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A Facile Microwave Method to Produce High Crystalline $CoFe_2O_4$ Nano-particles

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ABSTRACT

$CoFe_2O_4$ have been synthesized via a surfactant assisted gel microwave route with a molar ratio of Fe/Co= 2 and oleic acid (OA) was used as a surfactant. Fourier Transform Infrared spectroscopy (FTIR), X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) were used to consider the structural and morphological properties of $CoFe_2O_4$ nano-particles. Results demonstrated that oleic acid is an effective surfactant for producing high crystalline powders. The average particle size and the percentage of crystallinity were calculated 34.7 nm and 90%, respectively.

Keyword: Nanomaterial; Size Distribution; Cobalt Ferrite; Crystallinity; Microwave; Oleic Acid.

1. INTRODUCTION

During the last few decades, more attention has been focused on the preparation and characterization of super-paramagnetic metal oxide nano-particles such as spinel ferrites, MFe_2O_4 (M = Co, Zn, etc.) [1]. Among this material, cobalt ferrite has very specific properties, such as its high coercivity, moderate saturation magnetization, high chemical stability [2], good photo-catalytic activity [3] and high absorption capacity to remove heavy metal or toxic material from water [4].

Magnetic nano-structures have the ability to affect the relaxation process and thus may be used as contrast agents upon accumulation in tissue [5].

In addition of role of coating agent to provide a stable suspension, coating of magnetic nano-particles with a suitable biocompatible material is essential for in vivo applications. The coating is essential to prevent the formation of large aggregates, changes of the original structure and sedimentation and bio-degradation when exposed to the biological system [6].

Different methods have been developed to

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synthesize ferrite nano-particles such as solvothermal [7-9], low temperature combustion [10], microwave [11, 12], sol-gel [13] and co-precipitation [14-16]. Generally, in most types of nano-synthesis routes, control of size, distribution and crystallinity are not possible [17]. Among them, microwave synthesis has been shown not only to increase the rate of chemical reactions, but also to give better yields in some cases [11].

The purpose of this work was to develop a simple one-pot surfactant assisted-microwave route in aqueous media to produce a narrow size distribution and uniform nano-cobalt ferrite particles by using surfactant. This method is very attractive for its versatility, since it has been shown to be suitable to prepare high-quality $CoFe_2O_4$ nano-crystals [18].

In this work, OA was used for synthesis of $CoFe_2O_4$ nano-particles with simple gel-microwave technique. Characterization of nano-particles showed the high crystallinity and good average size by using the OA as surfactant.

2. EXPERIMENTAL

2.1. Materials

Iron (III) nitrate nona-hydrate (Merck 99-101%), cobalt nitrate hexa-hydrate (Merck 99%), urea ($(CO(NH_2)_2)$, Merck 99%), and special-grade of oleic acid ($C_{18}H_{32}O_4$, Merck 88%), ammonia (NH_4OH, Merck 25%) used without any purification.

2.2. Synthesize of $CoFe_2O_4$

Nano-particles synthesis in the presence of OA as a surfactant carried out as follow: Appropriate amounts of $Fe(NO_3)_3.9H_2O$, $Co(NO_3)_2.6H_2O$ and urea, in a molar ratio of 1:2:3 were first dissolved in a minimum amount of deionized water. Ammonia was added drop by drop to the mixed solution to adjust pH around 7. Then 0.3 mmol of OA added to the solution. During water evaporation, the solution was continuously stirred using a magnetic agitator and heated at 60°C to transform into a gel. Obtained viscous gel was poured into the wide head beaker and was irradiated at 500 W for 5 min in a microwave oven.

After solution reaches the point of spontaneous combustion, it began burning and released a great amount of heat, vaporized all the remaining water and became a solid burning at the high temperature. The nano-powders were calcined in 600°C with an electrical furnace for 2 hours.

2.3. Characterization process

X-ray diffraction (XRD) pattern was measured by a "Philips X'pert", using Cu Kα radiation at 40 kv and 30 mA. A "Philips XL-30" scanning electron microscope was used to characterizing the morphologies and microstructure of the samples. Fourier transform infrared spectra (FTIR) were measured with a "Thermo Nicolet Nexus 470 ESP" FT-IR within the wave number range of 5000-400 cm^{-1} using KBr pressed pellet technique.

