

BiFeO₃ Magnetic Nanoparticles: A Novel, Efficient and Reusable Magnetic Catalyst for the Synthesis of Polyhydroquinoline Derivatives

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ABSTRACT: *Herein, it has been shown that the bismuth ferrite magnetic nanoparticles (BFO-MNPs) are new, efficient and recyclable catalysts for the synthesis of polyhydroquinoline derivatives by the Hantzsch reaction. The one-pot four-component cyclocondensation reaction of dimedone, aromatic aldehydes, ethyl acetoacetate and ammonium acetate was carried out under solvent-free conditions. The desired products were obtained in very short reaction times with high yields. The magnetic nanocatalyst was characterized by the X-Ray Diffraction (XRD) and FT-IR analysis. For the first time, the bismuth ferrite magnetic nanoparticles were used as a catalyst in the Hantzsch reaction. The catalyst was found to be reusable, which showed considerable catalytic activity after the third run.*

KEYWORDS: *BiFeO₃ NMPs; Magnetic nanocatalysts; Polyhydroquinoline derivatives; Hantzsch reaction.*

INTRODUCTION

Multiferroic materials are compounds which show ferroic and antiferroic properties such as ferromagnetic, ferroelectric, ferroelastic, etc. In these materials, ferroic properties are coupled with each other [1]. Bismuth Ferrite (BiFeO₃) is one of multiferroic materials which shows G-type antiferromagnetic ordering below Neel temperature $T_N = 370$ °C and ferroelectricity below $T_C = 830$ °C [2, 3]. The structural and magnetic properties of

BiFeO₃ nanoparticles greatly depend on the particle size, morphology, doping, pressure which can be controlled by the synthesis procedure. BiFeO₃ nanoparticles have been synthesized by different techniques such as sol-gel method [4], tartaric acid [5], chemical coprecipitation process [6], sucrose [7], etc. Bismuth ferrite nanoparticles are very important material due to its applications like visible light photocatalytic activity [8], microwave

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absorption [9], gas sensing properties [10], etc. Furthermore, there have been no reports concerning the use of BFO-MNPs as catalysts for the multicomponent reactions.

Multi Component Reactions (MCRs) are known as a powerful tool for the synthesis of complex organic molecules from simple and readily available substrates. Also, this manner is very fast and impressive without the isolation of any intermediate [11-14]. In the mentioned reactions, three or more components are reacted to form ideally one product, which contains the essential parts of all the initial reactants. Synthesis of polyhydroquinolines *via* the unsymmetrical Hantzsch reaction is one of multicomponent reactions.

1,4-dihydropyridyl compounds (1,4-DHPs) contains a variety of significant biological activities such as antimicrobial and antioxidant agents [15], hypotensive agents [16], antitubercular agents [17]. Polyhydroquinolines are a class of fused 1,4-DHPs which involve the one-pot, four-component condensation of dimedone, aldehydes, ethylacetoacetate and ammonium acetate. The classical method for the synthesis of 1,4-DHP suffers from some limitations such as long reaction time, using hazardous organic solvents and poor yield [18-19]. The easiest and fastest procedure for the preparation of polyhydroquinolines involves a multicomponent reaction in the presence of various catalysts such as CAN [20], ionic liquids [21], organo catalysts [22], $\text{Yb}(\text{OTf})_3$ [23], and $[\text{TBA}]_2[\text{W}_6\text{O}_{19}]$ [24], sulphonic acid/SBA-15 [25]. In addition to the aforementioned catalysts, nanocatalysts such as Ni nanoparticles [26], $\text{Ru}/\text{Al}_2\text{O}_3$ nanocatalyst [27], $\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3$ nanocatalyst [28], carbon nanotubes supported alkalized MoS_2 catalyst [29], carbon nanotubes supported cobalt catalyst [30], cobalt oxid nanocrystallites LaCoO_3 catalyst [31], nano Fe_3O_4 [32-34] have shown the exclusive application and properties.

Because of the important biological activity of the polyhydroquinolines and nanoparticles as catalyst, herein we would like to report a new, efficient and reusable magnetic nanocatalyst for the preparation of polyhydroquinoline derivatives **5** by a one-pot four-component reaction including dimedone **1**, aromatic aldehydes **2**, ethyl acetoacetate **3** and ammonium acetate **4** under solvent-free conditions (Scheme 1).

