Research Article

Bismuth Iron Oxide Nanoparticles as Photocatalyst for Solar Hydrogen Generation from Water

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Abstract

Multiferroic materials such as bismuth iron oxide (BiFeO3/BFO) have strong potential for solar hydrogen generation. In this paper, we have described a sol-gel method using urea and polyvinyl alcohol at low temperature to synthesize high purity BFO nanoparticles of size 50–60 nm. A complicated and high temperature process is usually employed to synthesize BFO. It is observed that the material has an energy band gap of 2.1 eV which makes it a potential material towards solar applications. Photoelectrochemical (PEC) and photocatalytic tests are conducted to evaluate BFO’s performance towards hydrogen generation by splitting of water using simulated solar light. PEC generation of hydrogen using fabricated electrodes (BFO nanoparticles coated on titanium foil) shows that the material is photoactive and can evolve hydrogen from water using a visible light. Photocatalytic tests for hydrogen generation are also performed using the nanoparticles in 1(M) KOH solution under simulated solar light. Upon analysis of the evolved gases by gas chromatography (GC), hydrogen and oxygen are detected. Furthermore, it is also observed that BFO generates three times more hydrogen than commercial titania P25 catalyst under similar experimental conditions.

Keywords bismuth iron oxide; nanoparticles; photocatalysis; hydrogen generation from water

1 Introduction

Multiferroic materials, combining the properties of ferroelectricity, ferromagnetism and ferroelasticity, have been widely discussed in recent years because of their wide range of applications as additives, spintronics devices, data storage and magnetic sensors [13,21,39,40]. Currently, these types of materials are of great interest for solar applications due to their bulk photovoltaic effect. It is reported that the photocurrent of ferroelectric material arises due to depolarization of electric field which can separate the photogenerated charged carriers [2,14,22,23,31,33]. This helps in preventing electron-hole recombination loss present in conventional semiconductor photocatalytic materials. It is also suggested that the photocurrent in multiferroics is generated due to the delocalized band-to-band optical transition in polar crystals because of Frank-Condon relaxation of the excited state [6,20] or due to asymmetric momentum distribution of photoexcited carriers [15]. Bismuth iron oxide or BiFeO3 or BFO is an interesting multiferroic material for energy-related applications especially hydrogen generation through photocatalytic and photoelectrochemical (PEC) water splitting due to its small band-gap (∼2.2 eV) [10,30] with good carrier transport properties and large absorption of visible light extending up to 750 nm. Thus BFO seems to be an ideal material for visible light water photosplitting to evolve hydrogen [1,29,32,34].

Even though numerous typical ferroelectric materials including BaTiO3, SrBi2Nb2O9 [3,37], LiNbO3 and Pb(Zr, Ti)O3 have been investigated [36], much study has not been done on perovskite structured BiFeO3 as the isolation of the pure phase compound is very difficult to achieve [4]. BFO has been synthesized by a variety of methods, for example, pulsed laser deposition (PLD) [36], electro-spinning [43] and magnetron sputtering [25]. Various wet chemical routes have also been used to prepare BiFeO3 which include hydrothermal synthesis [7], co-precipitation [35], microemulsion technique [11], combustion synthesis [12], ferrioxalate precursor method [18], sol-gel process [19,41,44] and polyacrylamide gel route [42]. Although a number of methods have been reported, investigations carried out on the synthesis of pure phase BFO are limited apparently due to specific facility requirements. Preparation of single phase, nanosized and highly crystalline BFO using a low cost process is still an interesting research topic to fabricate cost-efficient devices on a large scale. In this present work, we report the synthesis of nanocrystalline BFO with water as reaction medium, polyvinyl alcohol (PVA) as an inhibitor and urea as a precipitating agent. Unlike other synthetic
procedures reported thus far, the current synthetic procedure only needs readily available standard lab equipments to get high purity and crystalline BiFeO₃. The total synthesis process reported here takes only few hours. Due to low synthesis temperature, the as-prepared sample is partially crystalline. To get fully crystalline material, the partially crystalline BiFeO₃ has been annealed at different temperatures (300–700 °C) and atmospheres (nitrogen (N₂), oxygen (O₂), argon (Ar) and air) which also allowed us to find out the effect of temperature and annealing atmosphere on the crystallization of BiFeO₃. Detailed characterization studies of the produced BiFeO₃ have also been reported. Powder XRD is used to find out the optimized condition to get pure phase and highly crystalline BFO.

