J. Mat. NanoSci. 2019, 6(2), 67-72 Article

Journal of
Materials NanoScience

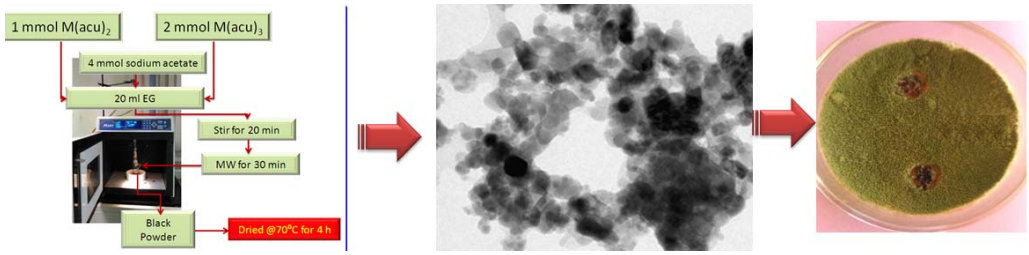
Low-temperature microwave-assisted synthesis and antifungal activity of $CoFe_2O_4$ nanoparticles

T. R. Ravikumar Naik*[1], Naveen Joshi,[1] S. A. Shivashankar,[1] P. J. Bindu[2]

[1]Centre for Nano Science and Engineering, Indian Institute of Science, Bangalore, India. [2]Department of Organic Chemistry, Indian Institute of Science, Bangalore, India

Submitted on: 16-Dec-2018 Accepted and Published on: 24-Sept-2019

ABSTRACT



Nanoparticle ferrite with chemical formula $CoFe_2O_4$ was prepared from the Co (II) and Fe (III) 3-acetyl-4-hydroxy-coumarin metal complexes by solution based one-pot microwave assisted technique. Single phase structure of $CoFe_2O_4$ ferrites nanoparticles was confirmed using FTIR, XRD, SEM, and EDX analysis. Transmission Electron Microscope (TEM) showed that the particle size of the samples in the range of (15 nm). The hysteresis studies showed ferromagnetic behaviour at room temperature. The antifungal activity of $CoFe_2O_4$ nanoparticle was investigated against *A.flavus* and *A. niger* by employing disc diffusion method. According to the results obtained, $CoFe_2O_4$ is a potential material for antifungal diseases. The $CoFe_2O_4$ nanoparticles could be readily separated from water solution after the disinfection process by applying an external magnetic field.

Keywords: Microwave-irradiation, Nanocrystalline $CoFe_2O_4$, Coumarin metal complexes, Antifungal activity

INTRODUCTION

In recent years, the spinel ferrites belonging to AB_2O_4 structure having A-site (metal) and B-site (iron) have drawn huge attention due to their fascinating properties to meet the requirements in various applications.[1,2] The cobalt ferrites have been found to be the most versatile ferrites systems from the perspective of their technological application because of its high electrical resistivity, high permeability, compositional stability and for high frequency applications.[1,2] The outstanding combination of these properties makes them attractive for potential applications in diverse field. The research and application of magnetic materials[3] have been developed considerably in the few past decades.[4,5] In order to discover new types of ferrites and develop their properties, scientific communities have also paid their significant attention.

Nanotechnologies have a great potential for various biomedical applications, including cancer diagnostics[6] and treatment.[7,8] Some specific characteristics are required for nanoparticles in biomedicine like, biocompatibility, heating ability,[9,10] morphology,[11] size. lipophilicity,[12] distribution, a ferrimagnetic/superparamagnetic behavior, hemocompatiblity, dispersibility in water and suspensions stability. Magnetite nanoparticles, with an inverse spinel structure, are the most studied ferrites for biomedical applications.[5]

$CoFe_2O_4$ (spinel-type ferrites), have many potential biomedical applications.[13] This is due to its high magnetic and thermal stability and high anisotropy field. These $CoFe_2O_4$ ferrites have potential applications in high-density magnetic recording,

*Corresponding Author: Dr. T. R. Ravikumar Naik
Centre for Nano Science and Engineering, Indian Institute of Science, Bangalore, India
Tel: +91 9900792675
E-mail: naikravi7@gmail.com

Cite as: *J. Mat. NanoSci., 2019, 6(2), 67-72.*
urn:nbn:sciencein.jmns.2019v6.108

 ISSN 2394-0867 http://pubs.iscience.in/jmns

microwave devices, magnetic fluids catalytic materials, gas-sensing materials.[14,15] Recently, cobalt ferrite ($CoFe_2O_4$) has attracted considerable research interest for visible-light-driven-photocatalyst due to its narrow band gap.[16]

