CHARACTERIZATION OF COFe$_2$O$_4$ NANOPARTICLES SYNTHESIZED BY CO-PRECIPITATION AND HYDROTHERMAL METHOD

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TÓM TẮT

CÁC ĐẶC TRƯNG VẬT LIỆU NANO CoFe$_2$O$_4$ TỔNG HỢP BẰNG PHƯƠNG PHÁP ĐỒNG KẾT TỦA VÀ PHƯƠNG PHÁP THỦY NHIỆT

CoFe$_2$O$_4$ là một vật liệu có rất nhiều ứng dụng trong các lĩnh vực công nghệ điện từ và gần đây cugnx rất được quan tâm trong lĩnh vực y sinh. Nano CoFe$_2$O$_4$ (CFO NPs) được nghiên tổng hợp theo hai phương pháp: Thủy nhiệt và đồng kết tủa. Trong đó, phương pháp thủy nhiệt đã đánh giá ảnh hưởng của nồng độ dung dịch kiềm, thời gian và nhiệt độ thủy nhiệt đến đặc trưng của CFO NPs thu được. Phương pháp đồng kết tủa cũng đã đánh giá ảnh hưởng của nồng độ dung dịch kiềm, nhiệt độ phản ứng, xử lý nhiệt sản phẩm. Các sản phẩm thu được đã được đặc trưng bằng các phương pháp nhiễu xạ tia X (XRD), chụp ảnh độ phân giải cao hình thái học bề mặt (SEM), phổ hồng ngoại (IR) và phân tích đường cong từ trễ M-H (VSM). Kết quả nghiên cứu XRD và SEM cho thấy: CFO NPs thu được là các sản phẩm sạch, có cấu trúc spinel, kích thước nano từ khoảng 6 đến 60 nm tùy thuộc điều kiện tổng hợp. Phổ IR chỉ ra rằng CFO NPs tổng hợp bằng phương pháp thủy nhiệt có cấu trúc tetrahedral (A) còn CFO NPs tổng hợp bằng phương pháp đồng kết tủa tồn tại đồng thời ở hai cấu trúc tetrahedral (A) và octahedral (B) nhưng khi nung lên 600^{o}C thì cũng chuyển dần sang cấu trúc tetrahedral (A). Đặc tính từ của vật liệu cũng phụ thuộc kích thước hạt và cấu trúc tinh thể.

***Từ khóa**: CoFe$_2$O$_4$, phương pháp thủy nhiệt, phương pháp đồng kết tủa.*

1. INTRODUCTION

CFO NPs has been known as chemical stability, mechanical hardness, high Curie temperature [1], strong magnetocrystalline anisotropy ($K_1 \approx 2\times10^6$ erg/cm^3), moderature saturation magnetization (80 emu/g) [2], high coercivity and large magnetostrictive coefficient [3]. So that, CFO NPs suitable for many applications: magnetic recording devices such as audio or video tapes [4], biomedical application as sensors, resonance imaging, magnetically guided drug delivery, and magnetic hyperthermia [3], [5] , energy storage fields [6], catalyst [7], antibacterial [8], …. These characteristic make CFO NPs becomes an attractive material for researchers and manufactures in recent years.

CFO NPs has synthesized by some common way as: co-precipitation, hydrothermal methods or sol-gel (combustion) [4], [6], [8], solvothermal [1] at many conditions. For example: co-precipitation Fe^{3+} and Co^{2+} by NaOH 3M for 9 hours under vigorous stirring with a magnetic stirrer under N$_2$ atmosphere and then stirred strongly for 8 hours at 80^{o}C, washed, dried and calcined at 600^{o}C for 2 hours [9]; or C.H. China et al [10] co-precipitate solution of Co^{2+} and Fe^{3+} by NaOH solution at different temperatures (40, 60, 80, 100^{o}C) for 1 hours, the as-prepare CFO are calcined at different temperatures (300, 450, 600, 750, 900, 1200^{o}C) for 12 hours. With Hydrothermal method, Le The Tam et al [9] used 3M NaOH solution reacted with solution of Fe^{3+} and Co^{2+} for 9 hours at room temperature and then transferred into a teflon-lined stainless steel autoclave and treated at 180ºC for 15 hours; Or Kinjal Gandha[11] treated as-prepare CFO at 200ºC for 10 hours; N S Gajbhiye [12] treated as-prepare CFO at 150ºC for 15 hours,…

The particle size, morphology and magnetic properties of CFO depend on the synthesized method. In this paper, we report the synthesis of CFO NPs by co-precipitation method and hydrothermal method at different concentration of sodium hydroxide and treatment temperatures to control size particles and magnetic properties by simple way.

