Laser assisted hydrothermal synthesis of magnetic ferrite nanoparticles for biomedical applications

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Abstract: In this work, copper substituted cobalt ferrite nanoparticles Co₁ₓCuₓFe₂O₄ (x = 0, 0.3, and 0.7), has been synthesized via laser assisted hydrothermal synthesis (LAHS) methods. The XRD patterns showed single phase spinel structure, comparative study between the two preparation methods, effect of laser irradiation on the structural properties, and average crystallite size that is evaluated from most intense peak (311) utilizing Scherrer formula. Further studies for laser assisted hydrothermal as-prepared ferrite samples using each of Field emission-scanning electron microscope (FE-SEM) which revealed the study of topography, particle size, vibrating sample magnetometer (VSM) with in 15kOe as maximum field. That was used to study the magnetic properties and confirmed the super-paramagnetic property of the prepared ferrite nanoparticles. Coercivity (Hc), remanence (Mr), saturation magnetization (Ms) and sequarness ratio were directly extracted from hysteresis loops. Moreover, results showed that the magnetic characteristics are on the basis of each particle size as well as cation distribution. In addition, the antibacterial property of the prepared nanoparticles against S. aureus and E. coli found to be improved after substitution of Cu in Co ferrite matrix.

Keywords: laser materials process; cobalt ferrite nanoparticles; magnetic properties; antibacterial activity.

1. Introduction

Recent years, there is a large and wondering interest for scientific community in the magnetic nanoparticles thanks to their fascinating unique chemical, thermal and magnetic properties [1]. Among these magnetic nanoparticles (NPs), the spinel ferrite nano-crystals with general formula MFe₂O₄ (in which M representing divalent cation regarding Zn, Mn, Co, Mg, and Ni) were the major significant materials due to their magnetic and electrical properties with high thermal and chemical stabilities [2], which make them suitable for several exceptional potential disciplines like magnetic fluids [3], catalysis [4], biotechnology/biomedicine [5], magnetic resonance imaging [6], data storage devices [7], transformers, disk recording, electric generators, and etc. [8]. From this ferrite materials, spinel cobalt ferrite (CoFe₂O₄) was major examined because of the high electromagnetic performance, considerable saturation magnetization, good chemical stability and mechanical hardness [9]. The physical properties regarding cobalt ferrite might be simply tuned through substitution, either completely or partially, the divalent ions without modifying the crystal structure by transition metal such as Zn²⁺, Cu²⁺, and Ni²⁺ ions to tune ability for specific application, then the general formula will be as CoMFe₂O₄ where M is the transition metal ions [10]. One of the most astonishing properties of cobalt ferrite NPs is the super-paramagnetism, a phenomenon observed when the crystallite size was
within single domain limits region (5-70nm) [11], so individual nanoparticles can be consider as a giant paramagnetic atom having a constant and large magnetic moment with fast response to utilized magnetic fields also possessing coercivity (field need to bring magnetization to 0) and negligible remanence (residual magnetism), such features are making super paramagnetic NPs extremely required for various biomedical applications since in spite of the risks of creating agglomerates at 25 Celsius [12].

With regard to biomedical applications, CoFe$_2$O$_4$ can be considered as a candidate of high importance because of 3 main reasons. Initially, they have sizes placing them at dimensions which are similar to those of gene 2nm, protein 5-50nm, virus 20-500nm, and 10-100nm long. Secondly, the NPs have large surface which might be suitably altered for attaching biological agents [13]. Thirdly, their capability for being detected and manipulated with external magnetic field. They might be utilized in various applications, both in-vivo and in-vitro, such as controlled and targeted drug delivery, magnetic separations, magnetic fluid hyperthermia (MFH) and biosensors [14]. In addition, finding new therapies in the field of biomedicine is always in demanded, for example chemotherapy in the hospitals as well as in the environmental settings often requires using antibiotics and that lead to an increasing the antibiotic resistance related to bacterial pathogens so that prompt the exploration of novel antimicrobials agents [15]. A study conducted by Sanpo et al. [16] suggested a novel approach for enhancing the antibacterial activity regarding ferrite NPs for the biomedical applications, the researchers indicated that the substitution related to the spinel ferrite with transition metal has the ability of enhancing the NPs antibacterial capability. Yet, this approach requires further study. Magnetic, electrical and structural characteristics of the cobalt ferrites NPs are on the basis of their microstructure and composition, so these properties were depending on the approach of synthesis [8]. Methods widely used to synthesize magnetic cobalt ferrite such: coprecipitation [17], hydrothermal [11], reverses micelles [18], sol-gel processing and etc. [19]. From sch approaches, the hydrothermal synthesis was of high importance because of its low costs and simplicity [20] and it is considered as significant route for producing weakly agglomerated and highly crystallized powders with narrow size distributions [21]. Significant stimulus regarding the laser ablation in liquid is the possibility of fast discovery of crystal structures and advanced materials. In addition, the major reason is that laser ablation is producing chemical conditions, thermodynamics and extreme kinetic, on short-time scales therefore chemically pure and well crystallized nanoparticles without by-products are obtained through continuously ablating metal target that is immersed in liquid [22-23], such approach has the ability of controlling NP size down to a few nanometers and ensuring elevated purity of the NPs with environmentally compliant characteristics. Therefore, it is providing fairly simply approach for preparing magnetic NPs [24].

