

Effects of the conditions of the microemulsion preparation on the properties of Fe₃O₄ nanoparticles

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Abstract. Fe₃O₄ nanoparticles have been prepared by the microemulsion technique with water as the aqueous phase, n-hexane as the oil phase and Span 80 as the surfactant. The reaction occurred under air, N₂ or high temperature and high pressure atmosphere. Particle size can be controlled by the concentration of the reactants dissolved in water, the ratio of water/surfactant and the atmospheric conditions. The particle size is of 6 - 20 nm. They are superparamagnetic with the saturation magnetization of 50 emu/g. Functionalization of the particle surface has been carried out by using a single layer of oleic acid for hydrophilic surface and double layer of oleic acid and sodium dodecyl sulfate for hydrophilic surface to disperse them in non-aqueous and aqueous solvents, respectively. Changing the conditions of the preparation affected to the properties of the product. This technique showed advantages such as simple, small size particles, monodisperse over the coprecipitation methods.

Keywords: Magnetite nanoparticles, microemulsion, superparamagnetic, Fe₃O₄.

1. Introduction

Magnetic fluids are of interest of many researchers due to their potential applications in physics and biology [1,2]. Magnetic fluids consist of magnetic nanoparticles, a surfactant and a carrier liquid. The magnetic properties of magnetic fluids are determined by magnetic nanoparticles (NPs). The surfactant helps

nanoparticles to disperse in the carrier liquid. The carrier liquid can be polarized or non-polarized depending on applications. As a result, it is necessary to choose a proper surfactant for nanoparticles disperse in the carrier liquid. Magnetic particles are normally required to have a high saturation magnetization M_s , biocompatibility, low-cost and stability under the working environment. Magnetite Fe₃O₄ are widely used to make magnetic fluid because that material can fulfill above requirements. For biological applications, two

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nano effects have been taken into account, which are high surface area and superparamagnetic property. Superparamagnetic NPs have no coercive field and no remanent magnetization but they do have high magnetization under a magnetic field. This fact is important for biological applications when it is desired to have high magnetization when a magnetic field is applied and to have no magnetization when the magnetic field is off. While magnetite particles are required to have the diameter less than about 20 nm in order to be superparamagnetic at room temperature, the surface effect is stronger when particle size is smaller. In addition, particle size distribution is very important for ensuring all particles have the same magnetic properties. The simplest way to make magnetite fluids is coprecipitation Fe^{3+} and Fe^{2+} ions by OH^- at room temperature [3]. However, this method has a problem to obtain particles with diameter of less than 10 nm and with small size distribution.

Microemulsion (inverse micelle) is suitable way for obtaining the uniform and size controllable nanoparticles [4]. A microemulsion may be defined as a thermodynamically stable dispersion of two immiscible liquids consisting of small droplets of one or both liquids stabilized by an interfacial film of surface active molecules (surfactant, stabilizer). In water-in-oil microemulsions, the aqueous (water) phase is dispersed as microdroplets surrounded by a monolayer of surfactant molecules in the continuous non-aqueous (hydrocarbon) phase. If a soluble metal salt is incorporated in the aqueous phase of the microemulsion, it will reside within the aqueous droplets surrounded by oil. These microdroplets continuously collide, coalesce and break again. If two identical microemulsions are produced

with a reactant P dissolved in the aqueous cores of one microemulsion and a reactant Q in the other microemulsion, upon mixing, they will form precipitate PQ, which will be contained entirely within the aqueous cores of the microemulsions. The growth of these particles in microemulsions is suggested to involve inter-droplet exchange and nuclei aggregation.

2. Experiment

The synthesis process occurred via the mixing of two microemulsion systems with identical compositions but different aqueous phase types – one containing metal ions (reactant A), the other, a precipitating agent (reactant B). The first one consisted of an aqueous solution of iron chloride salts ($\text{FeCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) dispersed in the Sorbian monooleate (Span 80)/n-hexane. The second system comprised a precipitating agent NH_4OH dispersed in the Span 80/n-hexane. The two microemulsions were mixed together under continuous stirring (typically 2 hr) to obtain nanoparticles. We obtained a water-in-oil reverse microemulsion system, in which Span 80 as surfactant to stabilize the emulsion state, n-Hexane as the continuous oil phase (o), and the aqueous phase (w) containing $c = 0.2 - 0.4$ M Fe^{2+} (the concentration of Fe^{3+} was adjusted to keep the ratio of $\text{Fe}^{3+}/\text{Fe}^{2+}$ to be 2:1 - reactant A), was used for synthesis of magnetite NPs. Particle size could be adjusted by changing concentration c of the reactant in the aqueous phase, changing the volume ratio of water and surfactant ($w/s = 20 - 100$), and the reaction atmosphere (300 K/1.0 at and 450 K/1.5 at). There were three types of samples: (A) mixing in air, (B) after mixing in air, the system was

