Bulletin of Faculty of Science, Zagazig University (BFSZU)
e-ISSN: 1110-1555
Volume2023-, Issue-4, pp-74-78
https://bfszu.journals.ekb.eg/journal
Research Paper DOI: **10.21608/bfszu.2023.198292.1258**

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Cobalt ferrite nanoparticles using the hydrothermal method and different bases

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***ABSTRACT* : Cobalt ferrite nanoparticles have been given special interest due to their unique properties, and they are considered an alternative to magnetite nanoparticles due to their chemical inertness to oxidation and unique magnetic characteristics, as magnetite is difficult to resist oxidation, giving rise to additional oxides with a lower magnetization response. The hydrothermal way succeeds in creating cobalt ferrite nanoparticles with highly crystalline nanoparticles at low temperatures, where a crystallization process directly occurs in solutions. This work introduces an eco-friendly hydrothermal method for preparing cobalt ferrite nanoparticles using different bases (NaOH, KOH, and NH_4OH). All the products were characterized by XRD and FTIR. The XRD analysis confirms the cubic spinel cobalt ferrite nanoparticles, and their average crystal sizes are 18.7, 18.1 and 12.9 nm for prepared samples using NaOH, KOH, and NH_4OH, respectively. The Fourier transform infrared spectra confirm the spinel cobalt ferrite nanoparticles by existence of two bands around 416 and 590 cm^{-1}.**

KEYWORDS: $CoFe_2O_4$ NPs, Hydrothermal, NH_4OH, NaOH, KOH

Date of Submission: 16-03-2023 Date of acceptance: 28-03-2023

I. INTRODUCTION

Magnetic nanoparticles have significantly developed new types of nano-systems that play a key role in different applications owing to their striking magnetic features, where an outer magnetic field is able to control them. Therefore, they are recycled a lot, which in turn supports the concept of sustainable growth. [1-3]. One of the magnetic nanoparticles that has captured significant researchers' interest is ferrite material [4]. On one hand, ferrite materials are classified on the basis of their structure into spinel, hexagonal, ortho ferrites and garnet. On another front, according to their coercivity values, some are soft (low coercivity) and the other ones are hard (high coercivity) ferrites [5]. Spinel ferrites and their nanocomposites are at the forefront of ferrite materials due to their superparamagnetic properties. Indicatively, bulk materials contain a multidomain phase, while the reduction in size from 15 to 100 nm allows spinel ferrites to change to a one-domain structure oriented in the same direction. When an external magnetic field is supplied, all single domains have an effective and quick magnetic response; nevertheless, they have no remaining magnetic momentum once the magnetic field is withdrawn [6]. These characteristics attracted the attention of researchers to spinel ferrites. The chemical formula of spinel ferrite is $(M)^A(Fe_2)^BO_4$, where M stands for any divalent metal, for example, Cu, Zn, Cd, Co and so on. Other trivalent cations, such as Ga and Al, can be used in place of the ferric cation. The cation distribution determines the spinel ferrite structure, whose structure is divided into normal, inverse and mixed spinel [4-6]. Basically, the spinel unit cell has eight formula units of AB_2O_4, which form 64 A locations (8 of them are filled) and 32 B places (16 of them are full) to preserve the anions in an electrically balanced state [4-6]. Among the various spinel ferrite systems are cobalt ferrite nanoparticles ($CoFe_2O_4$ NPs) [7, 8]. Cobalt ferrite has become the favored choice for wide utilizations like storage devices, water treatment, lithium-ion batteries, photocatalysis and biomedical applications like drug and gene delivery, biosensors, promising contract agents in imaging and magnetic fluid hyperthermia [9-12]. Amongst other methods, hydrothermal or solvothermal

synthesis is the most eco-friendly, energy-efficient and it can manufacture nanoparticles with precise form and tunable size [9, 13-15]. Despite the fact that there are several studies on cobalt ferrite nanoparticles, there is a dearth of research to understand their reaction conditions and effects on the rates of the cobalt ferrite nanoparticles and their composition and characteristics. In this paper, we were able to construct cobalt ferrite nanoparticles by hydrothermal technique using different base factors and investigated their effects on composition and crystal size by using XRD and FT-IR analyses.

II. MATERIALS AND METHODS

2.1. Chemicals: We consumed all of the supplies as they were given to us without purifying. Cobalt (II) nitrite was delivered by Alpha Chemika, India. Iron (III) nitrate was bought from Sd Fine Chem, India. Ammonia solution (25 %) and ethanol (70 %) were bought from El Nasr pharmaceutical chemicals, Cairo, Egypt. Sodium hydroxide pellets and potassium hydroxide were delivered from Sigma-Aldrich.

