In-situ precipitation of ultra-stable nano-magnetite slurry

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A B S T R A C T

In this contribution, we prepared water-based magnetic fluids of iron oxide nanoparticles using an in-situ precipitation method. The effect of dodecanoic acid addition as a surfactant on the physico-chemical and magnetic properties of iron oxide nanoparticles was investigated as well. The quantity of the surfactant was varied between 3 and 5 g. Raman spectroscopy and X-ray diffraction (XRD) were utilized to confirm the presence of spinel phase magnetites (Fe3O4). Dynamic light scattering (DLS) and transmission electron microscopy (TEM) were used to characterize the resulting magnetic nanoparticles' size and morphology. The results showed polydispersed hexagonal nanoparticles (average diameter of ca. 70 nm) as a result of the protocol. Moreover, the pH-dependent stability of the samples confirms that magnetite nanofluids were highly stable in the wide range of pH, from 4–12. The optimal amount of dodecanoic acid to produce ultra-stable nano-magnetite slurry with the highest saturation magnetization of 8.6 emu g−1 was determined to be 4.5 g.

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1. Introduction

Recently, many researchers have made attempts for understanding magnetic nanomaterials. The greatest innovation in this field has been the improvement of new measuring techniques and the regeneration of synthetic methods [1]. Nanofluids are defined as engineered colloidal suspensions of nanoparticles in a base fluid [2]. The magnetic nanofluid, or ferrofluid, is a specific smart material that its properties are adjustable via an external magnetic field [3]. These colloidal dispersions are composed of tiny single-domain magnetic particles, which are suspended in a continuous phase, whose rheological behavior is governed by external magnetic fields [4]. Ferrofluids are also known as magnetic-liquids, which refer to a stable colloidal system formed by nanoscaled magnetic particles in a liquid that are treated with surfactants to realize high levels of dispersion. In fact, the combination of magnetism of solids, along with the rheology of liquids, results in very unique physico-chemical properties, such as special magnetism, electricity, and magneto-optical features [5]. Nano-ferrofluids were proven applicable in technological, biological, and medical fields. Ferrofluids are also vastly utilized in magnetic hyperthermia, magnetic drug targeting, separation of cells and magnetic diagnostics (contrast enhancement for magnetic resonance imaging, MRI) [6]. Moreover, water-based magnetic nanofluids are defined as a particular category of magnetic fluids due to the specifications of stabilization mechanisms and structural coordination under different conditions as opposed to magnetic fluids utilizing organic polar carriers [7].

Currently, it is quite a challenge to control the size and the dispersity of nanoparticles in selected solvents. Nanoparticles possess high surface energies due to their large surface-to-volume ratio. They are also prone to agglomerate, as they are constantly trying to minimize these high energies. The inter-particle magnetic dipolar attraction also contributes to the total energy in the system, as their intrinsic magnetic properties attempt destabilization within a colloidal dispersion [8]. Most applications require that nanomagnetic particles be well-dispersed within a gravitational field, as aggregation will disrupt the formation of a single magnetic domain of the particles. This problem can be addressed by coating the nanoparticles with polymers, block copolymers, polyelectrolytes, surfactants, or inorganic materials. The stabilization of magnetic nanoparticles in a slurry can be done via in-situ and post-synthesis coatings [9].

One of the main surfactants that have been utilized for the preparation of ferrofluids are fatty acids. Fatty acids are generally divided into two main groups; unsaturated and saturated. Unsaturated fatty acids possess one or more double bonds in their carbon chain, while saturated fatty acids are long-chain carboxylic acids that normally possess between 12 and 24 carbon atoms with no double bonds. The most important unsaturated fatty acid that has been frequently used is oleic acid (OA) [10–13]. Moreover, ferrofluids can be synthesized using other surfactants accompanying oleic acid in the form of double layer surfactants [14–16]. In addition, dispersing magnetite nanoparticles using oleic acid...
and polymer matrix were already reported in literature [17–19].

