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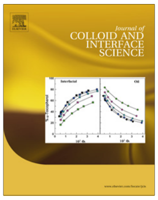

Self-suspended permanent magnetic FePt ferrofluids

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ABSTRACT

We present the synthesis and characterization of a new class of self-suspended ferrofluids that exhibit remanent magnetization at room temperature. Our system relies on the chemisorption of a thiol-terminated ionic liquid with very low melting point on the surface of L10 FePt nanoparticles. In contrast, all types of ferrofluids previously reported employ either volatile solvents as the suspending media or superparamagnetic iron oxide nanoparticles (that lacks permanent magnetization) as the inorganic component. The ferrofluids do not show any sign of flocculation or phase separation, despite the strong interactions between the magnetic nanoparticles due to the strong chemisorption of the ionic liquid as evidenced by Raman spectroscopy and thermal analysis. Composites with high FePt loading (40 and 70 wt%) exhibit a pseudo solid-like rheological behavior and high remanent magnetization values (10.1 and 12.8 emu/g respectively). At lower FePt loading (12 wt%) a liquid like behavior is observed and the remanent and saturation magnetization values are 3.5 and 6.2 emu/g, respectively. The magnetic and flow properties of the materials can be easily fine tuned by controlling the type and amount of FePt nanoparticles used.

1. Introduction

Colloidal magnetic fluids, or ferrofluids, are suspensions of magnetic particles, typically iron oxide (magnetite or maghemite) in a low viscosity medium. Particle agglomeration as well as flocculation due to gravitational or magnetic forces is prevented using suitable surfactants physically absorbed on the surface of the nanoparticles [1]. Specific applications like seals, lubrication fluids and heat transfer materials require that the nanoparticles are suspended in a carrier liquid that does not evaporate or decompose easily at high temperatures [2]. To that end, the magnetic nanoparticles are typically suspended in heavy paraffin oils with low vapor pressure and high thermal stability.

FePt in its ordered, tetragonal phase (L10) is considered as one of the most important magnetic materials mostly due to its potential applications in high density magnetic recording media such as hard disk drives [3], MRI contrast agents [4a] or drug delivery carriers [4b] and as electrocatalysts in fuel cells. [5] Intermetallic FePt and CoPt nanoparticles in the ordered (fct) phase combine chemical stability, high magnetocrystalline anisotropy ($Ku = 7 \times 10^6\ J/m^3$), and large coercivity [6].

The new ferrofluids described here distinguish themselves from those reported previously based on diluted dispersions of functionalized nanoparticles [7] in that they rely on the chemisorption of a low melting point thiol-terminated ionic liquid on the surface of FePt nanoparticles, which are annealed to obtain an ordered tetragonal structure (L10). It is a self-suspended ferrofluid, since it is free of any volatile solvent such as hexane or water, oftentimes employed as the suspending media [8,9]. Moreover, our system exhibits permanent magnetization stemming from the FePt nanoparticles, in contrast to systems based on iron oxide nanoparticles, which are superparamagnetic when their size falls below a critical value (in the range of 20–30 nm) [10]. With our method stable magnetic fluids with up to 70 wt% nanoparticles can by synthesized. This value is much higher compared to the ferrofluids reported previously in the literature for aqueous dispersions of superparamagnetic nanoparticles stabilized with polymers [11], surfactants [12] or ionic liquids [13].

The presence of the thiol group on the ionic liquid used in our system is critical, since thiols are known to form strong bonds with noble metals like Au, Pt and Ag. In contrast to nanoparticles physically dispersed in an ionic liquid (two-phase system), in our system the suspending medium is carried by the nanoparticles [14]. The thiol-based ionic liquid strongly interacts with the FePt nanoparticles leading to a stable system. Since the ratio of the ionic

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liquid to the inorganic cores can be easily controlled the magnetic properties and the fluidity of the ferrofluid are readily tunable. In contrast, the corresponding carboxylate-based ionic liquid interacts weakly with the FePt particles and can be easily removed upon washing with the appropriate solvent (see Supporting information, Fig. S1b).

Ionic liquids are low vapor solvents with potential in many important technological applications [15–17]. They are characterized by high thermal stability and very low melting points. In the field of ferrofluids, Jain et al. recently demonstrated the use of ionic liquids as stabilizing agents for the preparation of iron oxide ferrofluids. However, a thin polymer layer was necessary in order to make the ionic liquid compatible with the magnetic particles [18]. A different approach that expands the application of ionic liquids towards magnetically controlled fluids was recently reported by Brown et al. [20]. They have synthesized nanoparticle-free ferrofluids by mixing iron trihalides and cationic surfactants. The nanoparticles respond to the presence of a small magnet, indicating that their magnetization was sufficiently high. These molecular liquids exhibit paramagnetic behavior with susceptibility values similar to those for Fe^{III} ions without any remanent magnetization. The synthesis of ferrofluids based on superparamagnetic iron oxide nanoparticles coated with a carboxylated PEG based ionic liquids has been also presented [19]. However, in all these systems the magnetic particles are in the superparamagnetic state without any remanent magnetization.