In recent decades, much attention has been paid on their shape and size of the nanoparticles synthesis.[17,18–20] Therefore, the synthesis of small size and uniformly dispersed $CoFe_2O_4$ has been the target of materials chemists. In recent years, cobalt ferrite nanoparticles prepared using various methods, such as sol–gel technique, thermolysis, hydrothermal method, coprecipitation, microemulsions, solvothermal, have been extensively studied.[17] However, ferrite nanoparticles have been synthesized successfully through most of these methods, but these techniques involves, selection of metal precursors, high reaction temperatures, long reaction times, toxic reagents used, and the by-products produced that have the potential to harm the environment. Among all these techniques, microwave[21,22] route seems to be the most convenient for the synthesis of cobalt nanoparticles.[23,24] This convenience come from its homogeneity, simplicity, cost effectiveness, less time consuming, better control over morphology, crystallite size.[25]

In particular, the synthesis of $CoFe_2O_4$ was reported by traditional methods by using commercial metal acetates and metal halides. Even though, there have been a lot of effort in the synthesis of the $CoFe_2O_4$ nanostructures by using the precursors as described above, very little attention was undertaken for the design of a new precursor for the synthesis of $CoFe_2O_4$ nonomaterials.[26] Also, the use of 3-acetylcoumarin as precursors for the preparation of metal oxide nanomaterials, such as $CoFe_2O_4$ using microwave-assisted synthesis has not yet been investigated. Hence we made an attempt to synthesize $CoFe_2O_4$ nanoparticles using cobalt and iron complex of 3-acetylcoumarin as precursor for the first time. The thermal decomposition behavior of metal precursors was examined. The structure, size, morphology, magnetic properties of as-prepared powder material were examined. The antimicrobial performance[27] of as-synthesized $CoFe_2O_4$ nanoparticles is discussed, where the excellent selective antimicrobial performance is confirmed.

EXPERIMENTAL

Synthesis and Characterization of metal precursor material.

All the chemicals used in the present study are of AR grade. Whenever analytical grade chemicals were not available, laboratory grade chemicals were purified and used. All the chemicals and reagents were purchased from SDFCl chemicals and Sigma-Aldrich. We have employed β-diketonates complexes type Co(II) and Fe(III) 3-acetyl-4-hydroxy-coumarin metal complexes as precursor materials. The Co(II) and Fe(III) metal complexes were synthesized and purified in-house. The FTIR, ^{1}H-NMR, Mass, TGA and UV-analysis of in house synthesized metal complexes was performed. The metal–oxygen bond present in β-diketonates complexes makes them appropriate precursors for the synthesis of metal/metal oxide nanoparticles.

Synthesis of $CoFe_2O_4$ nanoparticles.

Solutions of 1 mmol of Cobalt (II) acetyl coumarin ($Co(acu)_2$) and 2 mmol of Fe (III) acetyl coumarin ($Fe(acu)_3$) dissolved in 30 mL of ethylene glycol and mixed together under constant stirring. The pH of the solution is adjusted to the desired value by 4 mmol of sodium acetate (alkaline source) with constant stirring for 20 min. The reaction mixture is irradiated into a MARS (Microwave Accelerated Reaction System, USA) microwave reactor (2.45 GHz) equipped with a water-cooled condenser and a fiber-optic temperature sensor. The solution was then irradiated for 30 min with the power set at 800 W and temperature at 250 °C, leading to a black precipitate. After completion of reaction, the powder materials was also collected by centrifugation, washed twice with deionized water, ethanol, acetone and dried in vacuum oven at 70 °C for 4h (Figure 1).

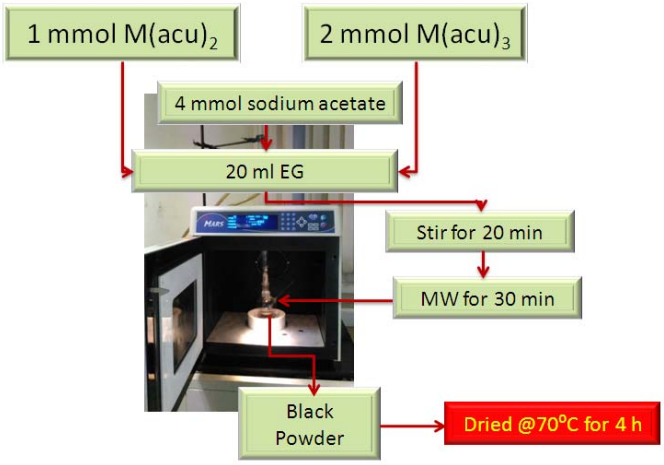


Figure 1. Flow chart for the synthesis of $CoFe_2O_4$ nanoparticles. Where M = $Co(acu)_2$ and $Fe(acu)_3$ metal complexes.