2. MATERIAL AND METHODS

2.1. Materials

In this report, all the materials used were of analytical grade and used without further purification. cobalt nitrate hexahydrate ($Co(NO_3)_2.6H_2O$), ferric nitrate nonahydrate ($Fe(NO_3)_3.9H_2O$), sodium hydroxide (NaOH) were purchased from Regenta (Hangzhou, China). Double distilled water was used as a solvent

2.2. Synthesis of CFO NPs by hydrothermal method

Equal quantities of Iron nitrate $Fe(NO_3)_3·9H_2O$ and Cobalt nitrate $Co(NO_3)_2·6H_2O$ were dissolved in 20 ml of double distilled water for 10 minutes by magnetic stirring, and then drop into 50 ml of the xM NaOH solution with stirred vigorously for another 10 minutes. The mixture was then poured into a Teflon lined stainless steel autoclave of 100 ml capacity. The autoclave was placed in an electric oven at a temperature of t°C for a specified time (T h) without any stirring. After that, the autoclave was cooled naturally to room temperature. The black precipitates were washed by distilled water until neutralization with assistant of a magnet. The precipitates were then dried at 70°C over the night to obtain the powder.

2.3. Synthesis of CFO NPs by co-precipitation method

Stoichiometric amounts of cobalt nitrate hexahydrate $Co(NO_3)_2.6H_2O$ and iron nitrate nonahydrate $Fe(NO_3)_3.9H_2O$ were dissolved in 20 ml double distilled water by magnetic stirring, and then drop into 50 ml of the xM NaOH solution at room temperatures or 80ºC with stirred vigorously for another 60 minutes. After cooling to room temperature, the precipitate was then washed by distilled water until neutralization with assistant of a magnet. Finally, the sample was dried at 70°C over the night to obtain the powder. A part of powders were calcined at t˚C for 1 hours.

The condition of synthesized process and sample symbol are summarized Table 1.

Table 1. Material synthesized conditions and samples symbols

Co-precipitation method				
Nº	C_M (NaOH)	T_R (ºC)	Calcined temperature (ºC)	Symbol
1	1M	25		1M25
2	3M			3M25
3	5M			5M25
4	1M	80		1M80
5	3M			3M80
6	5M			5M80
7	1M	25	450	1M25-450
8	1M		600	1M25-600
9	1M	80	450	1M80-450
10	1M		600	1M80-600

Hydrothermal method				
Nº	C_M (NaOH)	Reaction time (h)	T_R (ºC)	Symbol
11	5M	5h	200	5M5h 200
12			180	5M5h 180
13			160	5M5h 160
14	4M	5h	160	4M5h 160
15	4M	4h		4M4h 160
16	3M			3M4h 160
17	1M			1M4h 160
18	1M	2h		1M2h 160

$C_{M(NaOH)}$: concentration of NaOH solution; T_R: Reaction temperature

2.4. Characterization

The phase identification of the sample was performed by powder X-ray diffraction (XRD) using a Bruker AXS diffractometer with Cu-Kα radiation (λ=1.5406 Å) at 45 kV and 40 mA. The FT-IR spectra were recorded with an J∧sco FT/IR-4600 using KBr plate at room temperature in the range 4000-400cm^{-1} with a scanning rate of 4cm^{-1}/min to identify the presence of functional groups of ZnO-NPs. Particle size and shape were analyzed using a field emission scanning electron microscopy FESEM (Hitachi S-4800). Hysteresis loops were measured at room temperature to the highest field of 11 kOe using a vibrating sample magnetometer (VSM) option at room temperature.

3. RESULT AND DISSCUCSION

3.1. X-ray Diffraction Analysis

The XRD patterns of $CoFe_2O_4$ samples prepared by using hydrothermal and co-precipitation methods are shown in Fig. 1. The XRD data indicate that all the samples are single phase with no trace of any secondary phase of impurities; the diffraction peaks could be indexed to the expected crystal structure of inverse spinel cubic with the XRD pattern of standard CFO (ICDD card No: 22-1086).

