FACILE SYNTHESIS OF PRISTINE AND LANTHANUM MODIFIED BIFEO$_3$ NANOMATERIALS AND THE INVESTIGATIONS OF PHOTOCATALYTIC PROPERTIES

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We report here a facile synthesis of $La_xBi_{1-x}FeO_3$ (x=0.00, 0.10) by sol-gel technique. This route of synthesis provides better control on particle morphology and phase purity of $BiFeO_3$.Crysallographic analysis, particle morphology and optical propertied was tested by X-ray diffraction, scanning electron microscopy and UV-visible spectroscopy technique, respectively. The X-ray diffraction technique has confirmed the formation of pure phase of $BiFeO_3$.The prepared materials has exhibited good photo catalytic action under the irradiation of UV-vis spectrum. We have found that the doped material has better photo catalytic action in comparison of pristine.

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Introduction

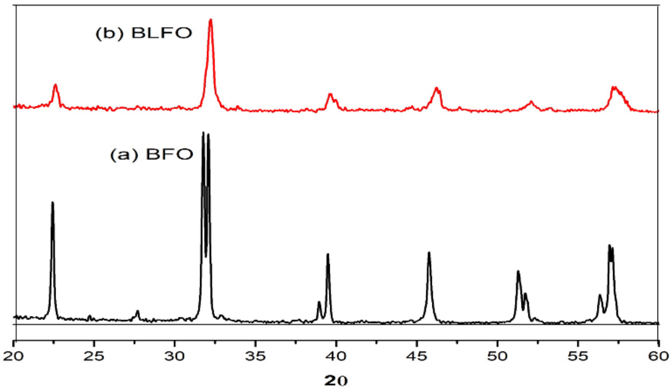
The sun is infinite source of energy. Sun energy can be harvest into another form of energy or energy carrier. To convert sun energy into solar electricity and solar hydrogen, a efficient photo catalyst material is required. A "Hydrogen" energy carrier that is sustainable could be created by combining the two sun energy and suitable photocatylyst [1]. One of the key types of solar cells is the photo electrochemical solar cell, which can split water to produce hydrogen. The two most crucial factors do not appear to have been handled together in the appropriate perspective, despite the fact that there are a number of parameters that need to be optimized for constructing effective and practical PEC solar cells. One of these is modifying the photo electrode's band gap to have the best solar spectral response. The other is a reduction in the recombination of electrons and holes, the carriers created by solar photons. For the same photo electrode, there are comparably few reviews that cover all of these aspects at once. In light of this, we will concentrate on band gap tailoring of photo electrode materials and lowering of carrier recombinations in this chapter. We will focus on the aforementioned qualities for oxide photo electrodes because they form one of the most stable photo electrodes, do not experience photo corrosion, and are stable. We will concentrate on two distinct oxide photo electrodes that can split water to produce hydrogen. One is TiO_2, the first and most extensively researched photo electrode material, which has a high band gap (3.20 eV) [2,3]. The highest documented STH efficiency for a TiO2-based PEC solar cell is 2.70 percent. The other is recently investigated $BiFeO_3$ and its customized variations. $BiFeO_3$ has a band gap of 2.23 eV, however it can be customized to have a smaller band gap up to 1.10eV [4,5]**.** In this research work we will focus on $BiFeO_3$ and its doped variants as photo catalyst. This is oxide based perovskite material with high chemical stability against photo corrosion. Reduction of the band gap of photo catalyst up to visible region near about 1.77eV may enhance photo catalytic activity[6,7,8]. The effective way to lower the band gap is doping of some suitable impurity in the host materials [9,10]. In this research work we will prepare pristine $BiFeO_3$ (BFO) material and lanthanum (La) doped material (BLFO) with low temperature sol gel method. Further will investigate and compare the photo catalytic activity.

