Synthesis and Characterization of Fe$_3$O$_4$ Nanoparticles for Nanofluid Applications-A Review

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Abstract. In this review, Fe$_3$O$_4$ metal oxide nanoparticle-water is used as nanofluids coolant for modern engine. The enhancement of thermal conductive mostly depends on size of metal oxide nanoparticles-water nanofluids. The major factors which control the thermal conductivity are (a) particles distribution of nanoparticles; (b) concentration of nanoparticles, (c) type of solvents, and (d) temperature and mixture of nanoparticles. The Fe$_3$O$_4$ magnetic nanoparticles (MNP) were synthesized by a co-precipitation method using sodium citrate and oleic acid as modifiers. Phase composition and microstructure analysis indicate that the sodium citrate and oleic acid have been successfully grafted onto the surface of Fe$_3$O$_4$ MNPs. The magnetic behaviors reveal that the modification can decrease the saturation magnetization of Fe$_3$O$_4$ MNPs due to the surface effect.

1. Introduction

Ultrahigh-performance cooling is one of the most vital needs of many industrial technologies. However, inherently low thermal conductivity is a primary limitation in developing energy-efficient heat transfer fluids that are required for ultrahigh-performance cooling. Modern nanotechnology can produce metallic or nonmetallic particles of nanometer dimensions. Nanomaterials have unique mechanical, optical, electrical, magnetic, and thermal properties. Nanofluids are engineered by suspending nanoparticles with average sizes below 100 nm in traditional heat transfer fluids such as water, oil, and ethylene glycol. The types of particles used in nanofluids may be categorized as follows: (i) Metals, such as Au, Ag, Cu, and Fe; (ii) Oxides, such as CuO, Cu$_2$O, Fe$_3$O$_4$, Al$_2$O$_3$, SiO$_2$, and TiO$_2$; (iii) Carbon nanotubes (CNTs), which have shown the highest conductivity enhancement: Single-walled (SWCNT), double-walled (DWCNT), and multi-walled (MWCNT) are three types of CNTs commonly used and (iv) Other particles, such as Si compounds. A very small amount of guest nanoparticles, when dispersed uniformly and suspended stably in host fluids, can provide dramatic improvements in the thermal properties of host fluids. Choi et al describe new class of nanotechnology-based heat transfer fluids that exhibit thermal properties superior to those of their host fluids or conventional particle fluid suspensions which is nanofluids [1]. Nanofluid technology, a new interdisciplinary field of great importance where nanoscience, nanotechnology, and thermal engineering meet, has developed largely over the past decade. The goal of nanofluids is to achieve the highest possible thermal properties at the smallest possible concentrations (preferably<1% by volume) by uniform dispersion and stable suspension of nanoparticles (preferably<10 nm) in host fluids. To achieve this goal it is vital to understand how nanoparticles enhance energy transport in liquids. In the review article we are described the synthesis and characterization of Fe$_3$O$_4$ nanoparticles.
2. Production Techniques:
The Fe$_3$O$_4$ nanoparticles were synthesized by wet chemical reduction technique. In the synthesis, 10 ml of 2.5 M sodium boro-hydride (NaBH$_4$; Sisco Chem, Mumbai, India) solution was prepared in a 100 ml clean glass beaker under magnetic stirring. Then 40 ml 0.1 M ferric chloride hexa-hydrate (FeCl$_3$·6H$_2$O; Loba Chemie, Mumbai, India) solution was prepared and added drop wise to the first solution under vigorous stirring. With gradual addition of ferric chloride solution the final solution became darker and eventually became complete black. Black precipitates were produced in less than 1 min after the addition of complete ferric chloride. The reaction proceeded by generation of bubbles. The reaction was presumed to be complete once bubble formation ceased. The Fe$_3$O$_4$ nanoparticles were filtered and given multiple wash using distilled water and absolute methanol. The particles were dried in oven for overnight at 50°C.

