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

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ABSTRACT

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 (Fe_3O_4). 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.

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

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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 findings of studies based on the application of multiple fatty acids in the synthesis of stable ferrofluids; Vékás et al. [7] reported that the OA surfactant with 18-carbon atoms and a double bond was more effective in producing a stable dispersion compared to shorter chain length surfactants, such as Luric acid and Myristic acid. 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 ($FeCl_2 \cdot 4H_2O$), ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$), ammonia solution (28% NH_4OH), dodecanoic acid ($C_{12}H_{24}O_2$, 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 $FeC1_2 \cdot 4H_2O$ and 24 g $FeCl_3 \cdot 6H_2O$ 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% NH_4OH) was gradually added while the solution was being vigorously stirred (addition rate of 1 ml min^{-1}). The precipitate was placed onto a permanent magnet to hasten the particles' sedimentation. After 5 min, the clear solution was decanted, and the precipitate was washed using a solution of 5% ammonium hydroxide in deionized water. This process is repeated to ensure that all impurities are removed. Different amounts of dodecanoic acid; 3.0, 3.5, 4.0, 4.5 and 5 g (mole ratio of dodecanoic acid to magnetite=0.3:1, 0.35:1, 0.4:1, 0.45:1, 0.5:1) were then added to the precipitate, and the final solution was adjusted to a volume of 50 ml. The mixture was heated at 80 °C for 10 min while stirring.

3. Characterization

The XRD patterns and crystal structure of the magnetite nanoparticles were recorded using Cu K_α 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, HNO_3 10^{-3} mol L^{-1} or NH_4OH 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 Fe_3O_4. However, it cannot be ascertained from the XRD diffractogram whether or not the further oxidized Fe_2O_3 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 (311) reflection, via the Debye–Scherer equation, $D = 0.9\lambda/B\cos\theta$, where B 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

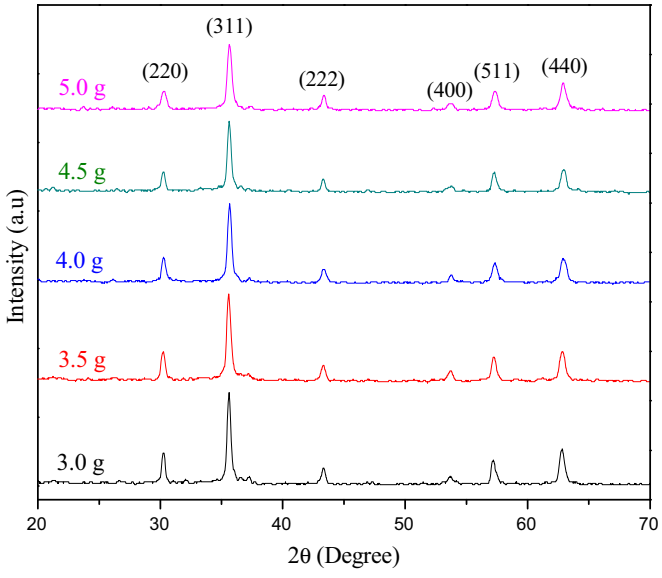

Fig. 1. XRD patterns for magnetite nanofluids synthesized using different amounts of dodecanoic acid as a surfactant (the diffraction peaks are labeled).