J. Nanostruct., 6(2): 121-126, Spring 2016
DOI: 10.7508/jns.2016.02.003

ORIGINAL RESEARCH PAPER

Effects of Capping Agent and Surfactant on the Morphology and Size of $CoFe_2O_4$ Nanostructures and Photocatalyst Properties

*Mazyar Ahmadi Golsefidi *, Farhad Yazarlou, Mehran Naeimi Nezamabad, B. Naeimi Nezamabad, M. Karimi*

Department of chemistry, Faculty of sciences, Gorgan branch, Islamic azad university, Gorgan, Iran

ARTICLE INFO.

Received 08/01/2016
Accepted 02/03/2016
Published online 01/04/2016

KEYWORDS
$CoFe_2O_4$
Electron microscopy
Hydrothermal
Photocatalytic degradation

ABSTRACT

In this work firstly $CoFe_2O_4$ nanoparticles were synthesized via a hydrothermal method. The temperature, surfactant and capping agent effects on the size of $CoFe_2O_4$ nanoparticles were investigated. 2-hydroxyacetophenone used as a good capping agent to produce cubic-like nanostructure. When SDBS used as surfactant, particles had spherical morphology. Nanoparticle was studied by scanning electron microscopy, X-ray diffraction, and Fourier transform infrared. We found that the $CoFe_2O_4$ nanoparticles were prepared exhibit a ferromagnetic behavior with a saturation magnetization of 20emu/g and a coercivity of 250 Oe. The photocatalytic behavior of $CoFe_2O_4$ was studied by the degradation of a methylene blue aqueous solution under ultraviolet light irradiation.

How to cite this article
Ahmadi Golsefidi M, Yazarlou F, Naeimi Nezamabad M, Naeimi Nezamabad B, Karimi M. Effects of Capping Agent and Surfactant on the Morphology and Size of $CoFe_2O_4$ Nanostructures and Photocatalyst Properties. J. Nanostruct.,2016; 6(1): 121-126. DOI: 10.7508/jns.2016.02.003

INTRODUCTION

Spinel ferrite has been widely used in many fields, such as message recording, microwave absorber [1], biology, medicine, magnetic sensors [2], magnetic drug delivery[3] and ferrofluids [4]. In the last few decades, Spinel ferrite nanoparticles have been the subject of much interest due to their unusual optical, electronic and magnetic properties, fine mechanical and chemical stability. Magnetic properties of nanoparticles is interesting research activity driven by a fundamental interest in the novel physical properties of the nanoscale system.

$CoFe_2O_4$ has received special attention because of its chemical stability, large magnet astrictive coefficient, mechanical hardness high coercivity, moderate saturation magnetization, and large magneto-crystalline anisotropy [5]. The magnetic properties are dependent to the particle size [6-8]. The energy of a magnetic particle was overall associated on the uniaxial anisotropy, magnetization direction, and easy axis aligned with the direction of external field. $CoFe_2O_4$ is a hard magnetic material with high coercivity and suitable magnetization. These characteristics, along with their tremendous physical and chemical stability, make $CoFe_2O_4$ nanoparticles suitable for applications such as high-density digital recording disks, and lithium batteries [9].

There are many procedures for the produce of nanoparticles, inclusive: hydrothermal, solvothermal, reverse micelle methods, sol-gel and sonochemical approach. A lot of methods for preparing nanosized cobalt ferrite have been presented. Zhang *et al.* [10]

*Corresponding author Email address: *mahmadig@gmail.com*

reported the nanoparticles of 2–35 nm in diameter which were prepared in normal micelle Similarly with the method of Pileni et al. Pileni et al. used oil-in-water micelle to prepare size-controlled Co-ferrite in the range of 2–5 nm [11]. Shah [12] and Ahn [13] used water-in-oil microemulsion to obtain the nanoparticles in the diameter of 50 and 4.9 nm, respectively. Properties of cobalt ferrite acutely depend on the preparation way [14]. Most recently, Co-ferrite nanocrystals have been prepared using various methods, such as chemical coprecipitation, method, combustion method, reverse micelle methods, solvothermal method and hydrothermal method. Amongst these Procedures, hydrothermal has been known as one of the accessible methods for synthesis of different nanoparticles.