3. Key Findings:
A wide variety of methods have been reported for synthesis of Fe$_3$O$_4$ nanoparticles, including co-precipitation [2], sol–gel method [3], flow injection [4], electrochemical [5], solvothermal [6], hydrothermal [7], microwave-assisted [8], thermal decomposition of iron (III) acetylacetonate in tri (ethylene glycol) [9] etc. Here we report the simple wet chemical reduction method for synthesis of Fe$_3$O$_4$ nanoparticles at ambient condition.

Figure 1: FESEM images of Fe$_2$O$_3$ nanoparticles [10]

Figure 1 shows all the Fe$_2$O$_3$ MNPs show homogeneously spherical shape with diameter about 12-15 nm, which is in agreement with the results of the XRD analysis. The Fe$_3$O$_4$ MNPs prepared without modification aggregate in deionized water. The sodiumcitrate and oleic acid -modified Fe$_3$O$_4$ MNPs show good dispersion capability in deionized water and oleic acid solution, which should be due to the fact that the high surface energy and dipolar attraction of the MNPs greatly reduced after modified by sodiumcitrate and oleic acid.

Figure 2 shows the sites and intensity of the diffraction peaks are consistent with the standard pattern for JCPDS Card No. (79 - 0417) magnetite - synthetic. The sample show very broad peaks, indicating the ultra-fine nature and small crystallite size of the particles. Cubic single phase nano sized Fe$_3$O$_4$ powder has been obtained. According to the Debye–Scherrer formula, the crystallite size $D_{hkl}$ for the sample nano sized Fe$_3$O$_4$ powder has been obtained. According to the Debye–Scherrer formula, the crystallite size $D_{hkl}$ for the sample is given by [11].
Figure 2: XRD diffraction of Fe₃O₄ nanoparticles [11]

Figure 3: FTIR spectra of Fe₃O₄ nanoparticles[12]

Figure 3 shows the FT-IR spectra of Fe₃O₄ MNPs of all samples. It can be seen that the characteristic absorption of Fe-O bond is at 580 cm⁻¹ and 634 cm⁻¹, while that of -OH bond is at 3398 cm⁻¹. The absorptions at 1393 cm⁻¹ and 1587 cm⁻¹ are characteristic peaks of the COO-Fe bond, which may be due to the reaction of hydroxide radical groups on the surface of Fe₃O₄ with carboxylate anion of sodium citrate. The peaks at 2855 cm⁻¹ and 2924 cm⁻¹ are from the vibration of in long alkyl chain -CH₂ and -CH₃. Furthermore, the characteristic peak of -OH bond at 3378 cm⁻¹ is obviously enhanced. These peaks reveal that sodium citrate has been successfully grafted onto the surface of Fe₃O₄ MNPs as well [13].

Figure 4: M-H hysteresis curves of all the Fe₃O₄ MNPs[13].

M-H hysteresis curves of all samples are shown in Figure 4. Symmetric hysteresis and saturation
magnetization can be observed, and all as-prepared Fe₃O₄ MNPs show ferrimagnetic behaviors. This is because that the diameter of MNPs is smaller with that of critical threshold of Fe₃O₄ (25 nm). The saturation magnetization of sample are 50.61, 61.36, 56.05 and 55.43 emu·g⁻¹ respectively, which are obviously lower than that of the bulk Fe₃O₄ (90 emu·g⁻¹). This phenomenon may attribute to the small particle size effect since a noncollinear spin arrangement occurs primarily at or near the surface, which results in the reduction of magnetic moment in Fe₃O₄ NPs. The saturation magnetization of which may be ascribed to the increase of particle size of Fe₃O₄ MNPs. The saturation magnetization decreases evidently when the Fe₃O₄ MNPs were modified with sodiumcitrate and oleic acid. This result could be attributed to the surface spin effect on Fe₃O₄ MNPs caused by modification, which subsequently decrease the saturation magnetization value. Nevertheless, compared to the decrease of saturation magnetization value in polymer-modification, the reduction by sodiumcitrate or oleic acid modification is significantly lower, showing the obvious advantage using small molecular compounds as modifiers[13].