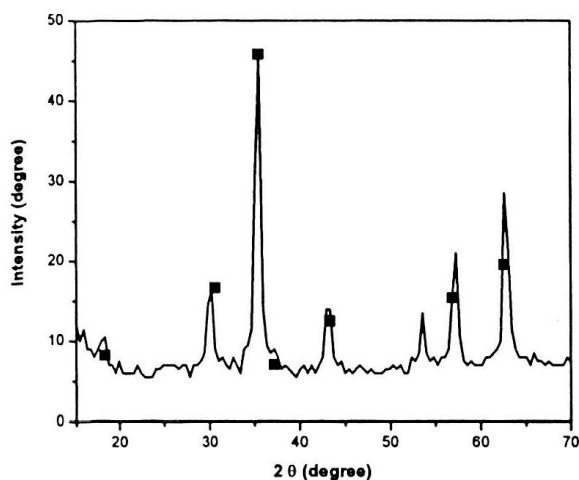


Fig. 1. XRD patterns of magnetite powder with concentration of Fe^{2+} of 0.2 M in the aqueous phase. The solid squares present the theoretical reflections of Fe_3O_4 (pdf # 790418).

submitted to an atmosphere with temperature of 180°C and pressure of 1.5 at for a time of 8 hr, and (C) mixing in N_2 . High temperature and pressure in case B fostered the reaction to form nanoparticles. In type B, we combined the microemulsion and the hydrothermal technique. When reaction completed, magnetic decantation was applied to remove NPs from the excess solution. Then oleic acid (OA) as a surfactant was mixed to coat NPs. Using magnetic decantation and washing by n-Hexane four times, OA-coated NPs dispersed in n-Hexane was made. The fact that Span 80 could not be used to coat NPs was due to the molecule of this surfactant could not create a chemisorption with magnetite surface while OA could [5]. For dispersing in water, Sodium dodecyl sulfate (SDS) was used as a second layer of surfactant. The hydrophobic part of SDS tended to the hydrophobic part of OA, which created a hydrophilic surface on nanoparticles (SDS/OA-coated nanoparticle).

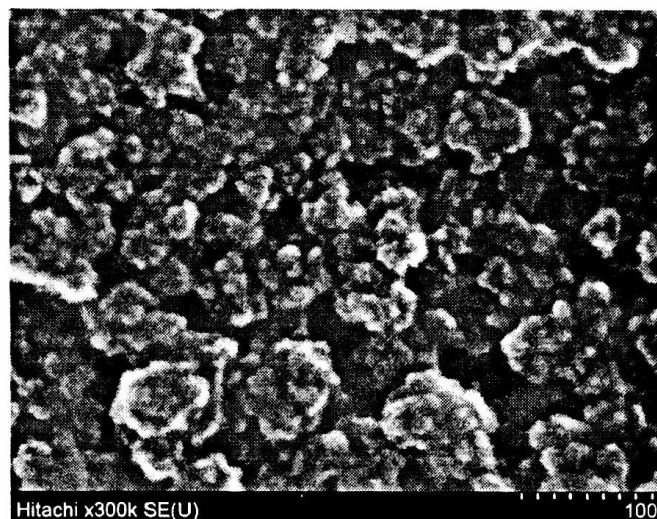


Fig. 2. Typical SEM image of magnetite nanoparticles (type C).

Structure analysis of the dried powder of non-coated NPs was conducted by using a D5005 X-ray diffractometer with $\text{Cu K}\alpha$ radiation. Magnetic properties were measured by a DMS 880 vibrating sample magnetometer. Morphology of NPs was examined by a JEOL 5410 LV scanning electron microscope. Weight loss (Thermal Gravity Analysis) as a function of temperature (heating rate of $10^\circ\text{C}/\text{min}$) was studied by a DSC SDT 2960 TA Instruments.

3. Results and discussion

The mechanism of formation of particles was understood as a short single burst of nucleation occurred when the concentration of constituent species reached critical supersaturation. Then, the nuclei so obtained were allowed to grow uniformly by diffusion of solutes from the solution or/and aggregation of other nuclei to their surface until the final size was attained. In conventional coprecipitation, size (d) can be controlled by concentration of reactants [5], pH and ionic strength [6]. Size of 12 - 100 nm could be made by this technique.

