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Development and characterization of nano-multifunctional materials for advanced applications

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Abstract

Multifunctional zinc oxide-bismuth ferrite and tin dioxide-bismuth ferrite have been synthesized using a double precipitation technique. The structural formation, chemical composition, morphology and thermal properties were characterized by Fourier transform infrared spectroscopy, X-ray diffraction, thermogravimatric analysis, scanning electron microscope with energy dispersive spectroscopy and transmission electron microscopy. Temperature-dependent magnetic behaviour of zinc oxide-bismuth ferrite and tin dioxide-bismuth ferrite were studied by vibrating sample magnetometer in the range 5K to 300K. The results indicate that zinc oxide-bismuth ferrite is a potential candidate for spintronics applications.

Keywords: Multifunctional; Zinc oxide-bismuth ferrite; tin dioxide-bismuth ferrrite

1. Introduction

Multifunctional nanomaterials have attracted huge interest, due to their excellent magnetic, electrical, optical and other properties[1,2]. Due to their characteristics, they are wieldy used in several advanced energy fields, such as: sensors, spintronic, transducers, memory and electronic filed controlled ferromagnetic resonance devices [3, 4]. Bismuth ferrite ($BiFeO_3$) is one of the multifunctional materials that have anti-ferroelectric, anti-ferromagnetism and anti-ferroelastic order in signal phase[4]. Owing to the functionalities of bismuth ferrite, such as: semi-conductive nature, wide band gap (2.0-2.20eV), and excitation binding energy (~60meV) at room temperature, it has ferro-electromagnetism property, which enhances its applicability in electromagnetic sensors, memory devices and electric energy harvesting in materials sciences [4,5]. In addition, their magnetic moment and magnetoelectric coupling offers several benefits in materials sciences and physics[6]. However, in order to enhance the applicability of $BiFeO_3$ in advanced nanotechnology, it can be modified with suitable metal-oxide semiconductor elements for pollutant degradation without any harmful residues.

Zinc oxide (ZnO) is one of the semi-conductive multifunctional materials. It has attracted attention for several potential applications due to its non-toxic nature, significant direct band gap [3.37eV], high electron mobility [$200cm^2\ V^{-1}\ s^{-1}$] and high excitation binding energy (60meV) at room temperature[7]. Due to its optimistic characteristics, it has been used for application in sensors, piezoelectric devices, optoelectronics, piezoelectric devices, medical, etc [8].

Tin oxide is another important inorganic-oxide. It is a suitable candidate for a range of applications, such as: sensor devices, transparent conductive coatings for displays, electrodes, light emitting diodes and solar cells, because of its excellent optical and electrical properties[9]. Thus, ZnO and SnO_2 are excellent choices for positive template for the development of multifunctional nanostructures for future advanced nanotechnology applications in advanced sciences.

In this scientific report, double precipitation method was used for the synthesis of possible nano-multifunctional zinc oxide-bismuth ferrite [(shell) ZnO-$BiFeO_3$ (core)] and tin dioxide-bismuth ferrite [(shell) SnO_2-$BiFeO_3$ (core)). The nano-multifunctional materials were characterized with fourier transform infrared spectroscopy, X-ray diffraction, thermogravimatric analysis, scanning electron microscope with energy dispersive spectroscopy and transmission electron microscopy and evaluated for their temperature- and magnetic field-dependent applications. The resulting nano-multifunctional materials have great potential for advanced functional applications.

2. Experimental

2.1. Materials

All the reactions processes were carried out at room temperature, under ambient reaction conditions. Bismuth (III) nitrate pentahydrate, Iron (III) nitrate nanohydrate, tin (IV) chloride, zinc nitrate, ammonium hydroxide, nitric acid and potassium hydroxide were obtained from Sigma Aldrich Chemicals Company.

