

Synthesis of CuFe_2O_4 Nanoparticles by a new co-precipitation method and using them as Efficient Catalyst for One-pot Synthesis of Naphthoxazinones

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ABSTRACT

This paper outlines the synthesis of CuFe_2O_4 nanoparticles and their catalytic applications. CuFe_2O_4 nanoparticles were synthesized via microwave-assisted co-precipitation method. The obtained nanoparticles characterized through Fourier transform infrared spectroscopy, X-ray diffraction, and scanning electron microscopy. Vibrating sample magnetometer shows nanoparticles exhibit ferromagnetic behavior. CuFe_2O_4 nanoparticles are used as an efficient and effective catalyst for the one-pot three-component synthesis of 2-naphthol condensed 1,3-oxazinone derivatives. This procedure includes some important aspects like the easy work-up, no need to column chromatography, simple and readily available precursors, and good to high yields.

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INTRODUCTION

CuFe_2O_4 is one of the most important magnetic materials, which has a normal spinel structure with tetrahedral A-sites occupied by Cu^{2+} ions and nanoparticles B-sites by Fe^{3+} ions. That can be expressed as $(\text{Cu}^{2+}_{0.8}\text{Fe}^{3+}_{0.2})_A(\text{Cu}^{3+}_{0.2}\text{Fe}^{2+}_{0.2}\text{Fe}^{3+}_{1.6})_B\text{O}_4$ [1]. The oxygen tetrahedral and octahedral with the central Fe^{3+} each contribute in a different way to magneto-optic Kerr effect (MOKE) spectra [2]. Nanoscale ferrite particles are of great interest due to their unique optical, electrical, and magnetic properties. These properties are strongly dependent on the particles size, shape, and dispersion, and therefore it is very important to carefully control the synthesis of particles of size distribution.

In recent years, various methods have been successfully used to synthesize different kinds of CuFe_2O_4 nanostructured materials such as

nanoparticles [3,4], nanorods [5,6], nanodisks [7], nanofibers [8], microspheres [9], and thin films [10,11]. CuFe_2O_4 was a well catalyst, which can be used in CO_2 , dimethyl ether steam reforming, and so on [12–14].

Recently new studies have been focused on the development of catalytic systems owing to their importance in synthetic organic chemistry. One of the most attractive synthetic strategies favored by organic chemists is the use of heterogeneous catalyst in increasing the efficiency of a wide range of organic synthesis. Heterogeneous catalysis is being used in the fine chemicals industry because of the need for more environmentally friendly production technology [15-17]. Heterocycles are of special interest because they constitute an important class of natural products, many of which exhibit useful pharmacological activities. Oxazinone, benzoxazin-

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one and their derivatives are a significant class of heterocyclic compounds, because many of these derivatives display biological activities, such as HIV-1 reverse transcriptase inhibitors [18] and anti-bacterial properties [19]. 1,3-oxazine compounds has shown that they possess varied biological properties such as anticonvulsant, antitubercular, antibacterial, analgesic and anticancer activity [20-23]. So several improved methodologies have been developed that are used for synthesis of [1,3] oxazine-3-one derivatives by multi- component reactions (MCRs) [24-30].

We aimed to demonstrate the CuFe_2O_4 nanoparticles are as an available, environmentally, friendly, non-volatile, reusable non-expensive, inexpensive catalyst [28,31].

We report herein, the synthesis of CuFe_2O_4 nanoparticles with size range from 19 to 25 nm were obtained by new co-precipitation method assisted by microwave with octanoic acid as an organic surfactant successfully. The obtained samples were characterized by scanning electron microscopy and X-ray diffraction pattern. The magnetic properties were investigated using a vibrating sample magnetometer.

Then obtained CuFe_2O_4 nanoparticles have been used as a nano- heterogeneous catalysis in a one-pot, three component reaction between aromatic aldehydes, β -naphthol and urea to produce aryl naphtho [1,2-e] [1,3] oxazine-3-one derivatives (Fig. 1).

MATERIALS AND METHODS

All chemicals were obtained from Merck or Fluka and were used without further purifications. XRD patterns were recorded by a Philips, X-ray diffractometer using Ni-filtered Cu K_β radiation. For SEM images the samples were coated by a very thin layer of Au to make the sample surface conductor and prevent charge accumulation, and obtaining a

better contrast. Room temperature magnetic properties were investigated using a vibrating sample magnetometer (VSM, made by Meghnatis Daghigh Kavir Company) in an applied magnetic field sweeping between ± 10000 Oe, and a Microwave Samsung (GE281) was used for microwave-assisted co-precipitation. Infrared (IR) spectroscopy was taken on Rayleigh (WQF-510A).