3. RESULTS AND DISCUSSION

Figure 1 illustrates X-ray powder diffraction pattern of obtained nano-powders. It is evident that produce powder contains only the spinel cubic ferrite. All the peaks in the pattern well matched with JCPDS (No. 22-1086) card.

Average crystallite sizes calculated from the full-width at half-maximum (FWHM) of diffraction peaks using Scherrer's formula (Eq. 1):

$$d= 0.9\, \lambda / \beta\cos\theta \qquad \text{(Eq.1)}$$

Where d is the grain diameter, β is half-intensity width of the relevant diffraction; λ is X-ray wavelength and θ the diffraction angle.

The percentage of crystallinity of sample calculated from ratio of net area to total area. Results shown that the good crystallinity about 90% was obtained. Using the Bragg law, for any cubic system, the lattice parameter calculated from Eq. 2.

$$\mathrm{Sin}^2\theta= \lambda^2\, (h^2 + k^2 + l^2)/ 4a^2 \qquad \text{(Eq. 2)}$$

Where λ is the lamp wavelength, ($h\ k\ l$) are the miller planes, θ is the maximum peak position and a is the lattice parameter. The measured value of this parameter for the sample is in good agreement with the reported value [19].

Figure 2 shows the SEM images of cobalt ferrite nano-particles. According to the images, cobalt ferrite nano-particles lead to formation of fine and uniform particles with a spherical shape. Some soft agglomeration was observed due to magnetic nature of the sample. The observed particle size, 35 nm, in these images confirmed with Scherrer's calculation from XRD data series.

Figure 3 illustrates the FTIR spectrum of un-calcined cobalt ferrite. Spectrum has a broad band around 3422.45 cm^{-1} which attributed to asymmetric and symmetric OH stretching vibration of lattice water. Characteristic vibrations around 2926 and 2853 cm^{-1} are indicated the stretching of asymmetric and symmetric vibrations of (-CH_2-) group of oleic acid, respectively. The weak peak at 2337.14 cm^{-1} confirmed by observed peaks at Limaye and et al. [20] work corresponds to

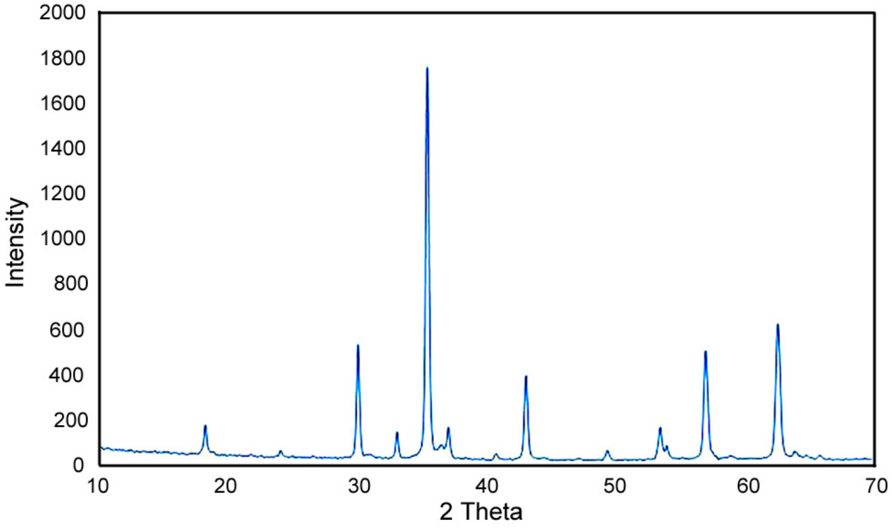

Figure 1: *X-ray diffraction pattern of* $CoFe_2O_4$ *synthesis in present of OA as a surfactant.*