Characterization of nanoparticles

The crystallinity and phase composition of the $CoFe_2O_4$ nanoparticles were investigated using an X-Ray Diffraction (XRD) - analysis was done with Rigaku X-ray difractometer, FT-IR studies were carried out using a Perkin Elmer Frontier FTIR spectrophotometer. The particle size and composition of CoFe2O4 nanoparticles were confirmed by using ULTRA55 FESEM equipped with EDS. The XPS analysis of $CoFe_2O_4$ nanoparticles was recorded by using kratos axis ultra dld spectrometer. The TGA of $CoFe_2O_4$ was recorded using Perkin Elmer STA 8000.

Antimicrobial assay

The antifungal activity of the as-prepared $CoFe_2O_4$ nanoparticles was assessed against *A. flavus* and *A. niger* through agar disk diffusion method. The pure fungal strains were maintained on nutrient agar and potato dextrose agar (PDA) respectively. The dried powder of $CoFe_2O_4$ was taken at the concentration of 50 µg/ml for the antimicrobial tests. Inoculum from the spore suspension cultures of the different fungal strains were spread onto the solidified agar plates. Distilled water poured disk was used as a negative control and Amphotericin B as a positive control. Plates were incubated at 37°C for 48 h. The diameter of zone of inhibition was measured for each compound in milimeter after 48 h.

RESULTS AND DISCUSSION

In the earlier work we have reported the efficient synthesis of metal β-diketonate complexes for materials synthesis.[28] The stability of the complexes has been influenced by the rigidity of the ligand backbone. As part of our continuing interest to synthesize metal complexes of β-diketonate type,[29] we have synthesized coumarin metal complexes with the similar ligand framework. As part of our continuing interest to synthesize metal complexes of β-diketonate type, we have reported 3-acetyl-4-hydroxy-coumarin metal complexes with the similar ligand framework. We described here a convenient approach to the preparation of $CoFe_2O_4$ nanoparticles using 3-acetyl-4-hydroxy-coumarin metal complexes by microwave method.[30]

From the results of FTIR, TGA and spectroscopic studies, the stoichiometry of the complexes has been deduced as $M(acu)_2$ and $M(acu)_3$. This coumarin entity has oxygen donor framework from hydroxyl and acetyl groups and, therefore, stabilizes comfortably the metal ions in their +2 and +3 oxidation state.

Magnetic $CoFe_2O_4$ nanoparticles were prepared via a rapid, facile and green microwave irradiation pathway with Co and Fe coumarin metal complexes as precursor materials, sodium acetate as an alkaline source and ethylene glycol (EG) as a reducing agent and microwave-absorbing solvent. As we know, microwaves are selectively absorbed by polar molecules, which are superheated through dipole rotation and ionic conduction, resulting in rapid heating and low thermal gradients. Briefly, EG has a high dielectric constant and therefore an excellent absorbing capacity towards microwaves, and has been frequently used as a microwave absorbent in microwave synthesis. Interestingly, compared with the previous results from our group, microwave irradiation dramatically accelerated the cluster formation process and the reaction occurred at a temperature of 250 ^{0}C within only 20 min, in striking contrast to the traditional methods.

The phase of the synthesized $CoFe_2O_4$ nanoparticles was identified by XRD characterization is as shown in Figure 2. All of

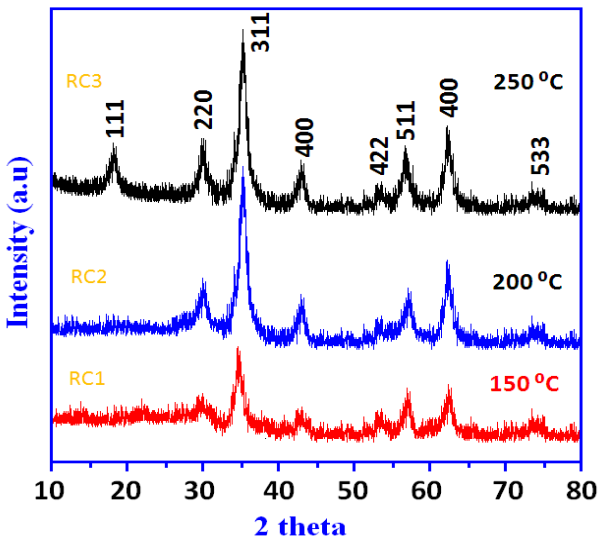


Figure 2. XRD of as-prepared $CoFe_2O_4$ nanoparticles at different temperatures by microwave assisted method.