In this work were investigated the surfactant and capping agent effects on the size and morphology of $CoFe_2O_4$ nanoparticles prepared by hydrothermal method. 2-hydroxyacetophenone used as a good capping agent to produce uniform cubic-like nanostructure. But when SDBS used as surfactant, particles had spherical morphology.

MATERIALS AND METHODS

$Fe(NO_3)_3.9H_2O$, Co $(acac)_2$.2H2O, ethanol and 2-hydroxyacetophenone were purchased from Merck and used without purification. Sodium dodecyl-benzenesulfonate (SDBS) as surfactant and NaOH for adjust pH and de-ionized water was used as solvent. XRD patterns were recorded by a Philips, X-ray diffractometer using Ni-filtered Cu Kα radiation. SEM images were obtained using a LEO instrument model 1455VP. Prior to taking images, the samples were coated by a very thin layer of Pt (using a BAL-TEC SCD 005 sputter coater) to make the sample surface conductor and prevent charge accumulation, and obtaining a better contrast. FT Infrared (FT-IR) spectra were obtained as potassium bromide pellets in the range of 400-4000 cm^{-1} with a Nicolet-Impact 400D spectrophotometer. The magnetic measurement was performed in a vibrating sample magnetometer (VSM) (BHV-55, Riken, Japan) at room temperature. The UV-vis spectra of the samples were taken on a UV-vis spectrophotometer (Shimadzu, UV-2550, Japan) + visible sources of 400 W Osram lamps.

Synthesis of $CoFe_2O_4$

The $CoFe_2O_4$ nanoparticles were synthesized using $Fe(NO_3)_3.9H_2O$, Co $(acac)_2$.2H2O, NaOH and de-ionized water as solvents. In a usual method, 0.32 g of $Fe(NO_3)_3.9H_2O$ and 0.1g Co $(acac)_2.2H_2O$ individually dissolved in 30 ml of de-ionized water and then two solutions are mixed on magnetic stirrer to achieved a homogeneous solution. Then we added NaOH to adjust pH solution (10-11). The obtained solution was stirred on stirring for 30 minutes. For investigation capping agent and surfactant functions, two solutions containing SDBS and 2-hydroxyaceto-phenone were added to above solution separately; in one beaker 0.1 ml 2-hydroxyacetophenone was added to the solution dropwise. In next beaker 0.07g SDBS dissolved in 50 ml methanol and added to the mixture. The achieved mixtures were stirred on the magnetic stirrer for 60 minutes. Finally the mixtures were heated in two autoclaves for 10 h at 160 °C separately and formed precipitates were washed with double distilled water and ethanol and were dried at 60 °C for 5 h.

Photocatalytic measurements

40 ml of the dye solution (10 ppm) was applied as a typical pollutant to determine the photocatalytic activity. 0.03 g catalyst was used for degradation of 40 ml solution. The solution was mixed by a magnet stirrer for 60 minutes in darkness to determine the adsorption of the dye by catalyst and better availability of the surface. Reaction carried out under the UV lamp irradiation, the mixture was placed inside the photoreactor in which the vessel was 40 cm away from the UV source of 400 W Mercury lamps. After each 10 minutes, sampling (about 10 ml) was performed and was centrifuged to separate the solid particles and after centrifuging, they were analyzed with the UV–Vis spectrometer.