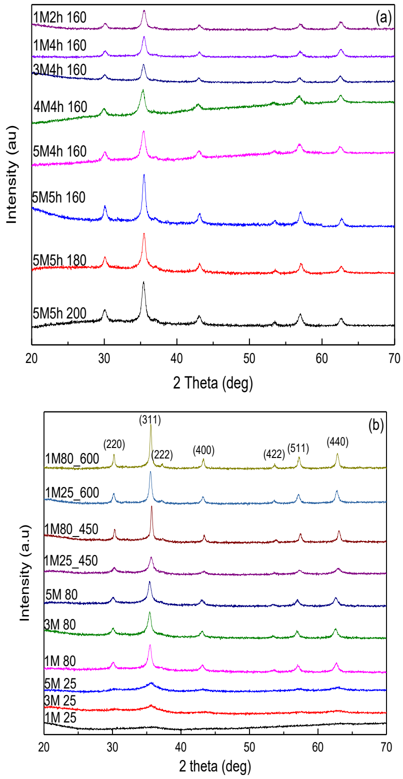


Fig. 1. XRD patterns of CFO samples prepared by using hydrothermal (a) and co-precipitation methods (b)

With hydrothermal method, the Fig.1a shown that: at the same alkaline concentration and hydrothermal time (5M5h), the temperature rise from 160 to 200°C, the intensity (I) of the peak slightly decreased, the peak width slightly increase, it mean the size particles decrease. At the same temperature, 160°C, the hydrothermal time reduced from 5 h to 4 h (5 M alkaline solution) or 4 h to 2 h (1 M alkaline solution), the intensity of peak significantly reduced, the peak width increase, demonstrated the degree of the crystallization decreases, the particle size decrease. As the hydrothermal condition was kept at 160°C for 4h, the alkalne concentration dcreased from 5 M to 1 M, the intensity peak decreased but not significantly, the peak width is almost unchanged, it demonstrate that the concentration of alkaline solution does not significantly affect the degree of crystallization and particle size in CFO synthesis by hydrothermal method. With co-precipitation method, the Fig. 1b shows: as the reaction occurs at the room temperature, the degree of crystallization is very poor. As the reaction occurs at 80°C, the intensity of peak sharply increased, the difference in concentration of alkaline solution (1 M, 3 M, 5 M) did not show any noticeable change in the XRD pattern. Samples 1M25 and 1M80 were heated to 450 or 600°C for 1h, the increasing of peak intensity (I) and the decreasing of peak width are both significant compared with 1M25 and 1M80 samples, the degree of crystallization of 1M-450 and 1M-600 is higher than 1M25_450 and 1M25_600 respectively.

The crystallite size D of the samples was calculated from the data of peak at 2θ ~ 35.5° with Miller indices by (311), using Scherrer equation, and show in Table 2:

$$d_{XRD} = \frac{0.89\lambda}{\beta\cos\theta} \qquad (1)$$

where d is the grain diameter, β is half intensity width of the relevant diffraction, λ is Xray wavelength and θ is the diffraction angle.

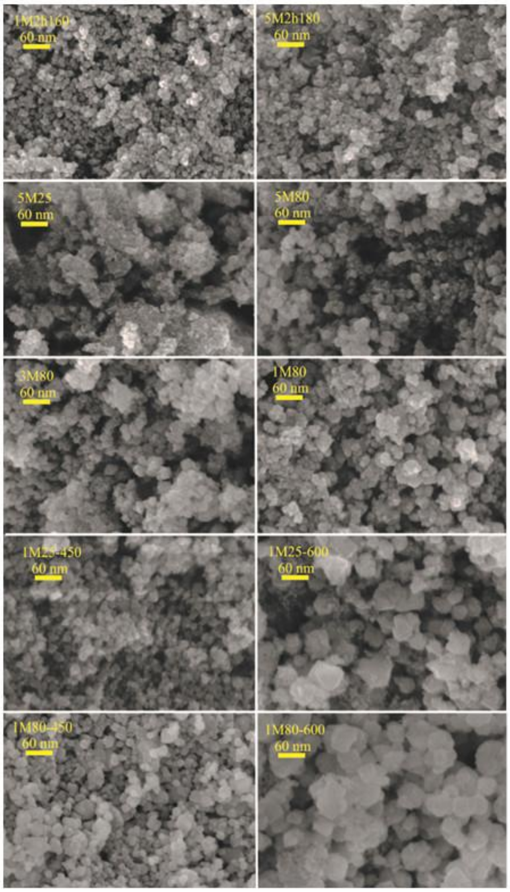
Table 2. Particles size of the $CoFe_2O_4$ NPs samples calculated from XRD pattern and SEM image

