FABRICATION OF Fe_3O_4 MAGNETIC FLUID BY POLY (ACRYLIC ACID) FOR BIOMEDICAL APPLICATIONS

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ABSTRACT

Fe_3O_4 nanosystems of different sizes were synthesized by thermal decomposition method in organic solvent. Magnetic fluid based on Fe_3O_4 nanoparticles was prepared by using poly acrylic acid (PAA) as a phase transfer agent. The structure, morphology and magnetic properties of samples were studied by: X-ray diffraction patterns (XRD), transmission electron microscope (TEM), and vibrating sample magnetometer (VSM). XRD results indicated that all samples had spinel single phase structure with average crystaline size less than 15 nm. TEM images showed that the average size of samples were nearly equal to those of XRD. The highest value of saturation magnetization obtained at room temperature for the sample synthesized at optimal reaction time and temperature (2 hours and 298 ^{o}C, respectively) after phase transferring was 75 emu/g. The linkage between magnetic nanoparticles' surface and functional groups of PAA was confirmed by FT-IR spectra. Simultaneously, the particle size and stability of magnetic fluid were evaluated by DLS and Zeta potential. These results demonstrated the narrow size distribution and high stability of nanosystem. The important point was that the phase transfer contributed to enhance of saturation magnetization of samples (about 5 % of the initial ones). Magnetic fluid based on Fe_3O_4 nanoparticles with high homogeneity, high saturation magnetization and good stability promised a potential application in biomedical, especially in magnetic hyperthermia and contrast-enhanced magnetic resonance imaging.

Keywords: Fe_3O_4 nanoparticles, thermal decomposition, poly (acrylic acid), phase transfer, magnetic fluid.

1. INTRODUCTION

In recent times, magnetic nanomaterials, typically ferrite spinel, have been specially of interest in research due to their outstanding physical and chemical properties which only appear in nano-size range as well as its large potiental applications in many fields such as: information technology, environment treatment, catalysis, especially in biomedical field [1 – 4].There are

many requirements for magnetic nanoparticles when they are applied in biomedicine. Among them, high saturation magnetization (MS > 70 emu/g), good dispersion and stablility in biomedical condition play important roles. For some special applications, magnetic nanoparticles must be small (about 10 nm) and uniform. For example, when applied in hyperthemia treatment of cancer, these two features contribute to enhancement of magnetic induction heating efficiency [5, 6]. Fe_3O_4 nanoparticles have been the most favored for biomedical applications thanks to their biocompability and simple synthesis.

Among many synthesis methods of Fe_3O_4 nanoparticles, thermal decomposition method is well known for its ability to generate uniform particles with high saturation magnetization [7, 8]. In our previous work [9], sodium dodecyl sulphate (SDS) was used as phase transfer agent in the synthesis of magnetic fluid. The magnetic heating study of this system showed that its specific absorption rate (SAR) was relatively high, but it was not time-stable.

Recently, many studies have shown that the coating layer can improve the stability due to the core – shell interaction and enhance the magnetic properties [10 – 12]. For instance, hydrophilic ligands carrying dopamine (DPA) have strong bonds between two OH groups of DPA molecule and the surface of magnetic nanoparticles and enhance their magnetism thanks to the appearance of the coating layer [13]. Beyond this ligand, such magnetic nanoparticles as Fe_3O_4 or $CoFe_2O_4$ can create strong bonds with carboxyl group (COOH) and phosphate (PO4) [14].

In this paper, we present the results of fabricating magnetic fluid based on Fe_3O_4 nanoparticles using organic solvent and PAA as the phase transfer ligand. Structure, morphology, particle size and magnetic properties of these samples were evaluated and discussed. Simultaneously, their stability was also studied and the manetic induction heating effect of these samples was determined and discussion.

2. EXPERIMENTAL

Chemicals used in our present synthesis of Fe_3O_4 nanoparticles are commercial products of Sigma-Aldrich with the purity of 99.99 %, including: Fe (III) acetylacetonate $Fe(acac)_3$, surfactants such as: oleylamine (OLA), oleic acid (OA) and some solvents: dibenzyl ether, ethanol, n-hexane. Chemicals used in phase transfer process are: Poly-acrylic acid (PAA) and Triethylenglycol (TEG).