The aim of this work is to synthesis copper substituted cobalt ferrite NPs with formula Co$_{1-x}$Cu$_x$Fe$_2$O$_4$ where $x=0, 0.3, \text{and} 0.7$ via LAHS methods, materials characterization by the structural, morphological, and magnetic properties and finally study the antibacterial property of the synthesized NPS as a biomedical application.

2. Experimental details
All reagents were of analytic grade, ultra-pure, and used as received without further purification, including cobalt nitrate hexahydrate (Co(NO$_3$)$_2$.6H$_2$O) manufactured by (General Co., England), Cupric sulfate pentahydrate (CuSO$_4$.5H$_2$O) manufactured by (Fluka Co., Switzerland), Ferric nitrate nonahydrate (Fe(NO$_3$)$_3$.9H$_2$O) manufactured by (Scharlau Co., Spain) and sodium hydroxide pellets (NaOH) manufactured by (G.T Baker Co., Sweden). The copper substituted ferrite nanoparticles
prepared by LAHS. The aqueous salts of cobalt nitrate, cupric sulfate, and ferric nitrate in molar ratio (1:1:2) see Table (1) dissolved in 50 ml of distilled water on a magnetic stirrer at moderate speed and temperature of (65°C), then these solutions mixed together in a (300ml) Pyrex beaker under constant stirrer for 15 minutes. (1.5M) of sodium hydroxide (NaOH) solution was add drop wise to the mixed metal solution under vigorous stirring for half an hour and the same temperature of (65°C), in the meanwhile we checked the PH which should be approximately equal to 12.

Table1. Precursor masses used in the synthesis process.

| Materials                  | Weight (g) |
|----------------------------|------------|
| For \( x = 0 \) (CoFe\(_2\)O\(_4\)) |            |
| Co(NO\(_3\))\(_2\).6H\(_2\)O    | 8.14       |
| CuSO\(_4\).5H\(_2\)O          | 0          |
| Fe(NO\(_3\))\(_3\).9H\(_2\)O  | 22.62      |
| For \( x = 0.3 \) (Co\(_{0.7}\)Cu\(_{0.3}\)Fe\(_2\)O\(_4\)) |         |
| Co(NO\(_3\))\(_2\).6H\(_2\)O    | 5.70       |
| CuSO\(_4\).5H\(_2\)O          | 2.09       |
| Fe(NO\(_3\))\(_3\).9H\(_2\)O  | 22.62      |
| For \( x = 0.7 \) (Co\(_{0.3}\)Cu\(_{0.7}\)Fe\(_2\)O\(_4\)) |          |
| Co(NO\(_3\))\(_2\).6H\(_2\)O    | 2.44       |
| CuSO\(_4\).5H\(_2\)O          | 4.89       |
| Fe(NO\(_3\))\(_3\).9H\(_2\)O  | 22.62      |

The copper substituted ferrite nanoparticles prepared by LAHS method which was irradiate with Nd:YAG laser wavelength 1064nm, pulse repetition rate 5Hz, pulse duration 9ns, the energy per pulse used was 360mJ and the number of pulses was 3000 pulse. After that, the irradiated solution is transferred into Teflon lined autoclave [25]. The anti-bacterial activity related to prepared copper substituted cobalt ferrite NPs was examined using well diffusion method. Gram-positive bacteria \( S. \) aureus and Gram-negative bacteria \( E. \) coli were taken from stock bacterial cultures by a loop. Planning the media surface has been by head of the loop touching the surface of the media lightly, then the perti dishe was closed directly. The agar wells with diameter of 6mm are punched into agar with the head of sterile micropipette tips. Also, the suspension of ferrite NPs was added into wells on plates. The plates containing the tested bacterials strain and ferrite NPs were incubated at 37°C for 24h [26]. In the case when bacteria were susceptible or sensitive to NPs, clear zone related to inhibition is going to occur, such inhibition zoe is specifying the that the bacteria weren’t existing in that area and thus, they were inhibited through NP. All experiments are achieved in triplicate and DMSO is applied as negative control [27].