BFO has potential applications in alternative energy harvesting [4]. Ramesh and his group have reported on the bulk photovoltaic properties of BFO where photocurrent can flow in a uniform material without the need to form an interface (p–n junction) [39,45,46]. In ferroelectric materials, the photovoltage magnitude is not limited by the band gap as it is in conventional semiconductor photovoltaic materials. Ji et al. [24] studied bulk photovoltaic phenomenon in a thin film made of epitaxially grown BFO. The as-deposited BFO films are completely self-polarized and produce large open-circuit photovoltage. They also reported on the bulk photovoltaic effect at visible wavelength in epitaxial ferroelectric BFO thin films [24].

BFO has also been used as a photocatalytic material. Liu and his group have observed the photoinduced oxidization ability of BFO nanowires [17] and significant photocatalytic pollutant decomposition properties of BFO nanoparticles [16], suggesting that BFO might be a promising material as for both photocatalysis and photoelectrolysis of water. They prepared BFO nanowires that showed the photoinduced oxidization ability to produce O₂ in AgNO₃/H₂O system [17]. The group has also shown the successful decomposition of methyl orange under UV-Vis light irradiation [16]. They reported that though both BFO bulk and nanoparticles decompose methyl orange photocatalytically, BFO nanoparticles are more efficient than that of bulk BFO due to the higher surface area of nanosized BFO [16]. Because of the small band gap, BFO nanoparticles show a significant degradation ability under visible light irradiation. Cho et al. [9] applied BFO nanopowders for the photocatalytic decomposition of RhB in water using visible-light illumination. Luo and Maggard demonstrated that SrTiO₃ coated BFO nanoparticles can produce H₂ under visible light irradiation while pure SrTiO₃ only responded to UV irradiation [28]. Joshi et al. [26] reported on the O₂ production ability of BFO nanocubes in the photocatalytic reaction from an aqueous FeCl₃ solution. This represents a half-cell reaction of photocatalytic water splitting. Photocatalytic tests have been carried out to evolve H₂ from water by using BFO. Gao et al. found that BFO nanowires failed to produce H₂ either from pure water or from Pt/CH₂OH/H₂O system under visible light irradiation and UV irradiation [17]. Luo and Maggard also found that BFO did not display any detectable photocatalytic activity for methanol oxidation [28].

Chen et al. prepared BFO films by pulsed laser deposition on Pt/TiO₂/SiO₂/Si substrates and studied them as photoelectrodes for water splitting [8]. They found that the incident photon to current conversion efficiency (IPCE) for the polycrystalline BFO electrode is approximately 16% at 350 nm and 7% at 530 nm at 1.5 V versus saturated calomel electrode. Joshi et al. also reported on the photocurrent generated by film photoelectrodes fabricated from BFO nanocubes and BFO bulk materials in water under visible light irradiation ≥ 420 nm. The photocurrents generated from BFO nanocube and bulk BFO electrodes at 1.0 V versus SCE are 5.2 and 4.7 μA/cm², respectively, while photocurrent is not generated in dark [26].

Thus it can be seen that not many studies have been done on the photocatalytic and photoelectrochemical (PEC) splitting of water by BFO. Though previous studies reported that no hydrogen (H₂) is evolved in the photocatalytic tests, we detected H₂ in the photocatalytic splitting of water by BFO. Both H₂ and O₂ are detected by gas chromatography (GC) analysis. H₂ is quantitatively measured and compared with commercially available Degussa P25 after 6 h of illumination. PEC measurements are also done and photocurrent is observed under AM 1.5 conditions and also with wavelength ≥ 420 nm (visible light). This article reports a systematic study on the synthesis, characterization and photocatalytic applications of BFO towards water splitting and also determines the best conditions to obtain the material in its purest form.

