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Silica encapsulation and magnetic properties of FePt nanoparticles

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Abstract

Core–shell nanoparticles have emerged as an important class of functional nanostructures with potential applications in many diverse fields, especially in health sciences. We have used a modified aqueous sol–gel route for the synthesis of size-selective FePt@SiO_2 core–shell nanoparticles. In this approach, oleic acid and olyel amine stabilized FePt nanoparticles are first encapsulated through an aminopropoxysilane (APS) monolayer and then subsequent condensation of triethoxysilane (TEOS) on FePt particle surface. These well-defined FePt@SiO_2 core–shell nanoparticles with narrow size distribution become colloidal in aqueous media, and can thus be used as carrier fluid for biomolecular complexes. In comparison, the scarce hydrophilic nature of oleic acid monolayers on FePt particle surface yields an edgy partial coating of silica when only TEOS is applied for the surface modification. The synthesized core–shell nanoparticles were characterized by direct techniques of high resolution transmission electron microscopy (HRTEM), EDS and indirectly via UV–vis absorption and FTIR studies. The FePt@SiO_2 nanoparticles exhibit essential characteristics of superparamagnetic behavior, as investigated by SQUID magnetometry. The blocking temperatures (T_B) of FePt and FePt@SiO_2 (135 and 80 K) were studied using zero field cooled (ZFC)/field cooled (FC) curves.

Keywords: FePt nanoparticles; Silica; Core–shell; Sol–gel; Colloids

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1. Introduction

The recent thrust to synthesize functional nanoscale particles stems from their fundamental and technological importance [1–4]. Nanoscale materials exhibit interesting electrical, optical, and magnetic properties which are often distinct from their bulk counterparts. Among these, magnetic nanoparticles with size range of 2–10 nm are of particular significance because of their potential applications in multiterabit magnetic storage devices and as carriers for biochemical complexes, MRI contrast enhancing agents, among many other applications [5]. These nanoparticles could also be used as ferrofluids, magnetic refrigeration systems, magnetic resonance imaging, magnetic carriers for drug targeting and catalysis [6,7]. However, some materials such as Co, Ni-based can be biohazardous and also prone toward easy oxidation or degradation at ambient conditions, hence an increased interest in coating their surface with a thin protecting shell for various biomedical applications. Current methods use micrometer-sized magnetic-polymer/silica particles which are too large for in vivo applications [8]. Recently, less than 20 nm size has been suggested for efficient diffusion of nanoparticles through tissues in MRI imaging [9]. Thus, developing nanometer scale encapsulated magnetic nanoparticles and the investigation of their properties are assuming greater importance.

Most of the work in the past has been on noble-metal nanocores and molecular shells, and monolayers anchored on metal cores have been used as precursors to make oxide shells [4,10]. An approach in this direction is to coat gold clusters with silica shell [10]. We have used an analogous approach to coat the magnetic FePt nanoparticles with silica shells, and focus the synthesis and characterization of colloidal and redispersable FePt@SiO_2 nanoparticles. The coating prevents the aggregation in liquid, has better chemical stability as compared to their bare counterparts and

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provides a biofunctional surface for modification and subsequent DNA/protein attachment.

In the recent past, various researchers have suggested encapsulation of magnetite and other ferrite materials [11,12]; however, the literature for the effective surface functionalization of metallic nanoparticles like FePt, Co, and Fe etc. is very sparse [13]. These metallic nanoparticles have higher performance because of their much higher susceptibility and saturation magnetization as compared to magnetite or ferrites. We have initiated this work on oxide protection of metallic/magnetic nanoparticles because this is a way to stabilize these particles under any extreme condition. This type of encapsulation also makes it possible to modify the surface of silica for bimolecular attachment, which can deliver specific ligands to target sites via the antibody–antigen recognition. Also, magnetic nanoparticles have fueled both fundamental and applied studies due to their magnetic properties (e.g., large uniaxial magnetocrystalline anisotropy, $K_u \cong 7 \times 10^6\ \mathrm{J/m^3}$) and enhanced stability [13].