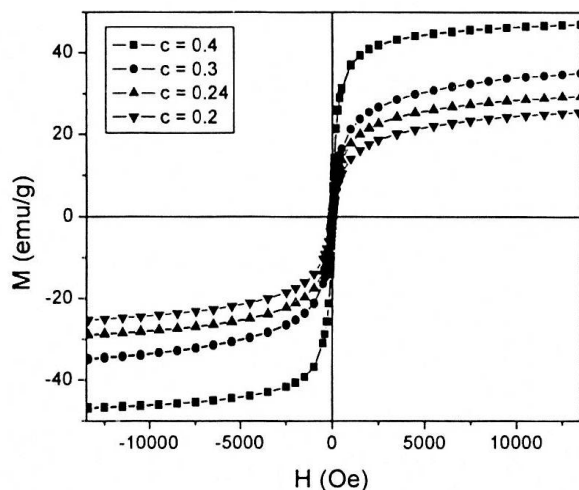


Fig. 3. Magnetization curves of of type C samples with different concentrations of the reactant.

Smaller particle size is difficult to obtain. Microemulsion can produce small particles with diameter can be less than 10 nm, which coprecipitation technique cannot do [7]. In microemulsion, amount of reactant is limited in a volume of the microdroplet, which can be controlled by water/surfactant ratio and atmospheric conditions.

XRD patterns of the dried non-coated NPs of type C sample with different concentration (0.2 and 0.4 M) of reactant ($w/s = 20$) were shown in Fig. 1. All reflections are of magnetite Fe_3O_4 . These indicated that the particles have the invert spinel crystalline structure as in the bulk phase. The width of peaks of the sample with higher concentration was broader than that of the peaks of sample with lower concentration. That means high concentration produced large particles. By controlling concentration, we could control the particle size. It suggested a way to obtain desired particles. Particle diameter can be determined by Cherrer formula [8]:

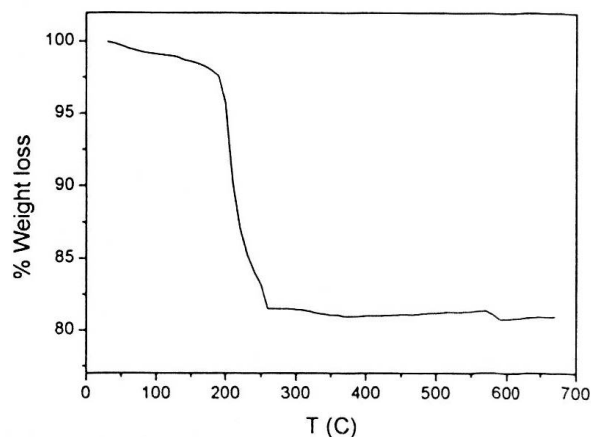


Fig. 4. Weight loss as a function of temperature of OA-coated NPs of type C sample with $c = 0.2$ M.

$$d = \frac{0.9\lambda}{B \sin \theta} \quad (1)$$

where λ is the wave length of the X-ray, θ is the reflection angle, and B is the full width at half maximum of the peak. The particle diameter obtained from that for all samples was in the range from 7 nm to 22 nm.

A typical scanning electron microscope (SEM) image of magnetite sample (type C, $w/s = 20$) coated by OA was presented in Fig. 2. Particle size was less than 10 nm which is in agreement with a value from XRD results. Some features of this image showed particle size can be 5-6 nm. Similar images were obtained for other samples.

Magnetic properties of sample of type A prepared under ambient conditions were non-ferromagnetic at room temperature, which can be understood by the fact that the reaction could not complete under these conditions. Whereas, magnetic properties of samples of type B were ferromagnetic with the saturation magnetization M_s of 50 emu/g and the coercive field H_c of 50 Oe at room temperature for sample with $c = 0.1$ M. M_s and H_c reduced when the concentration

of reactant lowered and reached 20 emu/g and 5 Oe, respectively, for sample with $c = 0.025$ M. The critical diameter d_c at which ferromagnetic property becomes superparamagnetic was determined from the equivalent condition of magnetic energy and thermal energy:

$$KV = 25kT \quad (2)$$

where K is anisotropy constant of material that makes NPs (magnetite), V is the volume of particle. V is proportional to d_c^3 , k is the Boltzmann constant and T is the absolute temperature. For magnetite, critical diameter is about 20 nm. The ferromagnetism in type B samples may come from the particles with the size d larger than the critical dimension. Large particles were formed when the microemulsion systems was under high temperature and high pressure, which made the microdroplets become bigger because the interfacial energy increased with the temperature and pressure. In some bioapplications such as hyperthermia, ferromagnetic behavior is required. So this type of sample can be applied for such applications. Samples of type C showed superparamagnetic behavior. The magnetization curve of these samples with concentration of 0.2 M - 0.4 M was given in Fig. 3. Highest M_s of 50 emu/g was reached for sample with $c = 0.4$ M. The value of M_s reduced to 35, 30, and 25 emu/g when the concentration was 0.3, 0.24, and 0.20 M, respectively. This can be ascribed to the smaller particle size in the sample with low concentration in which, amount of reactant limited in a droplet of microemulsion was smaller than that in the droplet of high concentration. As a result, smaller particles were formed in the low concentration samples. Small particle possesses larger surface layer whose magnetization was normally lower than

