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Facile synthesis of stable magnetic fluid using size-controlled Fe_3O_4 nanoparticles

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ABSTRACT

Magnetic fluids based on superparamagnetic, well-crystalline and mono-dispersed Fe_3O_4 nanoparticles are synthesized by a facile thermal decomposition method. Low-cost $Fe(oleate)_3$ is used as ferrous resource, and paraffin oil is introduced as solvent and carrier simultaneously. Fe_3O_4 nanoparticles with three kinds of different size (12, 16 and 20 nm), exhibiting different saturation magnetization of 65.51, 68.03 and 74.48 emu/g, respectively, are prepared easily by controlling the thermal decomposition time. Magnetic performance and viscosity-temperature characteristics of the magnetic fluid are also studied. It is found that the saturation magnetization of the magnetic fluid with 5% Fe_3O_4 mass percentage is 2.94 emu/g, which exhibits a good viscosity temperature characteristics compared with paraffin carrier.

1. Introduction

Magnetic fluids (ferrofluids) with a combined fluidic and magnetic properties have wide applications in industry and biomedicine [1]. It is a kind of stable suspension of magnetic NPs dispersing in liquid which is not destroyed even in the presence of centrifugal force or magnetic field [2,3]. Magnetic nanoparticles (NPs), such as magnetite (Fe_3O_4), iron (Fe), nickel (Ni), and cobalt (Co), can be applied in magnetic fluid preparing. Among these magnetic NPs [4–6], Fe_3O_4 has been extensively adopted in magnetic fluids for its tunable magnetic properties [7]. So far many synthetic strategies are proposed to prepare magnetic fluids of Fe_3O_4 NPs. Hereinto, co-precipitation method in oil or water with the presence of surfactants is a traditional route to prepare magnetic fluids [8]. However, the traditional multi-step preparing process of magnetic fluid is complex, which restrains its further application [9]. Therefore, simplifying its preparing technology is of great importance.

A great number of previous works focused on improving this method to obtain stable and high effective magnetic fluids. In the early 1980s, Shimoiizaka et al. developed a method for stable magnetic fluids preparation by dispersing Fe_3O_4 NPs in aqueous solutions [10]. Gregory G. Warr prepared a water based magnetic fluid with Fe_3O_4 [11]. Lucian Borduz prepared magnetic fluids using silicone oil, ester oil or hydrocarbon oil based carriers. There are many advantages of co-precipitation method in Fe_3O_4 preparing [12], such as high yields, cost-effectiveness and so on. Nevertheless, the disadvantages of the method are much in evidence. Firstly, the preparation process is a complex multi-step. Secondly, the size of Fe_3O_4 NPs is uniform and the stability is also poor. All of these shortcomings of co-precipitation method restrict their application in industry. Thus, developing a new route to prepare magnetic fluids in a facile, low-cost and effective way is a task of top priority.

Thermal decomposition method is found to be a simple route in magnetic fluids preparing, while the high cost of ferrous resource and solvent limits its application in magnetic fluids. This method may be regarded as a facile, cheap and effective route to prepare magnetic fluids if adopting a suitable ferrous resource and solvent. Luckily, $Fe(oleate)_3$ is founded as a good ferrous resource with its low-cost. Since the first report by Hyeon's group on the synthesis of monodisperse Fe_3O_4 NPs using 1-octadecene and iron-oleate complex as a reactant [13], the method has been utilized for the synthesis of many other binary metal oxides [14]. But it is difficult to choose a suitable low-cost solvent for $Fe(oleate)_3$ in thermal decomposition method. Firstly, the solvent must be cheap enough to fulfill the requirement of the industry. Secondly, the whole magnetic fluid preparing process may be greatly simplified if the solvent can also work as a carrier of magnetic fluid at the same time, which makes it possible to prepare stable magnetic fluids in

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facile route with thermal decomposition method by choosing a suitable solvent.

In the present work, a low-cost and facile method is suggested to synthesize magnetic fluid of uniform polyisobutenylsuccinimide (PIBSI) coated Fe_3O_4 NPs. Iron oleate is utilized as ferrous resource in the thermal decomposition method. The low-cost mineral oil (paraffin) is used as both solvent and carrier. The paraffin oil is the best choice as the solvent of this method for the reason of the high boiling point, good thermal stability and low-cost. Polyisobutenylsuccinimide (PIBSI) acts as a stabilizer to protect the NPs in preparing stable fluids. A stable paraffin based magnetic fluid with monodisperse Fe_3O_4 NPs is prepared via the thermal decomposition method. The paraffin oil plays a dual role as the solvent of the Fe_3O_4 NPs and the carrier of the magnetic fluid in this work.