RESULTS AND DISCUSSION

The $CoFe_2O_4$ nanoparticles were investigated by X-ray powder diffraction (XRD). Fig. 1 shows XRD patterns for $CoFe_2O_4$ nanoparticle was synthesized by hydrothermal procedure and calcinated at 550 °C for 3 hours when the Co precursor is Co $(acac)_2.2H_2O$ and Fe precursor was $Fe(NO_3)_3.9H_2O$. As shown in XRD pattern, the synthesized matter has crystal structure of $CoFe_2O_4$ (JCPDS card no. 01-1121) and according to XRD pattern, the synthesized product is quite pure the average crystal size was calculated by using the Debye-Scherrer equation:

$$D_{\mathrm{XRD}} = \frac{k.\lambda}{\beta.cos\theta} \quad (1)$$

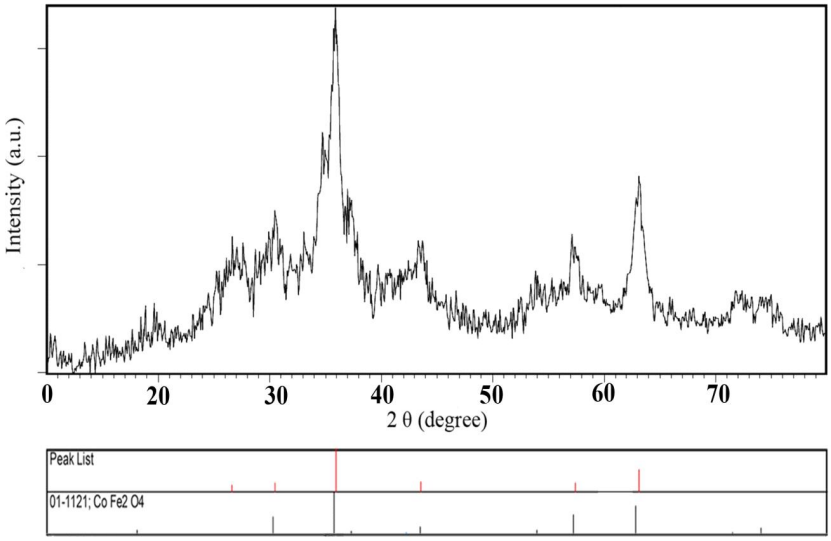

Fig. 1. XRD patterns for $CoFe_2O_4$ synthesized by hydrothermal method.

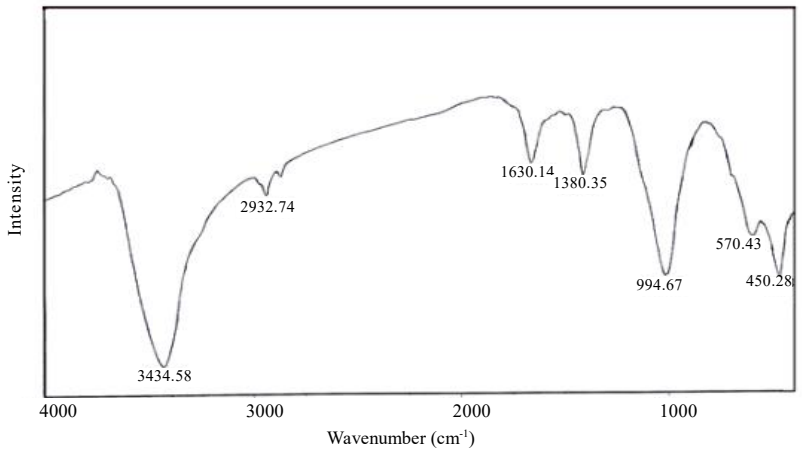

Fig. 2. IR spectrum for $CoFe_2O_4$ synthesized by hydrothermal method

Where D_{XRD} is the average crystallite diameter, k is a constant equal to 0.9, β is the full-width at half-maximal, λ is the wavelength of the X-ray used and θ is the diffraction angle. It is found that the average crystallite diameter of $CoFe_2O_4$ nanoparticle was calculated to be 15 nm at the temperature of 500 °C.

FT-IR spectrum demonstrates peaks at 1630 and 3434 cm^{-1} were related to the stretching vibrations of surface hydroxyl groups. The broad absorption at around 570 and 450 cm^{-1} were the stretching of Me-O, which is typical for $CoFe_2O_4$ molecules [15, 16](Fig. 2). Adsorbed water is featured by the band at 1380 cm^{-1}.