Amani et al.[14] investigated on Thermal conductivity measurement of spinel-type ferrite MnFe₂O₄ nanofluids in the presence of a uniform magnetic field, they found the thermal conductivity of MnFe₂O₄/water nanofluids in attendance of magnetic field. The MnFe₂O₄/water is synthesized and is prepared in different nanoparticles concentrations ranging from 0.25% to 3%. The thermal conductivity of nanofluids has been determined without magnetic field. Sha et al.[15] investigated on experimental investigation on the convective heat transfer of Fe₃O₄/water nanofluids under constant magnetic field, they found that in the experiment the effects of temperature and magnetic field strength on the convective heat transfer of the Fe₃O₄/water nanofluids were examined. Sha et al.[16] investigated on The effect of perpendicular, uniform and gradient magnetic field on the convective heat transfer of Fe₃O₄/Water nanofluids in a turbulent flow regime. The local convective heat transfer coefficients were measured at volume concentrations of 0.5, 1, 2 and 3% and temperatures of 20, 30 and 40°C, they found that It showed that the heat transfer coefficient increased with the increase of the Fe₃O₄/Water nanofluids concentration, temperature and magnetic field intensity Without the effect of the magnetic field, the maximum averaged convective heat transfer coefficient of Fe₃O₄/Water nanofluids over that of distilled Water was improved by 5.2% at the volume concentration of 3% and the temperature of 40°C. Bennia et al.[17] investigated on the nanofluid mixture of water and Fe₃O₄ with MHD effect. The simulation is performed in order to determine the turbulence forced convection heat transfer in a circular tube. The study is implemented by considering the single and two phase mixture, and the particle is considered in a spherical shape of diameter 36nm, they found that Nu and friction factor at fixed Reynolds number is proportional to the magnetic field. Sheikholeslami et al. [18] investigated on the forced convection heat transfer in Fe₃O₄-ethylene glycol nanofluid in a two-dimensional enclosure with Coulomb force. They found that the Coulomb forces impact on forced convective heat transfer in nanofluid is presented. Forced convection of Fe₃O₄-ethylene glycol nanofluid in the presence of an external electric field is presented. Khashan et al. [19] investigated at the The temperature rise characteristics of the nanofluids at different heights of the solar collector, for duration of 300 min, under a solar intensity of 1000 W m⁻². They come to the conclusion that the Fe₃O₄-SiO₂ NPs have a core/shell structure with spherical morphology and size of about 400 nm. nanofluid, since the silica coating improves both the thermodynamic stability of the nanofluid and the light absorption effectiveness of the NPs. At a concentration of 1 mg/1 ml of Fe₃O₄-SiO₂/H₂O. Ebrahimimi et al. [20] investigated on the role of external magnetic field with strength up to 0.2 T was studied on the thermal conductivity of the considered nanofluid with different basic parameters such as nanoparticle concentration and temperature of the base fluid. Mixed Fe₃O₄/CuO nanofluid was selected for conductivity of the pure and mixed Fe₃O₄ with CuO nanoparticle has significant enhancement at presence of the external magnetic field. By increasing the concentration of the Fe₃O₄ nanoparticle the coefficient of thermal conductivity is increased.
4. Conclusion 
In this review, The thermal conductivity of nanofluids has been determined without magnetic field. they found that friction factor at fixed Reynolds number is proportional to the magnetic field, the experiment the effects of temperature and magnetic field strength on the convective heat transfer of the Fe₃O₄/water nanofluids were examined. The local convective heat transfer coefficients were measured at volume concentrations of 0.5, 1, 2 and 3% and temperatures of 20, 30 and 40°C, Nu and friction factor at fixed Reynolds number is proportional to the magnetic field. When nanoparticle concentration is 2% by volume and it is kept at 20°C then its thermal conductivity is 1.25 and viscosity modulation is 2.088 and the ratio between thermal conductivity and viscosity modulation is 0.598 and if Fe₃O₄ with water nanofluid system is kept at 20°C-60°C then the thermal conductivity is increased by 25%.

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