2. Material and methods

2.1. Chemicals and materials

Ferric chloride ($FeCl_3{\cdot}6H_2O$, 99%), ethanol, sodium oleate, deionized water, and heptane were purchased from Sinopharm Chemical Reagent Co. Ltd. Polyisobutenylsuccinimide (PIBSI) and paraffin oil were purchased from China Petrochemical Corporation.

2.2. Synthesis of iron oleate

The iron oleate complex was prepared by reaction of sodium oleate and Fe^{3+} chlorides [11]. In a typical synthesis, 40 mmol of $FeCl_3{\cdot}6H_2O$, 120 mmol of sodium oleate, 100 ml of H_2O, 100 ml of ethanol, and 200 ml of hexane were mixed and refluxed at 70 °C for 4 h. The mixed iorn oleate complex was obtained after separated from water.

2.3. Synthesis of magnetic fluid

5 g of the iron oleate complex, 100 mL paraffin oil, and 5 g PIBSI dispersant were mixed and magnetically stirred for 1 h under flowing N_2. The mixture was then heated to 350 °C with a rate of 10 °C/min and maintained at this temperature for 40 (sample A), 80 (sample B) and 120 min (sample C), respectively, under N_2 with continuous stirring. The mixture was then stirred at 200 °C until the impurities were evaporated. Stable paraffin oil based magnetic fluid was obtained after the autoclave was naturally cooled to room temperature.

2.4. Characterization

X-ray powder diffraction (XRD) patterns were obtained by a Bruker D8 diffractometer using Cu Ka radiation (λ = 1.5406 Å). Transmission electron microscopy (TEM) experiment was performed on a JEM-2100 electron microscope (JEOL, Japan) with an acceleration voltage of 200 kV. Carbon coated copper grids were used as the sample holders. Fourier-transform infrared spectra (FT–IR) of the samples were acquired with a Spectrum One IR spectrometer. Magnetization was measured at 300 K with a Lake Shore Vibrating Sample Magnetometer Model 7404, applying field strengths up to 20 kOe. Rotating viscometer (NDJ-79) is a kind of measuring various newtonian fluid and non-newtonian fluid apparent viscosity of the precision instruments. So it is used to measure the viscosity of the magnetic fluid. In the test, the magnetic fluid is added in the tank of the rotating viscometer. A suitable rotor and measuring range is chosen (readings should be in the range of 20–30°). The viscosity of the magnetic fluid in different temperatures is achieved through the automatic temperature control part of the rotating viscometer.

3. Results and discussion

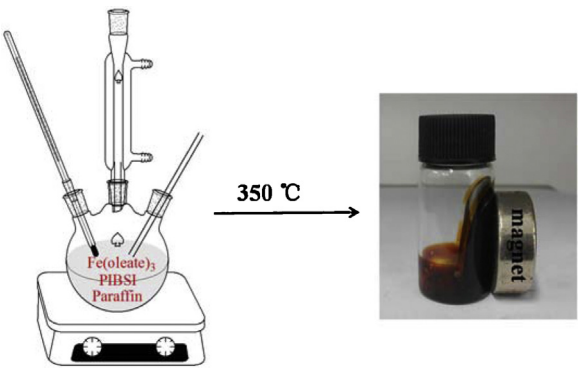
3.1. Characterization of magnetic nanoparticles

