

## STUDY ON PREPARATION OF MAGNETIC FLUID BASED ON SYNTHESIZED Fe<sub>3</sub>O<sub>4</sub> MAGNETIC NANOPARTICLES IN WATER AND ORGANIC SOLVENTS

Vuong Thi Kim Oanh<sup>1,5\*</sup>, Do Hai Doan<sup>1</sup>, Nguyen Xuan Truong<sup>1,5</sup>,  
Nguyen Xuan Ca<sup>2</sup>, Le The Tam<sup>3,5</sup>, Le Trong Lu<sup>4,5</sup>, Tran Dai Lam<sup>4,5</sup>

<sup>1</sup>Institute of Materials Science – VAST, <sup>2</sup>University of Sciences - TNU

<sup>3</sup>Vinh University, <sup>4</sup>Institute for Tropical Technology - VAST

<sup>5</sup>Graduate University of Science and Technology - VAST

### ABSTRACT

Fe<sub>3</sub>O<sub>4</sub> magnetic nanoparticles were synthesized by hydrothermal and thermal decomposition methods. Particles synthesized by hydrothermal method were water soluble meanwhile one by thermal decomposition method were organic soluble. Structure, morphology and magnetic properties of magnetic powders and magnetic fluid samples were characterized. The XRD results pointed out that all of prepared samples had ferrite spinel single phase. The field emission scanning electron microscope (FESEM) and transmission electron microscopy (TEM) images revealed that the as-synthesized nanoparticles were spherical in shape and fairly uniform in size. The mean particle size of the samples synthesized at optimal conditions by hydrothermal method (2 hours, 160 °C) and thermal decomposition (2 hours, 300 °C) were 15 nm and 13 nm, respectively. The saturation magnetization (M<sub>s</sub>) of as high as 63 emu/g and 70 emu/g corresponded to above samples. The magnetic fluid samples were treated with poly(acrylic acid) –PAA as the phase transfer ligand for a high stability with zeta potential values of about -40 to -50 mV. The magnetic fluid system has good dispersion and high stability, which open potential applications in biomedical.

**Keywords:** *hydrothermal method; thermal decomposition; magnetic fluid, phase transfer ligand; high stability*

### INTRODUCTION

During the time, nanomaterials, including ferit spinel, have attracted a great deal of attention thanks to potential applications in various fields, especially in biomedicine [1, 2]. To be a good candidate for being applied in biomedicine for example hyperthermia or MRI contrast enhancement, magnetic nanoparticles (MNPs) must hold a good quality (homogenous size and high saturation magnetization) and be superparamagnetism at room temperature [3, 4]. Although saturation magnetization value of Fe<sub>3</sub>O<sub>4</sub> MNPs is moderate, they are given considerable attention owing to their great compatibility, easy production and good stability during time.

Until now, almost all of publications about synthesis of Fe<sub>3</sub>O<sub>4</sub> MNPs has mentioned some methods such as: coprecipitation, sol – gel or reduction [5, 6]. Advantage of these

methods is: all of them is low-cost, environment friendly and easily synthesized. However, there is still some drawbacks of non-uniform particles size and low saturation magnetization because they are synthesized in water and at low temperature.

In this paper, we present two methods to fabricate Fe<sub>3</sub>O<sub>4</sub> MNPs at high temperature to obtain nanoparticles at excellent quality. Hydrothermal method, which was performed in aqueous solution, and thermal decomposition method, which was performed in organic solvent, were employed. Starch – a natural polymer, soluble in water and highly biocompatible – was used to coat MNPs synthesized in aqueous phase [7, 8]. Meanwhile, poly acrylic acid (PAA) contains numerous –COOH carboxylic functional groups, which contribute strong bonds with the particle's surface, therefore, PAA was used as a agent to transfer the MNPs from the organic phase to the aqueous phase [9].

\* Tel: 0979 054979, Email: oanhvtk@ims.vast.ac.vn

Results of the synthesis and also the coating and the phase transferring processes will be summarized, compared and discussed.

## EXPERIMENT

### Chemicals

Iron (III) acetylacetonate ( $\text{Fe}(\text{acac})_3$ ), oleylamine (OLA) and oleic acid (OA) purchased from Sigma-Aldrich.