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Synthesis of CuFe_2O_4 nanoparticles and nano-composites

In a typical experiment, aqueous solutions of 8.21 g of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.02 mol) (10 mL) and 1.72 g of CuCl_2 (0.01 mol) (10 mL) were prepared separately and mixed together in 2:1 molar ratio. 2 mL of octanoic acid was added to the solution as a surfactant. Then, NaOH solution (1.5 M) was slowly added into the solution until the pH of the mixture was 7–8. After complete precipitation, the liquid precipitate was then placed in a conventional microwave oven and the reaction was performed under ambient air for 5 min/180 °C (540 W).

The microwave irradiation time and power were found effective in the formation of the crystalline phase of nanoparticle. After cooling at room temperature, the

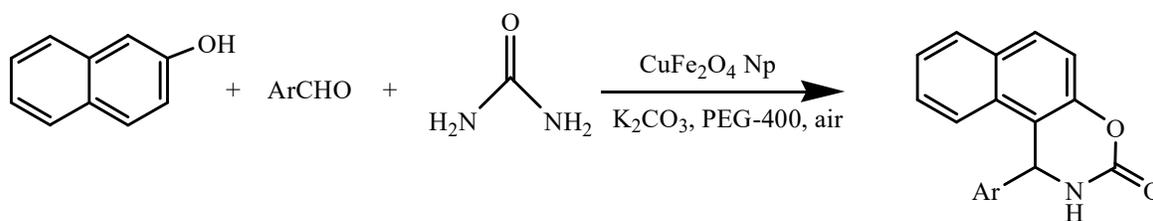


Fig. 1. Synthesis of oxazine-3-one derivatives the presence Of CuFe_2O_4 -nanoparticles as a catalyst

resulting products were centrifuged for 15 min at 3,000 rpm, washed with distilled water and ethanol several times to remove the excess surfactant from the solution. Then, precipitation was dried in an oven at 100 °C for for 3 h. The resulting red-brown powder was calcinated at 800 °C for 3 h to remove any organic residue.

Typical procedure for the CuFe₂O₄ nanoparticles catalyzed 1,3-oxazin-3-ones derivatives

To a mixture of benzaldehyde (2 mmol), urea (3 mmol) and K₂CO₃ (0.3 mmol) in PEG-400 (3 mL) CuFe₂O₄ nanoparticles (0.001 g) were added, ûnely mixed together and allowed to stir for 5 min at room temperature and then β-naphthol (2 mmol) was added. The resulting reaction mixture was stirred at room temperature for a speciûed period (Table 1). After complete conversion as indicated by thin layer chromatography (TLC), the mixture was filtered and the heterogeneous catalyst was recovered and was reused for evaluating the performance in the next reaction. The reaction mixture was dissolved in diethyl ether and the ethereal layer was decanted. The diethyl ether was evaporated and the crude product crystallized with ethanol to auord the pure products (Table 1).

RESULTS AND DISCUSSION

Characterization data of some important Compounds

1-Phenyl-1,2-dihydro-naphtho[1,2-e][1,3] oxazin-3-one (4a): Yield 94% as a white solid; mp. 217-218°C. IR (KBr, cm⁻¹): 3256 (N-H Str.); 3047 (C-H_{arom} Str.); 1725 (C=O Str.). ¹HNMR (400 MHz, CDCl₃, δ, ppm): 6.10 (1H, d,CH); 8.19(1H, s, 1NH); 7.11-7.82 (11H_{arom'}, m, 11CH_{arom}).

1-(4-Bromophenyl)-1,2-dihydro-naphtho[1,2-e][1,3]oxazin-3-one (4b): Yield 90% as a white solid; mp. 221-223°C; (KBr, cm⁻¹): 3223(N-H Str.); 3144(C-H_{arom} Str.); 1732(C=O Str.). ¹HNMR (400 MHz, CDCl₃, δ, ppm): 6.21(1H, d, 1CH); 8.94(1H, s, 1NH); 7.31-8.01(10H_{arom'}, m, 10CH).