2.2. Preparation of Oxide nanoparticles

2.2.1. Synthesis of single-phase bismuth ferrite ($BiFeO_3$): Bismuth ferrite was synthesized by a precipitation technique. Bismuth (III) nitrate pentahydrate (0.01M) and iron (III) nitrate nanohydrate (0.01M) were completely dissolved in 100ml of diluted nitric acid (6.3ml of HNO_3/93.7ml of distilled water) solution in a 500ml beaker under constant stirring condition at room temperature. To this solution, potassium hydroxide was slowly added drop-wise in order to obtain a co-precipitate (Fe^{3+}, Bi^{3+} ions) until a brown color precipitate was formed during which the pH was adjusted to ~9. After starring for 30 minutes, the precipitate formed was washed several times with distilled water in order to remove the K^+, NO and other unwanted materials and the pH of the filtrate was reduced to 7. The resultant mixture was dried at 120°C for 120min. Finally, it was cooled to room temperature. Subsequently, the possible powders were dried and heat-treated at different temperatures

2.2.2. Zinc Oxide (ZnO) nanoparticlels: 0.05M of zinc nitrate aqueous solution was prepared by adding of 14.87g zinc nitrate to 50ml of distilled water under the constant stirring condition at ambient temperature for 1h. Then, the solution pH was increased to 9 by adding ammonium hydroxide drop-by-drop with stirring for 3h until there was a white color precipitation. After the reaction was completed, the resulting final product was collected by filtration technique. The filtrate was thoroughly washed with distilled water and then dried at 120°C for 120min.

2.2.3. Tin dioxide (SnO_2) nanoparticles: SnO_2 was prepared by hydrothermal process. In a typical synthesis, 0.025m of tin(IV) chloride was dissolved in 100ml distilled water and stirred for 30min at ambient temperature and then (10 to 15ml) ammonium hydroxide was add drop-wise to this solution for the formation of a slurry-like white precipitation. After 20min of stirring, the resulting solution was washed, several times, with distilled water in order to remove the (chlorine and other ions) unwanted elements. Finally, it was filtered and dried at 120°C for 120min

2.3. Preparation of possible functional nanoparticles by double precipitation technique.

2.3.1. Method A: *Tin dioxide- bismuth ferrite* (SnO_2 - $BiFeO_3$) *nanoparticles***:** In this process, 0.025M of tin (IV) chloride was initially dissolved in 100ml distilled water under stirring condition. Secondly, the 30ml of bismuth ferrite (3g) solution was introduced to the above solution. Finally, it was precipitated with ammonium hydroxide solution, pH 9. After 30min of continuous stirring, the precipitated solution was washed with distilled water in order to remove the chloride ions and the unreached reactants from the precipitation. Then, possible core-shell was filtered, dried and heat-treated at 120°C for 120min.

2.3.2. Method B: *Zinc Oxide-bismuth ferrite ($ZnO-BiFeO_3$) nanoparticles:* 14.87g of zinc nitrate and 3g of bismuth ferrite were dissolved in 50ml of distilled water under constant stirring condition at ambient temperature for 1h. Subsequently, ammonium hydroxide solution was added drop-wise, until there was the formation of core/shell precipitation during which, the pH was adjusted to ~9. Here, the alkaline solution is increases the reaction rate to get a precipitation, since alkaline cations play vital role in the formation of $ZnO-BiFeO_3$. Furthermore, the core/shell precipitation was filtered and rinsed 3 times with distilled water to adjust the pH from 9 to 7 neutralize and wash-out any unreacted metal ions[10]. Finally, the washed powder was dried at ambient temperature and cooled to ambient temperature. The possible core-shell powders were dried and heat-treated at different temperatures.

2.4. Characterizations

The structures of the SnO_2-$BiFeO_3$, ZnO-$BiFeO_3$ possible core-shell nanoparticles formed were confirmed with electron microscopes (Scanning and Transmission electron microscopes (SEM and TEM)), X-ray diffraction (XRD) studies, Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA). In addition, their temperature-dependent magnetic properties were determined by vibrating sample magnetometer (VSM). SEM micrographs were recorded using a JEOL JEM 7500F (Tokyo, Japan) scanning electron microscope at 2 keV. Energy dispersive spectroscopy analyses were carried out on a JEOL JEM 7500F SEM. Transmission electron microscopes were recorded on JEM-1200EX, JEOL (Tokyo, Japan). The samples were dispersed in a 1:1 methanol and water solution and deposited on a 3 mm copper grid and dried at ambient temperature after removing the excess solution using filter paper. X-Ray diffraction measurements were carried out using a Rikagu diffractometer with Cu-K_α radiation and using a scan rate of 0.02^o s^{-1}. FTIR absorption spectra were recorded in a Perkin Elmer Model impact 410 (Wisconsin, MI, USA) spectrophotometer in order to identify the functional groups in the multifunctional materials. Thermal properties were determined from the TGA data, using SDT Q600 thermal analyzer (T.A. Instruments-water LLC, Newcastle, DE, USA), at a heating rate of 20 ^{0}C/min and passing N_2 gas at a flow rate of 100ml/min.