2.2. Procedures : The $CoFe_2O_4$ NPs were produced as described in our previous research [16]. As follows, 6.4 g of ferric nitrate and 2.305 g of cobalt nitrate (2:1 ratio) were added separately to 40 mL of distilled water and after that both solutions were stirred together. Drop by drop, (3 M, 50 mL) of ammonia were added to the red salt solution under constant shaking at 60 °C. Afterwards, the brown mixture was shacked for 30 minutes at 60 °C before being carried into an autoclave for 4 h at 180 °C. Cautiously, the black precipitate underwent ethanol and distilled water rinsing to achieve a neutral pH. The previously separated precipitate was dried for 5 h at 100 °C. Other samples were prepared with the same aforementioned procedures but using sodium hydroxide (3 M, 50 mL) and potassium hydroxide (3 M, 50 mL) for comparison. The samples were labelled as CF-NH_4OH, CF-NaOH and CF-KOH for ammonia, sodium hydroxide and potassium hydroxide, respectively.

2.3. CoFe2O4 NPs Characterization: An X-ray diffractometer (Bruker Co., D8Advaced) with Cu Kα source λ = 1.5406 Å, 40 mA and 40 KV was employed to record the crystal phase of produced samples. The bond formation and skeletal vibration of the prepared samples were obtained from Fourier transform infrared (FT-IR) spectra utilizing a ThermoFisher Nicolete IS10 spectrometer from 4000 to 400 cm^{-1}. Samples were created by blending the powders with KBr and pressing them into pellets.

III. RESULTS And DISCUSSION

3.1. X-ray diffraction investigation

We have demonstrated the impress of the type of base on the prepared cobalt ferrite nanoparticles hydrothermally using different types of bases, including NaOH, KOH and NH_4OH. The XRD patterns for three products are good matched at 2θ values of 18.2°, 30.08°, 35.4°, 43.05°, 53.4°, 56.9°, 62.5° and 74.01°, which correspond to (111), (220), (311), (400), (422), (511), (440) and (533) planes as shown in Fig. 1. These values fit the JCPDS file No. 022-1086 [17], which has a cubic cobalt ferrite spinel structure, the space group Fd3m 227 and lattice factors of a = b = c = 8.39 Å, α = β = γ =90. Applying the Debye-Sherrer equation (1), the average crystallite size of the produced materials was calculated [4, 9].

$$D = K\,\lambda/\beta\cos\theta \qquad (1)$$

Where, D represents crystal size (nm), β is the full width of the diffraction line at the half-maximum intensity (FWHM) in rad, K stands for the morphology of the crystal =0.89, λ is the wavelength = 1.5406 Å and θ refers to the angle of diffraction. The average crystallite size was estimated to be 18.7, 18.1 and 12.9 nm for CF-NaOH, CF-KOH and CF-NH_4OH, respectively. The samples prepared with strong bases (NaOH and KOH) have a higher crystallinity degree than those prepared with a weak base (NH_4OH). This might be attributed to the fact that the crystallinity may be increased by increasing the pH. This agreed with other reports; for example, Refat et al. prepared spherical cobalt ferrite nanoparticles by hydrothermal method and investigated the effect of pH factor using different amounts of 3 M ammonia solution. They indicated the crystallite size increased from 12.3, 12.7and 12.9 nm by increasing the pH degree from 8, 9 and 9.5, respectively [16].

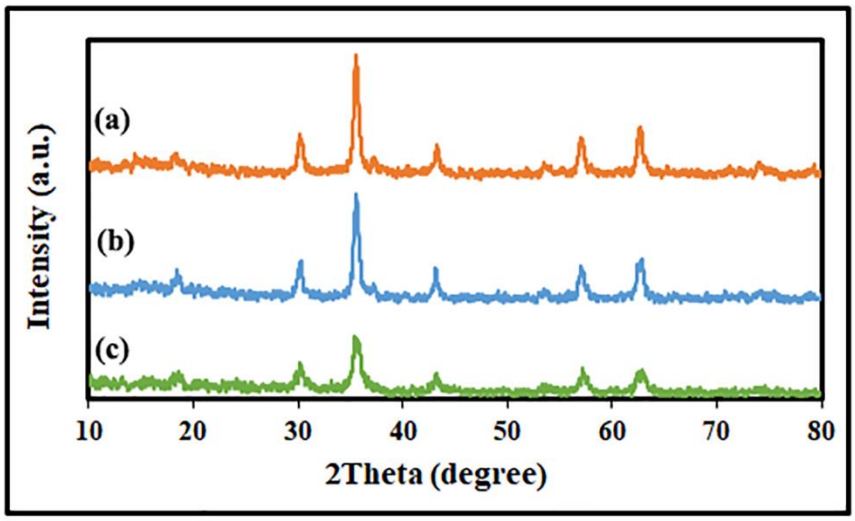

Fig.1. XRD diffractions of the prepared products (a), (b) and (c) using NaOH, KOH and NH_4OH, respectively.