that of the bulk material. With type C samples, value of M_s was also dependent on the ratio w/s in a way which was similar to other types of samples. The saturation magnetization reduced with w/s . With w/s smaller than 60, M_s of about 50 emu/g does not change significantly. However, at higher w/s , the value of M_s reduces faster and lowers to 35 emu/g at $w/s = 100$. The explanation for that is the same as the argument above. Therefore, the optimum ratio is chosen to be 20.

Among three ways for the preparation of magnetic nanoparticles, microemulsion in N_2 atmosphere was the best way to produce superparamagnetic particles. The particle size can be controlled by adjusting the concentration of reactants, volume ratio of water/surfactant.

Magnetic nanoparticles tend to form clusters to reduce surface energy. To disperse NPs in a solvent, we need a stabilizer. There are two types of solvents: polarized (such as water) and non-polarized (such as n-hexane). Each type of solvent requires suitable stabilizer (known as another name "surfactant"). Polarized and non-polarized solvent only allow hydrophilic and hydrophobic particles to be dispersed, respectively. Therefore, the particles must be coated by a surfactant which makes them hydrophilic or hydrophobic. That surfactant must have a strong contact with the particles. The contact that comes from hydrophobic affinity in such the case of Span 80 was much weaker than that came from chemisorption in such the case of OA. With OA, the hydrophilic carboxyl group attached to particle surface and left the hydrocarbon chain outward [5]. So that, OA-coated NPs have hydrophobic surface which makes them be dispersed in non-polarized hexane. Weight loss

of a typical OA-coated NPs of type C sample with $c = 0.2$ M was presented in Fig. 4. In the temperature range lower than 200°C , the loss was about 2% which can be explained by the evaporation of remained water. There was a 17 % weight loss appeared in the range $200^{\circ}\text{C} - 250^{\circ}\text{C}$, which resulted from the evaporation of OA coating NPs. From the weight loss of OA-coated NPs (17%) and supposing that there was a single layer of OA molecules around particles and the area of a OA molecule took place on the particle surface was about 0.3 nm^2 [9], we can estimate particle size of NPs was about 8 nm. The result is reasonably in agreement with SEM observation. To make NPs hydrophilic, we used double layer of surfactant by coating another layer of SDS on the OA-coated NPs. The hydrocarbon chain of SDS tended inward to the hydrocarbon chain of OA and gave the particle a hydrophilic surface. These SDS/OA-coated NPs can be dispersed in polarized liquid such as water. In many bioapplications, NPs are required to be dispersed in water, this way functionalizing of NPs is a potential for that. Especially, the double layer coated NPs have a hydrophobic space between the two layers. This space can be used as a carrier to load hydrophobic drug and with an assistance of an external magnetic field, the double layer coated NPs can be applied for magnetic drug delivery [10].

4. Conclusion

By adjusting concentration of reactant, water/surfactant ratio, reaction atmosphere in microemulsion method, we can produce magnetic nanoparticles with particle size of less than 10 nm. Microemulsion technique under N_2

atmosphere is a versatile way to produce magnetic nanoparticles. The particles can be dispersed in polarized or non-polarized solvents by coating a single layer or double layer of relevant surfactant around NPs. The nanoparticles are suitable for biological applications.

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Ảnh hưởng của các điều kiện chế tạo trong phương pháp nhũ tương lên tính chất của hạt nano Fe_3O_4

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Hạt nano Fe_3O_4 đã được chế tạo bằng phương pháp nhũ tương sử dụng nước, hexane và chất hoạt hóa bề mặt Span 80. Phản ứng tạo hạt nano xảy ra trong môi trường không khí (với áp suất và nhiệt độ khí quyển và áp suất và nhiệt độ cao) và khí nitơ. Kích thước hạt nano từ 6 đến 20 nm. Hạt có tính siêu thuận từ với từ độ bão hòa đạt đến 50 emu/g. Việc chức năng hóa bề mặt kỵ nước được thực hiện nhờ oleic acid, chức năng hóa bề mặt ưa nước bằng lớp hoạt hóa bề mặt kép gồm oleic acid và sodium dodecyl sulfate. Thay đổi điều kiện chế tạo ảnh hưởng nhiều đến tính chất hạt nano. Hạt nano tạo bằng phương pháp này có những tính chất ưu việt so với phương pháp đồng kết tủa là hạt nhỏ, độ đồng nhất cao.