1-(4-Chlorophenyl)-1,2-dihydro-naphtho[1,2-e][1,3]oxa-zin-3-one (4d): Yield 95% as a white solid; mp. 205-207°C. IR (KBr, cm⁻¹): 3223 (N-H Str.); 3144 (C-H_{arom} Str.); 1732(C=O Str.). ¹HNMR (400 MHz, CDCl₃, δ, ppm): 8.42(1H, s, 1NH); 6.91(1H, d, 1CH); 7.16-7.83 (10H_{arom'}, m, 10CH).

1-(2,4-Dichlorophenyl)-1,2-dihydro-naphtho[1,2-e][1,3]oxazin-3-one (4f): Yield 95% as a white solid; mp. 212-215°C. IR (KBr, cm⁻¹): 3228(N-H Str.); 3146 (C-H_{arom} Str.); 1739(C=O Str.). ¹HNMR (400 MHz, CDCl₃, δ, ppm): 8.22(1H, s, 1NH); 6.81(1H, dd, 1CH); 7.21-7.87(6H_{arom'}, m, 6CH); 7.82(2H_{arom'}, t, 2CH); 8.62(1H_{arom'}, d, 1CH).

The FT-IR spectra of organic surfactant, the product before and after calcination in the frequency range from 4200 to 400 cm⁻¹, are compared in Fig. 2. In FT-IR spectrum of pure organic surfactant, octanoic acid (Fig. 2a), the very broad feature from 3500 to 2500 cm⁻¹ is due to a very broad O–H stretch of the carboxylic acid. The sharp bands at 2929 and 2857 cm⁻¹ are assigned to the asymmetric and symmetric CH₂ stretch, respectively. The intense carbonyl stretch at 1711 cm⁻¹ is derived from the C=O of octanoic acid carbonyl.

The stretch at 1285 cm⁻¹ is assigned to a C–O stretch. The O–H in-plane and out-of-plane bands appear at 1459 and 937 cm⁻¹, respectively. In the FT-IR of product before calciation (Fig. 2b), the characteristic bands of surfactant are shown to be shifted to a lower frequency region relative to free surfactant. For example, the asymmetric and symmetric CH₂ stretch bands are shown to be shifted at 2922 and 2852 cm⁻¹, respectively. The O–H in-plane appears at 1448 cm⁻¹. The intense carbonyl stretch in free surfactant becomes weak in the product and shifted slightly to a lower frequency. In addition, the broad band in the range of 3400-3100 cm⁻¹ is due to υ(OH) of lattice water molecules. The results for FT-IR measurement indicate that there is an interaction between octanoic acid chain and the particles and the surface of the particles was partially covered with the organic ligands [32]. As can be seen from Fig. 2c,

Table 1. Perpration of Naphthoxazin-3-one Derivatives

product	Ar	Time/min	Yeild %	m.p °C
4a	C ₆ H ₅	30	94	217
4b	4-BrC ₆ H ₅	27	90	223
4c	4-NO ₂ C ₆ H ₅	35	93	204
4d	4-ClC ₆ H ₅	28	95	205
4e	4-MeOC ₆ H ₅	30	90	189
4f	2,4-DiClC ₆ H ₅	25	95	213
4g	2,3-DiMeOC ₆ H ₅	33	95	212
4h	4-MeC ₆ H ₅	29	92	164
4i	3-Me C ₆ H ₅	31	89	207

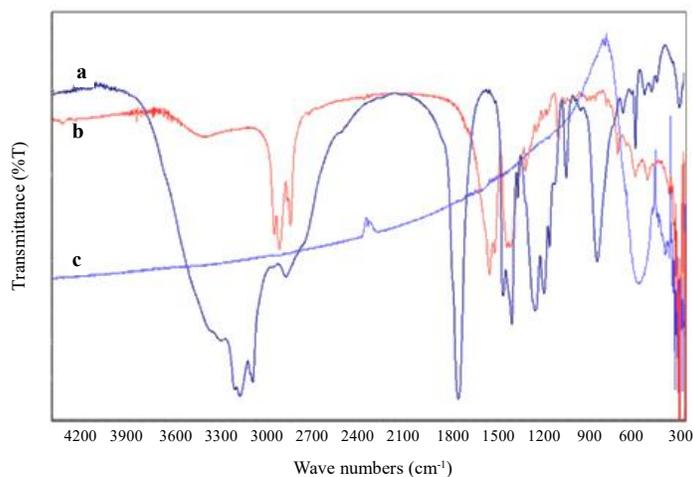


Fig. 2. FT-IR spectrum of (a) octanoic acid, (b) product before, (c) after calcination