3.2. FT-IR spectra

The produced samples were confirmed by FT-IR spectra, as seen in Fig. 2. The cobalt ferrite NPs phase was formed, as evidenced by the appearance of peaks about 416 and 590 cm^{-1}, which were caused by the octahedral position of the Co-O bond and the tetrahedral position of the Fe-O bond, respectively [18, 19]. Because the humidity, the bands at about 3385 and 1616 cm^{-1} are attributed to stretching and bending vibration of water, respectively [9, 20].

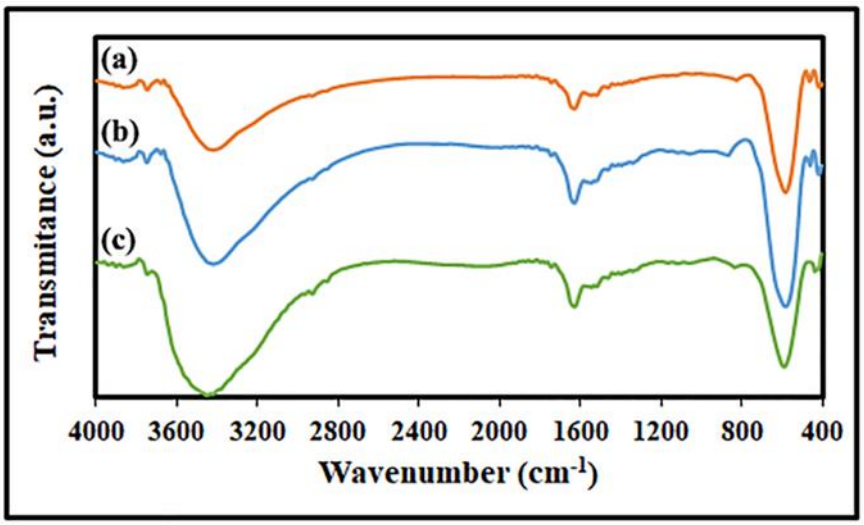

Fig.2. FTIR spectrum of the products (a), (b) and (c) using NaOH, KOH and NH_4OH, respectively.

REFERENCES

[1] Z. Liu, Y. Liu, S. Shen, D. Wu, Progress of recyclable magnetic particles for biomedical applications, Journal of Materials Chemistry B, 6 (2018) 366-380.

[2] E.P. Muniz, L.S.D. de Assunção, L.M. de Souza, J.J.K. Ribeiro, W.P. Marques, R.D. Pereira, P.S.S. Porto, J.R.C. Proveti, E.C. Passamani, On cobalt ferrite production by sol-gel from orange fruit residue by three related procedures and its application in oil removal, Journal of Cleaner Production, 265 (2020) 121712.

[3] T. Tatarchuk, A. Shyichuk, Z. Sojka, J. Gryboś, M. Naushad, V. Kotsyubynsky, M. Kowalska, S. Kwiatkowska-Marks, N. Danyliuk, Green synthesis, structure, cations distribution and bonding characteristics of superparamagnetic cobalt-zinc ferrites nanoparticles for Pb(II) adsorption and magnetic hyperthermia applications, Journal of Molecular Liquids, 328 (2021) 115375.

[4] Shyamaldas, M. Bououdina, C. Manoharan, Dependence of structure/morphology on electrical/magnetic properties of hydrothermally synthesised cobalt ferrite nanoparticles, Journal of Magnetism and Magnetic Materials, 493 (2020) 165703.

[5] V.V. Jadhav, S.D. Shirsat, U.B. Tumberphale, R.S. Mane, Chapter 3 - Properties of ferrites, in: R.S. Mane, V.V. Jadhav (Eds.) Spinel Ferrite Nanostructures for Energy Storage Devices, Elsevier, 2020, pp. 35-50.