Synthesis of Fe_3O_4: Firstly, such precursors as $Fe(acac)_3$ 4 mmol, oleic acid 20 mmol and oleylamine 20 mmol are put in a flask containing 40 ml of dibenzyl ether. This mixture was then stirred gradually for 30 minutes before a raise in the temperature of reaction to different temperatures (265 ^oC, 285 ^oC, 298 ^oC) in the same reaction time of 2 hours. After that, the obtained solutions were cooled naturally to room temperature, followed by being washed with ethanol and centrifuged before being dispersed in n-hexan. After they were dried and denoted as M1 M2, M3 corresponding to the increasing reaction temperatures, these samples were characterized with their structure (XRD), bonds (FT-IR), particle size (TEM) and magnetic feature (VSM) (consult reference [9] for more information).

Synthesis of Fe_3O_4 magnetic fluid: in the initial step, 2 gram of PAA was dissolved in 40 ml of TEG solution. Next, this mixture was heated to 110 ^oC. No sooner did it reach this temperature than 5 ml of the mixture of 100 mg magnetic nanoparticles dispered in n-hexane was injected quickly into the reaction mixture. It was continuously heated and maintained at 280 ^oC for 6 hours. After finishing the reaction, the obtained product was cooled to room temperature.

After removing the supernatant, the residue was redispered in water using ultrasound. These magnetic fluids were labeled as L1, L2, L3 coresponding for M1, M2 and M3.

The crystal structure of the samples before and after coating with PAA was determined by using the diffractometer SIEMENS D5000 with Cu-Kα radiation (λ = 1.5406 Å) at room temperature. The average crystal size was acquired from X'Pert HighScore Plus commercial image analysis software. The shell – core bonds were analyzed by Fourier transform infrared spectroscopy FT-IR (Nicolet 6700).

The morphology properties of these particles (size and shape) were obtained by using transmission electron microscopy TEM (JEM 1010) at National Institute of Hygiene and Epidemiology. Size distribution and stability of magnetic fluids were examined by the Zetasizer (Nano ZS – Malvem – UK). The saturation magnetization of these samples at room temperature was measured under the highest magnetic field of 10 kOe using a vibrating sample magnetometer (VSM) (home-made in institute materials science).

3. RESULTS AND DISCUSSION

The effect of reaction temperature to structure characteristics of Fe_3O_4 nanoparticles like phase and crystal size were published [9]. It can be observed, all three samples are monophase with spinel structure, size particles varies from 8 - 15 nm corresponding to the reaction temperature gradual increase from 265 ^oC – 298 ^oC. Beside, magnetic saturation also increased (from 54 -70 emu /g) according to the reaction temperature.

X ray diffraction pattern of L3 sample, M3 sample which was used to compare is ploted at Figure 1. It shows that both two samples appear feature diffaction peaks of Fe_3O_4 nanoparticles, or can be confirmed that samples after phase transfer are monophase of spinel structure. The average crytal size (D_{XRD}) of all samples were determined from the full width at hafl maximum of peak at $2 = 62,5^o$ with value 7, 10 and 1 2 nm according to M1, M2 and M3, respectively.

The information about the bond between PAA and magnetic nanoparticle of L3 sample after washing by water to remove free molecules was confirmed by FT-IR spectrum.

It can be seen from Figure 2, that there is the appearance of feature vibrations related to functional groups of Fe_3O_4 and OA, OLA shell. The peaks at 2920 cm^{-1} and 2850 cm^{-1} are
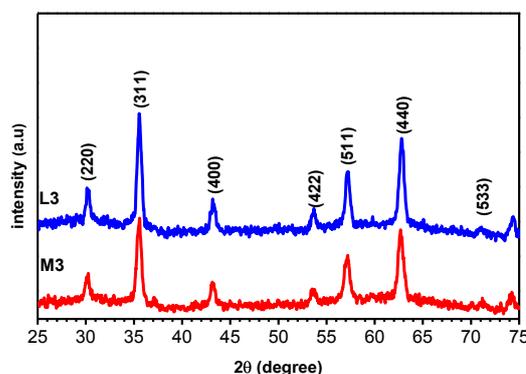

Figure 1. XRD patterns of L3 samples, M3 sample was used for comparison.
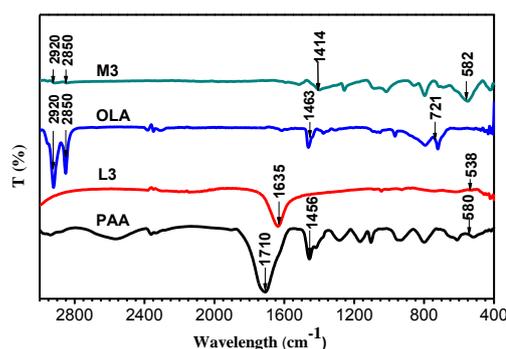
Figure 2. FT-IR spectra of Fe_3O_4 nanoparticles before (M3) and phase transition after (L3).

typically characteristic for C-H group. While, the two peaks at 1536 and 1414 cm^{-1} are due to asymmetrical stretching and symmetrical stretching vibrations of COO^- group on the particle

surface. In addition, the wavenumber separation between two peaks Δ (1536 cm^{-1} – 1414 cm^{-1} = 122 cm^{-1}), which is in the 120 – 190 cm^{-1} range, demonstrates the bond between OA molecules and Fe$_3$O$_4$ particle surface being bridging.