2 Materials and methods

2.1 Synthesis of BFO and optimization to get pure phase

All chemicals used are of analytical grade and used as received without further purification. An aqueous solution of ferric nitrate Fe(NO₃)₃·9H₂O (ACS grade, Fischer) is added to a solution of bismuth nitrate Bi(NO₃)₃·5H₂O (98%, Sigma-Aldrich) in dilute nitric acid in stoichiometric amounts. The resulting solution is heated up to 70 °C when the color of the liquid mixture changed from transparent to dark brown. At this time, polyvinyl alcohol (PVA, 99%, Sigma-Aldrich) is dissolved in distilled water (10% w/v) and added to the mixture while maintaining the optimum metal ion to vinyl alcohol monomer unit of PVA mole ratio of 1:2.5. Then a certain amount of urea (99.5%, Alfa-Aesar) is introduced to the above mixture. The mole ratio of (Fe³⁺ and Bi³⁺) to urea is 1:1. A strong smell of ammonia (NH₃) that is evolved from the reaction medium can be
easily identified. These are manifested by the formation of voluminous organic based fluffy brown mass as the end product. The fluffy mass is dried at 40 °C in a water bath for 4 h until the color becomes dark brown. The material when characterized proved to be BiFeO$_3$. This process presents the quickest and simplest way to synthesize BiFeO$_3$. The synthesis process and crystallization procedure of the material are optimized to get a pure phase. Annealing of the as-prepared materials is carried out in a chemical vapor deposition furnace (CVD, FirstNano). Annealing atmosphere, temperature and time are varied to get the purest form of material. The flow rate of the gases is always maintained at 400 sccm (standard cubic centimeters per minute).

2.2 Preparation of BFO nanoparticle coating on Ti foil (BFO-Ti)

A dip coating method was adopted to coat the above synthesized BFO nanoparticles (nitrogen annealed for 2 h at 600 °C) on titanium (Ti) foil. For this purpose, the BFO nanoparticles (10 mg) are dispersed in a solution containing ethylene glycol (10 mL), ethanol (5 mL) and polyvinylpyrrolidone (5 mg). The Ti foil (after nanoparticle coating) is dried in an air oven (120 °C) overnight, followed by annealing in an oxygen atmosphere for 3 h at 500 °C. This process removed the organics from the thin layer of BFO nanoparticles and a uniform film is formed on the Ti foil. In a similar way, P25 nanoparticles are also coated on Ti foil (for a comparison with BFO).

2.3 Characterization

All the materials are characterized by various analytical and spectroscopic techniques as discussed below. A scanning electron microscope (SEM; Hitachi, S-4700) is used to analyze the morphology of the materials. The images are taken in an operating accelerating voltage of 20 kV. Energy dispersive X-ray (EDX) analysis is obtained using an Oxford detector to determine the composition of the sample. Diffuse reflectance ultraviolet and visible (DRUV-Vis) spectra of the samples are measured (to understand the solar light harvesting properties of the materials) from the optical absorption spectra using a UV-Vis spectrophotometer (UV-2401 PC, Shimadzu). Fine BaSO$_4$ powder is used as a standard for the baseline measurements, and the spectra are recorded in a range of 200–800 nm. Transmission electron microscope (TEM, JEOL 2100F) images are taken by dispersing a small amount of sample in ethanol, followed by ultrasonication for few minutes (min) for proper distribution. A drop of ethanol (containing sample) is placed on a carbon coated Cu-grid and subjected to High Resolution Transmission Electron Microscopy (HRTEM), and Fast Fourier Transform (FFT) measurements. Powder X-ray diffraction (PXRD) measurement is carried out for optimization process to achieve high purity and crystalline compound. This is done using a Philips-12045 B/3 diffractometer. The target used in the diffractometer is copper ($\lambda = 1.54$ Å), and the scan rate is 1.2 deg/min. Thermogravimetric analysis (TGA, TGA-50 Shimadzu) is carried out over the temperature range of 0–600 °C in nitrogen atmosphere to understand the weight loss profile of the as-synthesized material. The heating rate is kept at 5 °C/min.

