Int. J. Bio-Inorg. Hybd. Nanomat., Vol. 1, No. 3 (2012), 193-197

International Journal of Bio-Inorganic Hybrid Nanomaterials

Surfactant-assisted Microwave Route to Fabricate $CoFe_2O_4$ Nanoparticles

Saeed Abedini Khorrami, Qazale Sadr Manuchehri*, Saber Sadeghipour

Chemistry Department, Azad University, North Tehran branch, Tehran, Iran

Received: 12 July 2012; Accepted: 16 September 2012

ABSTRACT

Glycerol mono-oleate (GMO) was produced by direct esterification reaction with amberlyst 16 resin catalysts with the efficiency of 86% and was used as a surfactant for synthesis of $CoFe_2O_4$ nano-particles by surfactant-assisted microwave method. Fourier transform infrared spectroscopy (FT-IR), 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 the average particle size and the percentage of crystallinity were 37.90 nm and 47.34%, respectively.

Keyword: Coblat Ferrite nano particle, Microwave, Glycerol mono-oleat, Sacrificial-core technique, GC-MS.

1. INTRODUCTION

Transition metal oxides with spinel structure MFe_2O_4 (M: Mn, Fe, Co, Ni, Zn, etc.) have attracted considerable interest during the last few decades due to their potential applications [1].

$CoFe_2O_4$ nano-particles have recently been developed as useful matter in many interesting biomedical applications. According to the unique magnetic properties of $CoFe_2O_4$, They are important nano particles for drug delivery, magnetic Resonance Image (MRI) contrast and DNA separation [2], hyperthermia [3], Microwave device and recording media [4].

Radiological technologies particular and cellular imaging such as MRI was emerging. MRI provides high spatial resolution and the opportunity to extract both anatomical and physiological information simultaneously [5]. It is based on the principle of nuclear magnetic resonance and uses radiofrequency waves to probe tissue structure and function without requiring exposure to ionizing radiation. Any local magnetic field variation leads to local variation in relaxation and that can demonstrate in corresponding image contrast. A large magnetic susceptibility difference between

(*) Corresponding Author - e-mail: gmanuchehri@yahoo.com

the nano-structures and their surrounding medium leads to a microscopic magnetic field gradient. More specifically, Protons move (oscillate) between two points and vibrate when they are exposed to a strong magnetic field.

Dephasing of the proton in magnetic moments lead to a negative contrasting effect (darkening of image) in MRI. Nanostructures that cause this are known as T_2 contrast agents [6]. Iron nano-particles have attracted much research attention in recent years due to higher magnetization that differ from their analogous systems containing iron oxides. These potential applications arise from higher T_2 relaxivity.

Furthermore, such systems efficiently induce local hyperthermia effects. Alloy-based nano-materials are good candidates for developing T_2 contrast agents with higher relaxivity. Several bimetallic ferrite nano-particles, including $CoFe_2O_4$, $MnFe_2O_4$, and $NiFe_2O_4$ have been investigated as potential T_2 contrast agents [7].

Recently, several methods have been reported to synthesize $CoFe_2O_4$ nano-particles. These include sol-gel method [8, 9], co-precipitation method [10], microwave [11], and solvothermal method [12, 13].

Glycerol mono-oleat (GMO) is the one of the non-ionic emulsifiers with the chemical formula ($C_{21}H_{40}O_4$ (which is synthesized as yellow solution from the reaction of oleic acid with glycerol by esterification method [14].

The challenge of this work is to develop a simple one-pot surfactant assisted-microwave route in aqueous media to fabricate fine $CoFe_2O_4$ magnetic nano-particles by using glycerol mono-oleat as surfactant. The surfactant-assisted method is very attractive for its versatility, since it has been shown to be suitable to prepare high quality $CoFe_2O_4$ nano-crystals.

In this work, glycerol mono-oleate (GMO) was produced by direct esterification reaction with amberlyst 16 resin catalyst with the efficiency of 89% and then used for synthesis of $CoFe_2O_4$ nano-particles with simple microwave route. Characterization of nano-particles showed the high crystallinity and good average size by using the GMO as surfactant.