3. Results and discussion

FTIR Study

Fig.1 shows the FTIR spectrum of $BiFeO_3$, ZnO, SnO_2, ZnO-$BiFeO_3$ and SnO-$BiFeO_3$ nanoparticles, representative of their perovskite type vibration. In **Fig.1A**, the absorption band observed at 850cm^{-1} indicates the symmetric stretching of Bi-O/Fe-O bonds in $BiFeO_3$[11,12]. The strong absorption band at 544cm^{-1} is attributed to Fe-O stretching of the $BiFeO_3$ group[13]. The band that appeared at 1365cm^{-1} is attributed to the strong vibration of NO_3^- [14]. The spectra of ZnO showed vital peaks at 452 cm^{-1} and 644 cm^{-1}, which indicates Zn-O stretching mode[15]. The bands at 3372 cm^{-1}, 1306cm^{-1} , 477 cm^{-1} are correlated to O-H, C=O vibration modes[16]. The SnO_2 spectra (**Fig.1B**) show absorption peaks at 497.67 and 610 cm^{-1} and are attributed to the stretching vibration of O–Sn–O and Sn–O[17].

Similar bands are observed in the case of ZnO-$BiFeO_3$ and SnO_2-$BiFeO_3$, but the bands appeared to have shifted positions and are attributed to the core/shell formation. The spectrum of ZnO-$BiFeO_3$ (**Fig.1A**) shows a characteristic peaks at around 857cm^{-1} and 697cm^{-1} and are assigned to the vibration frequencies of Bi-, Fe-O in the Zn-O lattice.

The main absorption band at 462cm^{-1} is attributed to Zn-O/Fe-O stretching of ZnO-$BiFeO_3$ group. SnO_2-$BiFeO_3$ spectra (**Fig.1B**) show absorption peaks at 466cm^{-1} (O-Sn-O, Fe-), 589cm^{-1} (Fe-), 677cm^{-1} (Sn-O) and around 846cm^{-1} (Bi-O/Fe-O) are attributed to the vibration of SnO_2-$BiFeO_{3.}$ Furthermore, these results are supporting XRD studies and nanostructure morphologies of pure ZnO, SnO_2 and $BiFeO_3$, and their nanocomposites.

SEM-EDS and TEM analyses

In order to obtain detailed information on the possible nano-multifunctional structure and morphology of the $BiFeO_3$, ZnO, SnO_2, ZnO-$BiFeO_3$ and SnO-$BiFeO_3$ nanoparticles synthesized, SEM and TEM studies were carried out. The SEM images of the nano-energy materials developed are presented in **Fig.2**. Fig A explains, the $BiFeO_3$ multifunctional nanoparticles have nano-flower structure with few spherical particles. From **Fig.2B,** it is evident from the SEM morphology that the ZnO nanoparticles are rods-like shape with excellent alignment, whereas ZnO-$BiFeO_3$ multifunctional nanomaterials (**Fig.2AB**) shows $BiFeO_3$ nano-flowers are highly curved with ZnO rods. **Fig.2C** shows the SEM image of SnO_2 nanoparticles developed which look like small spherical clusters on the surface. **Fig.2AC** illustrates the image of the SnO_2-$BiFeO_3$ core/shell nanoparticles prepared. The resulting images explain the fact that $BiFeO_3$ nanoparticles are covered with spherical SnO_2 clusters nanoparticles.