Synthesis protocol for pure and La doped $BiFeO_3$

All of the 99.9% pure raw ingredients purchased from Sigma Aldrich will be utilized. Stoichiometric amounts of bismuth nitrate penta was dissolved in 50 mL of distilled water while being stirred and heated to 80 °C in order to manufacture the substance. Bi loss during synthesis due to its volatile nature was compensated using a minor amount (5wt%) of bismuth nitrate. The stoichiometric amounts of iron nitrate nanohydrate were added to the aforementioned solution after 10 minutes. A few drops of concentrated HNO_3 were added. The solution was heated while being stirred constantly until a gel formed, and it was then dried in an air oven at 120 °C. After gathering the powder, pellets were created. The pellet was then annealed for two hours at 500 °C. In order to prepare La doped BFO same process was followed by adding and lanthanum nitrate hexa hydrate were dissolved in 50 mL of distilled water while being stirred and heated to 80 °C.

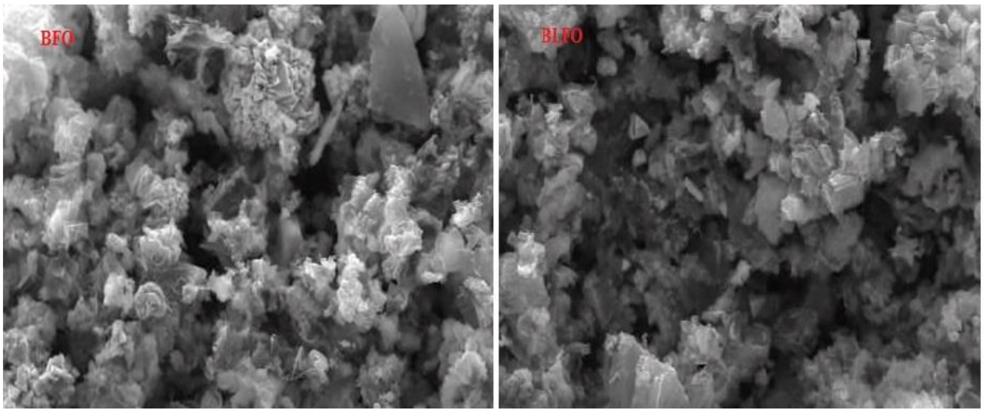
Result and discussion

Fig 1 shows the XRD patterns of pure BFO and La doped BFO. Fig 1 (a) revels the XRD profile pure BFO which confirms the formation BFO material. The XRD peaks of BFO could be indexed with rhombohedral lattice with R3c space group [12]. Besides of pure phase some impurity phase also appeared. The small intensity peak near two theta at 27 belongs to oxygen rich impurity $Bi_{25}FeO_{40}$. Fig 1 (b) revels the XRD profile La doped BFO. After doping 10% of La at Bi site two high intensity peaks merged into single peak. This indicated after doping lattice structure of BFO transformed from rhombohedral to orthorhombic [11]. After doping no any impurity phase has appeared.



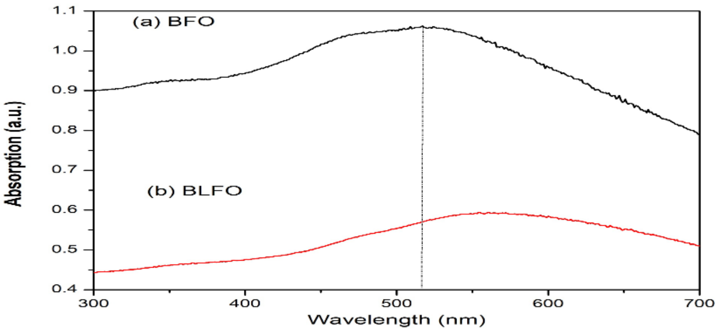
Fig;1 XRD patterns of (a) pure BFO and La doped BFO

The micrographic analysis of as prepared material was done by scanning electron microscopic technique which is shown in Fig 2(a,b). SEM images indicates that the BFO particle having various size in clustered form. After doping La it could be seen that the particles are less agglomerated and particles poses the structure like cube. This has indicated the doping may lead the nucleation, growth and hence crystallization in another way. These images have confirmed that the surface morphology can alter by doping some trace element in the host material. Doping can also affects the photo catalytic properties because it depends on surface morphology of the material.