### Synthesis of $\text{Fe}_3\text{O}_4$ nanoparticles

$\text{Fe}_3\text{O}_4$  MNPs were synthesized by hydrothermal and thermal decomposition methods as described in our previous publications [10, 11]. In those works, the both two methods were studied at different reaction temperatures. The best powder sample (uniform size and high saturation magnetization) of each method was selected to prepare ferrofluid and labeled M1F1 and M2F2 corresponding to samples synthesized by hydrothermal and thermal decomposition method, respectively.

### Coating of MNPs

$\text{Fe}_3\text{O}_4$  MNPs synthesized by hydrothermal method were redispersed in 50 ml of distilled water under sonication for 15 minutes following by continuously stirring and heating until 80 °C. At the time the solution reached 80 °C, 50 ml of starch solution of 10 mg/ml was added dropwise to the magnetic suspension, the mixture then was kept at this temperature during 2 h. After 2 h, the mixture was refrigerated at 0 °C for 24 h to let the MNPs well dispersed in the solution. Then, the starch-coating MNPs were refined until pH = 7 using a permanent magnet. The final product was washed again by magnet and dispersed in water at desired concentration.

### Phase transfer process

2 g of PAA was dissolved in 40 ml of triethylene glycol (TEG) solution. This mixture was heated to 110 °C, as soon as it reach this temperature, 5 ml of n-hexan solution containing 100 mg of MNPs was rapidly injected into the reaction mixture. The

mixture was conjunctively heated and kept at 280 °C for 6 h. After reaction, the mixture was natural cooled until room temperature. The phase transferred MNPs were separated from the TEG solution by adding an amount of HCl and centrifuging at 12000 rpm.

### Characterization of Magnetic Nanoparticles

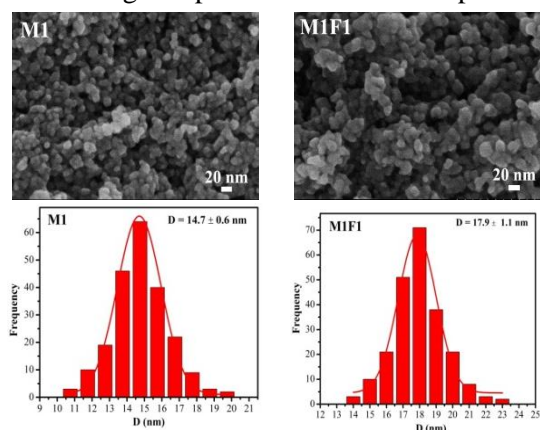
Morphology (size and shape) of the particles were obtained by field emission scanning electron microscopy FESEM (Hitachi S-4800), transmission electron microscopy TEM (JEM 1010). The saturation magnetization of the samples at temperature was measured under the highest magnetic field of 10 kOe using a vibrating sample magnetometer (VSM) (home-made). The size distribution and stability of the magnetic fluids were examined using the Zetasizer (Nano ZS-Malvern-UK).

## RESULTS AND DISCUSSION

To find out the best qualified sample (homogenous size, high magnetization), all the samples were examined at different conditions, for example: variation of precursor concentration, solvent, reaction time or temperature. Among these factors, temperature holds the most important roles in the changes of size, homogenization, and magnetism of magnetic materials. Therefore, in this work, both the hydrothermal and thermal decomposition methods were studied at different temperature for the same reaction time of 2 h. Hydrothermal method was performed at temperature of 120 °C, 140 °C, 160 °C and 180 °C, while thermal decomposition method was carried out at temperature of 265 °C, 285 °C and 300 °C. The best powder samples synthesized at 160 °C in 2 h by hydrothermal method and 300 °C, 2 h by thermal decomposition method were selected to prepare ferrofluids. The corresponding saturation magnetization and average size of these two MNPs samples were 63 emu/g, 15 nm and 70 emu/g, 13.9 nm, respectively.

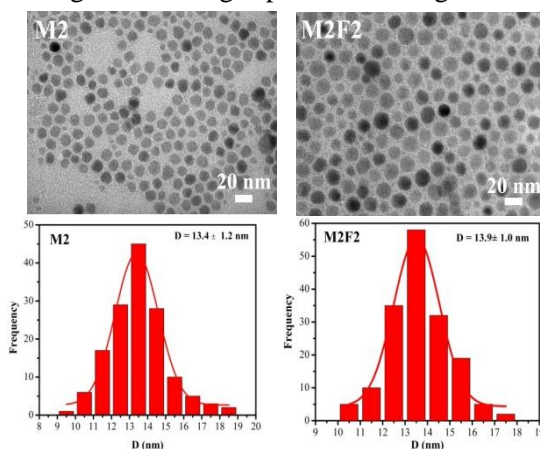
### Variation in particles size of samples before and after making ferrofluid

From FESEM images in figure 1, we can see the inevitable changes in particles size before and after coating. Boundary of particles in sample M1F1 (after coating) was blurred and not as clear as the pre-coating sample M1. From particles size diagram based on size calculated from FESEM images, samples before or after being coated by starch are spherical, the average particles size increased from 14.7 to 17.9 nm (increased 21.8%) after the coating compared to uncoated sample.