2. EXPERIMENTAL

2.1. Material and methods

Analytical grade of iron (III) nitrate nona-hydrate ($Fe(NO_3)_3.9H_2O$, Merck 99-101%), cobalt nitrate hexa-hydrate ($Co(NO_3)_2.6H_2O$, Merck 99%), urea ($(CO(NH_2)_2$), Merck 99%), and synthesized GMO, ($C_{21}H_{40}O_4$), special-grade of oleic acid ($C_{18}H_{32}O_4$, Merck 88%), and glycerol ($C_3H_8O_3$, Merck 99%), used without purification. Amberlyst 16 resin (Fluka, France) a nominal particle size of about 700 μm in the proton form was used as the cation-exchange resin catalyst.

2.2. Procedure of GMO synthesis

Glycerol mono-oleate (GMO) was synthesized using sacrificial-core technique. Oleic acid (16 mmol) and amberlyst resin-16 (1.6 g) were poured into the multi neck round bottom flask and placed at water bath with the temperature of 70°C for 15 minutes with the stirring speed of 600 rpm. Stirring was carried out for completion of the reaction of acid adsorption on the catalyst. Glycerol was then added to this solution and stirring was continued for 8 hours until a yellow compound solution was obtained.

2.3. Procedure of $CoFe_2O_4$ preparation

$CoFe_2O_4$ were synthesized using the synthetic GMO as a surfactant. Appropriate amounts of $Fe(NO_3)_3.9H_2O$, $Co(NO_3)_2.6H_2O$ and urea, were first dissolved in a minimum amount of deionized water in molar ratio of 1: 2: 3. Ammonia solution was added to the solution to adjust pH about 7. Then 0.3 mM of GMO added to the solution. During this procedure, the mixture was continuously stirred using a magnetic agitator and then heated at 60°C for 3 hours and continued to heat to gel the sample. Then, the gel mixture was put into a microwave worked at 2.45 GHz and a fixed power level of 500 Watts. After solution reached the point of spontaneous combustion, it began burning and released great amount of heat, vaporized all the remaining water and became a solid burning at the high temperature. Nano powders were calcined in 600°C in electrical furnace for 2 hours.

2.4. Characterization process and instruments

GC-MS analysis was performed with a Varian, cp3800. The chromatographic separation was performed using a VF-5 ms column of 30 m×0.25 mm×0.25 μm with helium as mobile phase 1 mL per min flow. The initial temperature was 50°C, with an increase of 15°C per min up to 180°C (ramp1), 7°C per min up to 280°C (ramp 2), and 10°C per min up to 350°C. The injection port temperature was 280°C, the injection volume was 2μL, and n-heptane used as solvent.

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 characterization 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

GC/MS Figure 1 show that no significant amount of other phases appears in the procedure mixture. Two peaks named from library β-glycerol mono-oleat and glycerol di-oleat.

The crystallographic phase of the samples has been examined from the X-ray diffraction (XRD) spectrum. The spectrum of each sample was recorded by using Cu Kα. Average crystallite sizes can be estimated from the full-width at half-maximum (FWHM) of the strongest diffraction peak using Scherer's formula:

$$d = 0.9\lambda / \beta\cos\theta$$

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 phase and purity of nano-powders were determined from the XRD patterns shown in Figure 2. Well-defined sharp peak indicate the good crystalline quality and confirm the formation of spinel magnetic ferrite and several peaks which were attributed to α-Fe_2O_3 sub-phase. The impurity phase was probably due to the occurrence of local combustion. The diffraction peaks appeared in the XRD patterns can be indexed with the standard patterns of $CoFe_2O_4$ (JCPDS No. 22-1086).

Figure 3 shows the SEM images of cobalt ferrite nano-particles. According to images, synthesis of $CoFe_2O_4$ in presence of GMO leads to formation of particles with spherical shape and agglomeration. Results clearly shows that in the presence of surfactant, surface tension of solution is reduced and this facilitates nucleation Formation of reverse micelles in gel can be effective in controlling the particles growth and the distance between particles.

The characteristic of some atoms and groups of

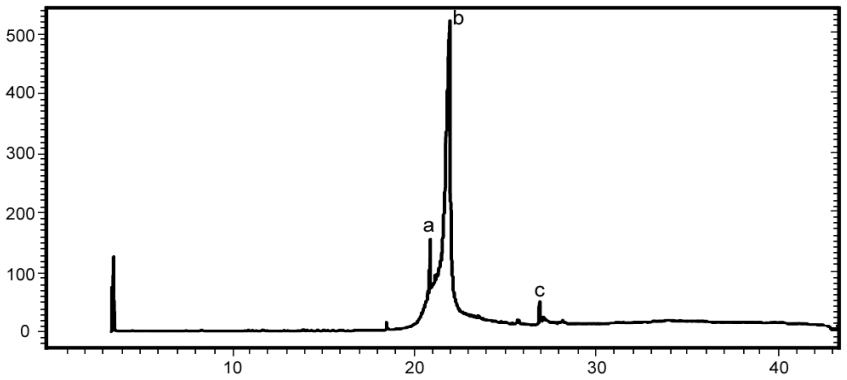

Figure 1: *GC spectrum of products a) glycerol monooleat, b) β-glycerol monooleat and c) glycerol dioleat.*

