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Magneto-optical properties and magnetic inductive heating of sodium oleate coated Fe_3O_4 magnetic fluid

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ABSTRACT

The Fe_3O_4 nanoparticles coated by sodium oleate (SO) were prepared by chemical co-precipitation method. Via Stokes polarimeter, the retardance of water-based SO coated Fe_3O_4 magnetic fluids (MFs with a mass ratio of 50% as SO to Fe_3O_4) with 1 g/ml is measured as 2.86° (dichroism is 0.064) under 64.5 mT. Next, the heating performance of SO coated MFs in the alternating magnetic field was investigated and the potential in the magnetic fluid hyperthermia was evaluated. According to TEM, the diameter distribution for the SO coated MF (mass ratio of 50%) is within 10–25 nm. When the concentrations of SO coated MFs are of 2 mg/ml and 50 mg/ml, under the external alternating magnetic field with applied apparent current of 210 A, after heating 200 s, the temperature of the coated MFs is greater than 45 °C, respectively, reached the requirements for the magnetic inductive heating treatment of medicinal cancer tumor.

1. Introduction

Investigations of a large variety of functionalized magnetic nanoparticles (MNPs) have been conducted to find new applications in academic and industrial applications, such as catalysis, magnetic storage, magnetic separation, wastewater treatment, tumor hyperthermia, and so on [1]. Among various methods for producing MNPs, 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 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, such as Fe_3O_4 (magnetite) MNPs are prone to aggregate. To avoid agglomeration of MNPs due to attractive van der Waals forces, the particles need to be coated with different complex agents that provide enhanced stability due to steric hindrance or combined electrostatic and steric stabilization. Further, to enhance the compatibility between MNPs and solvent, and tailor the surface properties or functionalization of MNPs, surface modification of MNPs is necessary. The surface of Fe_3O_4 MNPs can be stabilized in an aqueous dispersion by the adsorption of oleic acid [2,4] or sodium oleate (SO) [3,4] as an amphiphilic surfactant, has much higher affinity to MNP surfaces compared to other surfactants. In addition, to improve the stability of water-based biocompatible magnetic fluids (MFs), the surface of MNPs was coated with sodium oleate as the primary layer and polyethylene glycol (PEG) [5,6] or dextran [7] as the secondary layer. Magnetic and inductive heating properties of composite nanoparticles in the PEG/Fe_3O_4 are studied and found to be useful as good thermoseeds for localized hyperthermia treatment of cancers [6,7].

Due to the strong magnetic property and low toxicity, the application of Fe_3O_4 in biotechnology and medicine has attracted significant attention. Magnetic Fluid Hyperthermia (MFH) is an important application, which can increase the temperature of tumors to 41–46 °C and therefore kill tumor cells. This method involves the introduction of ferromagnetic or superparamagnetic particles (thermoseeds) into the tumor tissue and then irradiation with an AC (magnetic field that varies sinusoidally) magnetic field [8]. The particles transform the energy of the AC magnetic field into heat by several physical mechanisms, three independent mechanisms result in thermal energy upon stimulation: Néel relaxation, Brownian relaxation, and hysteresis loss [9], and the transformation efficiency strongly depends on the frequency and amplitude of the external field as well as the nature of the particles such as magnetism, surface modification [8], and concentration of MFs [10].

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In our previous study, 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 [11]. Further, the error analysis of retardance and dichroism measurements was performed. Compared to Taketomi method [12] in low magnetic field, the method proposed in [11] was validated to be more sensitive and accurate in magneto-optical properties such as magnetic-field-induced retardance and dichroism. Further, it is noted that small size, high dispersion, and high saturated magnetization (magnetic response) may dominate the magnetic-field-induced birefringence (principal axis and retardance) behavior of MFs. Moreover, the dichroism measurements may distinguish between MFs which exhibit either weak or strong clustering in the presence of magnetic field [11]. Hence via the magneto-optical measurement to find the water-based coated MFs with high retardance, may be suitable to be used in the study of hyperthermia, i.e. magnetic inductive heating of MFs.

In this research, the Fe_3O_4 MNPs coated by SO were prepared by an improved chemical co-precipitation method. Via Stokes polarimeter with a feasible algorithm [11], the retardance and dichroism of water-based SO coated Fe_3O_4 MFs is characterized. The heating performance of SO coated Fe_3O_4 MFs in the alternating magnetic field with different concentrations was investigated and the potential in the magnetic fluid hyperthermia was evaluated. According to the TEM (transmission electronic microscopy) results, the diameter distribution for the Fe_3O_4 MF coated by SO with a mass ratio of 50% to the Fe_3O_4 is within 10–25 nm. When the concentrations of SO coated MFs are of 2 mg/ml and 50 mg/ml, under the external alternating magnetic field with applied apparent current of 210 A, after heating 200 s, the temperature of the SO coated MFs is greater than 45 °C, respectively, reached the requirements for the heat treatment of medicinal cancer tumor.

2. Experiment

2.1. Materials

Ferric chloride ($FeCl_3$), ferrous sulfate ($FeSO_4{\cdot}7H_2O$), aqueous ammonia (NH_4OH), and ethyl alcohol were all analytic grade. Sodium oleate ($C_{18}H_{33}O_2Na$, TOKYO Chemical Industry, 97%) was reagent grade. Deionized water was industrial grade and used throughout the experiments.