Sample	**d_{XRD} (nm)**	**d_{SEM} (nm)**
5M5h 200	13.95	
5M5h 180	14.68	
5M5h 160	15.32	14.22
5M4h 160	12.15	
4M4h 160	11.36	
3M4h 160	13.05	
1M4h 160	12.52	
1M2h 160	10.05	9.66
5M25		6.61
1M80	19.34	18.07
3M80	18.73	19.57
5M80	18.28	21.05
1M25-450	21.06	22.12
1M80-450	25.37	26.75
1M25-600	41.46	47.28
1M80-600	51.64	57.54

We can concluded that, the CFO crystal formation by hydrothermal and co-precipitation methods is quite simple, it is easy to obtain the clean sample, the particle size can be controlled through the process temperature or time, and it is not necessary to use a high concentration NaOH solution.

3.2. Morphology characterizations

Fig. 2 show the FESEM images of the CFO NPs samples. The average size of nano-particles prepared by hydrothermal and co-precipitation method is ~ 6 to 60 nm, respectively. This result is matching with the calculations from the XRD data (Table 2).



The CFO NPs prepared by hydrothermal method are uniform polygonal blocks (4 edges (square, rhombus), individually with particles of 3, 5 or 6 edges) with a narrow size distribution. The morphology of nanoparticles obtained by co-precipitation method in non-calcined and calcined, which display as polygonal blocks, 5M25 sample is very small and indistinguishable to shape, xM80 samples observed particles of 4, 5 or 6 edges and be in state of agglomerated particles, with the calcined samples, the higher the calcined temperature is, the more uniform the particles, the particles gradually change from 4-sides polygons to hexagons, the state of agglomerated is also reduced.

3.3. Fourier transform infrared spectroscopy (FTIR) analysis

FTIR was performed for samples at room temperature in Fig. 3. It is well known that metal ions in ferrites are distributed between two lattice sites namely tetrahedral (A) and octahedral (B) depend on the bond between the oxygen atoms with their nearest neighbors is Fe or Co [13]. Therefore, two main metal-oxygen bands are expected to be present in IR spectra of the samples in the bands from 400-1000 cm^{-1}. The band (ν_1) appeared in the range 385-450 cm^{-1} indicates the presence of cation-anions stretching vibrations at octahedral sites (Co^{+2}-O^{-2}), and the band (ν_2) appeared in the range 500-600 cm^{-1} usually attributed to the intrinsic stretching vibrations of Fe^{+3} and O^{-2} at tetrahedral sites in spinel structure [14].

asy to see that: in the Fig.3a, all the sample synthesized by hydrothermal method have only been recorded the band appeared in the range 500-600 cm^{-1}, it mean that, the hydrothermal CFO NPs are primarily a tetrahedral (A) ferrite structure. And all these sample displayed a peak in the range 3000-3600 cm^{-1} due to the stretching of O-H. While, in the Fig.3b, all the CFO NPs synthesized by co-precipitation non-calcined are not only displaying the band in the range 500-600 cm^{-1} but also displaying the band below 450 cm^{-1}; but, as the calcined temperature increase, the band below 450 cm^{-1} decrease and in sample 1M25-600 and 1M80-600, the band below 450 cm^{-1} disappears. This result shows that, CFO NPs samples synthesized by co-precipitation at room temperature or 80^oC without calcination are distributed two lattice sites: tetrahedral (A) and octahedral (B) ferrite structure, and if the samples are calcined, it change gradually into tetrahedral (A) ferrite structure.

