SYNTHESIS OF BISMUTH FERRITE AND ITS APPLICATION IN SYNTHESIS OF 2-SUBSTITUTED BENZOXAZOLE

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A B S T R A C T

Bismuth ferrite ($BiFeO_3$/BFO) were synthesized via a wet chemical route using bismuth nitrate and iron nitrate as starting materials and excess citric acid as chelating agent, respectively, followed by thermal treatment.The prepared samples were characterized by X-ray diffraction of powder (XRD), scanning electron microscope (SEM) for extracting their surface morphology and their crystallographic structure. BFO has several applications in physics and device applications, which centred on spintronics and memory devices that can be addressed both electrically and magnetically. .Applications of BFO as a highly efficient heterogeneous and recoverable catalyst for organic reaction were remain unattended. So application of BFO for preparation of benzoxazole is explored using benzene diazonium salt. This protocol provides an efficient, economical, base free protocol for benzoxazole synthesis using cross coupling reaction is a powerful tool for the construction of C-N bond. It also adds to benefits of reactionat moderate temperature with shorter reaction time with good yield of the product. Product characterizations are done by GCMS, NMR, IR spectral techniques.

Keywords: Bismuth Ferrite, Benzoxazole, Benzene diazonium salt

1. INTRODUCTION:

$BiFeO_3$ (BFO) is perhaps the only material that is both magnetic and a strong ferroelectric at room temperature. As a result, it has an impact on the field of multiferroic that is comparable to that of yttrium barium copper oxide (YBCO) on superconductors, with hundreds of publications devoted to it in the past few years [1]. Application of mixed metal oxides (MMO) has an important role in organic transformations, due to their simplicity in handling, decreased reactor and plant corrosion problems, cost effectiveness and because most of the MMOs are reusable and recyclable. Ferrites containing mixed metal oxides (pervoskite ABO_3) can be used for various name reactions and other important organic conversions.[2] These ferrites containing mixed metal oxides can be separated magnetically and can be recycled. Synthesis of BFO has many alternatives with respect to its application. A facile sol–gel approach with a fixed calcination temperature is developed to prepare BFO nanoparticles, and the gel-drying temperature is adjusted to control the appearance of a g-Fe_2O_3 parasitic phase. The formation of a heterojunction structure between the BFO and g-Fe2O3 phases is proposed to be responsible for the enhanced photocatalytic activity. [3] The uniform multiferroic BFO nanoparticles with fairly narrow particle size distribution have been successfully synthesized by a simple glycol-based sol–gel route at relatively low temperature. The strong band-gap absorption at 2.55 eV and the enhanced photocatalytic activities of the BFO nanoparticles with H_2O_2 addition may bring some novel applications in water treatment field. [4]Ba-doped BFO ($Bi_{1-x}Ba_xFeO_3$) nanoparticles have been synthesized by sol–gel process using bismuth nitrate and iron nitrate as sources. [5] Heterostructures of

thin titania films on BFO substrates were grown by pulsed laser deposition. The heterostructures, when excited by visible light with energies between 2.53 and 2.70 eV, photochemically reduce aqueous silver cations from solution.[6] A facile aerosol-spraying approach was also developed to prepare mesoporous BFO hollow spheres with enhanced activity and durability in visible photocatalysis. [7] A BFO photocatalyst in the shape of uniform microspheres has been synthesized by solvothermal process assisted with chelating effect of citric acid. [8]Hydrothermal Synthesis and Photocatalytic Activities of $SrTiO_3$-Coated Fe_2O_3 and BFO [9]The single pervoskite BFO nanoparticles were prepared by a sol-gel process.[10]Microwave assisted hydrothermal (MAH) method was used to synthesize crystalline BFO nanoparticles at temperature of 180°C with times ranging from 5 min to 1 Hr.[11] Multiferroic BFO nanoparticles were prepared by a sol–gel rapid calcination technique with average diameter of 35nm with narrow size distribution. [12] In the present work BFO is prepared by using simple coprecipitation method using nitrate precursors and citric acid as chelating agent. It is found very robust and effective for synthesis of 2-substituted benzoxazole as catalyst. Benzoxazole is an important class of heterocyclic compound that are encountered in a number of natural products and are used in drug and agrochemical discoveries. As a consequence, much effort has been devoted not only to construct basic skeleton of benzoxazole molecules but also to prepare derivatives through C-C or C-N atom bond formation. Hence development of an efficient methodology for the preparation of benzoxazole and its derivatives has gained a lot of importance in current research. Benzoxazole is prepared previously by using 0-aminophenol and benzaldehyde [13]], copper-catalyzed intermolecular cross-coupling of 1,2-dihaloarenes with primary amides [14] and other precursors as shown in above figure. Transition metal-catalyzed synthetic transformations have been considered as one of the most powerful and reliable tools for those bond connections, giving complex molecular structures to be prepared in an efficient and economical manner. The first row transition elements such as Ni, Co, Fe, Mn and Cu are also used as alternative to palladium in cross coupling reactions. So we have taken oxide combination of transition and nontransition element in the form of BFO. The conventional reagents used for these coupling reactions are preactivated electrophiles such as aryl-, vinyl-, or alkyl (pseudo)halides, are employed to react with organometallic nucleophiles. Despite this splendid advance, preactivated reagents are replaced by simple primary aromatic amides and benzene diazonium salts.