Moreover, the strong absorption band at 582 cm^{-1} are associated with Fe-O bond, due to the presence of Fe$_3$O$_4$ magnetic nanoparticle. These results are in good agreement with the finding of author [8]. On the other hand, it can see the feature vibrivation peak of COOH group in PAA at 1710 cm^{-1}. Similar to, this peak also appears in L3 sample at 1635 cm^{-1}. The peak at 538 cm^{-1} is considered as Fe-O bond. As a results, Fe$_3$O$_4$ nanoparticles were functionalized successfully by PAA.

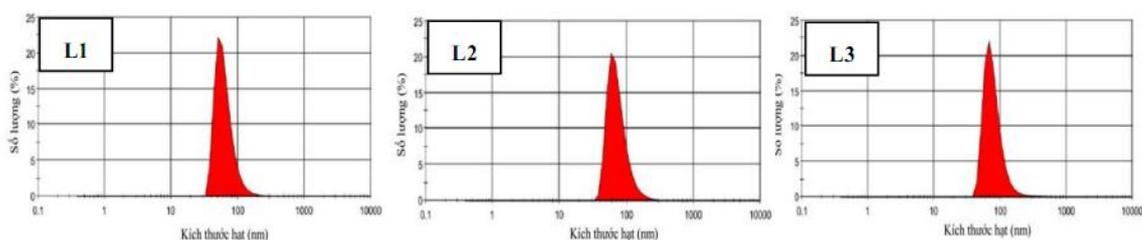To evaluate particle size as well as the stability of samples, they were measured by using a Zetasizer equipment.

Figure 3. The particle size distribution pattern of three samples: L1, L2, L3..

Figure 3 exhibits that both three samples only appear an unique peak. This proved nanoparticles have relatively uniform size with average size around 70 nm. The difference from particle size and moving size when assessed by DLS can be due to the influence of polymer in water. The Zeta voltage of all samples were over 40 mV, hence these samples are considered as high stability (in range about 40 - 50 mV) [15, 16].
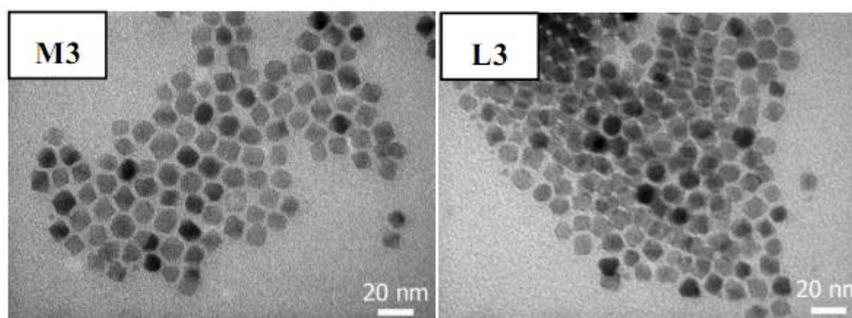

Figure 4. Typical TEM images of M3 and L3 sample.

Morphology and size of samples were studied by TEM image. Fig 4 is TEM image of L3 sample, it exhibits the nanoparticles after phase transition have size equivalent to initial particles (M3), this leads to the thickness of the shell is insignificant. Furthermore, obtained nanoparticles have relatively uniform size and ungathered. It demonstrated that Fe$_3$O$_4$ nanoparticles were dispersed well in water.
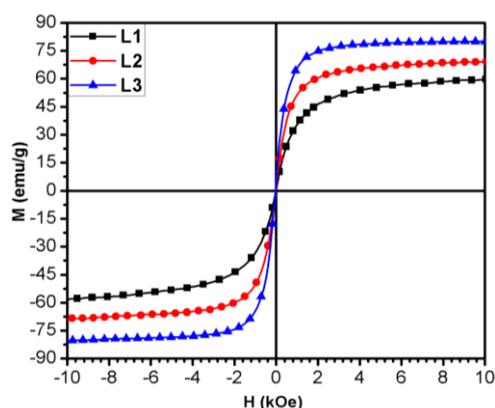
Figure 5. Hysteresis loops of L1, L2 and L3 sample synthesized by M1,M2 and M3 sample, respectively.