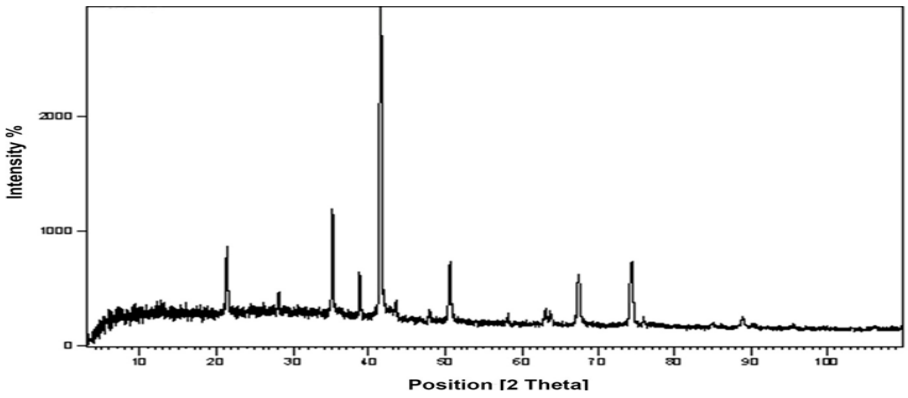

Figure 2: *X-ray diffraction pattern of $CoFe_2O_4$ synthesis in present of GMO as a surfactant.*

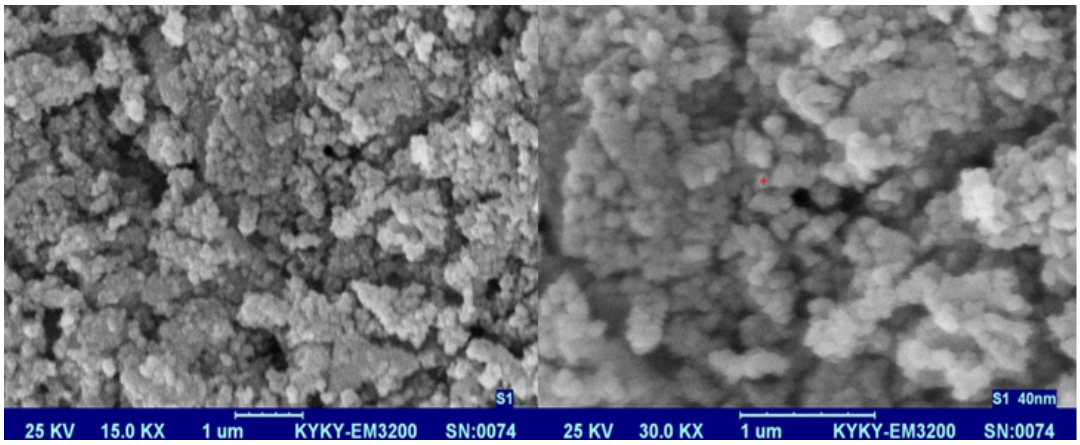

Figure 3: *SEM imagining of $CoFe_2O_4$ nanoparticles synthesized with GMO as surfactant.*