The scanning electron microscopy (SEM) images of $CoFe_2O_4$ nanoparticle at surfactant and capping agent was taken and used for synthesis condition optimization, therefore effect of surfactant and capping agent on the particle size and morphology was investigated. Here, we use the SDBS and 2-hydroxyacetophenone as surfactant and capping agent respectively. As shown in SEM photographs, when we use of SDS particles has spherical morphology (Fig. 3), but when we use the 2-hydroxyacetophenone, it is clear that the obtained nanoparticles are cubic-like (Fig. 4).

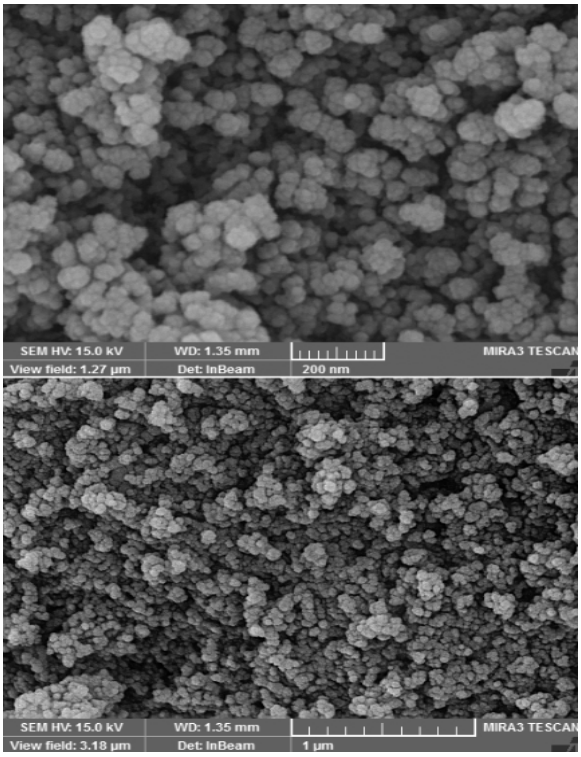

Fig. 3. SEM images of $CoFe_2O_4$ stabilized by SDBS

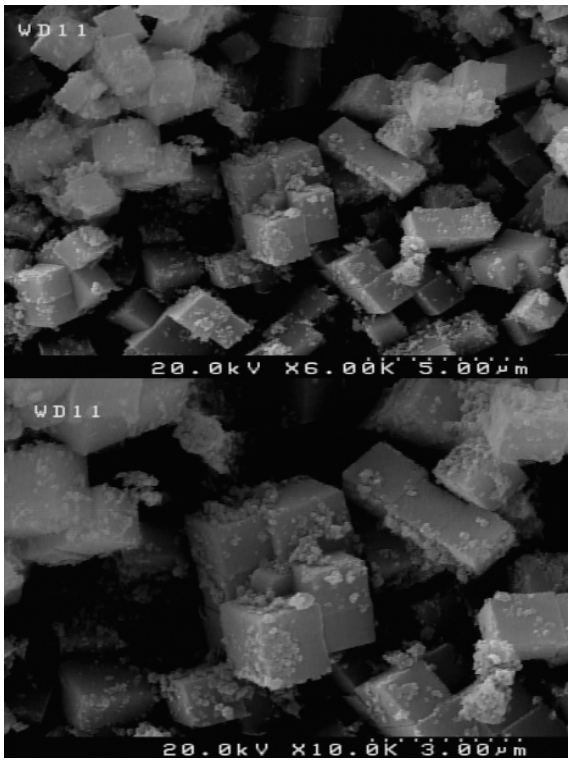

Fig. 4. SEM images of $CoFe_2O_4$ stabilized by 2-hydroxyacetophenone.

For investigation magnetization treatment of the $CoFe_2O_4$ nanoparticles Hysteresis loops were mentioned in magnetic curve (Fig. 5). Results indicate that $CoFe_2O_4$ nanoparticles synthesized show ferromagnetic behavior and have a saturation magnetization of 20 emu/g which is smaller than the bulk value (74.08 emu/g) [17, 18] and a coercivity of 250 Oersted.