2.1 Statistical Analysis:
Comparison between groups of data of three replicates was made by unpaired t test using graph pad prism (V5.01). A \( \rho \) value of less than 0.05 is significant [28].

3. Results and discussions:
3.1 XRD patterns analysis of the prepared samples
Fig (1) is showing XRD patterns related to synthesized samples CoFe$_2$O$_4$, Co$_{0.7}$Cu$_{0.3}$Fe$_2$O$_4$, and Co$_{0.3}$Cu$_{0.7}$Fe$_2$O$_4$ respectively, while all the samples are showing comparable diffraction peaks corresponding to cubic inverse spinel type lattice of the CoFe$_2$O$_4$. The average crystallite size ($D$) estimated utilizing Scherrer relation [29] was 15.58nm, 10.38nm and 9.49nm for compound Co$_{1-x}$Cu$_x$Fe$_2$O$_4$ at $x=0$, 0.3, and 0.7 respectively by LAHS method. All XRD patterns for the synthesized materials via LAHS confirmed that there is no existence of additional peaks indicates that all samples were of pure single phase cubic crystal structures, confirming that Cu ions have substituted Co sites with no considerable changes in crystal structures of the CoFe$_2$O$_4$, which means that Cu penetrated into Co ferrite crystal lattice and this related with the fact that the ionic radius of Cu$^{2+}$ (0.73Å) was extremely close to that of Co$^{2+}$ (0.70Å) [30]. The substitution of copper ions in cobalt ferrite led to increase in lattice constant, while crystallite size decrease with substitution of copper ions this refer to the copper ions replaced with cobalt ions which attributed to nearly ionic radii regarding Cu$^{2+}$ ions 0.73Å as compared to Co$^{2+}$ 0.70Å cations.

We also note a significant LAHS method in the intensity of diffraction peaks, lattice constant (a) and average crystallite size (D), can be assigned to IR laser photothermal effects which would be responsible for impart the energy required for structure refinement without altering the ferrite structure, in addition the floating ferrite particles are absorbing the subsequent laser pulses. Coupling the laser irradiation with suspended particles has the ability of reducing the particle size and narrowing the distribution (Table 2).

Figure 1. XRD pattern for Co$_{1-x}$Cu$_x$Fe$_2$O$_4$ samples at (A) $x=0$, (B) $x=0.3$ and (C) $x=0.7$ synthesized via LAHS method.

Table 2. The crystallite size and lattice constant of the ferrite samples synthesized via LAHS method.
3.2 Morphological properties

Figure (2) shows FESEM micrographs of (A) CoFe$_2$O$_4$, (B) Co$_{0.7}$Cu$_{0.3}$Fe$_2$O$_4$, and (C) Co$_{0.3}$Cu$_{0.7}$Fe$_2$O$_4$ synthesized via laser assisted hydrothermal method. They show the microscopic structure and morphology of the synthesized magnetic nanoparticles. Average particle size is decreasing from $\sim$30 nm to $\sim$15 nm with increasing the copper substituted concentrations into CoFe$_2$O$_4$ NPs. Particle size is decreased due to creating Cu–O–Fe on the surface related to substituted NPs, that will be retarding the growth of crystal grains as well as assisting the particle separation. Thus, the confined particles were appearing in small dimensions. It must be indicated that average particle size related to samples acquired from FE SEM images was large compared to nanocrystals size as estimated utilizing XRD measurements, indicating that each one of the grains was created via agglomeration of a number of nanocrystals because of the magnetic interactions between them in addition to the union regarding primary particles which are held together via weak surface interactions like van der Waals forces.