2.4 Photocatalytic hydrogen (H$_2$) generation

BFO and commercially available titania (Degussa P25) are examined for photocatalytic water splitting. Photocatalytic hydrogen generation experiments have been carried out in a slurry-type photochemical reactor (Ace Glass, 7840-340). In a typical experiment, 600 mg of photocatalyst (annealed BFO) is weighed and introduced into the reactor with 300 mL of 1(M) KOH. Under dark conditions, the slurry is mixed via magnetic stirring while the system is purged with nitrogen (N$_2$) for 25 min to remove any dissolved oxygen before illumination of the photocatalyst. A 400 W immersion-type medium pressure quartz mercury U/V-visible lamp is used for photoillumination of the slurry (Ace Glass, 7825-34). During all experiments, the temperature of the reactor is maintained at ~ 30 °C utilizing a circulating water quartz jacket.

2.5 Photoelectrochemical (PEC) H$_2$ generation

Experiments on H$_2$ generation from water are carried out in a glass cell with photoanode (BFO-Ti and Ti) and cathode (Pt foil) compartments. The compartments are connected by a fine porous glass frit. Ag/AgCl electrode is used as the reference electrode. The cell is provided with a 60 mm diameter quartz window for light incidence. The electrolyte used is 1(M) KOH. A computer-controlled potentiostat (SI 1286, England) is used to control the potential and record the photocurrent generated. A 300-W solar simulator (69911, Newport-Oriel Instruments, USA) is used as the light source. An AM 1.5 filter is used to obtain one sun intensity, which is illuminated on the photoanode (87 mW/cm$^2$, thermopile detector from Newport-Oriel is used for the measurements). The samples are anodically polarized at a scan rate of 5 mV/s under illumination and the photocurrent is recorded. All the experiments are carried out under ambient conditions. The effect of visible light ($\geq 400$ nm) irradiation is carried out by using a band-pass filter (Edmund optics) in combination with an AM 1.5 filter.

Electrochemical impedance spectroscopy (EIS) measurements are carried out to understand the charge transport properties of the BFO electrodes. The measurements are done at open circuit potential using similar conditions as described above for PEC tests. The amplitude of
Figure 1: PXRD patterns of BiFeO\(_3\) samples: (A) (a) as-prepared and (b) fired with alcohol and (B) annealed at 600 °C for 2 h under N\(_2\) atmosphere.

Figure 2: XRD patterns of BiFeO\(_3\) samples annealed in an air oven for 2 h at (a) 400 °C, (b) 550 °C and (c) 600 °C, respectively.

The sinusoidal wave is 10 mV and the frequency range examined is 100 kHz to 0.1 Hz. The Mott-Schottky analysis was carried out by conducting a standard electrochemical impedance spectroscopy at 3000 Hz in 1(M) KOH solution by scanning the potential from positive to negative direction in steps of 50 mV/s under illuminated conditions (by the simulated solar light using AM 1.5 filter).

3 Results and discussions

During synthesis, the reaction mixture is heated up to 120 °C after the addition of urea. During this time, the color of the reaction mixture became darker from light brown to dark brown and the mixture dried up until the volume of the reaction mass suddenly increased and consequently caught fire by itself. Then the dark brown fluffy mass is ground into fine powder to form the precursor material. The crystallization of the as-synthesized material is carried out in two ways. The first process deals with the room temperature firing of the as-synthesized powder using ethanol. This is carried out by adding ethanol to the fine, as-synthesized BFO powder followed by firing of the sample.