the peaks of the patterns of the calcined samples can be readily indexed to cubic $CoFe_2O_4$ with spinel structure (JCPDS file No. 22–1086), where the diffraction peaks can be indexed to the reflection of (220), (311), (400), (422), (511), and (440) planes of the spinel $CoFe_2O_4$, respectively. No impurity phase is found in the XRD patterns, indicating high purity of the products. The average crystallite size of the as-prepared cobalt ferrite nanomaterial was calculated from the width of the prominent (311) reflection using the Scherrer's equation. The size of the $CoFe_2O_4$ crystal is about 18 nm.

We have also studied the effect of microwave temperature and power on the synthesis of nanocrystalline cobalt ferrites. Figure 2 shows the XRD patterns of the cobalt ferrites synthesis at 150 °C (RC1), 200 °C (RC2) and 250 °C (RC3) with constant microwave power (800 W) and irradiation time (20 min) respectively.

The morphological studies of the obtained $CoFe_2O_4$ nanoparticles were investigated by the FE-SEM analysis. The highly agglomerated nanoparticle prepared by microwave method was shown in Figure 3. The results showed that grain sizes and morphology depended strongly on the microwave-assisted synthesis. The SEM of precursor material is as shown in figure 3(a), 3(b) and 3(c), respectively. High-resolution transmission electron microscopy (HRTEM) at an accelerating voltage of 200 kV was employed to know the morphology and size of prepared $CoFe_2O_4$ nanoparticles (Figure 3d). The particle diameters are in the range of 15 nm, which may be due to the preparation method and the presence of magnetic interactions among the particles.

Figure 3 (e) shows the EDX analysis of $CoFe_2O_4$ nanoparticles carried out at room temperature for the elemental confirmation and purity of the sample. The EDX spectrum confirms both the homogeneity and gradient of the elements Fe, Co, O present in the sample. The results suggested that the precursors have fully reacted in the microwave-irradiation to form the single phase $CoFe_2O_4$ nanoparticles and it confirms that there is no other impurity present in the samples. Further we investigated the chemical composition and oxidation state of the as-prepared $CoFe_2O_4$ nanoparticles (RC3) was by XPS analysis. The O1s peaks and regions were easily visible, and originated from the prepared $CoFe_2O_4$ oxides and surrounding environment. The XPS spectra of the primary Fe2p and Co2p core levels of Sample 3 (RC-3) of the prepared $CoFe_2O_4$ oxide nanoparticles are shown in figure S14 (see supplementary file). The Fe2p spectra in Fig. exhibited two peaks at 710.9 and 724 eV could be attributed to the $Fe2p_{3/2}$ and $Fe2p_{1/2}$ oxidized states of Fe^{3+} inside $Co^{2+}Fe^{3+}{}_2O_4$ oxide. The peak at 780.6 eV is from $Co2p_{3/2}$, and the peak at 796.8 eV is caused by $Co2p_{1/2}$. Further quantitative EDX analysis finds that the atomic ratio between Co and Fe is about 1:2, which is compatible with the data of XRD.

In addition the magnetic data of the as-prepared $CoFe_2O_4$ nanoparticles (RC3) was recorded at 30 K and is as shown in Fig. 4. The sample exhibits a ferromagnetic behavior at room temperature. The magnetic properties of the magnetic materials are dependent on the sample shape, crystallinity, magnetization direction, etc. The observed value of saturation magnetization (M_s), coercivity (H_c) and remanent magnetization (M_r) was