Owing to our interest in developing self-suspended ferrofluids with permanent magnetization at room temperature we present here the first example and a systematic study of stable ferrofluids based on noble metal magnetic alloys (fct FePt). In our system the ionic liquid is strongly absorbed (chemisorbed) on the surface of the nanoparticles preventing extensive aggregation of the strongly magnetic particles even at very high concentrations (up to 70 wt% FePt). To that end, we synthesized and used a new ionic liquid with a very low melting point (−68 °C), excellent thermal stability (no weight loss until 330 °C), which combined with its functional thiol terminal group make it a versatile tool for a wide range of self suspended fluids based on noble metal and metal chalcogenide nanoparticles.

2. Experimental section

2.1. Synthesis of ionic liquid

Trihexyl(tetradyl)phosphonium decanoate 1 mmol (CYTEC CYPHOS IL103, IL-C), a waxy solid with melting point 43 °C, was mixed with sodium 3-mercaptopropane sulfonate (1.5 mmol) (Sigma–Aldrich, 90%) in dichloromethane. After filtration in order to remove the white precipitate, the sulfonate form of the ionic liquid (S-IL) was isolated by evaporation of the solvent. The S-IL is a transparent liquid with a melting point of −68 °C.

2.2. Synthesis of FePt particles

The FePt nanoparticles were synthesized using the polyol method. Iron (III) acetylacetonate (0.26 mmol, Fluka) and platinum (II) acetylacetonate (0.26 mmol, Aldrich) were dissolved in 10 ml of polyethylene glycol (PEG, Aldrich, *mw* = 400) and heated to 230 °C under argon flow. PEG is serving as both a reducing agent and a solvent. After 1 h at this temperature the solution was cooled down to room temperature, and 15 ml of absolute ethanol were added in order to precipitate the particles and remove any byproducts. The FePt particles were isolated by centrifugation and washed with absolute ethanol. The as-made nanoparticles are obtained in the superparamagnetic disordered face-centered cubic phase. In order to obtain the ordered, face-centered tetragonal (L10) phase, the particles were annealed at 600 °C under an Ar/H_2 mixture for 45 min at a heating rate of 300 °C/h.

2.3. Synthesis of FePt ferrofluids

The ferrofluids were synthesized by first dispersing the FePt nanoparticles in anhydrous tetrahydrofuran and sonicating in order to obtain a fine dispersion. Any large aggregates that could not be dispersed in the solvent were discarded. Appropriate amounts of S-IL were dissolved in THF and added to the suspension of the nanoparticles followed by drying in a vacuum oven to evaporate the solvent. FePt12, FePt40 and FePt70 correspond to samples comprised of 12, 40, and 70 wt% of nanoparticles, respectively. In order to estimate the amount of ionic liquid chemisorbed on the surface of the particles, the samples were centrifuged and washed with THF. The amount of the S-IL that remains on the surface of the particles is calculated from TGA analysis to be 25 wt% for the ordered FePt, (Fig. S1a).

3. Characterization techniques

XRD patterns of powder samples were recorded on a Scintag Theta-Theta X-ray Diffractometer (XRD) on glass slides. TEM images were recorded in a FEI T12 Spirit TEM-STEM at 120 kV. The samples were cast on carbon grids from diluted THF solutions. Raman spectrum was recorded on Renishaw InVia Confocal Raman microscope with excitation wavelength of 488 nm and a spectral resolution of ~0.1 cm^{-1}. DSC scans were taken on a TA Q2000

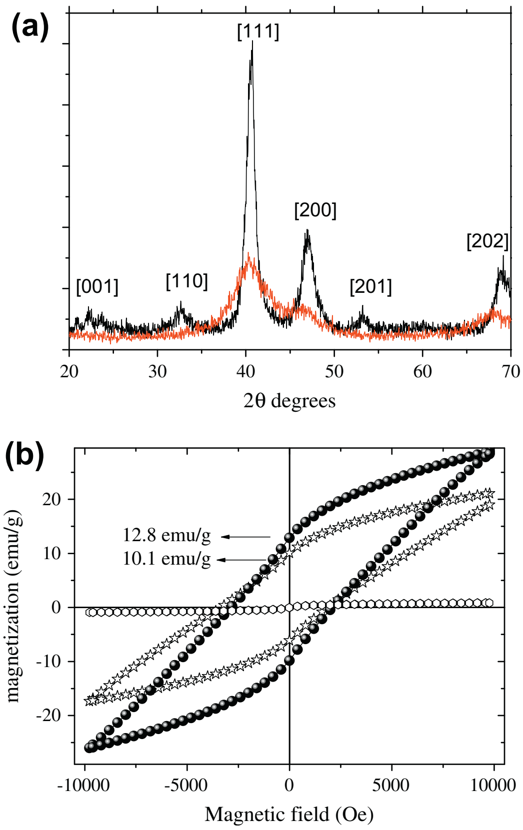

Fig. 1. (a) XRD pattern of the ordered L10 particles (black) and the disordered fcc FePt (red). (b) Magnetization curves recorded at room temperature for the disordered FePt (open circles), ordered FePt powders (spheres) and ordered FePt ferrofluids with 70 wt% FePt (stars). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)