2.2. Synthesis of MNPs

To synthesize Fe_3O_4 MNPs, in a typical experiment, a solution with 100 ml of $FeCl_3$ (1.75 mol/l) and 100 ml of $FeSO_4.7H_2O$ (1 mol/l), respectively, mixed with a molar ratio of 1.75:1 was prepared in a three-necked flask without N_2 protection, and was ultrasonically vibrated for 30 min. In a room temperature of 20 °C, ammonia aqueous solution (mass ratio, 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 mixture (precipitate) was collected and washed three times with deionized water and ethyl alcohol, respectively, and until the pH value of mixture was around 7. After magnetic separation, washing, and decanting, the colloidal suspensions of Fe_3O_4 MNPs were obtained.

Further, in a typical experiment for coating sodium oleate (SO) onto the Fe_3O_4 MNPs, the deionized water of 100 ml was added to the suspension of Fe_3O_4 MNPs of 6 g, and mechanical stirring of 900 rpm and ultrasonic vibration were done for 30 min. Then, mechanical stirring of 900 rpm was still on, and the hydrochloric acid was used to fix the pH value of the solution to be 5.5 [13] before coating. While mechanical stirring of 400 rpm was still on and the temperature was raised to 80 °C [13,14], the SO solution of 75 g/l (3 g SO dissolved in deionized water of 40 ml) was dropped into the solution at a rate of 1 ml/min. After the titration of SO solution was over, the reaction was done for a further 30 min. Then the resulted black mixture (precipitate) was collected and washed with 50 ml deionized water until the pH value was around 7. In order to get nanoparticles with smaller size and uniform particle size distribution, the double centrifugations before the ultrasonic vibration of SO coated suspensions is adopted, i.e. the first centrifugation is of 3000 rpm for 15 min, and the second centrifugation is of 6000 rpm for 20 min, respectively. Finally the ultrasonic vibration was done on the coated MNPs contained in deionized water for 30 min, and the stabilized SO coated Fe_3O_4 MFs were obtained. The pure and SO coated MFs of 1 g/ml were measured for their magnetic-field-induced retardance and dichroism.

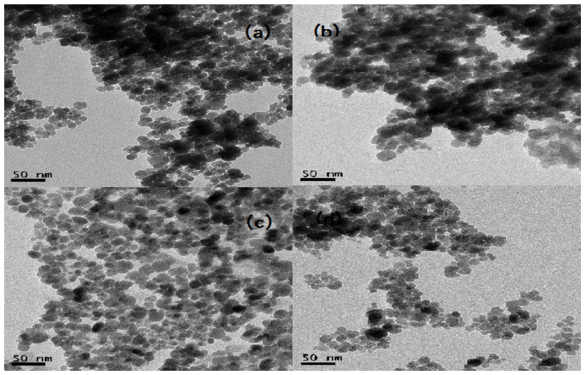

Fig. 1. TEM morphology of the nano magnetite (a) and magnetite under different amounts of sodium oleate with 2.7, 3, and 3.3 g, respectively (b–d).

2.3. Effects of the amount of surfactant

We consider the mass ratio between 6 g Fe_3O_4 (magnetite) MNPs and SO from 45% to 55% in increments of 5%. From the comparisons of TEM (JEOL, JEM-1400, Japan) micrographs, as shown in Fig. 1(a–d), the dispersibility for the amount of SO with 3 g (a mass ratio of 50% to Fe_3O_4 MNPs) in Fig. 1(c) is best and fewer agglomerations are found in 50 nm scale. The size range of SO coated MNPs is from 10 nm to 20 nm with near-spherical shape. It is noted that the MNPs without coating on SO aggregate heavily, as shown in Fig. 1(a). Fe_3O_4 MNPs with coating on appropriate amount of anionic surfactant SO in an acidic environment (pH value of 5.5), which have positive charges on their surfaces and combine with the carboxylic acid head groups of SO very well. Therefore the stability is improved. The detailed explanation could be described as the H^+ would adsorb on these hydroxyl groups under acidic environment, when added SO into solution, the electrostatic interaction between their carboxylic acid head groups and the hydroxyl groups will make them combine tougher [13].

Fig. 2 shows the XRD (X-ray diffractometry, Shimadzu, XRD-6000, Japan) patterns of the pure (uncoated) Fe_3O_4 MNPs and SO coated Fe_3O_4 MNPs (mass ratio of 50% as SO to Fe_3O_4 MNPs). From the patterns, it was found that all the different peaks at 2θ(crystal face) = 30.1°(2 2 0), 35.4°(3 1 1), 43.1°(4 0 0), 53.4°(4 2 2), 56.9°(5 1 1), 62.6°(4 4 0), and 73.9°(5 3 3) (not obvious) could be well indexed to the inverse cubic spinel structure of Fe_3O_4 (JCPDS card no. 85-1436) [15]. The average crystallite size D was obtained from Sherrer equation: $D = K\lambda/(\beta\cos\theta)$, where K is a constant of 0.89, λ is X-ray wavelength of 0.154056 nm, β is the peak width