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MỤC LỤC

trang

CHARACTERIZATION OF COBALT FERRITE $CoFe_2O_4$ NANOPARTICLES SYNTHESIZED BY CO-PRECIPITATION AND HYDROTHERMAL METHODS

Le The Tam [1], Nguyen Hoa Du [1], Le Thi Hong Nhung [1]
Duong Thi Ngoc Hang [1], Phan Thi Dung [2], Ngo Minh Duc [1], Tran Thi Phuong Thu [1]
[1]*School of Natural Sciences Education, Vinh University*
[2]*Nghe An College of Education*
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Abstract. Crystalline nanoparticles $CoFe_2O_4$ with a spinel structure were prepared by co-precipitation and hydrothermal methods. The magnetic properties of calcined cobalt ferrite formed from nano crystalline powders by these methods have been compared to each other. The dependence of the particle size and crystalline structure of obtained nanoparticles on the synthesis conditions was examined and characterized using field emission scanning electron microscope (FESEM), X-ray diffraction analysis (XRD) and energy dispersive X-ray spectroscopy (EDX). The XRD analysis revealed a high degree of crystallinity and confirmed spinel structure. The FESEM images showed the presence of spherical ferrite particles with an average diameter about 20-25 nm. The results also showed that the formation of cobalt ferrite spinel structures is affected by synthesis methods. Both prepared techniques were effective for the production of spinel crystalline nanoparticles. Magnetic hysteresis loop data confirmed that the magnetic properties of nanoparticles depend on the structure and size of particles. The materials prepared by hydrothermal route and calcination at 600°C have had higher magnetic saturation than the non-calcined and calcined co-precipitation method samples.

1. Introduction

In recent years, nanocrystalline materials are becoming a subject of intense research because of their unique properties. Magnetic nanoparticles have been of interest for their typical physical and chemical properties as well as their potential applications in various fields such as information technology, environmental treatment, catalysis, biomedicine (extraction of biomolecules, targeted drug delivery, magnetic resonance imaging (MRI) contrast enhancement and thermal magnetic therapy) [1-3]. In particular, magnetic spinel ferrites ($M_xFe_{3-x}O_4$, where M = Fe, Co, Ni, Mn, or Zn) are emerging as innovative nanostructures for many biological applications, where a superparamagnetic behavior, a high magnetization value, a diameter smaller than a critical value (typically around 10-20 nm), a narrow size distribution, and an appropriate surface coating are required. Among magnetic spinel ferrite nanoparticles (NPs), $CoFe_2O_4$ has received a lot of attention because of its unique magnetic properties, such as a large anisotropy energy, tunable coercivity, and high saturation magnetization, that make $CoFe_2O_4$ NPs become a good candidate for many applications such as in magnetic resonance image (MRI).

There are some common ways to synthesize $CoFe_2O_4$ nanoparticles, including co-precipitation, sol-gel or hydrothermal methods [4-7]. Among these techniques, chemical co-precipitation has been reported to be the most economical one. In addition, hydrothermal method has been confirmed to be a high rate of production and simplicity.

Email: tamlt@vinhuni.edu.vn (L. T. Tam)

In this paper, we reported the effect of structural properties on magnetic properties of cobalt ferrite samples, prepared by hydrothermal and co-precipitation processes.

2. Chemicals, instruments and measurements

$CoFe_2O_4$ NPs were prepared by hydrothermal and co-precipitation method using the analytically pure grade ferric chloride hexahydrate ($FeCl_3.6H_2O$), cobalt(II) chloride tetrahydrate ($CoCl_2.4H_2O$) and sodium hydroxide. All chemicals were purchased from Merck chemical company. Ultra-pure nitrogen gas (99.99%) was used to provide anaerobic condition in solution. Distilled deionized water was used to prepare all the solutions. All the synthesis experiments were conducted in the laboratory of Inorganic Chemistry at Vinh University.

2.1. Synthesis by co-precipitation method

Superparamagnetic $CoFe_2O_4$ nanoparticles were prepared by co-precipitation of cobalt (II) and ferric chloride in nitrogen atmosphere. The chlorides of cobalt and iron were dissolved in deionized water at the determined molar ratio (Fe/Co = 2) under N_2 with stirring at 400 rpm for 25 minutes. Aqueous solution of NaOH 3M was used as the precipitating agent. The obtained solution was added by dropwise into 15 ml sodium hydroxide (NaOH 3M) solution with rate of 3 ml/min, under vigorous stirring with a magnetic stirrer under N_2 atmosphere, after which the color of the mixture turned to black and the pH value was higher than 12. Large pH values (above 12) were used because it controls the process of nucleation rate and reduces the particles sizes. The obtained solution was maintained at a fixed temperature for 9 hours under vigorous stirring with a magnetic stirrer under N_2 atmosphere [4, 5]. This precursor (denoted A) was used for hydrothermal synthesis. For co-precipitation, the mixture was stirred strongly for 8 hours at 80°C. The synthesized $CoFe_2O_4$ NPs were washed by decanting with assistant of magnet, using distilled deionized water until neutralization, and was dried at 80°C for 8 hours (denoted as M1). A half of M1 was calcined at 600°C for 2 hours and denoted as M2.