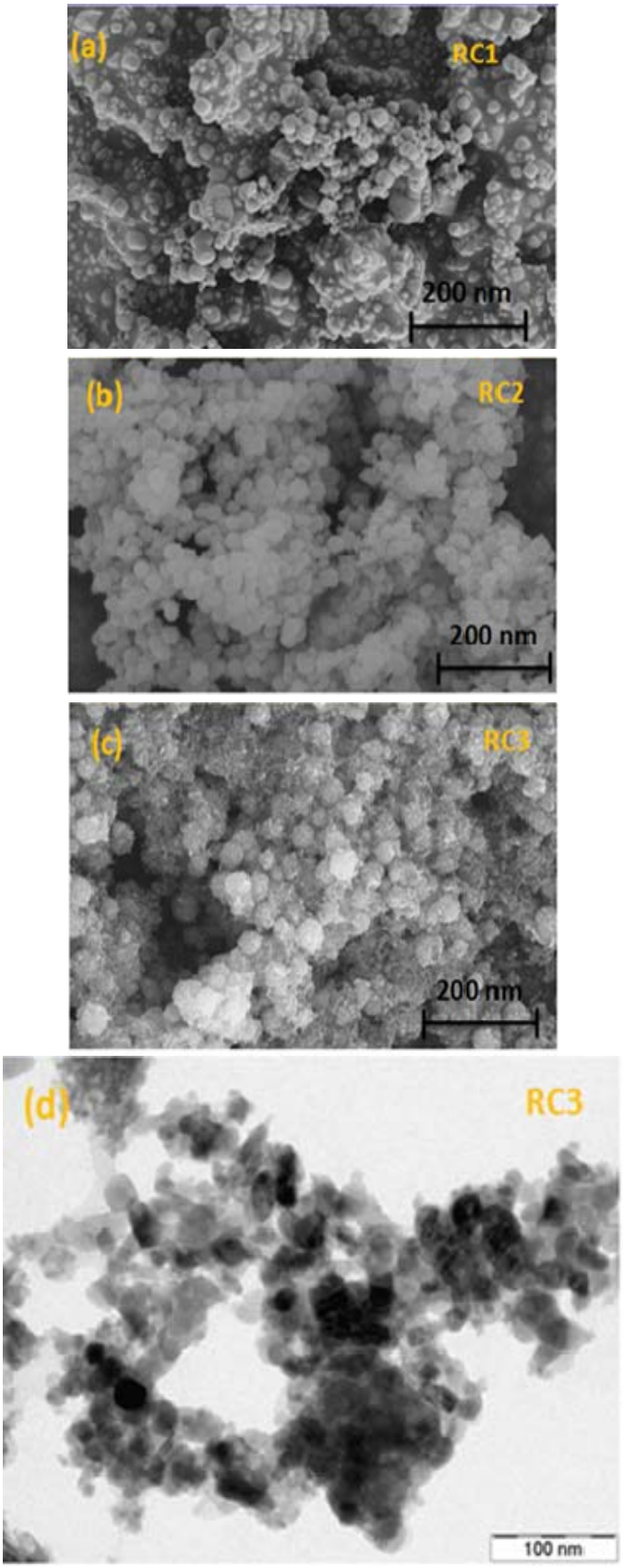


Figure 3. SEM of as-prepared $CoFe_2O_4$ by microwave method (a) RC1 at 150 °C, (b) RC2 at 200 °C (c) RC3 at 250 °C (d) TEM of RC3

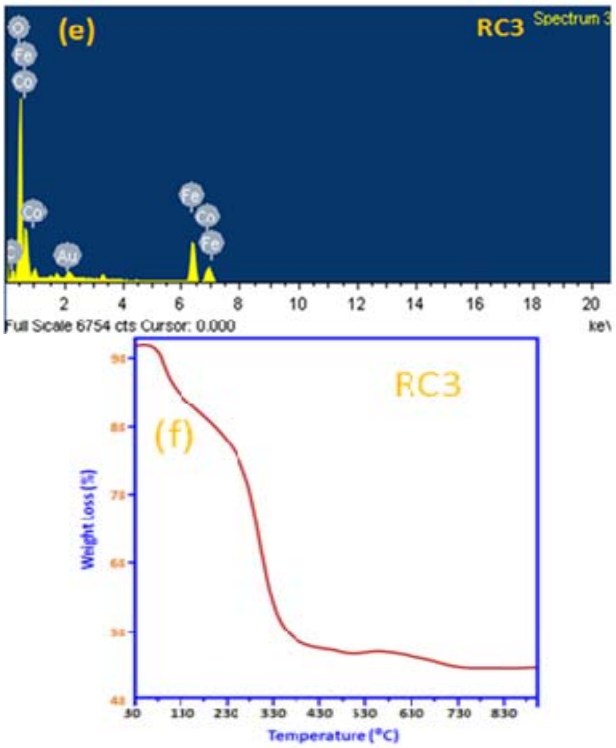


Figure 3. (e) EDX of RC3, (f) TGA of RC3

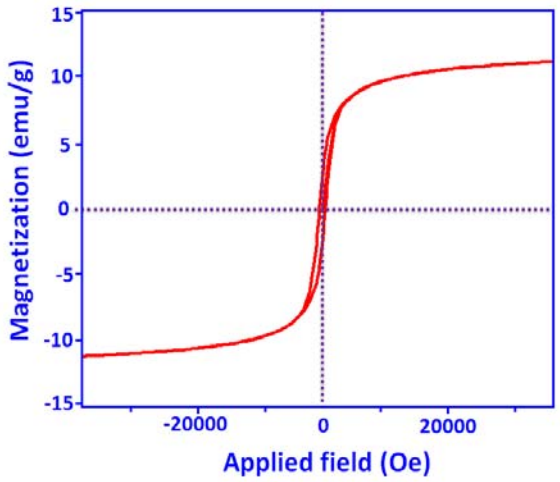


Figure 4. M-H curve of as-prepared $CoFe_2O_4$ measured at 30 K (RC3).