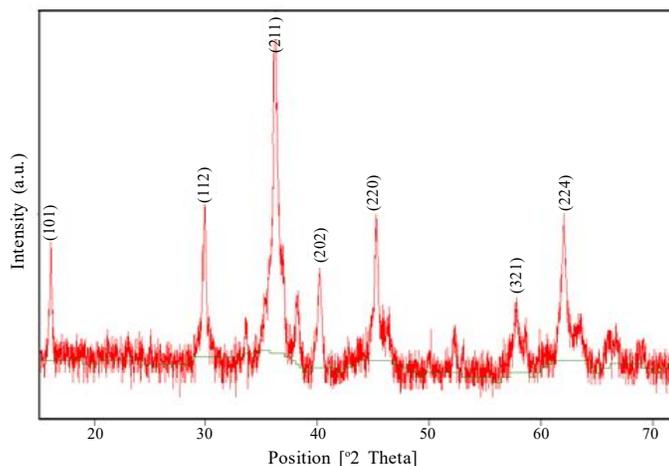


Fig. 3. XRD pattern of the CuFe_2O_4 nanoparticle

all above bands were disappeared when the product was calcinated. We can see after calcination, the characteristic bands of OH groups disappeared and only strong bands due to the metal oxide appeared. In the FT-IR spectrum of the product after calcinations, there are two strong absorption bands at about 590 and 408 cm^{-1} which correspond to M–O stretching vibration and O–M–O bending vibration of CuFe_2O_4 , respectively. Their positions are in good agreement with those reported in the literature [33].

Fig. 3 shows the XRD patterns of the CuFe_2O_4 nanoparticles prepared at $800\text{ }^\circ\text{C}$ for 3 h. The peak position and relative intensity of all diffraction peaks for the product match well with standard powder

diffraction data. All the diffraction peaks in the XRD pattern can be indexed to those of the tetragonal structure of copper ferrite CuFe_2O_4 according to JCPDS file No. 34-0425. It is indicated that pure CuFe_2O_4 can be obtained at $800\text{ }^\circ\text{C}$ for 3h.

Fig. 4 illustrates SEM images of synthesized CuFe_2O_4 nanoparticles that confirm average diameter size of product is 20 nm.

Microwave method propose easy manipulation in particle size and so magnetic properties by a simple change in power of pulsation and time of irradiation.

Fig. 4 illustrates SEM images of CuFe_2O_4 nanoparticles. Average size of nanocrystals from SEM images is 20 nm.

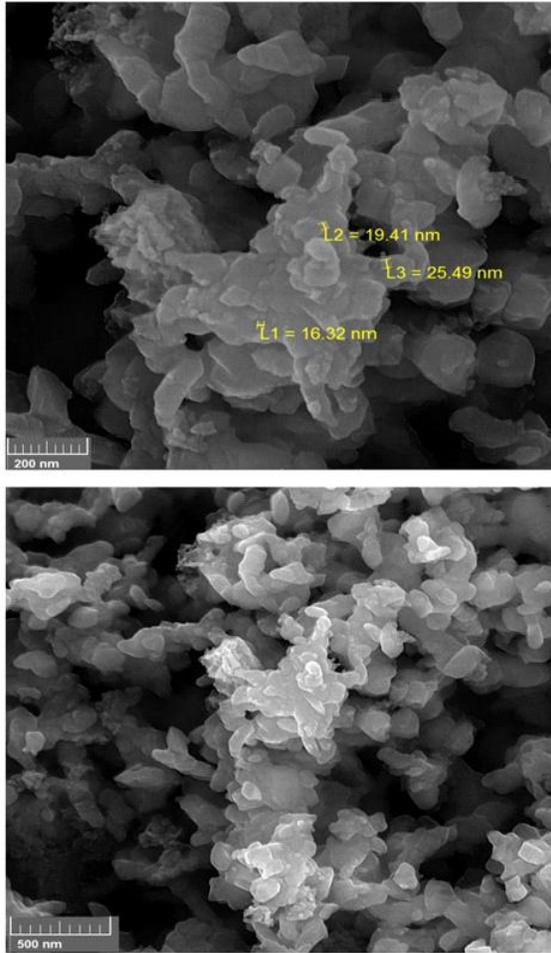


Fig. 4. SEM images of CuFe₂O₄ nanoparticles

Fig. 5 shows the magnetic hysteresis curves measured at room temperature for the CuFe₂O₄ nanoparticles obtained at 800°C. The CuFe₂O₄ microcrystal exhibited a weak ferromagnetic behavior with coercive force (H_c) value of 133.50 Oe, saturation magnetization (M_s) value of 32.43 emu/g and remanent magnetization (M_r) value of 2.68 emu/g, which was comparable to the value 39 emu/g for CuFe₂O₄ nanoparticles (crystallite size of 50 nm) [12] and higher than the value of 30 emu/g for CuFe₂O₄ nanoparticles (crystallite size of 10–20 nm), [34] 23.98 emu/g for CuFe₂O₄ nanoubers (diameter of 60–200 nm) [9]. These results are consistent with the reports that the magnetization is strongly dependent on their particle size.