EXPERIMENTAL SECTION

All chemicals were commercially available and used without further purification. The BFO-MNPs was synthesized and characterized according to Ref. [35]. The Melting points were recorded using a Stuart SMP3 melting point apparatus. The IR spectra were obtained on a Tensor 27 Bruker spectrophotometer as KBr disks. The ^1H NMR spectra (400 MHz) were recorded on a Bruker DRX400 spectrometer. X-ray diffraction (XRD) was performed with a Philips PAN analytical X'Pert X-ray diffractometer.

Preparation of BFO-MNPs

BiFeO_3 nanoparticles were prepared from bismuth and iron nitrates through a chemical coprecipitation process, while NaOH was used as precipitant. Firstly, $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ with 1:1 molar ratio were dissolved in 2 mol/L HNO_3 solution at room temperature. After complete dissolution, the precursor solution was mixed for another 40 min for homogenization. Then 2 mol/L NaOH solution was slowly dripped into the precursor solution under intensive stirring conditions. After the metal precursors were completely precipitated, the coprecipitated product was filtered and washed three times with de-ionized water, and dried at 30 °C for 5 days. Finally, the remains were grounded for 0.5 h and then loaded into a furnace, where the temperature was maintained at 600 °C for 120 min before quenching to room temperature in air. So pure-phase BiFeO_3 nanoparticles were obtained.

General procedure for the synthesis of polyhydroquinoline derivatives using BFO-MNPs as catalyst

A mixture of dimedone **1** (1mmol), aromatic aldehydes **2a-2k** (1 mmol), ethyl acetoacetate **3** (1mmol), ammonium acetate **4** (1mmol) and BFO-MNPs (0.02 g) was heated on the oil bath at 110 °C for 15-30 min. The reaction progress was monitored by TLC. After the completion of the reaction, the reaction mixture was cooled to room temperature and boiling ethanol was added. The solid residue was dissolved in boiling ethanol and filtered off. The catalyst was separated by a magnet. Then, crude product was collected from the filtrate after cooling to room temperature and recrystallized from ethanol to give compounds **5a-5k** in high yields (Table 2).

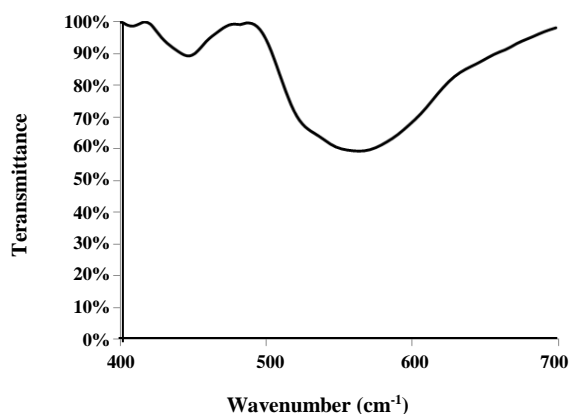
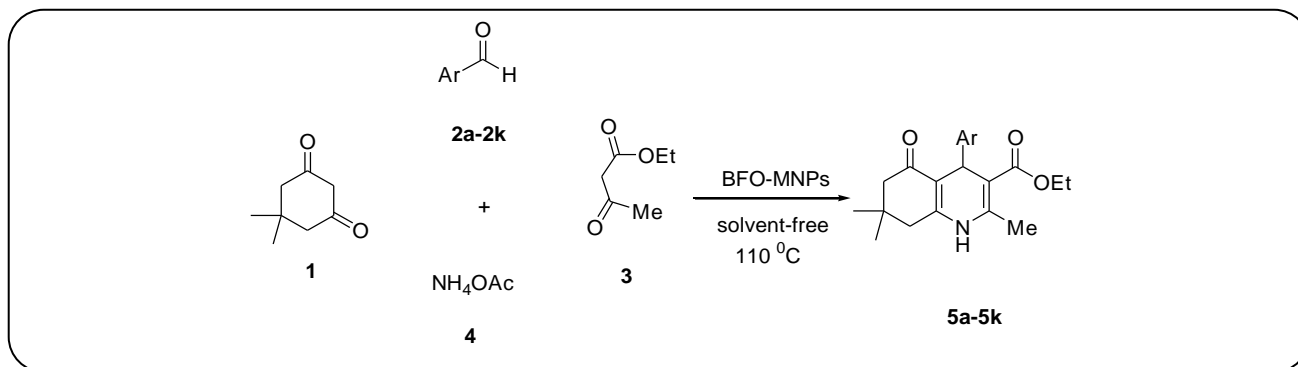


Fig. 1: The FT-IR spectrum of fresh BiFeO₃ MNPs.