Fig;2 Scanning electron micrograph (SEM) of (a) pure BFO and La doped BFO

The photo catalytic properties of as prepared materials were tested by using UV-Vis spectrophotometer. UV-Vis spectrum of materials was taken in absorbance mode. Fig 3(a) indicates that the absorption peak of BFO was found at wave length 524 nm which corresponds to the band gap of the semiconductor material 2.36eV. After doping 10% of La the absorption peak shifts towards red region which is shown in Fig 3(b). BLFO material shows absorption peak at 560 nm which corresponds to the energy band gap 2.20eV. This shifting of peak has confirmed that doped material can absorb much photons in comparison of pure BFO and hence doped material exhibited better photo catalytic activity.



Fig; 3 UV-Vis absorption spectrum of (a) pure BFO and La doped BFO

Conclusions:

We have successfully prepared pure and La doped BFO by low temperature sol gel method**.** All the prepared materials were gone through various characterization techniques. After in depth comparative study we have found that the doping may lead enhance in photo catalytic activity of semiconductor material. We have found that 10% La doped BFO material has better photo catalytic action in comparison of pristine.

References:

1. Rengui L.Latest progress in hydrogen production from solar water splitting via photocatalysis,photoelectrochemical, and photovoltaic-photoelectrochemical solutions. Chin. J. Catal. 2017; 38: 5–12.
2. Khaselev O,Turner JA. A Monolithic Photovoltaic-Photoelectrochemical Device for Hydrogen Production via Water Splitting. Science. 1998; 280:425-427.
3. Li J, Wu N.,Semiconductor-based photocatalysts and photoelectrochemical cells for solar fuel generation: a review., Catal. Sci. Technol., 2015, 5, 1360.
4. Leng WH, Barnes PRF, Juozapavicius M, Regan OBC, Durrant JR. Electron diffusion length in mesoporous nanocrystalline TiO2 photoelectrodes during water oxidation. J Phys Chem Lett 2010;1:967-72.
5. Lakshmana RN, Emin S, Valant M, Shankar MV. Nanostructured Bi2O3@TiO2 photocatalyst for enhanced hydrogen production. Int J. Hydrogen enegy 2017; 42:6627 -6636.
6. Li Z, Luo W, Zhang M, Feng J, Zou Z. Photoelectrochemical cells for solar hydrogen production: current state of promising photoelectrodes, methods to improve their properties, and outlook. Energy Environ. Sci. 2013,6, 347-370.
7. Rajeshwar K. Materials aspects of photoelectrochemical energy conversion. J Appl Electrochem 1985; 15:1–22.
8. Longzhu L, Changhai L, Yangyang Q, Naotoshi M, Zhidong C. Convex-nanorods of a-Fe2O$_3$/CQDs heterojunction photoanode synthesized by a facile hydrothermal method for highly efficient water oxidation. Int J Hydrogen Energy 2017; 42:19654-63.
9. Joy J, Mathew J, George C. Nanomaterials for photoelectrochemical water splitting – review. . Int J Hydrogen Energy 2018; 43:4804-4817.
10. Müller A, Kondofersky I, Folger A, Rohlfing D F, Bein T, Scheu C. Dual absorber Fe2O3/WO3 host-guest architectures for improved charge generation and transfer in photoelectrochemical applications. Mater. Res. Express. 2017;4: 016409.
11. Chen Z B, Jaramillo T F, Deutsch T G. Accelerating materials development for photoelectrochemical hydrogen production: standards for methods, definitions, and reporting protocols. *J. Mater. Res.*, 2010, 25: 3–16.
12. Dong P, Hou G, Xi X, WO3-based photocatalysts: morphology control, activity enhancement and multifunctional applications. *Environ. Sci.: Nano*, 2017, 4: 539–557.