| Co$_{1-x}$Cu$_x$Fe$_2$O$_4$ | 2θ (deg.) | FWHM (deg.) | Intensity (counts) | d$_{hkl}$ (nm) | a (nm) | D (nm) |
|---------------------------|-----------|-------------|--------------------|---------------|--------|--------|
| x= 0                      | 35.61     | 0.5300      | 70                 | 0.2518        | 0.8354 | 15.58  |
| x= 0.3                    | 35.51     | 0.7950      | 51                 | 0.2525        | 0.8376 | 10.38  |
| x= 0.7                    | 35.56     | 0.8700      | 64                 | 0.2522        | 0.8365 | 9.49   |

**Figure 2.** FE-SEM images of Co$_{1-x}$Cu$_x$Fe$_2$O$_4$ samples (A) x= 0, (B) x= 0.3, and (C) x= 0.7 synthesized via LAHS method.
3.3 Magnetic properties:

Figure (3) shows the variation of magnetization as a function of applied magnetic field at room temperature for $\text{Co}_{1-x}\text{Cu}_x\text{Fe}_2\text{O}_4$ samples was studied using VSM curve. The magnetization curve for $x=0$ has a small broad result of small coercivity while $x=0.3$ and $x=0.7$ clearly trace an ‘S’ shape, which indicating virtually no hysteresis at room temperature and hence no thermal effect from hysteresis loss would be expected for these materials. The $M_s$, $M_r$, and $H_c$ values have been directly obtained from the scurves, and have been listed in various ($x$) values in Table (2). The maximum magnetization achieved at an applied magnetics field ranging from $-15$ to $+15$ kOe are about 46 emu/g, 47 emu/g, and 32 emu/g for $x=0$, 0.3, and 0.7 respectively. There will be an increase in the saturation magnetization due to the increase in Cu content up to $x=0.3$ and decreases rapidly for large value of Cu concentration while coercivity is drastically decreases. The behavior of the saturation magnetization can be attribute to three reason, first the modest degree of crystallization because the $M_s$ values increase with the enhancement of crystallinity [21], second the cations distribution and the misbalance of $\text{Fe}^{3+}$ ions that occurred in tetrahedral and octahedral sites, and super-exchange interactions. There will be an increase in the $H_c$ values with the increase in copper content which can be indicated based on domain structures as well as the critical diameter of crystal. Also, the $H_c$ was in direct proportion to single-domain grains value. Thus, $H_c$ is gradually smaller with the decrease in single domain particle.

![Figure 3. Magnetic hysteresis loop for $\text{Co}_{1-x}\text{Cu}_x\text{Fe}_2\text{O}_4$ samples at $x=0$, 0.3 and 0.7 synthesized via LAHS method.](image)
The reduction in size of ferrite nanoparticles will enhance the super-paramagnetic behavior. One of the important reasons for this enhancement will be the migration of Fe$^{3+}$ ions into the tetrahedral site, which eventually restructure the magnetic interaction between the octahedral as well as tetrahedral sites. In order to explain the effect of reducing domain, squareness ratio (Mr/Ms) was calculated for each sample, which defined in Table (3). Values of squareness ratio of Co$_{1-x}$Cu$_x$Fe$_2$O$_4$ samples $x=0$, 0.3, and 0.7 exhibited below 0.5 (vary between 0.068 and 0.425) which mean that the samples have single domain structures [31], this effect can be seen in Figure (4).

![Figure 4. variation of squareness ratio with Cu concentration in Co$_{1-x}$Cu$_x$Fe$_2$O$_4$.](image)

| Co$_{1-x}$Cu$_x$Fe$_2$O$_4$ | Ms (emu/g) | Mr (emu/g) | Mr/Ms | Hc (Oe) |
|--------------------------|-----------|-----------|-------|---------|
| $x=0.0$                  | 46.30     | 19.7      | 0.425 | 860     |
| $x=0.3$                  | 46.82     | 4.84      | 0.103 | 76.4    |
| $x=0.7$                  | 31.98     | 2.20      | 0.068 | 32.5    |

3.4 Antibacterial Activity:

In vitro antibacterial activity of Co$_{1-x}$Cu$_x$Fe$_2$O$_4$ ferrite NPs for *S. aureus* and *E. coli* was examined utilizing agar well-diffusion technique. Figures (5) and (6) clarify the inhibition-zone results on *S. aureus* and *E. coli* bacteria strains respectively, after 24 hours at 37 °C incubation with all Co$_{1-x}$Cu$_x$Fe$_2$O$_4$ samples (A) $x=0$, (B) $x=0.3$, and (C) $x=0.7$ of concentrations of 62.5, 125, 250, and 500 μg/mL for each of them. In addition, the bars are means of 3 independent experiments. The symbol **, *** as well as **** are considerably different from the negative control. $p<0.05$, $p<0.01$, $p<0.001$.