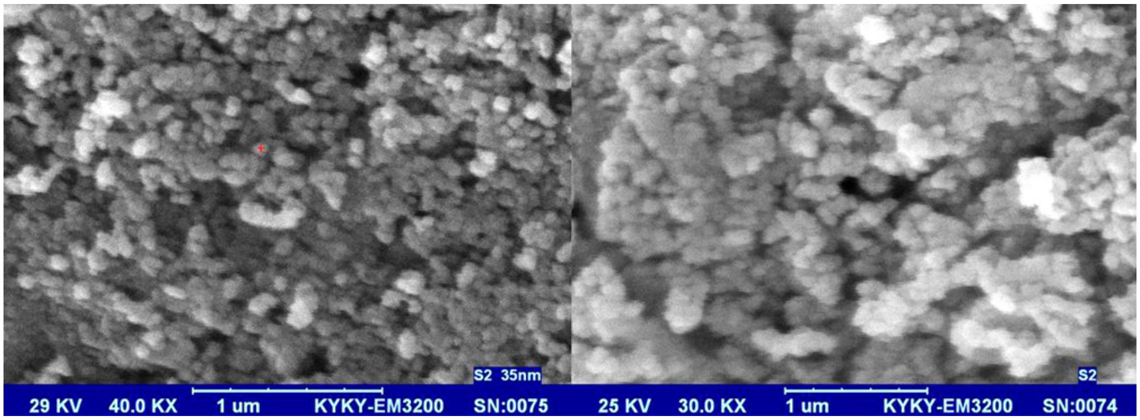

Figure 2: *SEM imagining of* $CoFe_2O_4$ *nano-particles synthesized with OA as a surfactant.*

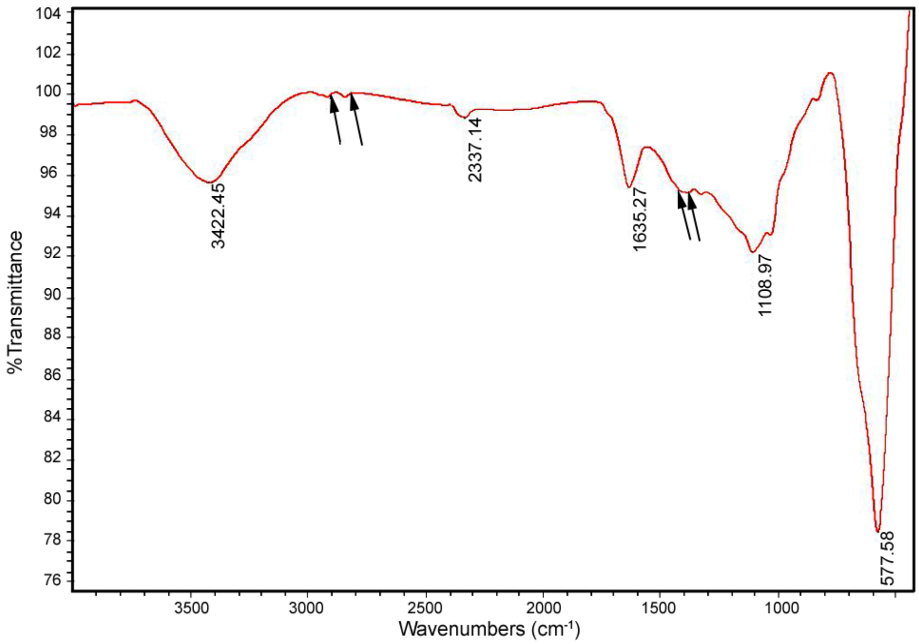

Figure 3: *FTIR spectrum of un-calcined $CoFe_2O_4$ nano-particles.*

gas-phase CO_2. This phenomenon may be due to adsorption of gas in the porous structure of cobalt ferrite from air. Also the peak at 1635.27 cm^{-1} has been assigned to H-O-H vibration bending of the absorbed water. In the region of 1000-1400 cm^{-1} some peaks overlapped. OA coated $CoFe_2O_4$ nano-particles show two distinct vibrations at 1583 and 1413 cm^{-1} and are attributed to asymmetric and symmetric vibrations of COO, receptively [21]. The peak at 1108.97 cm^{-1} characteristic of C-O, C-C or C=O Vibration bands. At last, the sharp peak at 577.58 cm^{-1} demonstrate Metal-O (Fe-O or Co-O) stretching band.