2.2. Synthesis by hydrothermal method

The resulting suspension A was transferred into a teflon-lined stainless steel autoclave with a capacity of 50 ml, and treated at 180°C for 15 hours. After the hydrothermal reaction time, the autoclave was taken out and cooled at room temperature naturally. The synthesized $CoFe_2O_4$ NPs were washed by decanting with assistant of a magnet, using distilled deionized water until neutralization. The obtained dark product was dried at 80°C for 8 hours. This product was denoted as M3. A half of M3 powders were calcined at 600°C for 2 hours and the obtained product was denoted as M4.

2.3. Measurements

The crystal structures of the samples were characterized by XRD using diffractometer XD8 Advance Bruker with Cu-Kα radiation (λ=1.5406 Å) (Faculty of Chemistry, Vietnam National University, Hanoi). The morphology (size and shape) of the particle materials was obtained by field emission scanning electron microscopy FESEM (Hitachi S-4800) and hysteresis loops were measured at room temperature to the highest field of 11 kOe using a vibrating sample magnetometer (VSM) (Institute of Materials Science, Vietnam Academy of Science and Technology).

3. Results and discussion

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 Figure 1. These patterns confirmed the formation of cubic spinel type lattice of $CoFe_2O_4$, which matches well with the XRD pattern of standard $CoFe_2O_4$ (ICDD card No: 22-1086), no other crystalline phase presented in the samples.

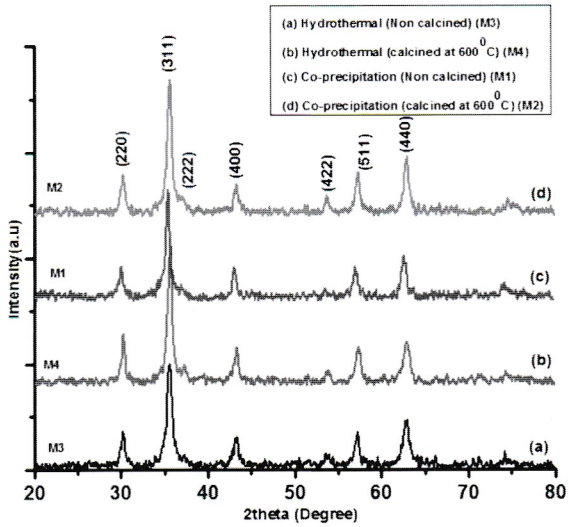

Figure 1: *XRD patterns of the $CoFe_2O_4$ NP samples prepared and treated with various conditions*

The crystallite size D of the samples was calculated from the data of peak at $2\theta = 35.5^o$ with Miller indices by (311), using Scherrer equation.

$$D_{XRD} = \frac{0.89\lambda}{\beta\cos\theta} \quad (1)$$

where D is the grain diameter, β is half intensity width of the relevant diffraction, λ is X-ray wavelength and θ is the diffraction angle. The lattice parameter was calculated according to the Eq. (2):

$$a = d_{hkl}(h^2+k^2+l^2)^{1/2} \quad (2)$$

The crystallite size and lattice constants of the cobalt ferrite nanoparticles have been summarized in Table 1.

Table 1: *Characteristics of the $CoFe_2O_4$ NPs samples*

Sample	Synthesis method	Lattic parameter, a (Å)	d_{311}(Å)	Particle size, (nm)	
				$D_{(XRD)}$	D_{FESEM}
M1 (non-calcined	Co-precipitation	8.381	2.527	27.06	25.5±1,6
M2 (calcined)		8.356	2.520	23.22	22.7±1.9
M3 (non-calcined	Hydrothermal	8.381	2.525	21.32	21.4±0.6
M4 (calcined)		8.351	2.518	24.31	23.4±1.5

3.2. Morphology characterizations

Figures 2 and 3 (a, b) show the FESEM images of the $CoFe_2O_4$ NP samples. The average size of nano-particles prepared by hydrothermal and co-precipitation method is ~ 20 and 25 nm, respectively. This result is matching with the calculations from the XRD data (Table 1). The $CoFe_2O_4$ NPs prepared by hydrothermal method are uniform with a narrow size distribution. The size and size distribution have a dependence on nucleation and growth rates during the reaction, which may be controlled by concentration of reagents and reaction conditions. Smaller particles were obtained if the nucleation rate was higher than growth rate [8, 9].