Dodecanoic acid or Lauric acid (LA) is a saturated fatty acid with a 12-carbon atom chain that has been clinically endorsed for both pharmaceutical and the food industry. They are also capable of synthesizing water-based colloidal suspension of MNPs that are highly stable [15,20]. MNPs coated with dodecanoic acid at low concentrations were proven to be biocompatible for in-vitro applications [21]. However, there are still some controversies on the concentrations were proven to be biocompatible for in-vitro applications. However, Khalafalla and Reimers [22] claimed that for water-based magnetic fluids, 12-carbon atoms are more efficient for stabilization. Herein, we synthesized ultra-stable water-based magnetic nanofluids (MNFs) using an in-situ precipitation method, employing different amounts of dodecanoic acid as a surfactant. The advantage of the in-situ generation of nano-precipitations as a second phase is the fact that the nanostructures can be naturally formed, which will allow us to eschew complicated post-synthesis treatments [23].

2. Experimental procedure

2.1. Materials

Ferrous chloride tetrahydrate (FeCl₂·4H₂O), ferric chloride hexahydrate (FeCl₃·6H₂O), ammonia solution (28% NH₄OH), dodecanoic acid (C₁₂H₂₄O₂, 99%) were all purchased from Sigma-Aldrich Co., (USA). All the chemicals and solvents were used without further purification. Moreover, during the experiments, Millipure water with a resistivity of greater than 18.0 MO/ cm was used.

2.2. Preparation of nano-magnetite slurry

In a typical method [22], 12 g FeCl₂·4H₂O and 24 g FeCl₃·6H₂O were separately dissolved in 50 ml of deionized water. The solutions were mixed into a 500-ml beaker, and then 50 ml of ammonium hydroxide (28% NH₄OH), dodecanoic acid (C₁₂H₂₄O₂, 99%) were all purchased from Sigma-Aldrich Co., (USA). All the chemicals and solvents were used without further purification. Moreover, during the experiments, Millipure water with a resistivity of greater than 18.0 MO/ cm was used.

2.3. Characterization

The XRD patterns and crystal structure of the magnetite nanoparticles were recorded using Cu Kα radiation on a Rigaku RU2000 rotating anode diffractometer. The FTIR spectra were obtained using a Perkin-Elmer 100 spectrophotometer (Waltham, MA, USA) over the range of 400–4000 cm⁻¹ under standard conditions. The structural properties were also investigated using a Raman microscope, Renishaw (Gloucestershire, UK), in the range of 100–800 cm⁻¹. The TEM images of the nanoparticles were taken with JOEL TEM 2010, operated at 200 kV. Zeta potential and particle size were measured using a Zetasizer Nano ZS apparatus.

The Zeta potential and hydrodynamic diameter of the different coated nanoparticles were measured by dispersing 0.5 mL of magnetite slurry in 100 mL distilled water, followed by using the DLS to probe the response of the ferrofluid. In order to adjust the pH of the solution for zeta potential measurements, HNO₃ 10⁻³ mol L⁻¹ or NH₄OH 10⁻³ mol L⁻¹ was added to the aforementioned solution. The DLS measurements used a 632.8 nm He-Ne laser to illuminate the sample, with the scattered light collected at 90°. To evaluate the influence of various amounts of surfactants on the magnetic behavior of the samples, the full magnetization curves of nano-magnetite slurry samples were examined using a vibrating sample magnetometer (VSM 880, DMS/ADE Technologies, USA).

4. Results and discussions

4.1. X-ray diffraction

The XRD patterns for the magnetite nanofluid samples are shown in Fig. 1, which can be fully indexed to the Bragg reflections expected for Fe₃O₄. However, it cannot be ascertained from the XRD diffractogram whether or not the further oxidized Fe₂O₃ phase exist in the samples due to similar lattice types or constants. As seen from Fig. 1, although the crystallinity of the samples decreased with increasing amounts of applied surfactants, the width of the peaks broadens, which might be representative of decreased crystal size. The size of the nanoparticles was estimated using the width of the most intense diffraction peak, the (3 1 1) reflection, via the Debye–Scherer equation, \( D = 0.9/\beta \cos \theta \), where \( \beta \) is the full width half-maximum of the peak. The results are shown in Table 1.