4. CONCLUSIONS

Cobalt ferrite nano-particles were produced successfully in microwave system using the oleic acid as a surfactant. Results demonstrated that obtained $CoFe_2O_4$ nano-particles by combination of applied surfactant and microwave irradiating, have high crystallinity and uniform morphology. In addition, FTIR spectrum of the microwave irradiated sample has an oleic-cape layer that allows homogenous particle size and uniform shape. The average particle size and percent crystallinity were calculated from X-ray powder diffraction data 34.7 nm and 90%, respectively.

REFERENCES

1. Liu C., Rondinone A.J., Zhang Z.J., *Pure Appl. Chem.*, **72** (2000), 37.
2. Kim C.H., Myung Y., Cho Y.J., Kim H.S., Park S.H., Park J., Kim J.Y., Kim B., *J. Phys. Chem. C*, **113** (2009), 7085.
3. Casbeer E., Sharma V.K., Li X.Z., *Sep. Purif. Technol.,* **87** (2012), 1.
4. Zhang S., Niu H., Cai Y., Zhao X., Shi Y., *Chem. Eng. J.*, **158** (2010), 599.
5. Joshi M., Lin H., Aslam Y.P., Prasad M., P.V., Schultz-Sikma, E.A., Edelman, R., Meade, T., Dravid, V.P., *J. Phys. Chem. C*, **113** (2009), 17761.
6. Terreno E., Castelli D.D., Alessandra Viale A., Aime S., *Chem. Rev.*, **110** (2010), 3019.
7. Zhao D., Wu X., Guan H., Han E., *J. Super. Fluid*, **42** (2007), 226.

8. Yanez-Vilar S., Sanchez-And ujar M., Gomez-Aguirre C., Mira J., Senaris-Rodriguez M.A., Castro-Garcia, S., *J. Solid State Chem.*, **182** (2009), 2685.
9. Repko A., Niznansky D., Poltierova-Vejpravova J., *J, Nanopart Res*, **13** (2011), 5021.
10. Xiao S.H., Jiang W.F., Li L.Y., Li X.J., *Mater. Chem. Phys.,* **106** (2007), 82.
11. Bensebaa F., Zavaliche F., L'Ecuyer P., Cochrane R.W., Veres T., *J. Colloid Interf. Sci.*, **277** (2004), 104.
12. Ibrahima A.M., Abd El-Latif M.M., Mahmoud M.M., *J. Alloy. Compd.*, **506** (2010), 201.
13. Gopalan E.V., Joy P.A., Al-Omari I.A., Sakthi Kumar D., Yoshida Y., Anantharaman M.R., *J. Alloy. Compd.*, **485** (2009), 711.
14. Chena Y., Ruan M., Jiang Y.F., Cheng S.G., Li W., *J. Alloy. Compd.*, **493** (2010), 36.
15. Tartaj P., Morales M.P., Veintemillas-Verdaguer S., Gonzalez-Carreno T., J Serna C., *J. Phys. D. Appl. Phys.*, **36** (2003), 182.
16. El-Okr M.M., Salema M.A., Salim M.S., El-Okr R.M., Ashoush M., Talaat H.M., *J. Magn. Magn. Mater*, **323** (2011), 920.
17. Maaz K., Mumtaz A., Hasanain S.K., Ceylan A., *J. Magn. Magn. Mater*, **308** (2007), 289.
18. Khorrami S.A., Sadr Manuchehri Q., Sadeghipour S., *Int. J. Bio-Inorg. Hybd. Nanomat*, **1** (2012), 193.
19. Ayyappan S., Philip, J., Raj, B., *Mater. Chem. Phys.*, **115** (2009), 712.
20. Limaye M.V., Singh S.B., Date S.K., Kothari D., Reddy V.R., Gupta A., Sathe V., Choudhary R.J., Kulkarni S.K., *J. Phys. Chem. B*, **113** (2009), 9070.
21. Ayyappan S., Mahadevan S., Chandramohan P., Srinivasan M.P., Philip, J., Raj, B., *J. Phys. Chem. C*, **114** (2010), 6334.