Thermal decomposition method is used to prepare stable magnetic fluid just in a facile route, and paraffin is chosen as the solvent. The preparing process is shown in Scheme 1. Fe_3O_4 NPs are obtained by suspending the decomposed $Fe(oleate)_3$ in a solvent (paraffin) with a surfactant (PIBSI) to get stable magnetic fluid. The whole preparing process is greatly simplified to obtain functional magnetic fluid from size-controllable Fe_3O_4 NPs just in one step. The synthesis of Fe_3O_4 with controlled size tends to attract attention because of their broad applications. Size controlled Fe_3O_4 NPs with a high level of monodispersity can be obtained by high-temperature decomposition of iron organic precursors [15–18], but the high cost of solvent limits their application. In this paper, monodispersed magnetite NPs based on high temperature (350 °C) reaction of iron oleate dispersed in paraffin oil are successfully prepared in the presence of PIBSI. PIBSI is amphiphilic molecular composed of two long non-polar tails and a polar head. The polar heads can attach to the oleic acid coated Fe_3O_4 NPs. It is significant to utilize inexpensive paraffin oil as the substitute of expensive 1-octadecene (the traditional solvent) to prepare Fe_3O_4 in thermal decomposition method. Moreover, the particle size can be controlled from 12 to 20 nm.

The Fe_3O_4 NPs are characterized in detail by TEM. Three representative TEM images of samples a–c together with the corresponding particle size histograms are shown in Fig. 1. The average size is 20 nm for sample a, 16 nm for sample b and 12 nm for sample c, which are obtained by measuring particles at random [19]. Fig. 1 shows that the particle size of the Fe_3O_4 NPs could be controlled by adjusting various reaction time. Fe_3O_4 NPs with sizes of 12, 16 and 20 nm are synthesized under different reaction time of 40 min, 80 min and 120 min, respectively.

As shown in Fig. 2, the Fe_3O_4 NPs are characterized by XRD. And all the diffraction peaks in Fig. 2 can be indexed as the face-centered magnetite (Fe_3O_4) crystallite compared with the literature (JCPDS card No. 74-0748), which indicates the obtained NPs are magnetite. The average particle size of the NPs is calculated to be about 20.8, 17.1 and 13.2 nm by using Scherrer's equation [20]. The result matches well with that of the TEM images. The diffraction peaks of the Fe_3O_4 NPs at 30.0, 35.5, 43.0, 53.0, 57.0, and 62.6 are respectively ascribed to the (2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1) and (4 4 0) planes of the magnetite, which are consistent with pure spinel Fe_3O_4 [21].

The well monodispersion Fe_3O_4 NPs with small sizes make them exhibit excellent magnetic properties. Magnetization properties of the as-prepared magnetite NPs are investigated at 300 K by measuring magnetization curves, and the maximum magnetic



Scheme 1. Reaction setup for preparation of magnetic fluid.