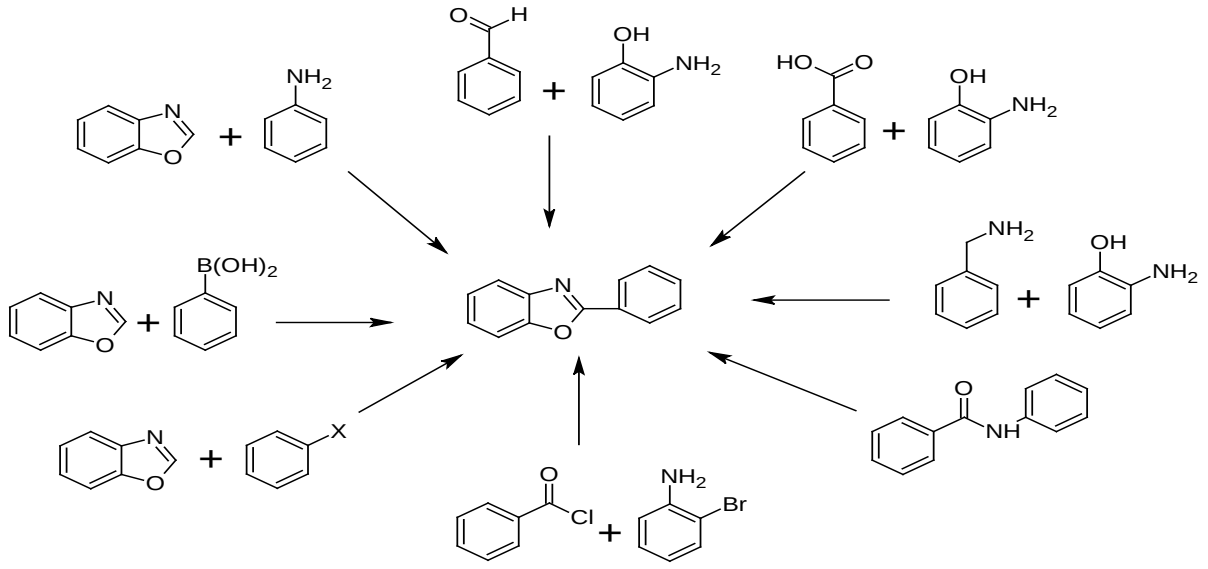


Fig.3. Reported ways to synthesize benzoxazole.

2. Experimental:

2.1. Catalyst preparation

All source chemicals (analytical grade) are purchased from Sigma Aldrich and used without further purification. In a typical run of synthesis, 0.040 mol/L bismuth nitrate ($Bi(NO_3)_3 \cdot 5H_2O$), iron nitrate ($Fe(NO_3)_3 \cdot 9H_2O$) with a molar ratio of 1:1 are added to form a solution using 10.0mL glycerol and 30.0mL ethanol. After 10 minutes of sonication, citric acid was added in the same molar ratio drop wise to form a fluffy precipitate. This precipitate was subjected to digestion for 1 Hr. at 80^0C. It is then filtered and dried at 150^0C for 2 hrs. The brown coloured lump was well grind and calcined directly at 450^0C for 2 Hrs. and taken to 450^0C slowly with heating rate of 5^0/5min. This well grinded powder of BFO is directly used in reactions as catalyst.

2.2. Characterizations

The sample composition is determined by EDAX. The catalyst structure is investigated by X-ray diffraction (XRD, Cu Kα radiation). The grain size is calculated by using Scherrer equation based on the principal XRD peak. Surface morphology and particle size are observed through scanning electron microscopy SEM. N_2 adsorption–desorption isotherms are measured using Brunauer–Emmett–Teller (BET) method and is used to calculate the specific surface area.