4.2. Raman spectroscopy

Raman spectroscopy was carried out to investigate the phase of iron oxide. Magnetite is poorly scattered, especially at low laser powers, which are required to keep the sample from undergoing laser irradiation induced phase transformations. The theoretical analysis based on the factor-group approach predicts five Raman-active bands; \( A_{1g} \) and \( E_g \). However, at ambient conditions, the non-polarized spectrum of magnetite shows 4 out of 5 theoretically predicted phonon bands at 668, 538, 306, and 193 cm⁻¹ [24]. As
clearly shown in Fig. 2, a characteristic band at 670 cm\(^{-1}\) identifies the presence of magnetite in the samples. Moreover, another broadband at 540 cm\(^{-1}\) may further assist in the discovery of the magnetite phase. Additionally, two more weak bands at about 308 cm\(^{-1}\) and 195 cm\(^{-1}\) confirmed the presence of the magnetite phase under the conditions of our study, which agrees with Gasparov et al. [25]. Shebanova and Lazor [24] reported on the Raman mode frequencies from different studies, pointing out that while there is an acceptable consistency for the strongest modes (at 668, 538, and 503 cm\(^{-1}\)), the agreement for the remaining modes is less satisfactory.

4.3. FTIR spectroscopy

To study the adsorption of the surfactants on the surface of iron oxide nanocrystals, FTIR analysis was conducted within the range of 400–4000 cm\(^{-1}\). Fig. 3 shows the FTIR spectra of the magnetite nanofluid samples using different amounts of dodecanoic acid as surfactants. The spectra show the peaks that correspond to both iron oxide and dodecanoic acid, proving that iron oxide was functionalized by dodecanoic acid. The bands at about 430 and 580 cm\(^{-1}\) were assigned to the Fe–O bond of magnetite, while bands at 1340–1470 cm\(^{-1}\) and 2850–2970 cm\(^{-1}\) were attributed to C–H bending and stretching of dodecanoic acid’s alkane chain, respectively. Moreover, bands at 1690–1760 cm\(^{-1}\) correspond to the C=O bond of dodecanoic acid, and finally, 1633 and 3400 cm\(^{-1}\) were attributed to O–H stretching and bending vibration of the adsorbed water, respectively.

<table>
<thead>
<tr>
<th>Magnetite nanofluid samples</th>
<th>D(_{XRD}) (nm)</th>
<th>D(_{DLS}) (nm)</th>
<th>D(_{TEM}) (nm)</th>
</tr>
</thead>
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<tr>
<td>3.0 g</td>
<td>36.4</td>
<td>75</td>
<td>37.2</td>
</tr>
<tr>
<td>3.5 g</td>
<td>36.1</td>
<td>75</td>
<td>37.2</td>
</tr>
<tr>
<td>4.0 g</td>
<td>35.8</td>
<td>75</td>
<td>36.4</td>
</tr>
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<td>4.5 g</td>
<td>35.3</td>
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<tr>
<td>5.0 g</td>
<td>35.5</td>
<td>72</td>
<td>35.5</td>
</tr>
</tbody>
</table>

4.4. Morphology and particle size

Fig. 4 shows the TEM images of Fe\(_3\)O\(_4\) nanoparticles without (a, and b) and with dodecanoic acid (c, and d). As shown in Fig. 4a and b, low and high magnifications of naked magnetite nanoparticles show polydisperse hexagonal particles with an average size of 50 nm. Fig. 4c and d shows TEM images of magnetite nanoparticles using 4.5 g of dodecanoic acid. It can be clearly seen that the shape of each nanoparticle remains hexagonal; however, the size of the particles decreased to 35 nm. Details on the particle size of the samples synthesized using different amounts of dodecanoic acid are listed in Table 1. The particular reaction environment explains the particles’ morphologies. The proposed growth mechanisms are divided into two general categories; one is based on the presence of organic molecules in the reaction system to reduce or speed up the addition of adatoms to specific crystal faces, while the second suggests that high concentrations of a surfactant encourage the formation of micelles, which function as templates for crystal growth and space-confining structures that physically shape the particles [26].