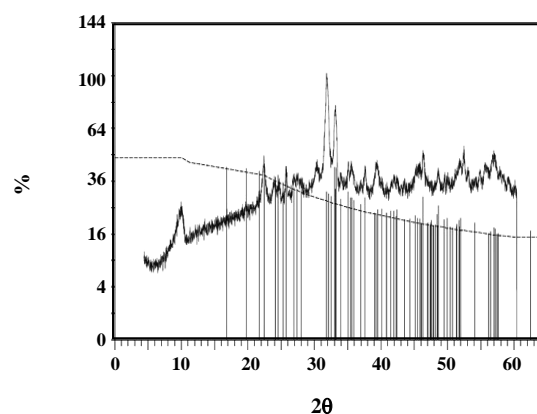


Fig. 2: The XRD pattern of BFO-MNPs.

RESULTS AND DISCUSSION

Characterized results of BiFeO₃ magnetic nanocatalyst

The BiFeO₃ magnetic nanocatalyst was characterized by X-Ray Diffraction (XRD) and FT-IR spectroscopy. The FT-IR spectrum of nano powder BFO is shown in Fig. 1. The strong absorption peaks at 400-600 cm⁻¹ are attributed to the Fe-O stretching and bending vibrations. Also, the XRD pattern of BFO-MNPs catalyst (Fig. 2) revealed seven diffraction peaks at $2\theta = 22.2848^\circ$, 31.6817° , 33.053° , 41.6418° , 46.2228° , 52.3547° and 56.9402° . All of the reflection peaks are accordance with the JCPDS card no. 71-2494, which confirm a rhombohedrally distorted perovskite structure belonging to the space group of polar R3c [36].

Evaluation of catalytic activity of BiFeO₃ magnetic nanoparticles (BFO-MNPs)

The catalyst BFO-MNPs was prepared according to a chemical coprecipitation process. We first selected a model reaction including the synthesis of **5d** to optimize

the reaction conditions. Therefore, a mixture of dione (1mmol), 4-chlorobenzaldehyde (1mmol), ethyl acetoacetate (1mmol) and ammoniumacetate (1mmol), in the presence of various amounts of BFO-MNPs was heated in different solvents and under solvent-free conditions (Table 1). As can be seen from Table 1, no product was produced in the absence of BFO-MNPs even after 2h (Entry 1). The effect of reaction temperature and amount of catalyst on the output was investigated. The shortest time and best yield were achieved in the presence of 0.02 g of the catalyst at 110 °C as optimal temperature (Entry 8).

In order to determine the generality of the novel protocol, we prepared a range of polyhydroquinoline derivatives with 0.02g of the catalyst at 110 °C as the optimized reaction conditions (Table 2). All the products were characterized by their IR spectral data and a comparison of their melting points with those of authentic samples. The structures of some products were also confirmed by ¹H NMR analysis.

Table 1: Optimization of reaction conditions for synthesis of compound 5d catalyzed by BFO-MNPs.

Entry	Catalyst	Solvent	T (°C)	Time(min)	Yield ^a (%)
1	----	----	120	120	----
2	0.01	----	60	40	54
3	0.01	----	90	40	66
4	0.01	----	110	20	70
5	0.01	----	130	20	76
6	0.02	----	60	30	60
7	0.02	----	90	20	72
8	0.02	----	110	15	95
9	0.02	----	130	15	93
10	0.03	----	60	30	55
11	0.03	----	90	20	53
12	0.03	----	110	15	80
13	0.03	----	130	15	75
14	0.05	----	110	20	70
15	0.02	H ₂ O	Reflux	240	42
16	0.02	CH ₂ Cl ₂	Reflux	240	63
17	0.02	CH ₃ CN	Reflux	240	65
18	0.02	EtOH	Reflux	240	75

Reaction conditions: dimedone **1** (1 mmol), 4-chlorobenzaldehyde **2d** (1 mmol), ethyl acetoacetate **3** (1 mmol), and ammonium acetate **4** (1 mmol).