**Figure 1.** FESEM images and size distribution diagram of samples before (M1) and after (M1F1) the coating process

The phase transferred sample using PAA was also under consideration about shape and size through TEM images presented in figure 2.



**Figure 2.** TEM images and size distribution diagram of samples before (M2) and after (M2F2) the phase transfer using PAA

From figure 2 we can see that after the phase transfer using PAA, the particles still have spherical shape, good dispersion. The particles were also monodispersion which was presented as clear boundary. From size distribution diagram which calculated from TEM images we find that after the phase transfer, particles size increased insignificantly from 13.4 nm to 13.9 nm (only 3.7 %). We also conclude that MNPs synthesized by thermal decomposition method were more uniform and more monodispersed than one by hydrothermal method. It can be explained as the thermal decomposition was performed at high temperature of 300°C which is much higher than 160 °C in hydrothermal process. On the other hand, there were two surfactants used in thermal decomposition, oleic acid (OA) and oleylamine (OLA). These two surfactants prevented the particles from aggregating and formed a very thin coating layer.

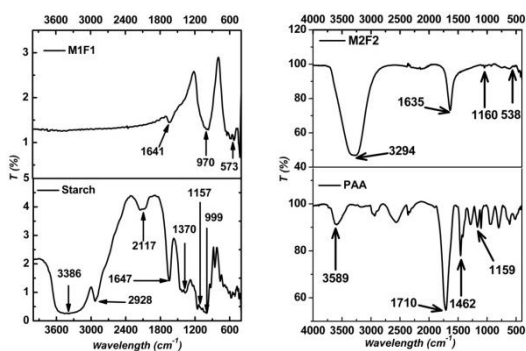
Thus, through FESEM and TEM images and size distribution diagrams we can indicate that Fe<sub>3</sub>O<sub>4</sub> MNPs coated by starch or phase transferred by PAA had uniform size and Gauss distribution of size. These ferrofluids with desired size could be suitable for biomedical application.

### Interaction between the coating layer and MNPs surface

To confirm the interaction between the coating layer and particles surface, FT-IR spectra of the ferrofluid M1F1 and M2F2 were carried out and presented in figure 3. We can obtain that in the spectrum of M1F1 there are clear evidences of the appearance of starch with its specific peaks for C-O, O-H (O-H stretching shows a vibration band at 3386 cm<sup>-1</sup> and OH bending peak at 1647cm<sup>-1</sup>) and CH (2928 cm<sup>-1</sup>) bonds. In this spectrum, there are also peaks corresponding to both starch and Fe<sub>3</sub>O<sub>4</sub>, peak at 573 cm<sup>-1</sup> attributes to Fe-O bond. Moreover, the OH bending peak is shifted in the spectrum of M1F1

sample (from  $1647\text{ cm}^{-1}$  to  $1641\text{ cm}^{-1}$ ), this change indicates the chemical absorption of starch on the surface of the MNPs through OH groups [12, 13].

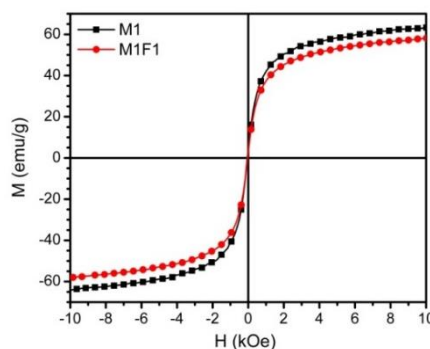
Similarly, in the spectrum of PAA, peaks at  $1710\text{ cm}^{-1}$  and  $1159\text{ cm}^{-1}$  are typically characteristic for C=O bond and C-O-C bond. Meanwhile, these two peaks of PAA also appear in the spectrum of M2F2 but are shifted to  $1635\text{ cm}^{-1}$  và  $1160\text{ cm}^{-1}$ . On the other hand, in the spectrum of M2F2 there is a peak at  $538\text{ cm}^{-1}$  can be attributed to the Fe-O bond [14, 15]. From these results we can assume that starch and PAA were successfully coated on the surface of the MNPs.