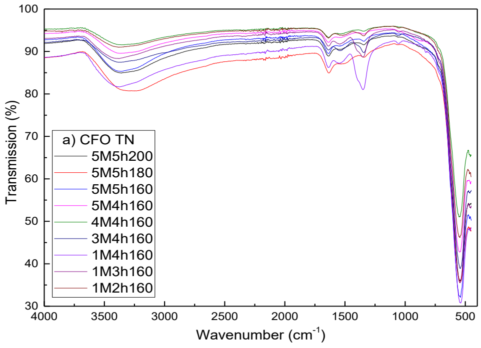


Fig. 2. FESEM imagine of CFO NPs samples

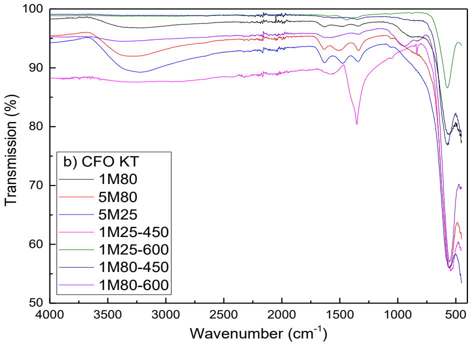


Fig.3. FTIR spectra of CFO NPs synthesized by hydrothermal method (a) and co-precipitation method (b) non-calcined and calcined.

3.4. Magnetic analysis

The magnetic hysteresis loops of all samples at room temperature are plotted in Fig. 4. The M-H curves of CFO NPs show typical hysteresis characteristics.

The saturation magnetization M_S values for the CFO NPs are in the range of 20 - 54 emu/g while those for the CFO bulk is 80 emu/g [2]. All the characteristic parameters of CFO samples (such as M_S, H_C, M_R) are summarized in table 3. As shown in Tab. 3, the coercivity (Hc) strong decreases from 3400 Oe for the 1M80 sample to 710 Oe for the 5M80 sample while the M_S increases from 20 emu/g for the 1M80 sample to 51 emu/g for the 5M5h180 sample. In addition, the difference in the M_S values of the CFO NPs are attributed to the variation in the size of NPs and other prepared methods.

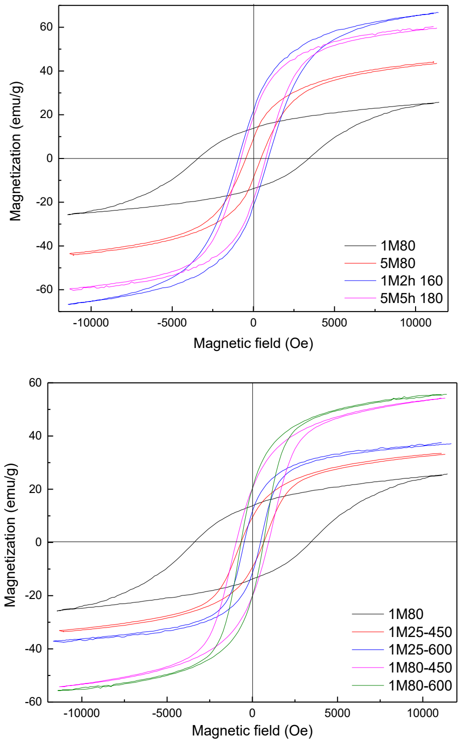


Fig.4. MH loops of CFO NPs with maximum applied field of ±11 kOe taken at room temperature

Table 3. Magnetic parameters of CFO NPs

Tên mẫu	M_s (emu/g)	M_r (emu/g)	H_c (Oe)
1M80	20.0	13.8	3400
5M80	32.0	11.6	710
1M2h160	54.0	21.5	920
5M5h180	51.0	18.0	760
1M25-450	24.5	9.5	660
1M25-600	41.0	20.8	950
1M80-450	29.0	11.2	470
1M80-600	45.0	20.0	665

4. CONCLUSION

Single phase cubic spinel structure CFO was successfully prepared by hydrothermal and co-precipitation method with nano-size dimension. The CFO synthesized by hydrothermal state in tetrahedral structure, high uniformity. The CFO synthesized by co-precipitation non-calcined state in both of octahedral and tetrahedral structure, is less homogeneous than hydrothermal samples, the particles size is approximately, the samples calcined lead to the changing the structure into tetrahedral and the size sharply increase, the particles shape also gradually transform into hexagonal with increasing the temperature. The magnatic properties depend on structure and the size of CFO NPs.

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