The inhibition zone was estimated from clear area edge, across the well to other clear area edge. Notably, higher concentrations of each Co$_{1-x}$Cu$_x$Fe$_2$O$_4$ samples (A) $x=0$, (B) $x=0.3$, and (C) $x=0.7$ have higher effect (higher inhibition zone) on both bacteria strains than smaller concentrations. Also, the antibacterial activity of cobalt ferrite NPs is improved (had greater inhibitory effects) after substituting with Cu content for both gram-negative and gram-positive bacteria. The impact of all such
NPs is maximum on *S. aureus*, in which *E. coli* is considered to be more resistant to NPs. The increased resistance related to Gram-negative bacteria might be due to the existence of outer lipopolysaccharide (LPS) membrane. While, *S. aureus* was more sensitive to nanoparticles due to lack of LPS, and outer membrane in their cell wall. A lot of approaches are accountable for the impact of Cu substituted into Co$_{1-x}$Cu$_x$Fe$_2$O$_4$ NPs against bacteria that result in creating inhibition zone like, electrostatic interaction of nanomaterials with cell wall, decompositions of Fe$_2$O$_4$ and creating reactive oxygen species, micro-organism DNA destroyed by ferrite NPs which stops the bacteria duplication, and photocatalytical light activation of nanoparticles [32-33]. Generally, NPs small size is the major significant feature to penetrate bacterial membrane. Also, the external cell membranes had nano sized pores, thus the NPs are penetrating the cell membrane due to their small diameter compared to pores, after that, the thick and coarse bacterial cell wall will be destroyed leading to disappearance and degradation of cytoplasm, thus leading to cell’s death.

![Figure 5. Antibacterial activity of samples](image-url)

Figure 5. Antibacterial activity of samples (A) CoFe$_2$O$_4$, (B) Co$_{0.7}$Cu$_{0.3}$Fe$_2$O$_4$, and (C) Co$_{0.3}$Cu$_{0.7}$Fe$_2$O$_4$ against *S. aureus*. (1) Negative control, (2) concentrations 62.5 µg/ml, (3) concentrations 125 µg/ml, (4) concentrations 250 µg/ml, (5) concentrations 500 µg/ml.
Figure 6. Antibacterial activity of samples (A) CoFe$_2$O$_4$, (B) Co$_{0.7}$Cu$_{0.3}$Fe$_2$O$_4$ and (C) Co$_{0.3}$Cu$_{0.7}$Fe$_2$O$_4$ against E. coli. (1) Negative control, (2) concentrations 62.5 µg/ml, (3) concentrations 125 µg/ml, (4) concentrations 250 µg/ml, (5) concentrations 500 µg/ml.

Conclusion

From this work, copper substituted cobalt ferrite Co$_{1-x}$Cu$_x$Fe$_2$O$_4$ (x=0, 0.3, and 0.7) were successfully synthesized using laser assisted hydrothermal method. The structural and morphological characteristics of synthesized materials are characterized utilizing FE-SEM, FT-IR and XRD approaches. The results showed the formation of the spinel single-phase cubic crystal structure of all samples with average lattice parameter of ~8.36 Å and we have observed a decreasing of the average particle size with increasing of Cu concentration. The obtained NPs are higher peak intensities and less average particle size, which they are spherical with a percent of aggregation because of the magnetic nature of the ferrite NPs which confirmed by FE-SEM images. In addition, there is a significant structure refinement of the synthesized materials after using pulse laser irradiation via pulsed nanosecond Nd:YAG laser at 1064 nm. This preparation procedure was attractive and promising to optimize the preparation parameters for producing such materials with desired properties, also it can be concluded that the magnetic characteristics of nanosized particles is depending on particle size. The saturation magnetization, remanence and coercivity of the materials varied by different concentrations of Cu. Moreover, the hysteresis loops of samples confirmed the super-paramagnetic behavior of the cobalt ferrite nanoparticles. The substitution regarding Cu in cobalt ferrite NPs is considerable enhancing the anti-bacterial activity against S. aureus and E. coli. Also, it was anticipated that the copper substituted cobalt ferrite NPs might be replacing a few antibiotic medicines utilized for combatting types of pathogenic bacteria in addition to other biomedical applications.

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