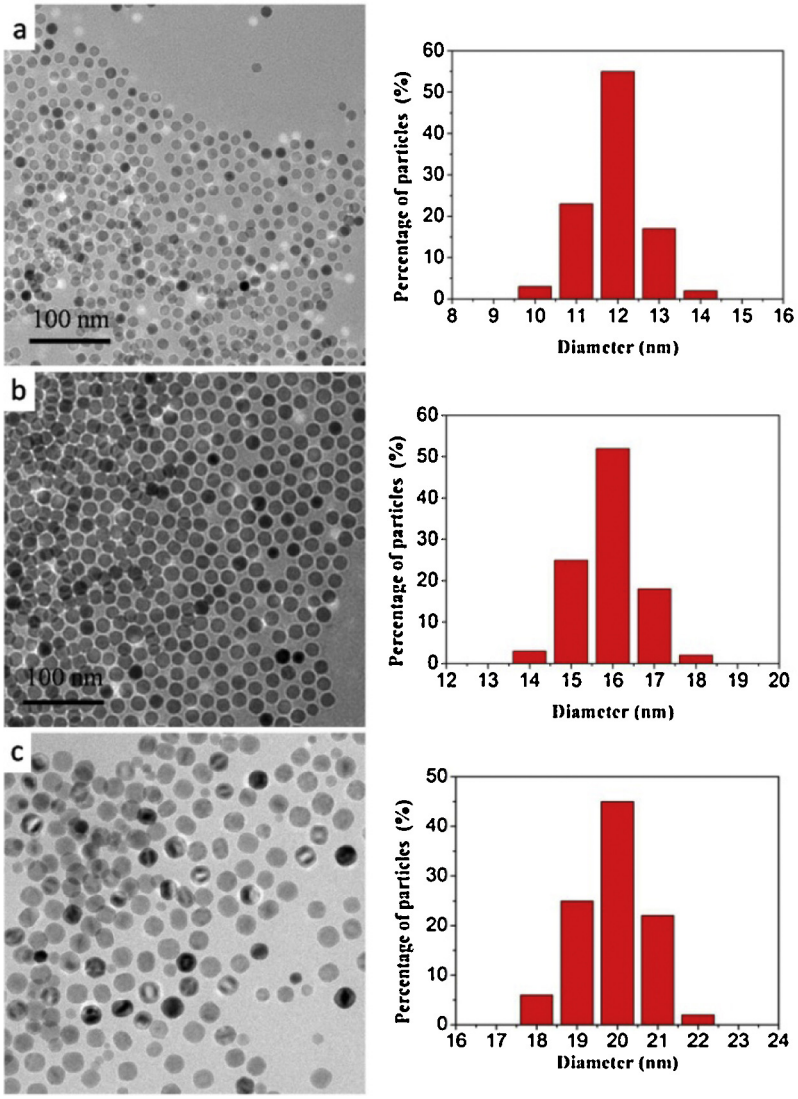


Fig. 1. TEM image and the corresponding particle size histogram of Fe_3O_4 (a) 12 nm (b) 16 nm and (c) 20 nm.

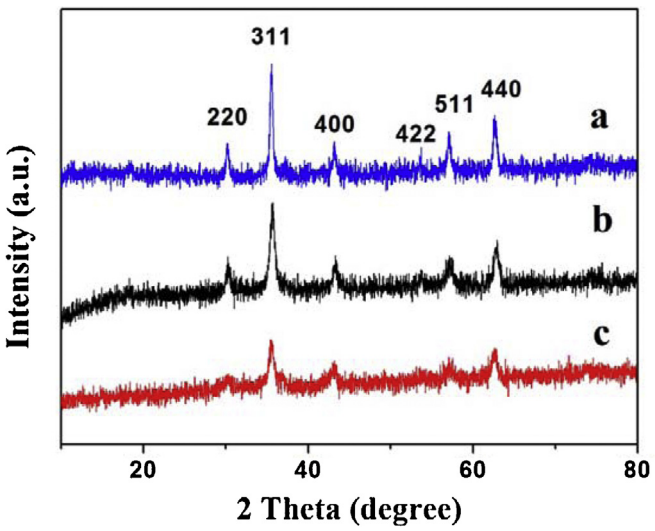


Fig. 2. X-ray diffraction of Fe_3O_4 NPs (a) 20 nm (b) 16 nm and (c) 12 nm.

field is 20 kOe (Fig. 3). The magnetization curves of the three different sizes of spherical Fe_3O_4 demonstrate typical superparamagnetic behaviour with negligible coercivity and remanence, in accordance with the theory that superparamagnetic behaviour is often observed at room temperature with magnetite NPs [22]. The saturation magnetization of 12, 16 and 20 nm Fe_3O_4 is 65.51, 68.03 and 74.48 emu/g, respectively. The saturation magnetization is smaller than that of the theoretical value of bulk magnetite (98 emu/g) [23].

The presence of abundant surface organic groups is significant for Fe_3O_4 NPs in stabilizing magnetic fluids. An FT–IR spectrometer is applied to research the surface organic groups of the Fe_3O_4 NPs. The prepared magnetic fluid was transferred to a 50 mL centrifuge tube, washed three times with a mixture of hexane and ethanol at a concentration of 1:2, and Fe_3O_4 NPs were obtained by centrifugating at 8000 rpm for 10 min. The Fe_3O_4 NPs were further FT–IR spectrum measured, which is shown in Fig. 4. The strong characteristic peaks at 590 cm^{-1} can be ascribed to Fe—O stretch. The peaks at 2922 and 2850 cm^{-1} can be ascribed to —CH_2 stretch of the PIBSI, which is absorpted on the surface of Fe_3O_4 NPs produced by thermal decomposition of the Fe(oleate)$_3$. And for the

