoparticles with a hierarchical structure were obtained by a simple solvo-thermal method. Both SEM and TEM images helped to confirm the unique hierarchical morphology for the synthesized $FeBiO_3$ nanoparticles. Under electric fields, the obtained hierarchical $FeBiO_3$ nanoparticles exhibit a good ER behavior. There experiments were performed at atmospheric pressure conveniently making them suitable for materials physics and materials chemistry laboratories.

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