The EDS patterns of the precipitate synthesized SnO_2, ZnO and $BiFeO_3$, and double precipitate synthesized ZnO-$BiFeO_3$ and SnO_2-$BiFeO_3$ possible core-shell nanocomposites are presented in **Fig.3**. The EDS spectra of pure ZnO (Fig B) and SnO_2 (Fig C) have accounted for elements of Sn, Zn, O, respectively presence and have not shown any foreign metals or elements presence, and thus pure composition formation at nano-scale has been witnessed and thus pure ZnO and SnO_2 compositions have formed with stoichiometric end products. It is clearly seen that $BiFeO_3$ mainly contains bismuth, iron and oxygen elements (**Fig.3A**), whereas ZnO-$BiFeO_3$ (**Fig.3AB**), SnO_2-$BiFeO_3$ (**Fig.3AC**) have additional (Zn, Sn) elements in addition to Bi, Fe and O, which are clearly observed in the EDS spectrum of possible core-shell nanofunctional materials respectively.

The TEM images of typical ZnO as shell material, SnO_2 as shell material and $BiFeO_3$ as core material, ZnO (shell)-$BiFeO_3$(core), SnO_2(shell)-$BiFeO_3$(core), sample are shown in **Fig.4**. **Fig. 4A, B and C** show the TEM image of $BiFeO_3$, ZnO and SnO_2 samples, developed by precipitation technique. It can be seen that the developed nanocrystalline are spherical in shape and are highly agglomerated with a diameter of 15±9nm, 30nm, and 3±1nm, respectively. At higher magnification, the inter-planar d-spacing of 0.397nm, 0.246nm and 0.319nm are clearly visible in **Fig.4A, B and C**, corresponding to the (012), (110) and (001 or 110) planes of $BiFeO_3$, ZnO and SnO_2, respectively, which is in agreement with previously reported values[18-20]. **Fig.4 AB and BC** shows the different shapes of ZnO-$BiFeO_3$ and SnO_2-$BiFeO_3$ nanoparticles, which show that $BiFeO_3$ nanoparticles are covered with ZnO and SnO_2. These studies clearly indicate that co-precipitation route supports the formation of well-defined core-shell structures of multifunctional materials, which enhances their applicability in energy, materials sciences and medical applications.

Thermal characterization of nano-functional materials

The TGA spectra of $BiFeO_3$, ZnO, SnO_2, SnO_2-$BiFeO_3$ and ZnO-$BiFeO_3$ are shown in **Fig.5A**.In the case of developed nanoparticles, high rate of weight loss has occurred in the range of 75^0C to 100^0C due to the evaporation of the water in the samples. TGA analysis of the precipitated ZnO and $BiFeO_3$ samples exhibited (**Fig.5Aa**) significant degradation at 317.6 ^{0}C with greater mass losses: 37.7 % (ZnO) and 5.49% ($BiFeO_3$), whereas the weight loss observed for ZnO-BiFeO$_3$ at same temperature is 23.03% which is due to the volatilization and combustible organic species present in the sample. However, this study indicates that ZnO added nano-multifunctional material have higher weight loss when compared BiFeO$_3$ and less weight loss than ZnO. This is due to the semi-conductive behaviour of ZnO which may cause the changes in weight loss that fallows this order: ZnO(37.7%)>ZnO-BiFeO$_3$(23.03%)>BiFeO$_3$(5.49%). Similarly, this phenomenon was observed in the case of SnO$_2$, SnO$_2$-BiFeO$_3$ and BiFeO$_3$. As shown in **Fig.5Bb**, the weight loss of the nano-materials follows the order: SnO$_2$(8.93%)>SnO$_2$-BiFeO$_3$ (8.04%)>BiFeO$_3$ (5.49%) occurred at 317.6^{0}C. For SnO$_2$, SnO$_2$-BiFeO$_3$, shows a comparatively very low weight loss at 317.6^{0}C, which was due to the partial decomposition of the SnO$_2$ nanoparticles[21].