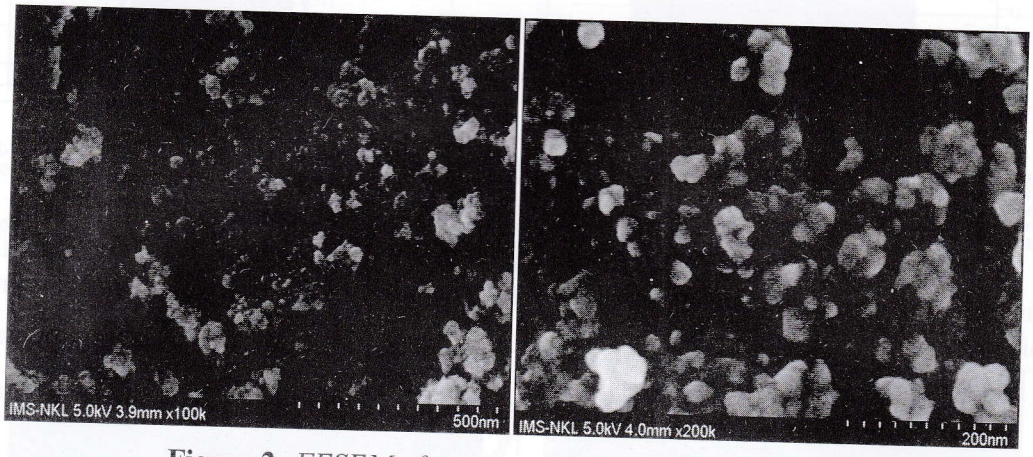

Figure 2: *FESEM of non-calcined samples: a) M1 and b) M3*

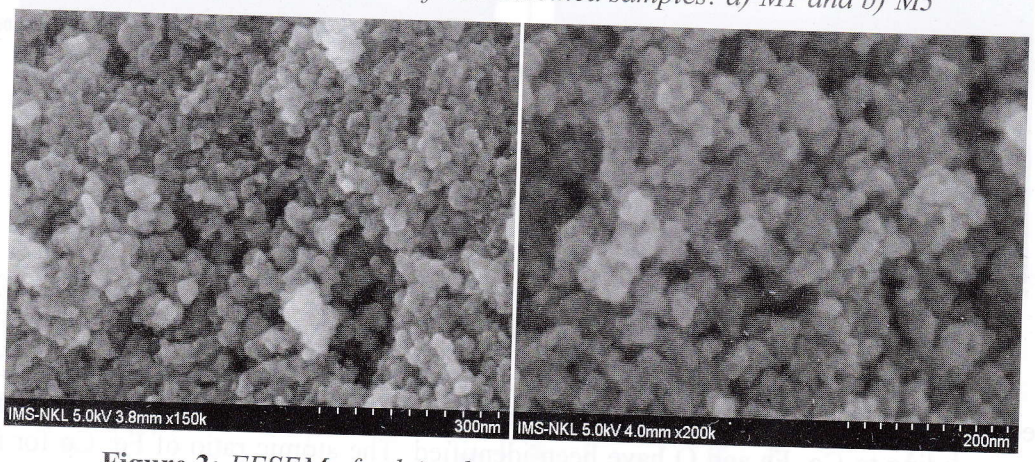

Figure 3: *FESEM of calcined at 600°C samples: a) M2 and b) M4*

The uniform spherical morphology of nanoparticles obtained in non-calcined and calcined at 600°C for 2 h as indicated in Figures 2 and 3, which display a spherical morphology with size of 27.06 nm (M1), 23.22 nm (M2), 21.32 nm (M3) and 24.31 (M4). It is interesting to note that the size distribution (Fig. 4) is more narrow for particles synthesized via hydrothermal than that via co-precipitation route.