**Figure 3.** FT-IR spectra of M1F1, M2F2 ferrofluid and starch, PAA

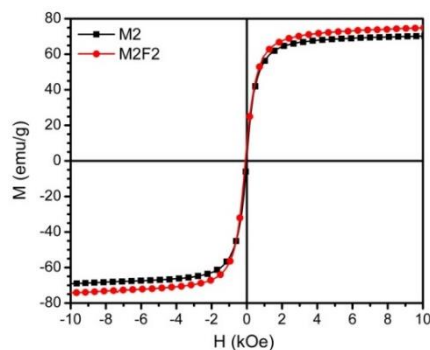
**Magnetic properties of the sample before and after making ferrofluid**

Influence of the coating layer on magnetic properties of the samples were carried out by comparing the samples before and after making ferrofluid using M(H) measurement. Figure 4 shows the hysteresis loop of pre- and post-starch coated samples. We can find from figure 4 that after the starch coating process, the saturation magnetization of sample decreased from  $63\text{ emu/g}$  to  $58\text{ emu/g}$  (decreased 8%). This reduction is exactly a result of the non-magnetic coating layer, starch. This result is also in constant with FESEM images in figure 1 which showed that samples after coating had size increased by 21.8%.



**Figure 4.** Hysteresis loop of  $Fe_3O_4$  MNPs before (M1) and after (M1F1) being coated with starch

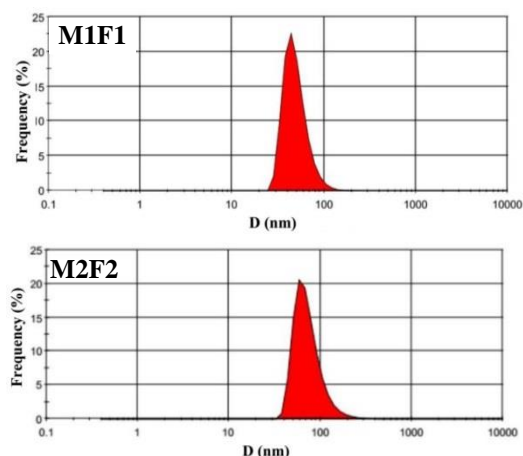
Figure 5 shows the hysteresis loops of the samples before and after the phase transfer with PAA. An interesting result was obtain: after being transfer to the water phase, the saturation magnetization of the sample increased from  $70\text{ emu/g}$  to  $75\text{ emu/g}$ . Hence, the phase transfer process increased the magnetization of the sample by about 7.1%. This can be explained as some functional groups, for example COOH, OH..., changed direction of spins on the surface of the nanoparticles following the direction of the coil of the particles with a similar mechanism as effects of dopamin (DPA) groups explained in the publication of Sridhar et al. [16].



**Figure 5.** Hysteresis loop of  $Fe_3O_4$  MNPs before (M2) and after phase transfer with PAA (M2F2).

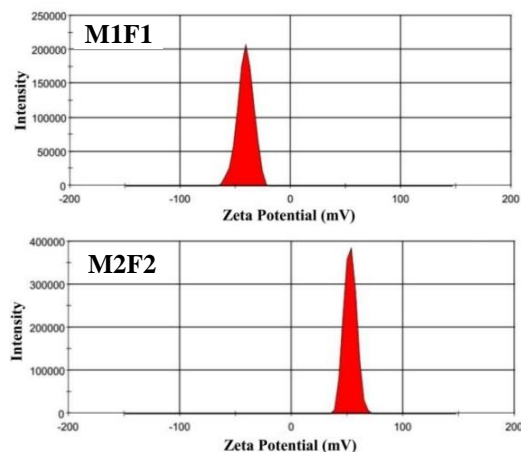
**Particles size and stability of the ferrofluids**

The ferrofluid is considered as at good quality when it reaches requirement about size distribution and high zeta potential. Dynamic light scattering (DLS) on Zetasizer was used to examine the samples, results were presented as size distribution and zeta potential in figure 6 and 7.



**Figure 6.** Size distribution diagram of the ferrofluids M1F1 and M2F2

From the size distribution diagram in figure 6, we can determine the average size of the ferrofluid M1F1 of about 74.53 nm and about 49.86 nm of sample M2F2, indicated that particles size in liquid of sample M1F1 was bigger than that of sample M2F2. This results are consistent with what we obtain from images in figure 1 and 2.