[6] T.N. Pham, T.Q. Huy, A.-T. Le, Spinel ferrite (AFe_2O_4)-based heterostructured designs for lithium-ion battery, environmental monitoring, and biomedical applications, RSC Advances, 10 (2020) 31622-31661.

[7] T.C. Coutinho, J.O.D. Malafatti, E.C. Paris, P.W. Tardioli, C.S. Farinas, Hydroxyapatite-$CoFe_2O_4$ Magnetic Nanoparticle Composites for Industrial Enzyme Immobilization, Use, and Recovery, ACS Applied Nano Materials, 3 (2020) 12334-12345.

[8] A. Das, S. Mohanty, R. Kumar, B.K. Kuanr, Tailoring the Design of a Lanthanide Complex/Magnetic Ferrite Nanocomposite for Efficient Photoluminescence and Magnetic Hyperthermia Performance, ACS Applied Materials & Interfaces, 12 (2020) 42016-42029.

[9] M.Y. Nassar, M. Khatab, Cobalt ferrite nanoparticles via a template-free hydrothermal route as an efficient nano-adsorbent for potential textile dye removal, RSC Advances, 6 (2016) 79688-79705.

[10] S.Y. Srinivasan, K.M. Paknikar, D. Bodas, V. Gajbhiye, Applications of cobalt ferrite nanoparticles in biomedical nanotechnology, Nanomedicine, 13 (2018) 1221-1238.

[11] H. Tombuloglu, Y. Slimani, T.M. AlShammari, G. Tombuloglu, M.A. Almessiere, H. Sozeri, A. Baykal, I. Ercan, Delivery, fate and physiological effect of engineered cobalt ferrite nanoparticles in barley (Hordeum vulgare L.), Chemosphere, 265 (2021) 129138.

[12] S. Williams, C.L. Okolie, J. Deshmukh, L. Hawco, J. McNeil, A.C. Nganou Assonkeng, C. Bennett, M. Mkandawire, Magnetizing Cellulose Fibers with $CoFe_2O_4$ Nanoparticles for Smart Wound Dressing for Healing Monitoring Capability, ACS Applied Bio Materials, 2 (2019) 5653-5662.

[13] S.M. Ansari, K.C. Ghosh, R.S. Devan, D. Sen, P.U. Sastry, Y.D. Kolekar, C.V. Ramana, Eco-Friendly Synthesis, Crystal Chemistry, and Magnetic Properties of Manganese-Substituted $CoFe_2O_4$ Nanoparticles, ACS omega, 5 (2020) 19315-19330.

[14] A. Chaudhuri, K. Mandal, Dynamic magnetic properties of monodisperse $CoFe_2O_4$ nanoparticles synthesized by a facile solvothermal technique, Physica B: Condensed Matter, 575 (2019) 311640.

[15] Z.E. Gahrouei, S. Labbaf, A. Kermanpur, Cobalt doped magnetite nanoparticles: Synthesis, characterization, optimization and suitability evaluations for magnetic hyperthermia applications, Physica E: Low-dimensional Systems and Nanostructures, 116 (2020) 113759.

[16] N.M. Refat, M.Y. Nassar, S.A. Sadeek, A controllable one-pot hydrothermal synthesis of spherical cobalt ferrite nanoparticles: synthesis, characterization, and optical properties, RSC Advances, 12 (2022) 25081-25095.

[17] P.A. Asogekar, S.K. Gaonkar, A. Kumar, V.M.S. Verenkar, Influence of Co over magnetically benign Zn ferrite system and study of its structural, dielectric, superparamagnetic and antibacterial efficacy, Materials Research Bulletin, 141 (2021) 111330.

[18] M. Ghanbari, F. Davar, A.E. Shalan, Effect of rosemary extract on the microstructure, phase evolution, and magnetic behavior of cobalt ferrite nanoparticles and its application on anti-cancer drug delivery, Ceramics International, 47 (2021) 9409-9417.

[19] Z. Mahhouti, H. El Moussaoui, T. Mahfoud, M. Hamedoun, M. El Marssi, A. Lahmar, A. El Kenz, A. Benyoussef, Chemical synthesis and magnetic properties of monodisperse cobalt ferrite nanoparticles, Journal of Materials Science: Materials in Electronics, 30 (2019) 14913-14922.

[20] J. Giri, T. Sriharsha, D. Bahadur, Optimization of parameters for the synthesis of nano-sized $Co_{1-x}Zn_xFe_2O_4$, ($0 \leq x \leq 0.8$) by microwave refluxing, Journal of Materials Chemistry, 14 (2004) 875-880.