Fig. 6 illustrate UV–Vis spectrum Diffuse Reflectance spectroscopy (DRS) for $CoFe_2O_4$. Band-gap of $CoFe_2O_4$ nanoparticle was estimated by Tauc's equation using the absorption data $\alpha = \alpha_0 (h\nu - Eg)^n / h\nu$ where α is absorption coefficient, α_0 and h are the constants, hν is the photon energy, Eg is the optical band gap of the material, and n depends on the type of electronic transition and can have any value between 0.5 to 3 eV. The cubic-shape nanoparticles of $CoFe_2O_4$ have the strong band edge absorption in the wavelength region of < 700 nm as illustrated in Fig. 7. The direct (allowed) energy gap (*Eg*) of the sample was distinguished by extrapolating the linear portion of the plots of $(ahn)^2$ *vs*. *h*n to the energy axis (2 eV). The nanoparticles are

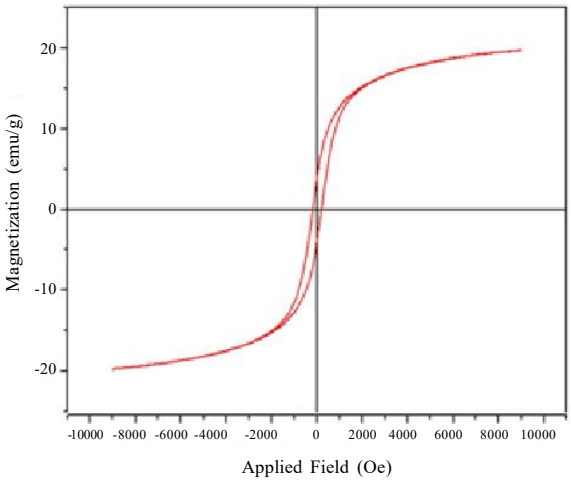

Fig. 5. Room temperature hysteresis loops of $CoFe_2O_4$ nanoparticles

photoresponsive in the UV ranges, and as shown $CoFe_2O_4$ has absorption in the UV area. The first wavelength of absorption was used to calculate the optical band gap. Calculated band gap in onset (l)

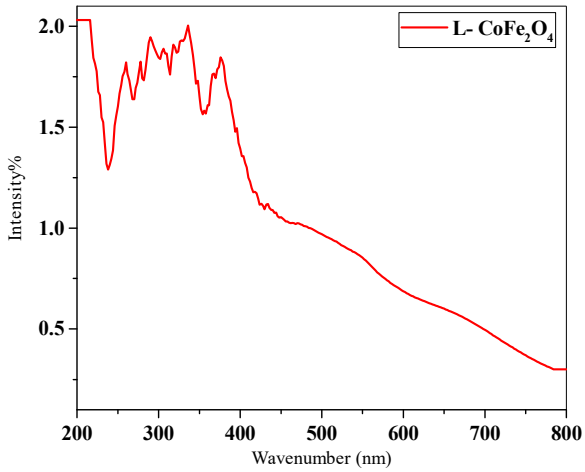

Fig. 6. UV–vis spectrum (DRS) for 2-hydroxyacetophenone -$CoFe_2O_4$ nanoparticle.

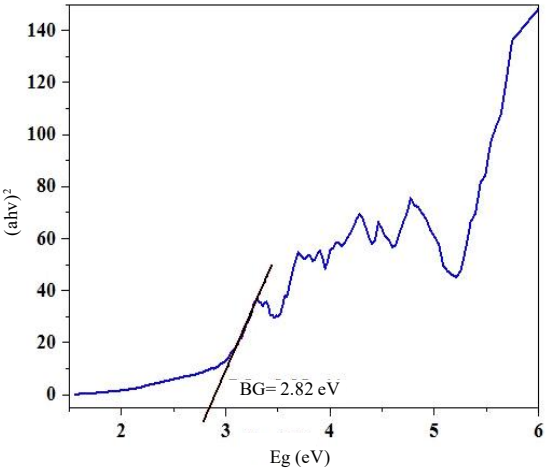

Fig. 7. The calculated band gap for 2-hydroxyacetophenone -$CoFe_2O_4$

for $CoFe_2O_4$ revealed that this nanostructure have good potential to acting as appropriate photocatalyst (Fig. 7).