^a Measured yields.

Table 2: BFO-MNPs catalyzed synthesis of polyhydroquinoline derivatives 5a-5k.

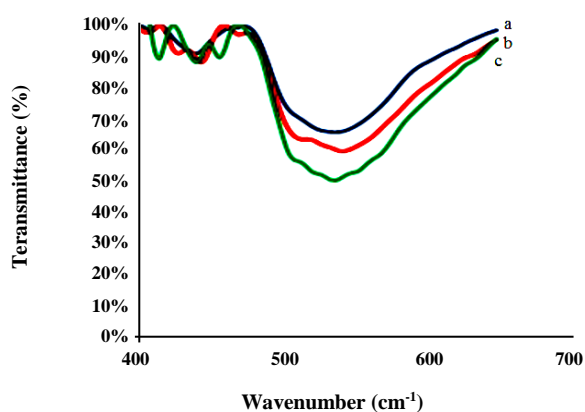
Entry	Ar	Products	Time (min)	Yields ^a (%)	m.p. (°C)	
					Found	Reported [17, 22]
1	C ₆ H ₅	5a	15	85	214-216	209-210
2	4-BrC ₆ H ₅	5b	10	95	259-260	254-255
3	2-ClC ₆ H ₅	5c	20	75	206-208	206-208
4	4-ClC ₆ H ₅	5d	15	95	246-248	244-246
5	3-OHC ₆ H ₅	5e	25	75	225-227	218-220
6	4-OHC ₆ H ₅	5f	30	70	239-241	237-238
7	4-OMeC ₆ H ₅	5g	10	95	257-259	257-258
8	4-MeC ₆ H ₅	5h	10	90	257-260	260-261
9	3-NO ₂ C ₆ H ₅	5i	25	75	181-183	178-180
10	4-NO ₂ C ₆ H ₅	5j	20	80	245-247	244-246
11	Furyl	5k	15	80	240-243	245-247

Reaction conditions: dimedone **1** (1 mmol), aromatic aldehyde **2a-2k** (1 mmol), ethyl acetoacetate **3** (1 mmol), ammonium acetate **4** (1 mmol), BFO-MNPs (0.02 g), 110 °C, solvent-free.

^a Measured yields

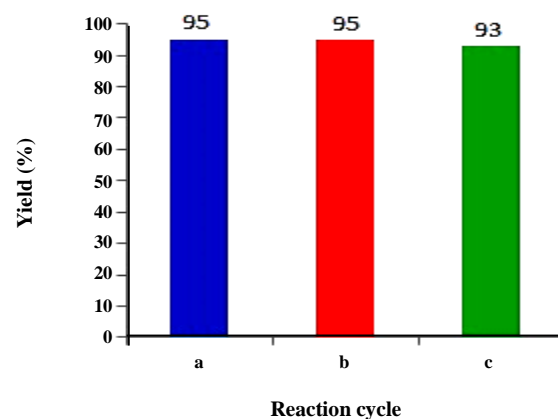
Table 3: Comparison of the efficiencies of different catalysts for the one-pot four-component synthesis of polyhydroquinolines.

Catalyst	Conditions		Time (min)	Measured Yields (%)
	Solvent	T/°C		
L-proline	EtOH	Reflux	360-420	81-92
Sc(OTf) ₃	EtOH	r.t	120-360	86-95
I ₂	---	25-40	30-150	92-97
K ₇ [PW ₁₁ CoO ₄₀]	CH ₃ CN	Reflux	25-60	75-85
CAN	---	r.t	35-120	85-98
[TBA] ₂ [W ₁₉ O ₆]	---	110	20-40	82-95
PPA-SiO ₂	---	140	40-60	85-92
[(CH ₂) ₄ SO ₃ HMIM][HSO ₄]	EtOH	Reflux	60-120	75-93
BFO-MNPs	---	110	10-30	70-95