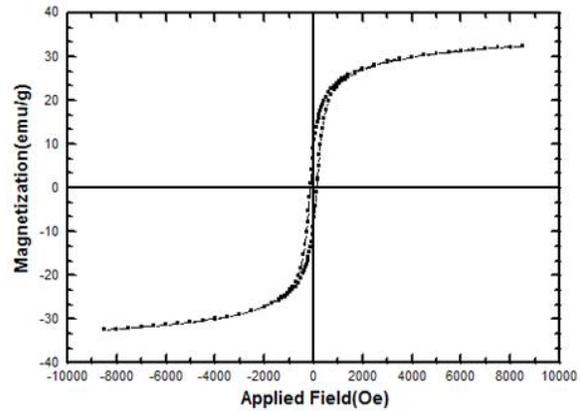


Fig. 5. Hysteresis curve of CuFe₂O₄ nanoparticles

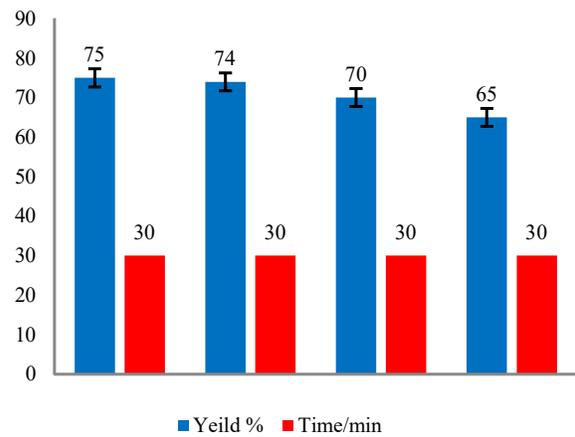


Fig. 6. Recyclability of catalyst for the synthesis of 4a

Mechanism

The experiment results indicated that CuFe₂O₄ nanoparticles can be obtained via microwave assisted co-precipitation product, which were synthesis by reaction of Cu²⁺ and Fe³⁺ ions in alkaline condition. The CuFe₂O₄ formation proceeds may be as these: first, Cu²⁺ and Fe³⁺ ions reacted to OH⁻ in aqueous ethanol solution formed Fe(OH)₃ and Cu(OH)₂ co-precipitation product, respectively (Eqs. 1 and 2). Subsequently, CuFe₂O₄ can be obtained from the reaction of Fe(OH)₃ and Cu(OH)₂. (Eq. 3)

The chemical reaction can be expressed as



Finally, CuFe_2O_4 nanoparticles were obtained via microwave-assisted co-precipitation products in a high temperature condition.

The size of CuFe_2O_4 nanoparticles was dependent on the formation of nucleus. It is believed that the absence of octanoic acid can reduce the formation speed of $\text{Cu}(\text{OH})_2$ and $\text{Fe}(\text{OH})_3$ nucleus and growth.

In order to explore the recyclability of the catalyst, the CuFe_2O_4 nanoparticles were used as catalyst for the same reaction repeatedly and the change in their catalytic activity was studied. The relation between the number of cycles of the reaction and the catalytic activity in terms of yield of the products is presented in the Fig. 6. It was found that copper nanoparticles could be reused for four cycles with negligible loss of their activity.

CONCLUSION

In summary, CuFe_2O_4 nanoparticles have been successfully prepared via microwave-assisted co-precipitation products in high temperature condition. These CuFe_2O_4 nanoparticles have potential applications in design of nanoscale devices, ultrahigh density magnetic storage devices, catalyst, and biomedicine for targeted drug delivery fields. We have also demonstrated that CuFe_2O_4 nanoparticles are a novel, an efficient and environmentally friendly catalysts for the synthesis of one-pot three-component condensation of aryl naphtho-xazine-3-one derivatives. The advantages of this method are shorter reaction times, simple work-up, environmentally benign, high yield, and reusability of catalyst in comparison with the other reported methods.

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CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

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