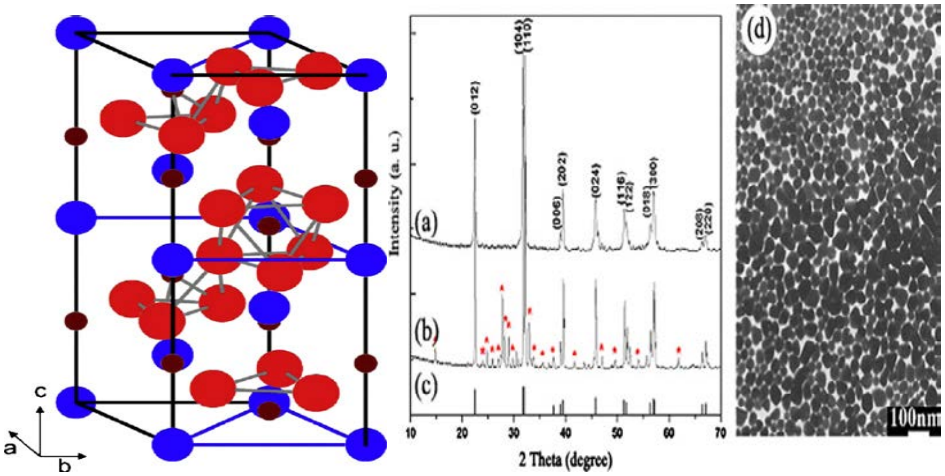


Fig1. **Fig.2**

Fig 1. Structure of perovskite-type $BiFeO_3$(Blue = Bi, Red =O, Brown = Fe).

Fig. 2 XRD patterns of the samples obtained from different calcination processes:
(a) Directly maintained at 450^0C for 2 hrs; (b) heated to 450^0 C with a heating rate of 5^0C/min, and held for 2 hrs. (c) Standard reflection lines from JCPDS: 86-1518. (d) TEM image of the obtained nanoparticles

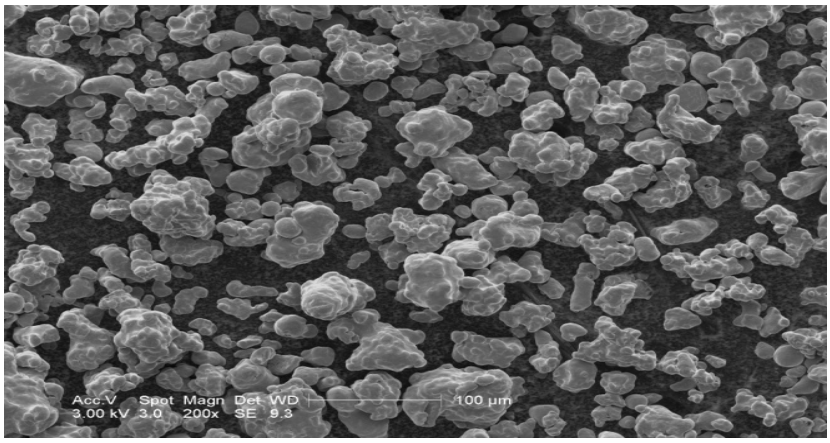
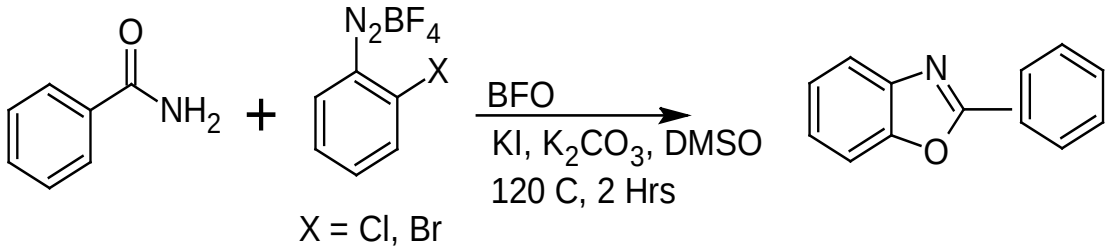


Fig 3: SEM image

2.3 Application of BFO as catalyst in the preparation of Benzoxazole



Scheme 1: BFO catalysed benzoxazole synthesis

Table 1.

Entry	catalyst	solvent	Catalyst loading (mol %)	Temp (^{0} C)	Time (Hrs)	Yield (%)
Screening of the catalyst						
1	-	DMSO	-	110	2	10
2	Mn2O	DMSO	2	110	2	40
3	CuO	DMSO	2	110	2	46
4	Nio	DMSO	2	110	2	50
5	BFO	DMSO	2	110	2	58
Effect of equivalent of BFO						
1	BFO	DMSO	1	110	2	45
2	BFO	DMSO	2	110	2	58
3	BFO	DMSO	4	110	2	66
4	**BFO**	**DMSO**	**4**	**120**	**2**	**72**
Effect of solvent						
1	BFO	DMSO	2	110	2	66
2	BFO	ACN	2	110	2	48
3	BFO	H2O	2	110	2	28
4	BFO	MeOH	2	110	2	34

3. Result and Discussion:

It has seen from the XRD that BFO has pervoskite structure and SEM reveals nanoparticle formation. When BFO is applied as catalyst to the synthesis of benzoxazole, it has given 72% yield of the product. This yield is comparatively better than other catalyst.

4. Conclusion:

Here, we have developed an efficient, recyclable route for 2-substututed benzoxazole synthesis using BFO as catalyst. Replacement of aryl halide by diazonium salt and transition metal by mix of transition- nontransition oxide has made the present protocol cost effective. Recyclability of the catalyst and insitu formation of aryl iodide are merits of this

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