Optik 124 (2013) 6910–6914

Contents lists available at ScienceDirect

Optik

journal homepage: www.elsevier.de/ijleo

Study on the optically linear birefringence and dichroism properties of Fe_3O_4 magnetic nanoparticles

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ARTICLE INFO

Article history:
Received 12 January 2013
Accepted 25 May 2013

Keywords:
Birefringence
Co-precipitation
Dichroism
Nanoparticle
Retardance

ABSTRACT

We adopt an improved co-precipitation method to prepare the Fe_3O_4 magnetic nanoparticles (MNPs). Influence factors such as the reaction temperature, the pH value of the solution, and the Fe^{3+}/Fe^{2+} molar concentration are considered. Via the transmission electronic microscope and X-ray diffractometry, we characterize the dispersibility and size of the products. The reaction temperature and the pH value of the solution have a great influence in the dispersibility and size of MNPs. The diameter of Fe_3O_4 MNP, produced under Fe^{3+}/Fe^{2+} molar concentration of 0.25 mole/l and molar ratio of 1.9:1, the reaction temperature is 80 °C, and the pH value reaches 9, is close to 11 nm. Above all, considering the variation of molar concentrations in Fe^{3+}/Fe^{2+}, the linear birefringence and dichroism of the kerosene-based ferrofluids are investigated by a Stokes polarimeter.

1. Introduction

Fe_3O_4 magnetic fluid or ferrofluid (MF, FF) is a colloidal suspension consisting of magnetite nanoparticles with a typical dimension around 10 nm and carrier liquid [1]. The preparation methods of magnetite powders mainly include co-precipitation, oxidation of $Fe(OH)_2$ by H_2O_2, microemulsion, and thermal decomposition of $Fe(CO)_5$ [2–4]. The chemical co-precipitation method is frequently used because of its advantages of low cost, simple equipment, usual raw materials, easy control of the size and shape of the nanoparticles, and precise control of the property and chemical composition of the product. Due to the high ratio of surface to volume and magnetization, Fe_3O_4 nanoparticles are prone to aggregate. To enhance the compatibility between the Fe_3O_4 magnetic nanoparticles (MNPs) and water or oil, and to control and/or tailor of the surface properties of the nanoparticles, the surface modification for Fe_3O_4 magnetic nanoparticles is a necessity.

Further, as for the linear birefringence and linear dichroism measurements in magnetic fluids, Taketomi [5] proposed a simple experimental setup for the study of birefringence in a magnetic fluid thin film. To substitute four parameters' values including the two absorption coefficients of magnetic fluids with respect to the ordinary ray and extraordinary ray and the maximum and minimum transmitted intensities when rotating the analyzer, the birefringence (the difference between the refractive indices for extraordinary and ordinary light, respectively) can be easily obtained by this experimental setup and method.

Afterwards, Di et al. [6] discussed the particle agglomeration in magnetic fluids using the structure proposed in [5]. Further, Pu et al. developed a simple optical configuration based on a polarizer and derived the analytical expression of the transmitted elliptically polarized light in [7]. From the rotation angle of the principal axis of the ellipse and the degree of polarization of the elliptically polarized light after magnetic fluids, the magnetic-field-induced linear birefringence and dichroism are investigated by numerical simulation. The results indicate it is usually improper to ignore the linear dichroism for some applications. In our previous study in [8], an optical scheme based on Stokes–Mueller formalism and rotating-wave-plate Stokes polarimeter was successfully developed for obtaining concurrent measurements of the linear birefringence and dichroism, and three probed lights, linearly polarized orientated at 0°, 45°, and circularly polarized, respectively, are utilized.