The firing process not only changed the color of BFO from light to deep brown but also changed the nonmagnetic powder to a magnetic one (tested by a magnetic needle). Figure 1(A) shows the PXRD pattern of the BiFeO\(_3\) powder before and after firing. It can be seen that the sample before firing treatment is amorphous in nature and has no distinct peaks Figure 1(A)-(a). However, after firing with alcohol distinct peaks are observed Figure 1(A)-(b). It can be inferred from Figure 1(A) that amorphous BiFeO\(_3\) powder can be crystallized by firing treatment but it still possesses a significant amount of other phases. It is well-known that other phases including Bi\(_2\)O\(_3\), Bi\(_2\)Fe\(_4\)O\(_9\), Bi\(_{25}\)FeO\(_{40}\) and Bi\(_{36}\)Fe\(_{24}\)O\(_{57}\) are repeatedly obtained during synthesis of BiFeO\(_3\) especially in the bulk form [4]. To minimize the presence of secondary phases, the other way of crystallization at high temperature and under controlled atmosphere is applied. Different portions of the precursor material are annealed under different temperatures and gas atmospheres for various durations of time to optimize the condition for obtaining highly crystalline and pure phase BiFeO\(_3\) nanoparticles. XRD patterns of the samples annealed at different temperatures and under different atmospheres have been obtained. Figure 2 shows the XRD patterns of BiFeO\(_3\) samples annealed in an air oven for 2 h at 400 °C, 550 °C and 600 °C, respectively. The peaks representing BiFeO\(_3\) are found in all the samples. At 400 °C, peaks from secondary phases are observed and the peak of BiFeO\(_3\) at 2θ ≈ 22° is not very prominent. However, as the annealing temperature is increased to 600 °C, strong peaks characteristic of BiFeO\(_3\) are obtained and the peak observed at 2θ ≈ 27° due to the presence of secondary phase is reduced substantially. Figure 3 shows the XRD patterns of BiFeO\(_3\) samples annealed under different atmospheres, namely, N\(_2\), O\(_2\) and Ar. Characteristic peaks from BiFeO\(_3\) are detected in every sample annealed under different atmospheres. The sample annealed under N\(_2\) atmosphere showed the smallest peak from the secondary phase at 2θ ≈ 27°. Thus the sample annealed under N\(_2\) showed the purest phase
Figure 3: XRD patterns of BiFeO$_3$ annealed at 600 °C for 2 h under (a) N$_2$, (b) air, (c) O$_2$ and (d) Ar atmospheres, respectively.

Figure 4: XRD patterns of BiFeO$_3$ annealed under N$_2$ at 600 °C for (a) 15 min, (b) 30 min, (c) 1 h, (d) 4 h and (e) 2 h.

Figure 5: SEM images of BiFeO$_3$: (a) as-synthesized and (b) annealed at 600 °C for 2 h under N$_2$ atmosphere.

Scanning electron microscope (SEM) images of BiFeO$_3$ powders both as-synthesized and after annealing in N$_2$ at 600 °C for 2 h are displayed in Figure 5. Both forms of material show a similar morphology. It is found that the size of nanoparticles ranges 50–60 nm. The high resolution TEM (HRTEM) image of annealed BiFeO$_3$ obtained under an accelerating voltage of 200 kV is shown in Figure 6. Both SEM and TEM images confirm that the BiFeO$_3$ nanoparticles are well crystallized with a single-phase perovskite structure (known from XRD). Figure 6(b) shows the HRTEM image of the BiFeO$_3$ nanoparticle as well as the selected FFT pattern (inset). The inter planar spacing of about 4.04 Å and 2.76 Å (corresponding to the 101 and 012 planes) are in accordance with single-phase perovskite structure of BiFeO$_3$ [38]. Figure 6(c) shows the energy dispersive X-ray (EDX) spectrum of annealed BFO material averaged over four different samplings. From the values of the peak intensities obtained from the EDX spectrum the atomic ratio of Bi:Fe:O is found to be approximately 1:1:3. This is also supported by the elemental composition of the material (Figure 6(d)). The above characterization studies confirm that the BiFeO$_3$ samples prepared are highly crystalline with single-phase perovskite structure and have consistent fixed stoichiometry.