12 emu/g and 6.3 Oe respectively. Consequently, the smaller the grain size, the better the magnetic property. When the grain size is beyond the single-domain size, the coupling effect of ferromagnetic exchange between the grains cannot significantly reduce the magnetocrystalline anisotropy of local regions within the grains. In this case, the domains in the material have distinctly non-uniform states of magnetization. Since the spin magnetic moments in the grain boundary regions are randomly distributed, it is difficult to magnetize these regions. Moreover, the randomly distributed magnetic moments can be counteracted each other to some degree.

Further, the in vitro antifungal activity of the $CoFe_2O_4$ nanoparticles was evaluated by disk diffusion method and is as shown in figure 5a). The $CoFe_2O_4$ nanoparticles RC2 and RC3 displayed antifungal activity toward the tested pathogenic strains of *A. flavus* (19 mm), (23 mm) and *A. niger* (17 mm), (20 nm) respectively. On the other hand, the negative control (distilled water) did not exhibit any zone of inhibition. The positive control showed antifungal activity against both the fungi. In this article, bactericidal activities of $CoFe_2O_4$ nanoparticles against the above mentioned bacteria were evaluated by determining the presence of inhibition zones (Figure 5b).[31]

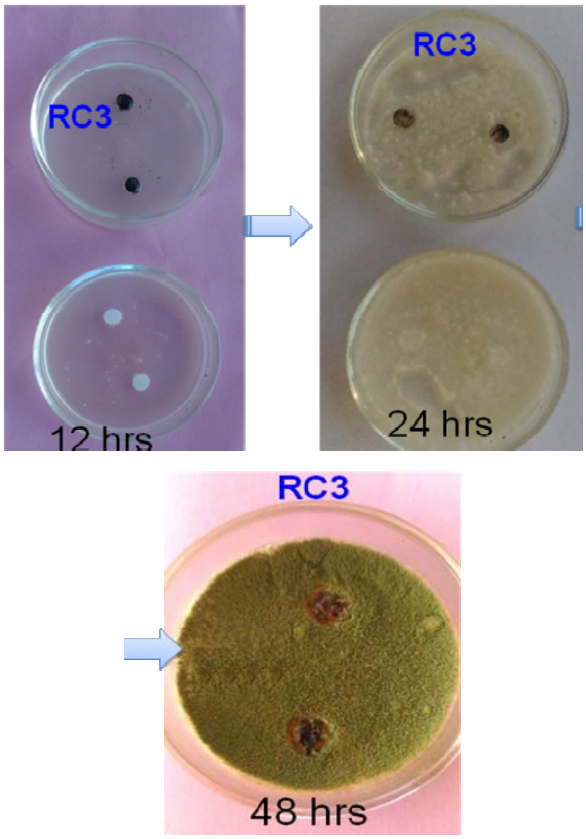


Figure 5a. Antifungal activity of RC3 at different time interval.

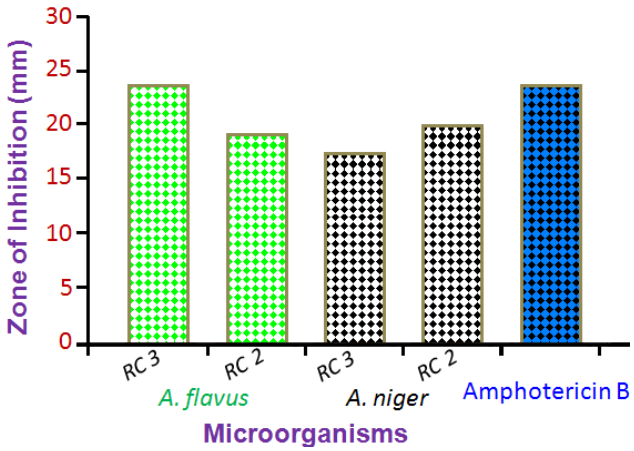


Figure 5b. Zone of inhibition of antifungal activity $CoFe_2O_4$ NPs.