**Figure 7.** Zeta potential of the ferrofluid M1F1 and M2F2

We can observe from figure 7 that the both two ferrofluids have zeta of high absolute value of 40 - 50 mV. According to some standard evaluations through zeta potential, these ferrofluid are high stability [17, 18]. Therefore, starch and PAA are suitable for particles coating and phase transfer purpose for MNPs synthesized in water and also in organic solvent.

## CONCLUSION

The  $\text{Fe}_3\text{O}_4$  MNPs were successfully synthesized by hydrothermal and thermal decomposition method. The ferrofluids were also well fabricated by coating MNPs synthesized in water by starch and by transferring the MNPs synthesized in organic phase into water using PAA. The interactions between the particles surface and the coating layer were confirmed through FT-IR spectra. Particles size of the samples after the coating process increased compared to one before the coating, which are presented in FESEM, TEM. The saturation magnetization grew up to 75 emu/g (about 7.1 %) when MNPs was synthesized in organic phase and transferred to water phase with PAA. DLS and zeta potential of these two ferrofluid indicate that they are at high quality and could be good candidates for biomedical applications.

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## TÓM TẮT

### NGHIÊN CỨU CHẾ TẠO CHẤT LÔNG TỪ TRÊN NỀN HẠT NANO TỪ $\text{Fe}_3\text{O}_4$ ĐƯỢC TỔNG HỢP TRONG DUNG MÔI NƯỚC VÀ HỮU CƠ

Vương Thị Kim Oanh<sup>1,5\*</sup>, Đỗ Hải Doan<sup>1</sup>, Nguyễn Xuân Trường<sup>1,5</sup>,  
Nguyễn Xuân Ca<sup>2</sup>, Lê Thế Tâm<sup>3,5</sup>, Lê Trọng Lưu<sup>4,5</sup>, Trần Đại Lâm<sup>4,5</sup>

<sup>1</sup>Viện Khoa học vật liệu - Viện Hàn lâm Khoa học và Công nghệ Việt Nam,

<sup>2</sup>Trường Đại học Khoa học - ĐH Thái Nguyên, <sup>3</sup>Đại học Vinh,

<sup>4</sup>Viện Kỹ thuật Nhiệt đới - Viện Hàn lâm Khoa học và Công nghệ Việt Nam,

<sup>5</sup>Học viện Khoa học và Công nghệ - Viện Hàn lâm Khoa học và Công nghệ Việt Nam

Hạt nano từ  $\text{Fe}_3\text{O}_4$  được chế tạo bằng hai phương pháp thủy nhiệt và phân hủy nhiệt. Phương pháp thủy nhiệt được tổng hợp ngay trong dung môi nước trong khi đó phương pháp phân hủy nhiệt được tổng hợp trong dung môi hữu cơ. Cấu trúc, hình thái và tính chất từ của các mẫu bột và mẫu chất lỏng từ được khảo sát trên các thiết bị hiện đại. Phân tích kết quả trên phổ nhiễu xạ kế tia X (XRD) cho thấy các hệ hạt thu được đều có cấu trúc đơn pha ferit spinel. Từ các ảnh hiển vi điện tử quét (FESEM) và hiển vi điện tử truyền qua (TEM) có thể thấy các hạt có dạng hình cầu, kích thước khá đồng đều. Kích thước hạt trung bình của các mẫu được chế tạo ở điều kiện tối ưu nhất bằng phương pháp thủy nhiệt (2 giờ, 160°C) và phân hủy nhiệt (2 giờ, 298°C) tương ứng là 15 nm và 13 nm. Giá trị từ độ bão hòa ( $M_s$ ) cao nhất thu được là 63 emu/g và 70 emu/g tương ứng với các mẫu trên. Mẫu chất lỏng từ được sử dụng poly axit acrylic (PAA) làm tác nhân chuyển pha cho độ bền cao với thế zeta trong khoảng từ - 40 mV đến -50 mV. Hệ chất lỏng với độ phân tán tốt, độ bền cao mở ra khả năng ứng dụng tốt trong y sinh.

**Từ khóa:** Phương pháp thủy nhiệt, phương pháp phân hủy nhiệt, chất lỏng từ, chuyển pha ligand, độ ổn định cao

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\* Tel: 0979 054979, Email: oanhvtk@ims.vast.ac.vn