Figure 7 shows the TGA curve of the as-prepared (A) and annealed (B) BFO samples. Figure 7(A) shows the absence of precursor material after 380 °C. Thus it can be
Figure 6: TEM images of BFO annealed at 600 °C for 2 h under N\textsubscript{2} atmosphere. (a) Particles of size ~ 50 nm, (b) HRTEM image of BFO nanoparticles showing interplanar distances of 4.04 and 2.76 Å, respectively, (c) EDX graph indicating that the material is composed of Bi, Fe and O, (d) EDX data showing elemental composition of the material to be approximately 1:1:3 (Bi:Fe:O).

Figure 7: TGA curve of BFO (heating rate is 5 °C/min): (A) as-prepared and (B) annealed in N\textsubscript{2} atmosphere.

deduced that in order to obtain pure BFO, the as-synthesized sample needs to be heated at ≥ 400 °C. Figure 7(B) shows that the annealed sample at 600 °C is stable and free of any precursor material.

As the UV-Vis absorption edge of a semiconductor catalyst corresponds to its energy band, it is important to record the optical absorption of the BFO nanoparticles for photocatalytic application. Figure 8 shows the DRUV-Vis absorption spectrum of BiFeO\textsubscript{3} and the inset shows the plot of \((\alpha h \nu)^2\) as a function of photon energy for BFO (UV-2401 PC). The absorption cut-off wavelength of BFO is about 620 nm suggesting that BiFeO\textsubscript{3} can absorb a considerable amount of visible light. According to the classical Tauc approach [38], the energy band gap of the BiFeO\textsubscript{3} nanoparticles is estimated to be about 2.1 eV which is close to the literature value [16,27].

The applicability of BFO as a potential candidate for photocatalytic water splitting for hydrogen generation is examined under AM 1.5 conditions. BFO material annealed at 600 °C for 2 h under N\textsubscript{2} is used for this application. A schematic of the set-up can be seen in Figure 9(A). The results (Figure 9(B)) show that BFO generates nearly three times the hydrogen than that of commercially available Degussa P25 after 6 h of illumination. A blank experiment
Figure 8: DRUV-Vis absorption spectra of BiFeO$_3$. The inset shows the BiFeO$_3$ plot of $(\alpha h\nu)^2$ as a function of photon energy ($h\nu$).

without any photocatalyst has also been performed in 1(M) KOH and no hydrogen evolution is detected. During the whole process, the pH of KOH solution does not change and the crystal structure of BFO remains the same. Figure 10 shows the XRD patterns of BFO before and after hydrogen generation. No significant change is observed from the two plots. No hydrogen is detected under dark condition. Hence it can be concluded that BFO can be used as an effective photocatalyst to generate H$_2$ from water under solar light illumination. The possible reasons for BFO nanoparticles being a better photocatalyst than P25 TiO$_2$ nanoparticles are firstly, due to the visible light contribution of BFO. P25 TiO$_2$ nanoparticles show negligible contribution towards visible light. The second reason may be due to the efficient separation in charge in BFO being a multiferroic material. Thus recombination loss is much less in BFO than TiO$_2$.