In the present investigation, Fe_3O_4 MNPs were prepared by an improved co-precipitation, using NH_4OH as the precipitating agent to adjust the pH value. The effects of the reaction temperature, the pH value of the solution, and the molar concentration of Fe^{3+}/Fe^{2+} salts in dispersibility and size of MNPs are studied. It is noted that the effects of surfactant amount in [9] is also mentioned in this paper. Mechanical stirring with appropriate speed and ultrasonic vibration are adopted in the titration and surface coating processes. Afterwards, the Fe_3O_4 MNPs were used as the precursor of oil-based FFs. We used oleic acid as surfactant and

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http://dx.doi.org/10.1016/j.ijleo.2013.05.130

kerosene as solvent. Characterization of the dispersibility and size in MNPs involved using transmission electronic microscope (TEM) and X-ray diffractometry (XRD). Finally, the linear birefringence and dichroism measurements of FF samples are executed for different molar concentrations of Fe^{3+}/Fe^{2+} salts with a molar ratio of 1.9:1 by our developed Stokes polarimeter [8].

2. Synthesiss of MNPs

To synthesize the Fe_3O_4 MNPs, in a typical experiment, a solution with 25 ml of $FeCl_3$ (2 mole/l) and 25 ml of $FeSO_4{\cdot}7H_2O$ (1 mole/l), respectively, mixed with a molar ratio of 2:1 (ideal ratio) was prepared in a three-necked flask without N_2 protection, and was ultrasonically vibrated for 30 min. In a room temperature, ammonia aqueous solution (25%) of 20 ml was then charged into the mixed solution at a rate of 0.15 ml/s with vigorously mechanical stirring of 1000 rpm and ultrasonic vibration, until the pH value of the solution reached 9. Thereafter, the temperature was raised to 70 °C and the solution was kept on stirring for additional 30 min. The resulted black precipitate was collected and washed three times with deionized water and ethyl alcohol, and until the pH value of the mixture was around 7. Then the deionized water of 100 ml was added to the mixture. Mechanical stirring of 900 rpm and ultrasonic vibration were done for 30 min. While the mechanical stirring is still on, and the temperature was raised to 80 °C, the oleic acid is dropped into the solution by four times, total volume of 1.2 ml were used. Finally, the reaction was done and then dried under vacuum at 60 °C for 12 h. The MNPs with 1000 mg was added to the kerosene of 20 ml, ultrasonic vibration is done for 30 min, and the FFs were obtained.

From our previous study considering the effects of the amount of surfactant in producing MMPs [9], we fix the molar ratio between Fe^{3+} and Fe^{2+} salts as an ideal value of 2:1, the stirring speed is set as 800 rpm in titration, the operating temperature is set as 70 °C, the reaction temperature in surface coating is set as 80 °C, and only change the amount of surfactant as oleic acid from 0.8 ml to 2 ml in increments of 0.4 ml. It is noted that the dispersion mode is chosen as only ultrasonic vibration when surface coating is done.

The effect of the amount of surfactant is studied through performing TEM (JEOL, JEM-1400, Japan) and XRD (Shimadzu, XRD-6000, Japan) analysis. From the comparisons of TEM micrographs [9], the dispersibility for the amount of oleic acid with 1.2 ml is best and fewer agglomerations are found in 100 nm scale. In addition, from the XRD patterns of Fe_3O_4 MNPs [9], it was found that all the different peaks at $2\theta = 30.1°$, 35.4°, 43.1°, 53.4°, 56.9°, 62.6°, and 73.9° could be well indexed to the inverse cubic spinel structure of Fe_3O_4. The average crystallite sizes of Fe_3O_4 MNPs obtained under different amounts of oleic acid (0.8, 1.2, 1.6, and 2.0 ml) were determined to be 12.5, 13.0, 15.2, and 17.3 nm, respectively. The sizes of these MNPs, respectively, are close to the critical size of 15 nm and lower diameter as 13.0 nm is obtained when the amounts of oleic acid is 1.2 ml.