X-ray diffraction

The structural analyses of the possible core-shell nano-multifunctional materials synthesized were carried out by using powder X-ray diffraction, which is a suitable technique for identifying the structural crystalline nature of the nano-multifunctional materials synthesized. The XRD patterns of ZnO, SnO$_2$, ZnO-BiFeO$_3$, SnO$_2$-BiFeO$_3$ nanomaterials are shown in **Fig.5B**. The XRD pattern are shows well intensified peaks of possible core/shell nanoparticles developed. We have identified the pure ZnO (JCPDS card no. 71-2494), SnO$_2$ (JCPDS card no. 41-1445) and BiFeO$_3$ (JCPDS card no 86-1518), and nanocomposites by using WinXPow software. It is evident that the intensities of clean peaks of ZnO, SnO$_2$, and BiFeO$_3$ are slightly modified in nanocomposite powders due to formation of possible core-shell structured nanopowders as supported by TEM pictures. Moreover, Bragg angel of pure peaks are slightly (with-in 0.002 θ) shifted towards higher angles than their pures. We have compared and justified by JCPDS standard files. In **Fig.5B I and II,** the sharp peaks identified at: 2θ =

32.35^0 and 57.47^0, are the vital characteristics of $BiFeO_3$ crystal planes (110) and (300), respectively[2122]. The other diffraction peaks (ZnO, SnO_2) are highly significant to the formation of ZnO-$BiFeO_3$ and SnO_2-$BiFeO_3$ materials [23,19,24]

VSM studies

The main emphasis of these possible core-shell nanocomposites developments is to understand magnetic properties with two distinct semiconductive shells materials in forming possible core-shell structured nanocomposite powders. Accordingly, we have investigated nanocomposites magnetic properties and since semiconductive SnO_2 and ZnO are feeble to show magnetic nature when compared to $BiFeO_3$. In order to investigate the nature of the ferromagnetism character in ZnO-$BiFeO_3$ and SnO_2-$BiFeO_3$, magnetic measurements were carried out on wide range of temperature, in the range of between 5-300 K. **Fig.6** shows the temperature-dependence of magnetizations for ZnO-$BiFeO_3$, and SnO_2-$BiFeO_3$, which exhibited a saturation magnetization against sufficiently external magnetic field. The zero-field-cooling magnetization of ZnO-$BiFeO_3$ sample (**Fig.6a**) shows a broad peak feature around 5K with decreasing order until 50K (the so-called blocking temperature at 50K) and decreased thereafter from 100K to 300K. However, the field-cooled magnetization exhibited similar behaviour as zero-field-cooled magnetizations above blocking temperature. However, fluctuation in the magnetization of SnO_2-$BiFeO_3$ (**Fig.6b**), arising from weak moment of the sample and interfacial effects between core BFO and semiconductive shell was observed. The magnetization of ZnO-$BiFeO_3$ is higher than SnO_2-$BiFeO_3$, which can make it to be a better magneto-electric interactive candidate.

4. Conclusion

In this scientific paper, zinc oxide-bismuth ferrite and tin dioxide-bismuth ferrite possible nano-multifunctional materials were successfully prepared by double precipitation technique. The nano-multifunctional materials were characterized by spectral, thermal techniques and the temperature-dependent magnetic behavior was studied. Heat-treated nano-multifunctional materials are highly crystalline, as supported by powder XRD studies. The zinc oxide-bismuth ferrite nano-multifunctional materials synthesized, exhibited good temperature-dependent magnetic behaviour for possible spintronic and energy applications.

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Caption for Scheme 1

Scheme 1. Schematic diagram for the formation of possible core-shell nano-multifunctional materials.

Caption for Figures

Fig 1. FTIR spectra of A) $BiFeO_3$, ZnO and ZnO-$BiFeO_3$. B) SnO_2 and SnO_2-$BiFeO_3$ nano-functional materials.

Fig 2. SEM image of nano-functional materials.

Fig 3. EDS images of A) $BiFeO_3$, B) ZnO, C) SnO_2, AB) ZnO-$BiFeO_3$ and AC) SnO_2-$BiFeO_3$.

Fig 4. TEM images of nano-functional materials

Fig 5. A) TGA curves of: a) $BiFeO_3$, ZnO, ZnO-$BiFeO_3$ and b) $BiFeO_3$, SnO_2, SnO_2-$BiFeO_3$; B) XRD patterns of: I) ZnO, ZnO-$BiFeO_3$ and II) SnO_2, SnO_2-$BiFeO_3$

Fig 6. M-H curves of a) ZnO-$BiFeO_3$ and b) SnO_2-$BiFeO_3$