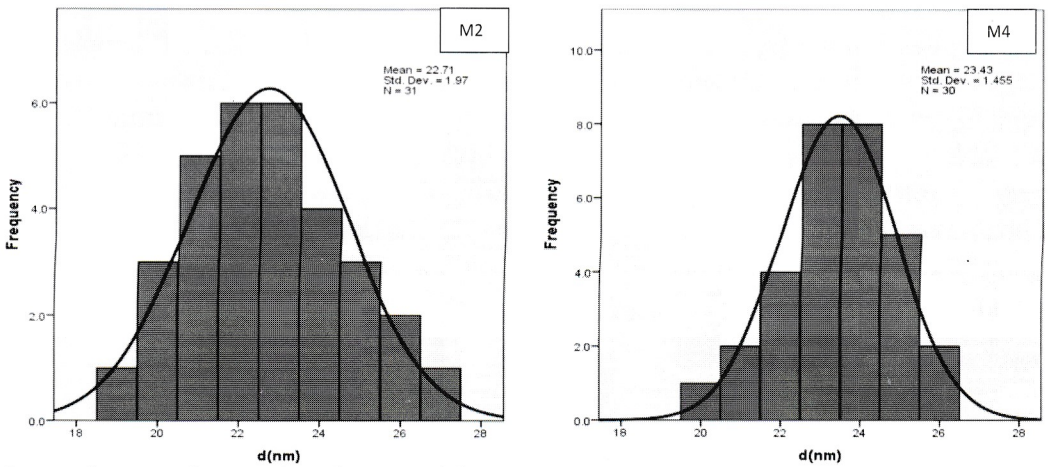

Figure 4: *Particle size distribution of the samples calcined at 600°C for 2 h (M2 and M4)*

3.3. EDX spectrum

Figure 5 shows the EDX spectra of the $CoFe_2O_4$ NPs samples and confirms the ratio of the transition metal atoms in each material according to the nominal stoichiometry.

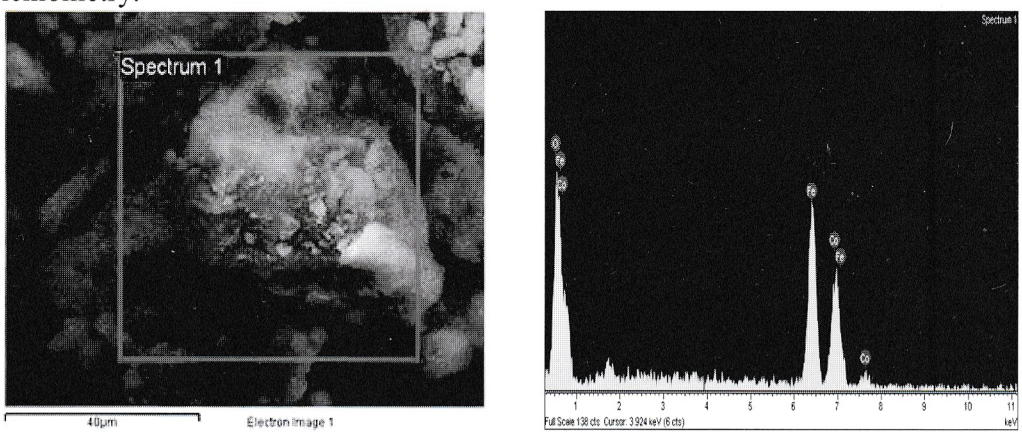

Figure 5: *The qualitative EDX analysis for $CoFe_2O_4$ powder of M3*

The EDX analysis is considered a semi-quantitative analysis. A typical EDX spectrum obtained from the analyzed samples is presented in Figure 5 where the peaks corresponding to Co, Fe and O have been identified. The atomic ratio of Fe: Co for the entire calcined sample is ~ 2:1, according to the nominal stoichiometry of $CoFe_2O_4$ materials (Table 2).

Table 2: *Elemental composition of M3 from EDX data*

Element	Weight%	Atomic%
O	30.53	60.98
Fe	45.13	25.82
Co	24.34	13.20
Total	**100.00**	**100**

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TÓM TẮT

ĐẶC TÍNH HỆ HẠT NANO $CoFe_2O_4$ CHẾ TẠO BẰNG PHƯƠNG PHÁP THỦY NHIỆT VÀ ĐỒNG KẾT TỦA

Trong nghiên cứu này, các hạt nano $CoFe_2O_4$ với cấu trúc spinel được tổng hợp bằng phương pháp thủy nhiệt và phương pháp đồng kết tủa với định hướng ứng dụng trong y sinh. Các đặc trưng cấu trúc, kích thước hạt và tính chất từ của vật liệu thu được bằng các phương pháp đã được so sánh với nhau. Sự thay đổi về kích thước tinh thể được khảo sát và đánh giá bằng phương pháp nhiễu xạ tia X (XRD), hiển vi điện tử kiểu quét phát xạ trường (FESEM) và phổ tán xạ năng lượng tia X (EDX). Phân tích kết quả XRD cho thấy tất cả các mẫu thu được đều đơn pha và có cấu trúc spinel. Kích thước tinh thể trung bình thu được từ XRD tương đương với kích thước hạt xác định từ các hình ảnh FESEM (20-25 nm). Kết quả cho thấy việc hình thành các hạt nano từ với cấu trúc spinel phụ thuộc vào phương pháp tổng hợp. Kết quả đo từ kế mẫu rung (VSM) cho thấy tính chất từ phụ thuộc vào cấu trúc, kích thước hạt và cách chế tạo vật liệu. Các mẫu chế tạo theo phương pháp thủy nhiệt và được thiêu kết ở 600^0C có giá trị từ độ bão hòa cao hơn so với các mẫu theo phương pháp đồng kết tủa.