Conclusion

In conclusion, we have developed a new cobalt and iron complex of 3-acetylcoumarin precursor materials for the synthesis of metal oxide nanomaterials by microwave method. The spectroscopic studies show that metal to ligand ratio is 2:1 and 3:1. The thermal behavior of the new metal precusors was characterized by TGA analysis. Further, we have developed a simple and rapid one-step microwave-assisted method for the synthesis of $CoFe_2O_4$ nanoparticles with the diameter approximately 15 nm. The results assure that the preparation method served as a facile tune for obtaining the desired morphology and microstructure of the ferrite nanocrystals. Finally, we investigated the antifungal activity of as synthesized $CoFe_2O_4$ nanoparticles. The offered nanoferrite crystals are recommended for versatile applications in biomedicine as they displayed good antimicrobial activity. Thus, coumarin metal complexes were found to be one of the potential metal precursor materials for the synthesis of metal oxide nanostructures.

Acknowledgments

The authors thank DeitY, Govt. of India, for a research grant and the Department of Organic Chemistry, Indian Institute of Science, Bangalore for providing the NMR and mass spectra of metal complexes and CeNSE for materials characterization.

Supplementary Information

The synthesis and characterization of Coumarin molecules used as metal complexation have been provided as supplementary file. Details of nanoparticle sytnesis and analysis data (XPS, TGA) is included in supplementary file. The file can be downloaded from article page on journal site free of charge.

Conflict of Interest Declaration

The authors declare no conflict of interest.

References and Notes

1. T. Sodaee, A. Ghasemi, R. Shoja Razavi. Shape factors dependence of magnetic features of CoFe2−xGdxO4 nanocrystals. *J. Alloys Compd.* **2017**, 693, 1231–1242.
2. X. Ni, Z. He, X. Liu, et al. Ionic liquid-assisted solvothermal synthesis of hollow CoFe2O4 microspheres and their absorbing performances. *Mater. Lett.* **2017**, 193, 232–235.
3. L. Khanna, N.K. Verma, S.K. Tripathi. Burgeoning tool of biomedical applications - Superparamagnetic nanoparticles. *J. Alloys Compd.* **2018**, 752, 332–353.
4. P.M. Raj, D. Mishra, S. Sitaraman, R. Tummala. Nanomagnetic Thinfilms for Advanced Inductors and EMI Shields in Smart Systems. *J. Mater. Nanosci.* **2014**, 1 (1), 31–38.
5. I. Roy, A. Anuradha. Synthesis and characterization of iron phosphate NPs and applications in magnetically guided drug delivery. *J. Mater. Nanosci.* **2016**, 3 (1), 1–7.
6. S.S. Malapure, S. Bhushan, R. Kumar, S. Bharati. Radiolabelled nanoparticles in cancer management: current status and developments. *Chem. Biol. Lett.* **2018**, 5 (1), 25–34.
7. Z. Hedayatnasab, F. Abnisa, W.M.A.W. Daud. Review on magnetic