The photo-catalytic activity of the $CoFe_2O_4$- 2-hydroxyacetophenone nanoparticle was evaluated by monitoring the degradation of methylene blue in an aqueous solution under irradiation with UV light. The methylene blue destruction percentage in time of t (DP (t)) was calculated as follows:

$$DP(t) = \frac{A_0 - A_t}{A_0} \times 100 \qquad (2)$$

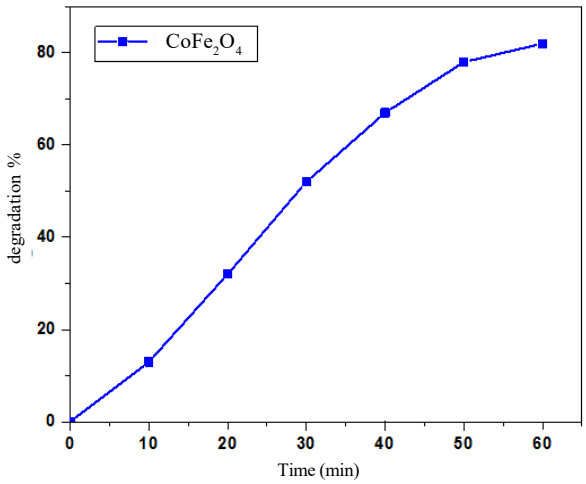

Fig. 8. Photodegradation of methylene blue by 2-hydroxyacetophenone- $CoFe_2O_4$ nanoparticle, inset: Methylene blue after 60 minutes photodegradation in the presence of 2-hydroxyacetophenone- $CoFe_2O_4$ nanoparticle

Where A_0 and A_t are the absorbance value of the solution at 0 and t minute, respectively. Dye was not depredated after 60 minutes in the absence of UV light and presence of nanostructured photocatalysts, so, the contribution of self-degradation was insignificant. The changes in the concentration of dye after 1 h under UV irradiation were illustrated in Fig. 8. By passing time, dye was adsorbed on the nanoparticles catalyst more and more and was degraded until the color of dye mixture solution was faded (inset of Fig. 8). Just after 45 minutes degradation percentage for $CoFe_2O_4$ was obtained 70%. Over time, the rate degradation decreased because of decrement of available dye molecules surrounds the catalyst nanoparticles. According to photocatalytic calculations by Eq. (2), the methylene blue degradation by $CoFe_2O_4$-2-hydroxyacetophenone nanoparticle was about 80%.

CONCLUSION

$CoFe_2O_4$ nanoparticle was prepared by hydrothermal method and characterized by XRD, SEM, DRS, VSM and IR techniques. The effects of surfactant and capping agent were investigated. In order to optimize morphology, after completing each step, SEM image were taken from the synthesized nanoparticles. $CoFe_2O_4$ synthesized by hydrothermal method studied for photocatalitic activity. Methylene blue was degraded by catalysts $CoFe_2O_4$. Previous

investigations proved that heterogeneous photocatalytic processes consists of diffusion, adsorption and reaction steps and suitable distribution of the pore will improve the diffusion of reactants, which increase the rate of photocatalytic reaction.

ACKNOWLEDGEMENT

The authors are grateful to University of Islamic Azad for providing financial support to undertake this work.

CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

REFERENCES

1. R.C. Che, L.M. Peng, X.F. Duan, Q. Chen, X.L. Liang. Microwave Absorption Enhancement and Complex Permittivity and Permeability of Fe Encapsulated within Carbon Nanotubes. Adv. Mater. 2004; 16 (5): 401-405.
2. N.E. Osman, N. Thapliyal, W. Alwan, R. Karpoormath, T. Moyo. Synthesis and characterization of Ba0.5Co0.5Fe2O4 nanoparticle ferrites: application as electrochemical sensor for ciprofloxacin. J Mater Sci: Mater Electron. 2015; 26 (7): 5097-5105.
3. C. Brazel. Magnetothermally-responsive nanomaterials: combining magnetic nanostructures and thermally-sensitive polymers for triggered drug release. Pharm Res. 2009; 26(3): 644-656
4. F. Tourinho, R. Franck, R. Massart. Aqueous ferrofluids based on manganese and cobalt ferrites. J Mater Sci. 1990; 25(7): 3249-3254.
5. G.A. El-Shobaky, A.M. Turky, N.Y. Mostafa, S.K. Mohamed. Effect of preparation conditions on physicochemical, surface and catalytic properties of cobalt ferrite prepared by coprecipitation. J Alloy Compd.2010; 493(2): 415-422.
6 J. Huo, M. Wei. Characterization and magnetic properties of nanocrystalline nickel ferrite synthesized by hydrothermal method. Mater Lett. 2009; 63(14): 1183-1184.
7. N. Li, M. Zheng, X. Chang, G. Ji, H. Lu, L. Xue, L. Pan, J. Cao. Preparation of magnetic CoFe2O4-functionalized graphene sheets via a facile hydrothermal method and their adsorption properties. J Solid State Chem. 2011; 184(4): 953-958.
8. G.B. Ji, S.L. Tang, S.K. Ren, F.M. Zhang, B.X. Gu, Y.W. Du. Simplified synthesis of single-crystalline magnetic CoFe2O4 nanorods by a surfactant-assisted hydrothermal process. J Cryst Growth. 2004; 270(2): 156-161.
9. Y.-Q. Chu, Z.-W. Fu, Q.-Z. Qin. Cobalt ferrite thin films as anode material for lithium ion batteries. Electrochim Acta. 2004; 49(27): 4915-4921.
10. C. Liu, B. Zou, A.J. Rondinone, Z.J. Zhang. Chemical Control of Superparamagnetic Properties of Magnesium and Cobalt Spinel Ferrite Nanoparticles through Atomic Level Magnetic Couplings. J Am Chem Soc. 2000; 122(26): 6263-6267.
11. N. Moumen, P. Veillet, M.P. Pileni. Controlled preparation of nanosize cobalt ferrite magnetic particles. J Magn Magn Mater. 1995; 149(2): 67-71.
12. V. Pillai, D.O. Shah. Synthesis of high-coercivity cobalt ferrite particles using water-in-oil microemulsions. J Magn Magn Mater. 1996; 163 (2): 243-248.
13. Y. Ahn, E.J. Choi, S. Kim, H.N. Ok. Magnetization and Mössbauer study of cobalt ferrite particles from nanophase cobalt iron carbonate. Mater Lett. 2001; 50 (1), 47-52.
14. D. Peddis, C. Cannas, A. Musinu, A. Ardu, F. Orrù, D. Fiorani, S. Laureti, D. Rinaldi, G. Muscas, G. Concas, G. Piccaluga. Beyond the Effect of Particle Size: Influence of CoFe2O4 Nanoparticle Arrangements on Magnetic Properties. Chem Mater. 2013; 25(10): 2005-2013.
15. A. Abbasi, H. Khojasteh, M. Hamadanian, M. Salavati-Niasari. Synthesis of CoFe2O4 nanoparticles and investigation of the temperature, surfactant, capping agent and time effects on the size and magnetic properties. J Mater Sci: Mater Electron. (2016); 27 (5): 4972-4980.
16. B. Gillot, F. Jemmali, A. Rousset. Infrared studies on the behavior in oxygen of cobalt-substituted magnetites: Comparison with zinc-substituted magnetites. J Solid State Chem. 1983; 50 (2), 138-145.
17. M.P. Gonzalez-Sandoval, A.M. Beesley, M. Miki-Yoshida, L. Fuentes-Cobas, J.A. Matutes Aquino. Comparative study of the microstructural and magnetic properties of spinel ferrites obtained by co-precipitation. J Alloy Compd. 2004; 369 (2), 190-194.
18. Z. Jia, D. Ren, R. Zhu. Synthesis, characterization and magnetic properties of CoFe2O4 nanorods. Mater Lett. 2012; 66 (1): 128-131.