3. Results and discussion

3.1. Effects of the reaction temperature

In this part, the molar ratio between Fe^{3+} and Fe^{2+} salts is fixed as 2:1 and the amount of oleic acid is 1.2 ml, the dispersion mode is changed as simultaneous ultrasonic vibration and mechanical stirring of 900 rpm for 30 min when surface coating is done, and the stirring speed in titration is 1000 rpm. The reaction temperature ranges from 75 °C to 90 °C. From the TEM micrographs, as shown in Fig. 1, it is found that when the reaction temperature is 80 °C or 85 °C, as shown in Fig. 1(b) and (c), good dispersibility (with clear boundary and few agglomerations) is obtained and compared to the other figures, as shown in Fig. 1(a) and (d) in 20 nm scale. Most of the particle's diameter in Fig. 1(b) and (c) is below 20 nm and with near-spherical shape. It is known that the low reaction temperature will induce process slower, and while the high temperature will induce larger diameter and the chance for collisions between particles and results in agglomeration. The reaction temperature is too low or too high, which are not good for dispersibility. Therefore, the appropriate reaction temperature is required to set carefully for the dispersion, the diameter, and even the magnetization.

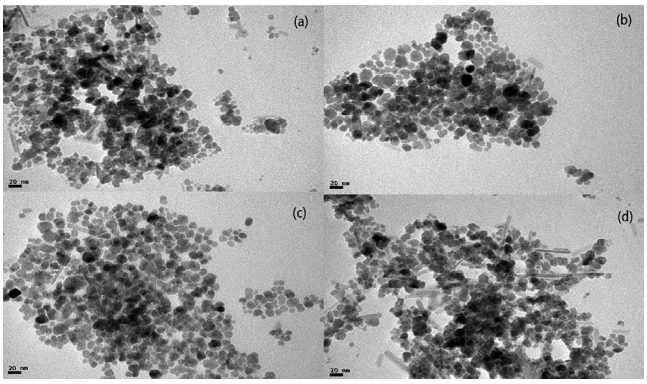

Fig. 1. TEM images under different reaction temperatures, (a) 75 °C, (b) 80 °C, (c) 85 °C, (d) 90 °C.

Fig. 2 shows XRD patterns of Fe_3O_4 MNPs, synthesized under different reaction temperature, it was found that all the different peaks at $2\theta = 30.1°$, 35.4°, 43.1°, 53.4°, 56.9°, 62.6°, and 73.9° could be well indexed to the inverse cubic spinel structure of Fe_3O_4. The average crystallite sizes of Fe_3O_4 MNPs obtained under different reaction temperature (75, 80, 85, and 90 °C) were determined to be 13.1, 10.3, 10.9, and 11.5 nm, respectively. The lowest diameter of these MNPs is obtained when the reaction temperature is 80 °C. The sizes of these MNPs are all below the critical size of 15 nm, the superparamagnetic iron oxides are therefore obtained. It is noted when the reaction temperature is 85 °C or 90 °C, there are a peak found at 32.7°, which is resulted from the oxidation effect of high temperature, and the Fe_2O_3 may arise.

3.2. Effects of the pH value

In this part, we fix molar concentration of 0.25 mole/l for $FeCl_3$ and $FeSO_4{\cdot}7H_2O$ (76 ml and 40 ml, respectively) and the amount of oleic acid is chosen as 0.5 ml. The molar ratio between Fe^{3+} and Fe^{2+} salts is fixed as 1.9:1, the dispersion mode is changed as

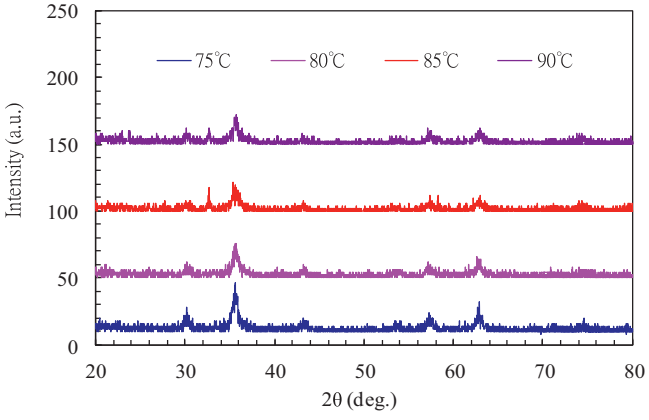

Fig. 2. XRD patterns of Fe_3O_4 nanoparticles synthesized under different reaction temperatures from 75 °C to 90 °C.