Figure 5 shows hysteresis loops of three samples L1-L3 at room temperature. We can observe that the 10 kOe magnetic field was not strong enough to the L1, L2 and L3 samples obtain saturation state. This can be associated with the particle size effect, in which, small particles need a larger magnetic field to turn the spins at the shell of the particles toward the direction of the external magnetic field. Magnetic of three sample are shown detail on the Table 1. It can be seen that the phase transfer took a role in the enhancement of the samples' magnetization of about 5 %, this may be due to the action of COOH function group, which changed the spin orientation on the surface of particles toward the direction of the core as the effect of DPA studied in the work of Sridhar et al [13].

Table1. Average size particles D$_{TEM}$ and magnetic saturation Ms of three samples before and process phase transfer after.

Samples	D$_{TEM}$ (nm) [9] (before phase transfer)	D$_{TEM}$ (nm) (after phase transfer)	M$_s$ (emu/g) [9] (before phase transfer)	M$_s$ (emu/g) (after phase transfer)
L1	8	8	54	58
L2	11	12	66	69
L3	13	13	70	75

In addition, when compare to the same size particles (of 13 nm [17]), which were synthesized by co-precipitation method and coated with poly (styrene – co – axit acrylic), we can observed that their particles had the magnetization of only 70 emu/g which was smaller than our particles, based on magnetic nanoparticles (synthesized by thermal decomposition method) coated with PAA, with the saturation magnetization of 75 emu/g).

4. CONCLUSIONS

In this work, we synthesized successfully magnetic fluid by thermal decomposition method in organic solvent and it was transferred phase by using PAA polymer. Used PAA being phase transfer substance because it allows to create magnetic fluid with good dispersion as well as

higher durability than SDS. The saturation magnetization of PAA-coated magnetic fluid enhanced, which will be clarified in further studies. The Successful fabrication of magnetic fluid with appropriable parameters is a good premise for biomedical applications.

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TÓM TẮT

CHẾ TẠO CHẤT LỎNG TỪ Fe₃O₄ BẰNG POLY(AXIT ACRYLIC) CHO ĐỊNH HƯỚNG ỨNG DỤNG Y SINH

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Hệ hạt nano Fe₃O₄ với kích thước khác nhau đã được tổng hợp bằng phương pháp phân hủy nhiệt trong dung môi hữu cơ. Chất lỏng từ trên nền hạt nano Fe₃O₄ đã được chế tạo bằng cách dùng poly-axit acrylic (PAA) như chất chuyển pha. Cấu trúc, hình thái và tính chất từ của mẫu được khảo sát bằng các thiết bị như: Nhiễu xạ kế tia X, hiển vi điện tử truyền qua (TEM) và từ kế mẫu rung (VSM). Phân tích kết quả XRD cho thấy tất cả các mẫu đều đơn pha với cấu trúc spinel và kích thước tinh thể trung bình dưới 15 nm. Phân tích các ảnh TEM chỉ ra rằng kích thước hạt trung bình của các mẫu có giá trị gần tương đương với kết quả tính toán từ XRD. Giá trị từ độ bão hòa cao nhất tại nhiệt độ phòng sau khi chuyển pha cho mẫu có thời gian và nhiệt độ phản ứng tối ưu (2 giờ, 298 °C) là 75 emu/g. Sự liên kết giữa bề mặt hạt từ với các nhóm chức của PAA đã được thể hiện qua phổ hồng ngoại Fourier. Đồng thời, kích thước hạt và độ bền của chất lỏng từ được đánh giá qua phổ tán xạ laser động và thế zeta, cho thấy hệ hạt có phân bố kích thước hẹp với độ bền cao. Điểm đáng chú ý là quá trình chuyển pha đã góp phần làm tăng giá trị từ độ bão hòa (khoảng 5 % so với mẫu ban đầu). Chất lỏng từ trên nền hạt nano Fe₃O₄ với độ đồng đều, từ độ cao và độ bền tốt mở ra khả năng ứng dụng trong y sinh, đặc biệt trong nhiệt từ trị và tăng tương phản ảnh cộng hưởng từ.

Từ khóa: hạt nano từ Fe₃O₄, phương pháp phân hủy nhiệt, poly(acrylic acid), quá trình chuyển pha, chất lỏng từ.