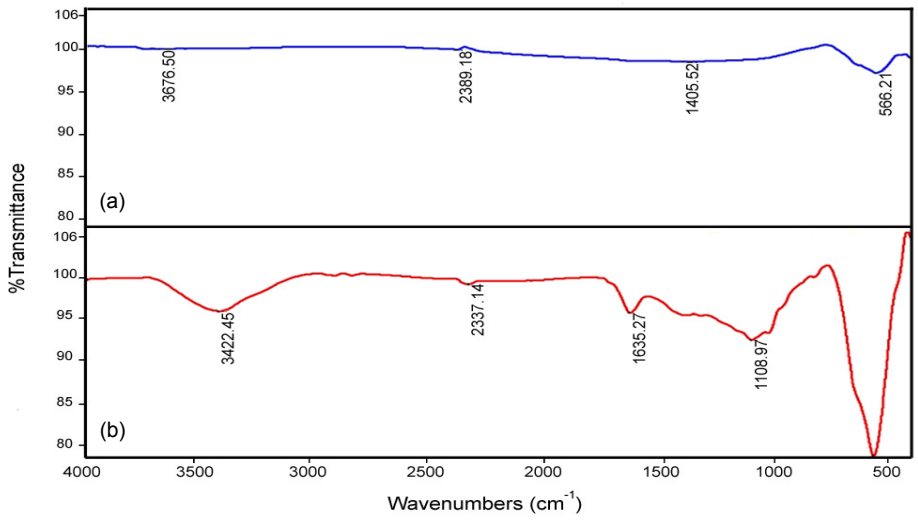

Figure 4: *FTIR spectrum of $CoFe_2O_4$ nanoparticles (a) without and (b) with calcination.*

atoms, as regarding the chemical bonds, are evident by FTIR spectrometry in Figure 4 (a and b). FTIR spectrum of cobalt ferrite which was prepared without calcination (Figure 4a) has a broad band in the region 1638.55 cm^{-1} which was demonstrated the H-O-H bending vibration of the absorbed water due to washing and drying of powders with deionized water and ethanol. While the spectrum of sample which was obtained after heat-treatment (Figure 4b) shows the weak band about 1633.69 cm^{-1} lead to formation of H-O-H bending vibration. Also the peaks in 3411.76 and 3414.43 cm^{-1} have been assigned to asymmetric and symmetric OH stretching vibration of lattice water. Compare these results clearly confirmed that calcination is efficient in removing absorbed water from nano-powders.

4. CONCLUSIONS

Glycerol mono-oleate (GMO) was produced by direct esterification reaction with the efficiency of 86%. GC/MS analysis showed that this is an ideal method for preparing the GMO. Results demonstrated successfully synthesize of $CoFe_2O_4$ nano-particle. The average particle size and percent crystallinity was 37.19 nm and 47.34%, respectively.

REFERENCES

1. Wang W.W., *Mater. Chem. Phys.*, **108**(2008), 227-231.
2. Ayyappan S., Mahadevan S., Chandramohan P., Srinivasan M.P., Philip J., Raj B., *J. Phys. Chem. C*, **114**(2010), 6334-6341.
3. Liu C.J., Rondinone A., John Zhang Z., *Pure Appl. Chem.*, **72**(2000), 37-45.
4. Olsson T.R., Salazar-Alvarez G., Hedenqvist M.S., Gedde U.W., Lindberg F., Savage S., *J. Chem. Mater.*,**17**(2005), 5109-5118.
5. C.S.S.R. Kumar, J. Hormes, C. Leuschner, Eds., 2005. *Nanofabrication towards biomedical applications: Technique, Applications, and Impact.* Wiley-VCH.
6. Joshi H.M., Po Lin Y., Aslam M., Prasad P.V., Chultz-Sikma E.A., Edelman R., Meade T., Dravid V.P., *J. Phys. Chem. C*, **113**(2009), 17761-17767.
7. Terreno E., Castelli D.D., Viale A., Aime S., *Chem. Rev.*, **110**(2010), 3019-3042.
8. Xiao S.H., Jiang W.F., Li L.Y., Li X.J., *Materials Chemistry and Physics*, **106**(2007), 82-87.
9. Rajath Varma P.C., Manna R.S., Banerjee D., Varma M.R., Suresh K.G., Nigam A.K., *J. Alloy .Compd.*, **453**(2008), 298-303.
10. Musat V., Potecasu O., Belea R., Alexandru P., *Mater. Sci. Eng. B-Solid.*, **167**(2010), 85-90.
11. Liu Y.C., Fu Y.P., *Ceram. Int.*, **36**(2010), 1597-1601.
12. Vilar S.Y., Andujar M.S., Gomez-Aguirre C., Mira J., Senaris-Rodriguez M.A., Castro-Garcs., *J. Solid State Chem.*, **182**(2009), 2685-2690.
13. Bucko M., Haberko K., *J. Eur. Ceram. Soc.*, **27**(2007), 723-727.
14. S. Tursiloadi, 2007. *Pemanfaatan hasil samping industri biodiesel dan industri ethanol serta peluang pengembangan industri integratednya*, Jakarta, Indonesian.