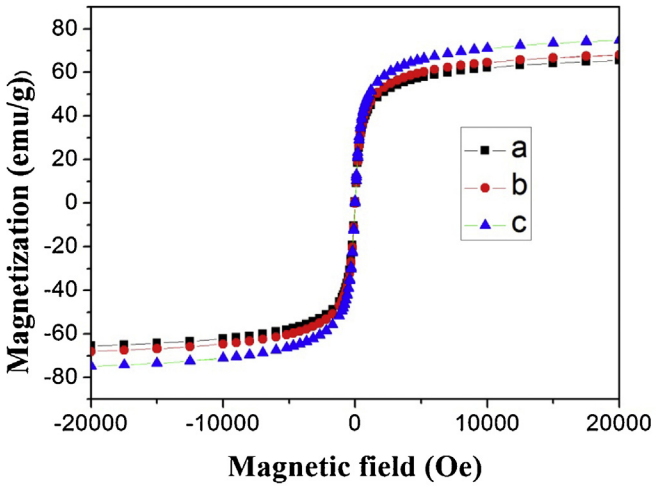


Fig. 3. Magnetic hysteresis curves of Fe_3O_4 (a) 12 nm (b) 16 nm and (c) 20 nm.

PIBSI coated Fe_3O_4 NPs, the peak at 1404 cm^{-1} is assigned to the CH_2 bending vibration of the PIBSI [24].

3.2. Characterization of magnetic fluids

Magnetic fluids are differentiated with magnetorheological fluid, in which magnetic fluids are suspensions of magnetic nanoparticles with size of about 10 nm in an appropriate carrier liquid like water, kerosene or various oils, while magnetorheological fluids are suspensions of magnetic particles mainly on the micro-scale. Compared with magnetic particles in magnetorheological fluids, the magnetic field with each particle containing only a single magnetic domain in the ferrofluids is permanent and the nanoparticles rotate randomly under Brownian motion because of their small size [24,25].

The stable magnetic fluids are prepared by thermal decompose method in one-pot. The as-prepared magnetic fluids exhibit good magnetic properties. And Fig. 5 shows the initial magnetization curve of magnetic fluid with 5% mass percentage (12 nm Fe_3O_4). We can draw from Fig. 5 that the magnetic fluid has superparamagnetic property, and the magnetization of the fluid increases with the increasing of magnetic field (H) simultaneously until it tends to be saturated. The saturation magnetization of the magnetic fluid with 5% mass percentage Fe_3O_4 of 12 nm is 2.94 emu/g.

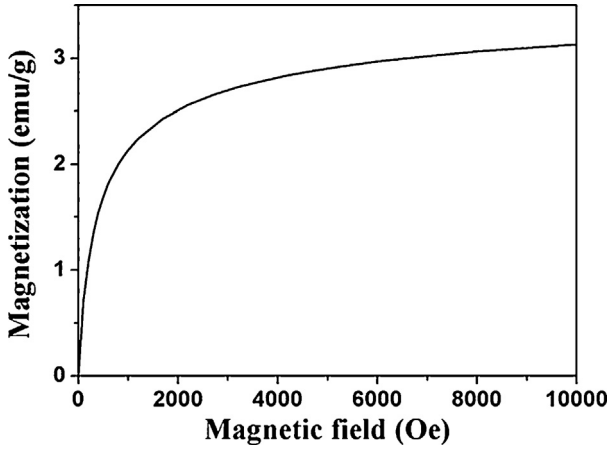


Fig. 5. Magnetization curves of Fe_3O_4 NPs in paraffin.

The viscosity dependence on temperature is studied by comparing the pure paraffin with paraffin based magnetic fluid, as shown in Fig. 6. It is found that the viscosity of both the pure paraffin and paraffin based magnetic fluid decreases sharply with the increasing of temperature before 40 °C, and then as temperature further increases, the viscosity changes little. The viscosity difference between the paraffin based magnetic fluid and the pure paraffin, pure paraffin is 24 cP at 25 °C, and it turns to 1.5 cP at 95 °C. The viscosity of paraffin based magnetic fluid is bigger than that of pure paraffin at the same temperature. The paraffin based magnetic fluid is a typical suspension system that Fe_3O_4 nanoparticles and surfactant are uniformly suspended in carrier paraffin, suspension system exhibits an increase of suspension viscosity compared to the medium liquid, especially at a low volume fraction it simply follows an Einstein equation [26,27]. In Fig. 6, the viscosity increases bigger than general suspension effect, mainly because of the high viscosity of surfactant PIBSI using in the suspension. From the result, it can be concluded that the magnetic fluid exhibits a relative bigger viscosity and a lower viscosity-temperature relationship than paraffin carrier.