nanoparticles for magnetic nanofluid hyperthermia application. *Mater. Des.* **2017**, 123, 174–196.
8. A.B. Salunkhe, V.M. Khot, S.H. Pawar. Magnetic Hyperthermia with Magnetic Nanoparticles: A Status Review. *Curr. Top. Med. Chem.* **2014**, 14 (5), 572–594.
9. P. Kumari, R. Gautam, A. Milhotra. Application of Porphyrin nanomaterials in Photodynamic therapy. *Chem. Biol. Lett.* **2016**, 3 (2), 32–37.
10. A. Patsha, S. Dhara, S. Chattopadhyay, K.-H. Chen, L.-C. Chen. Optoelectronic properties of single and array of 1-D III-nitride nanostructures: An approach to light-driven device and energy resourcing. *J. Mater. Nanosci.* **2018**, 5 (1), 1–22.
11. B.S. Chhikara, S.K. Misra, S. Bhattacharya. CNT loading into cationic cholesterol suspensions show improved DNA binding and serum stability and ability to internalize into cancer cells. *Nanotechnology* **2012**, 23 (6), 065101.
12. B.S. Chhikara, D. Mandal, K. Parang. Synthesis, anticancer activities, and cellular uptake studies of lipophilic derivatives of doxorubicin succinate. *J. Med. Chem.* **2012**, 55 (4), 1500–1510.
13. N. Sangeneni, K. Taddei, N. Bhat, S. Shivashankar. Magnetic properties of superparamagnetic, nanocrystalline cobalt ferrite thin films deposited at low temperature. *J. Magn. Magn. Mater.* **2018**, 465, 590–597.
14. L. Thakur, B. Singh. Study of magnetic properties of mixed Cobalt-Zinc Ferrites synthesized by solid state reaction technique. *Integr. Res. Adv.* **2014**, 1 (1), 5–7.
15. S. Kumar, G. Kumar, M. Singh. Effect of temperature on structural and electrical properties of Mn0.6Zn0.2La0.2Fe2O4 Nanoferrite. *J. Integr. Sci. Technol.* **2015**, 3 (1), 1–5.
16. C.-J. Li, J.-N. Wang, B. Wang, J.R. Gong, Z. Lin. A novel magnetically separable TiO2/CoFe2O4 nanofiber with high photocatalytic activity under UV–vis light. *Mater. Res. Bull.* **2012**, 47 (2), 333–337.
17. A. Hajalilou, S.A. Mazlan. A review on preparation techniques for synthesis of nanocrystalline soft magnetic ferrites and investigation on the effects of microstructure features on magnetic properties. *Appl. Phys. A* **2016**, 122 (7), 680.
18. S. Rastogi. Controlled Aqueous Phase Synthesis of Gold Nanoparticles using Fruit extract of Momordica charantia. *J. Mater. Nanosci.* **2016**, 3 (1), 11–13.
19. B.S. Chhikara, R.S. Varma. Nanochemistry and Nanocatalysis Science: Research advances and future perspectives. *J. Mater. Nanosci.* **2019**, 6 (1), 1–6.
20. B.S. Chhikara. Current trends in nanomedicine and nanobiotechnology research. *J. Mater. Nanosci.* **2017**, 4 (1), 19–24.
21. B.S. Chhikara, V. Tandon, A.K. Mishra. Impact of microwave radiations on macrocyclization reactions: Solvent free synthesis of 1,4-benzothiazin-3-one derivatives on basic alumina. *Heterocycl. Commun.* **2004**, 10 (6), 441–446.
22. M.S. Rao, B.S. Chhikara, R. Tiwari, et al. Microwave-assisted and scandium triflate catalyzed synthesis of tetrahydrobenzo[a]xanthen-11-ones. *Monatshefte fur Chemie* **2012**, 143 (2), 263–268.
23. J.C. Fariñas, R. Moreno, A. Pérez, et al. Microwave-assisted solution synthesis, microwave sintering and magnetic properties of cobalt ferrite. *J. Eur. Ceram. Soc.* **2018**, 38 (5), 2360–2368.
24. A.L. Gurgel, A.E. Martinelli, O.L. de A. Conceição, et al. Microwave-assisted hydrothermal synthesis and magnetic properties of nanostructured cobalt ferrite. *J. Alloys Compd.* **2019**, 799, 36–42.
25. Y.-J. Zhu, F. Chen. Microwave-Assisted Preparation of Inorganic Nanostructures in Liquid Phase. *Chem. Rev.* **2014**, 114 (12), 6462–6555.
26. C.L. Londoño-Calderón, A. Londoño-Calderón, S. Menchaca-Nal, et al. Magnetic properties of cobalt ferrite octahedrons obtained from calcination of granular nanotubes growing on bacterial nanocellulose. *J. Magn. Magn. Mater.* **2020**, 495, 165899.
27. A.H. Ashour, A.I. El-Batal, M.I.A.A. Maksoud, et al. Antimicrobial activity of metal-substituted cobalt ferrite nanoparticles synthesized by sol–gel technique. *Particuology* **2018**, 40, 141–151.
28. T.R. Ravikumar Naik, S.A. Shivashankar. Heterogeneous bimetallic ZnFe2O4 nanopowder catalyzed synthesis of Hantzsch 1,4-dihydropyridines in water. *Tetrahedron Lett.* **2016**, 57 (36), 4046–4049.
29. P.J. Bindu, T.R.R. Naik, K.M. Mahadevan, G. Krishnamurthy. Synthesis, DNA photocleavage, molecular docking and anticancer studies of 2-methyl-1,2,3,4-tetrahydroquinolines. *Chem. Biol. Lett.* **2019**, 6 (1), 8–13.
30. M.G. Naseri, M.K. Halimah, A. Dehzangi, et al. A comprehensive overview on the structure and comparison of magnetic properties of nanocrystalline synthesized by a thermal treatment method. *J. Phys. Chem. Solids* **2014**, 75 (3), 315–327.
31. N.L. Naveena, R. Naik, R. Pratap, S.A. Shivashankar. Microwave assisted greener synthesis of silver nanoparticles using Karanjin and their antifungal activity. *J. Mater. Nanosci.* **2018**, 5 (1), 23–28.