In addition to the above photocatalytic test on BFO, we have also performed PEC experiments on BFO. In this process, BFO coated on Ti foil (BFO-Ti) as catalyst (exposed area = 1.0 cm$^2$) is used as photoanode in the PEC cell to evaluate its activity for water photoelectrolysis in 1(M) KOH electrolyte under simulated solar light illumination (87 mW/cm$^2$). The photoelectrochemical (PEC) tests are carried out using Pt as cathode and Ag/AgCl as reference electrode. The PEC activities of BFO-Ti under intermittent illumination conditions are presented in Figure 11(A). The photocurrent is recorded as a function of the applied potential. The potential is increased gradually (5 mV/s) from the open circuit condition until 0.2 V$_{Ag/AgCl}$. The maximum photocurrent density obtained from BFO-Ti photoanode is 0.36 mA/cm$^2$ at 0.5 V$_{Ag/AgCl}$. Under the same illumination conditions, oxygen annealed Ti photoanode showed $\sim$ 0.3 mA/cm$^2$ photocurrent density. The superior activity of the coupled photocatalyst is due to good charge separation as well as efficient solar light harvesting. The dark current density (without illumination) is always found to be $\sim$ 0.05 $\mu$A/cm$^2$. This indicates that the photocurrent obtained from the system is mostly due to the photocurrent generated by the illumination of light on the photoanode.

To find the contribution of the visible-light components on the total activity of the BFO-Ti photoanode, we carried out experiments with UV filters (only $\lambda \geq 400$ nm is illuminated). It is interesting to note that 36% of the photocatalytic splitting of water. It is seen that BFO generates 3 times more H$_2$ than commercial P25 titania nanoparticles.

Figure 9: (A) Photocatalytic H$_2$ generation using BFO as a catalyst in 1(M) KOH; (a) solar simulator light source, (b) reactor, (c) burette for collecting gas by downward displacement of water, (d) N$_2$ cylinder for purging, (e) gas collection outlet, (f) petridish containing water. (B) Volume versus time graph showing the volume of H$_2$ evolved during the photocatalytic splitting of water. It is seen that BFO generates 3 times more H$_2$ than commercial P25 titania nanoparticles.
changes observed in the absorption intensity (DRUV-Vis), surface morphology (SEM) and elemental composition (B/F/O ratio) of the composite photoanode after the sample has been used for photoelectrochemical tests. These results show that the composite photocatalyst is having potential for long-term operation with good photoactivity. The less value of photocurrent obtained upon irradiation of simulated light over BFO-Ti anode may be due to the low thickness of BFO and due to poor mobility of electrons through the material. This can be overcome by fabricating BFO electrodes of a certain thickness and also by doping with other elements, for example, silicon (Si). Grätzel et al. showed improved photocurrent of thin film hematite (Fe₂O₃) photoanode towards water photosplitting by doping Fe₂O₃ with Si and forming a thin film of a certain thickness on transparent, conducting oxide-coated glass [5].

4 Conclusions

Single-phase BFO nanoparticles have been successfully synthesized by a simple and cost effective sol-gel method based on PVA by annealing at a temperature as low as 600 °C under nitrogen atmosphere for time duration of 2 h. This process is the quickest and simplest way to make high quality BiFeO₃ material. The extent of purity of the sample and the rhombohedral phase of BiFeO₃ are determined by an X-ray diffraction pattern. Images from SEM and TEM show that the material is highly crystalline with a single phase perovskite structure. The chemical composition of BiFeO₃ is found from EDX measurements with a ratio of Fe:Bi:O = 1:1:3. The inter-planar spacing values obtained from HRTEM are of 4.04 Å and 2.76 Å which are in accordance to literature values of single phase perovskite structure. The cost effective and easy synthesis of highly crystalline, single phase BiFeO₃ opens the avenue for large-scale applications of the material. DRUV-Vis absorption spectrum indicates that the absorption cut-off wavelength of the nanoparticles is about 620 nm corresponding to the energy band gap of 2.1 eV. This material showed a highly efficient photocatalytic activity of water decomposition under simulated solar light 34 mL of H₂/g of BFO as catalyst after 6 h run. It showed three times better photocatalytic activity than P25 Degussa TiO₂ nanoparticles. PEC measurements indicate that BFO shows ∼ 36% visible light activity and is moderately effective in splitting water. The enhanced photocatalytic activity of BFO than TiO₂ nanoparticles can be attributed to the visible light contribution and efficient charge separation in BFO. This information coupled with the cost efficient synthesis process may lead to the fabrication of new devices for harvesting solar energy and other optoelectronic purposes.

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