In addition, low magnification TEM images of water-dispersed magnetite nanoparticles with 4.5 g dodecanoic acid are shown in Fig. 4c. There are no indications of aggregation as opposed to the naked magnetite nanoparticles dispersed in water (Fig. 4a), or any reduced polydispersion of the colloid. The aqueous samples of the nanoparticles were stable as suspensions even after being stored for a month at room temperature. It can be surmised that the addition of dodecanoic acid as a surfactant led to the production of highly stable aqueous magnetite nanofluids. According to Table 1, the size of magnetite nanoparticles was decreased with the addition of fatty acids; however, these changes are small and insignificant.

4.5. Magnetizations

The magnetic behavior of the magnetite nanofluid samples synthesized using different amounts of dodecanoic acid was examined using a vibrating sample magnetometer (VSM) at room temperatures, as shown in Fig. 5. The synthesized magnetite samples show a superparamagnetic behavior, with no coercivity or magnetic remanence observed. As clearly seen from the
magnetization curves, saturation magnetization was enhanced by increasing the amount of dodecanoic acid from 3.0 to 4.5, which then decreased when 5 g of dodecanoic acid was used. It can be assumed that enhancement in the saturation magnetization values is associated with decrease in the magnetite’s particle size. The improvement of magnetization can be explained using the crystal structure of magnetite. The presence of impurities should also be taken into account, due to the decreasing magnetic components in the sample. Magnetite is a ferrimagnetic iron oxide possessing a cubic inverse spinel structure, with oxygen anions forming an fcc closed packing structure, and iron (cations) situated at the interstitial tetrahedral and octahedral sites. The electron can simply bounce between Fe(II) and Fe(III) ions in the octahedral sites at room temperature, which provides half of the metallic property of the magnetite.

The magnetic moment of the unit cell was only raised by Fe$^{2+}$ ions. When the particle size decreases, the oxygen content in the sample will correspondingly decrease, which consequently lead to lowering of the valence state of the cations. The observed increase in the unit cell volume with the reduction in particle size of Fe$_3$O$_4$ particles implies an increase in the Fe$^{2+}$ content [ionic radius of Fe$^{2+}$ is larger than that of Fe$^{3+}$]. Since the resultant magnetic moment in Fe$_3$O$_4$ is assumed to be due to the divalent ions (Fe$^{2+}$), the increase in magnetization with a decrease in size is justified [27]. The saturation magnetization of magnetite nanofluid samples is shown in Fig. 6. The maximum value was obtained when 4.5 g of dodecanoic acid was used.

4.6. Stability

Zeta potential was used to analyze the colloidal stability of the magnetite nanofluid samples synthesized using different amounts of dodecanoic acid. The zeta potential value normally represents the surface charge density that can be determined via detailed oxide stoichiometry, the degree of order at the particle surface, and adsorbed molecules [28]. The variation of the zeta potential as a function of pH is shown in Fig. 7 for magnetite nanofluids with no dodecanoic acid (naked magnetite), as opposed to dodecanoic acid-coated magnetite nanoparticles.
5. Conclusion

Ultra-stable water-based magnetite suspension was successfully synthesized using the co-precipitation method and the application of different amounts of dodecanoic acid as a surfactant. Dodecanoic acid, with relatively short carbon chain length, ensured the stable dispersion of magnetite nanoparticles in the slurry, and also reduced the polydispersive character of the colloid. On the basis of the zeta potential results, the highest stability of magnetite nanofluids was obtained for the sample synthesized using 4.5 g of dodecanoic acid in a wider pH range of 4–12. Moreover, the highest saturation magnetization (8.6 emu g⁻¹) took place when 4.5 g of dodecanoic acid was used. Therefore, the optimum amount of 12-carbon chain saturated fatty acid to prepare highly dispersed nano-magnetic slurry with super-paramagnetic behavior is 4.5 g under our experimental conditions.

Conflict of interests

The authors declare that there are no conflict of interests regarding the publication of this paper.

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References