**Fig. 3: FTIR spectra of the BFO-MNPs, a: first recovery, b: second recovery, c: third recovery.**

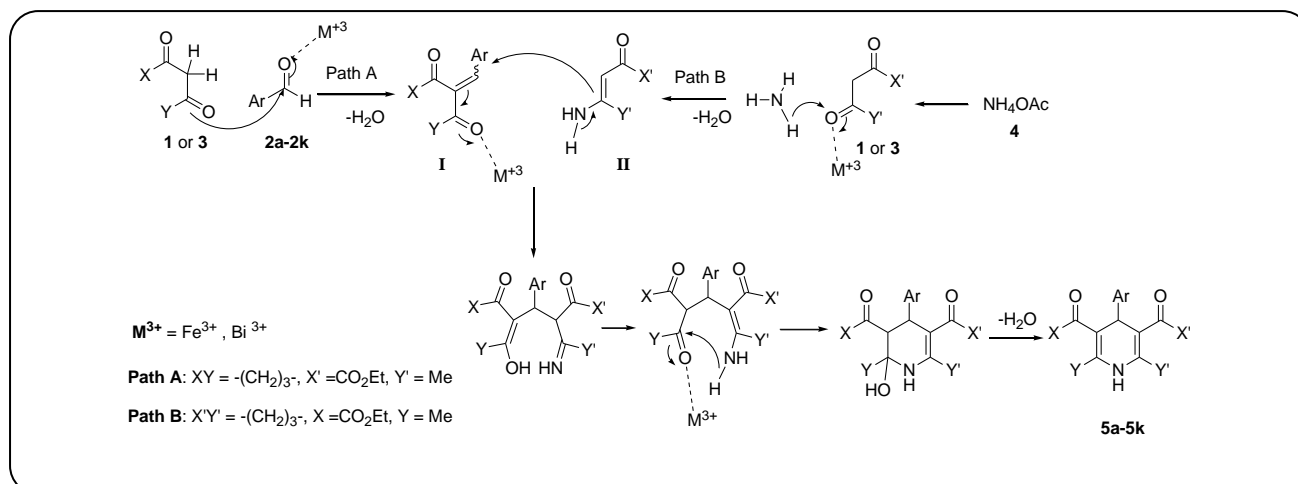
For further evaluation, we compared the reaction times and the yields of product **5** in the Hantzsch reaction under various conditions (Table 3). As can be seen, our method reduces reaction times significantly and produces high yields of the products.

One of the important properties of magnetic nanocatalysts in organic transformations is their reusability. The catalyst was easily separated by a magnet, because it was not dissolved in organic solvents. The recovered catalyst was washed with boiling ethanol and then dried under vacuum at 100 °C and reused. The catalyst could be used at least three times with only a slight reduction in the catalytic activity. As seen in Fig. 3, the FT-IR spectrums of **a**, **b** and **c** are belonging to the catalyst after first, second and third recovery, respectively.

**Fig. 4: Effect of recycling on the catalytic performance of the BFO-MNPs in the synthesis of 5d.**

The retention of the catalyst structure was confirmed by comparing the FT-IR spectrum of the recovered catalyst with the fresh catalyst (Fig. 1) for the model reaction. Furthermore, the **a**, **b** and **c** diagrams show the efficiency of the **5d** species after using the recovered catalyst (Fig. 4).

A plausible mechanism for the synthesis of polyhydroquinoline derivatives by the BFO-MNPs catalyst is shown in Scheme 2. According to the structure of nanocatalyst [36], the existence of the Bi⁺³ and Fe⁺³ ions in the structure makes it a good Lewis acid. As shown in Scheme 2, the metal ions activate the carbonyl groups as an electrophile in aromatic aldehydes **2** and 1,3-diketone compounds (**1** or **3**). Therefore, the intermediate **I** has obtained *via* a Knoevenagel condensation reaction



Scheme 2: Plausible mechanism for the formation of polyhydroquinolines in the presence of the BFO-MNPs as catalyst.

(path A). On the other hand, the 1,3-diketone compounds react with amine species **4** and produce the intermediate **II** (path B). The reaction of intermediates (**I** and **II**) results in the production of the **5** species by a cyclocondensation reaction.

CONCLUSIONS

In conclusion, we have shown that the BiFeO₃-MNPs are a new-efficient catalyst for one-pot four-component reaction of dimedone, aromatic aldehydes, ethyl acetoacetate and ammonium acetate under solvent-free conditions. Furthermore, the BiFeO₃-MNPs as a catalyst can be recycled after a simple workup, and used for three times with only slight reduction in its catalytic activity.

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