Stability is one of the most important technical indexes of fluids, which can be easily reflected by density testing. If the density of a fluid does not change for a long time and no particles precipitated in the fluid [28], it is proved to be stable. The density of the Fe_3O_4 fluid remains 0.905 g cm^3 even for 90 days (Fig. 7) with no Fe_3O_4 precipitated out, indicating that the PIBSI-coated Fe_3O_4

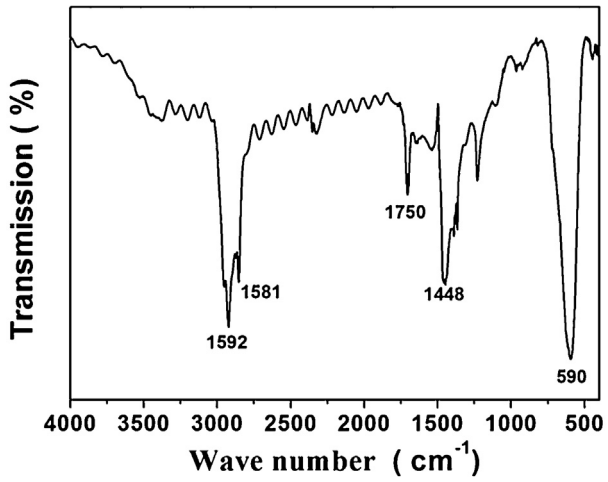


Fig. 4. FT–IR spectra of coated Fe_3O_4 NPs.

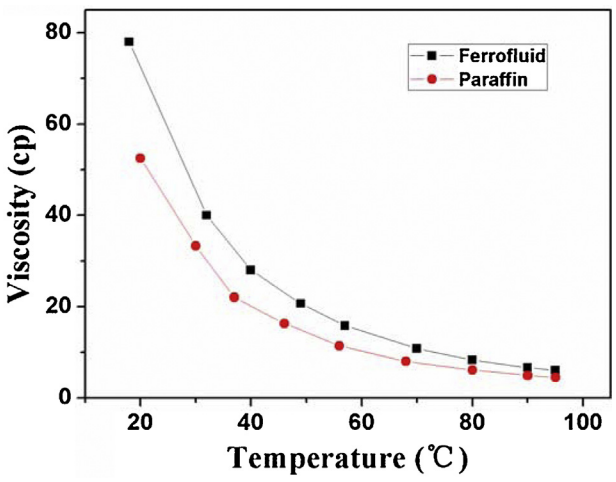


Fig. 6. The relationship of viscosity and temperature.

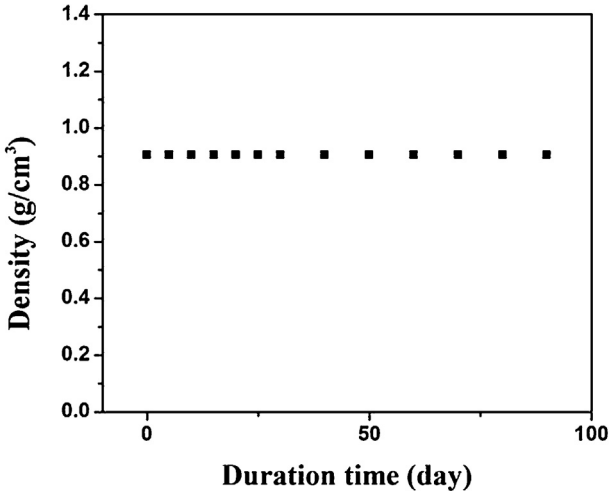


Fig. 7. Stability index of magnetic fluid.

NPs are not separated from paraffin for such a long time and the stability of the paraffin based Fe_3O_4 fluid is very good.

4. Conclusions

In summary, a facile thermal decompose method is developed to synthesize size-controlled Fe_3O_4 NPs magnetic fluids with good magnetic properties and high monodispersity. The prepared magnetic fluids display excellent magnetic properties with the special saturation magnetization (5% Fe_3O_4 mass percentage) being 2.94 emu/g. Particle size of the Fe_3O_4 NPs could be controlled by adjusting various reaction time. Fe_3O_4 NPs with average diameter of 12, 16 and 20 nm are synthesized under the reaction time of 40 min, 80 min and 120 min, the saturation magnetization of which is 65.51, 68.03 and 74.48 emu/g, respectively. The paraffin-based magnetic fluids have a good viscosity temperature characteristics compared with paraffin oil carrier.

Acknowledgments

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