This is the first report where we elucidate the homogeneous and uniform encapsulation of monodispersed FePt nanoparticles with controlled thickness of silica. Since surface functionalization plays an important role in many biological systems, such type of core–shell structures are key in designing complicated multilayer structures with promising applications in biomolecular therapeutics. We use high resolution electron microscopy (HRTEM), UV–vis spectroscopy, infrared spectroscopy (FTIR), and magnetic measurements (SQUID) as the characterization tools to reveal the core–shell structure formation in magnetic nanoparticles.

2. Experimental

The FePt nanoparticles synthesis was carried out using standard airless procedures and commercially available reagents [5]. Phenyl ether (99%), 1,2-hexadecanediol (90%), oleic acid (90%), iron pentacarbonyl ($Fe(CO)_5$), oleylamine (70%), and platinum acetylacetonate ($Pt(acac)_2$) were purchased from Aldrich Chemical Co.

A typical synthesis route is as follows: 0.5 mM $Pt(acac)_2$ and 1.5 mM hexadecanediol were mixed in 20 ml diethyl ether and heated up to 110 °C. Equal amount (1 mM) of oleic acid and oleyl amine were then added with $Fe(CO)_5$ and this mixture was heated up to 300 °C for 1 h. The reaction was carried out under N_2 atmosphere. The black colored solution was allowed to cool to room temperature and precipitated by adding excess ethanol. The magnetic particles were separated using a strong magnet. Dark-yellow supernatant was discarded. After washing several times with ethanol, the precipitate was uniformly dispersed in hexane with small amount of surfactants.

Further, these FePt nanoparticles were encapsulated using two different sol–gel processes. A 0.5 ml hexane based FePt solution was added in 20 ml ethanol containing 0.1 ml triethoxysilane (TEOS). Under continuous mechanical stirring, 1 ml NH_4OH solution (30%) was added slowly to this rigorously stirred mixture. After 3 h, the encapsulated particles were separated using magnet and the excess silica formed during the hydrolysis–condensation was washed off using extensive ethanol washing [11a]. In comparison to direct TEOS condensation, in yet another process the FePt particles with a mean size of ∼5.5 nm in hexane were mixed with 1 mM APS and the suspension was left for 2 h for place exchange with oleic amine monolayers [11b]. APS monolayers are covalently attached onto the surface of nanoparticles. The APS modified nanoparticles are then used as a source of nucleation of TEOS condensation. A strong magnet was used to separate these APS monolayer covered particles and the particles were subsequently suspended in 100 ml ethanol containing 14 µl TEOS. The solution was stirred continuously while adding 10 ml deionized water for the hydrolysis of TEOS. The final solution was stirred 3 h. The particles were collected with a magnet and repeatedly washed with ethanol. This approach provides great flexibility in the selection of magnetic core. Consequently, magnetic tunability is able to be introduced into these core–shell nanoparticulate systems to achieve the desired superparamagnetic response.

High resolution electron microscopy (HRTEM) measurements were performed on FePt and FePt@SiO_2 samples which were drop-casted onto a carbon-coated Au grid (Hitachi HF-2000 TEM, Japan). Elemental analysis was performed using EDS system attached to the same instrument. FTIR spectra were acquired with a Bio-Rad Win-IR spectrometer with a resolution of 2 $\mathrm{cm^{-1}}$. The samples were prepared by dropcasting the particle solutions in hexane and alcohol (FePt@SiO_2) onto a KBr plate to form a thick film, and further dried in a gentle N_2 stream. UV–vis spectroscopy was carried out with an UV–vis Czerny–Turner double beam spectrometer with a 1-cm quartz cuvette. Solutions were prepared typically at a concentration of 0.1 mg/ml in hexane and water respectively for FePt and FePt@SiO_2 particles. Magnetic measurements of FePt and FePt@SiO_2 were done using SQUID analyzer (Quantum Design, MPMS). The magnetization was measured from room temperature to low temperature. Hysteresis was measured at room temperature. Blocking temperature (T_B) was measured using ZFC and FC measurements with M vs T curve at an external magnetic field of 500 Oe.

3. Results and discussion

We first focused our attention to synthesize uniformly distributed FePt nanoparticles using the route which Sun et al. [5] have reported earlier. While they used size-selective precipitation to obtain monodispersion (std. deviation ∼10%), we acquired a fairly uniform distribution by controlled addition of a reducing agent. These particles are stabilized using a small amount of oleic acid and olyel amine in hexane. Fig. 1A shows the TEM image of uniform distri-