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Large scale solvothermal synthesis and a strategy to obtain stable Langmuir–Blodgett film of $CoFe_2O_4$ nanoparticles

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ABSTRACT

Nearly monodisperse oleic acid coated cobalt ferrite nanoparticles were synthesized in large scale by a simple solvothermal method utilizing N-methyl 2-Pyrrolidone (NMP) as a high boiling solvent. The magnetic oxide was further investigated by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), transmission electron microscopy (TEM), high resolution transmission electron microscopy (HRTEM) and vibrating sample magnetometer (VSM). Langmuir–Blodgett (LB) technique is discussed to obtain a 2D assembly of oleic acid coated $CoFe_2O_4$ nanoparticles over a large area. We describe a method to obtain stable, condensed three layers of cadmium arachidate on a piranha treated glass substrate. The hydrophobic surface thus obtained was subsequently used for forming a stable monolayer of oleic acid stabilized cobalt ferrite nanoparticles at the air–water interface. The stability of the LB films at the air–water interface was studied by pressure–area isotherm curves and atomic force microscopy (AFM) cross sectional height profile analysis. 2D organization of the magnetic nanoparticles at different surface pressures was studied by TEM. Preparation of large area LB films of $CoFe_2O_4$ nanoparticles is reported for a surface pressure more than 15 mN/m.

1. Introduction

For last few decades, significant effort is devoted to fabricate large scale 2D assemblies of tiny magnetic nanoparticles for their potential applications such as in high density magnetic storage media, magneto optical devices, electronic logic devices and sensors [1–3]. Recently, protein cage-guided formation of magnetic nanoparticle superlattices was reported for their potential applications in biological systems [4]. Among the various techniques reported for the 2D assembly of nanoparticles, Langmuir–Blodgett (LB) technique has proved to be the most versatile technique to form homogenous thin films of controlled thickness [5–7]. So far, several achievements have been made in forming LB monolayer or multilayers of highly monodisperse magnetic nanoparticles [8–14]. A theoretical result on magnetic nanoparticles of modeled 2D LB films consisting of different types of stable π-monoradicals was reported [15]. In spite of being interesting, these studies have not addressed the physical properties, structure and stability of the LB films, which strongly governs their potential applications. The substrate surface condition, hydrophobic or hydrophilic, also plays an important role in achieving a stable LB film. Therefore, it is important to select an appropriate substrate for lifting the magnetic oxide monolayer to achieve stable LB films of magnetic nanoparticles. Earlier, few promising attempts were made to stabilize LB films by utilizing ionically cross linked (gluing) monolayers and via small supramolecular clips based on dicarboxylates [16,17]. It is also known that the incorporation of divalent cations to the long chain saturated carboxylic acids dramatically increases the ease of deposition on one hand and the stability of their LB films on the other [18,19]. In most of these studies, cadmium arachidate is chosen as the prototypical material to enhance the hydrophobicity and stability of the LB films.

In the present investigation, we utilized this strategy to get a stable hydrophobic glass substrate and subsequently deposit the hydrophobic magnetic nanoparticles onto it. Three layers of cadmium arachidate LB films were built up by successively dipping piranha treated glass substrate following Y-dipping protocol [20]. This allows the methyl end of the alkyl chain face the interface, thereby enhancing the hydrophobicity and stability of the glass substrate. Reorganization density of the cadmium arachidate LB films was studied at different pH of the subphase divalent cations (Cd^{2+}).

Synthesis of high quality monodisperse nanoparticles is a key to achieve stable self-assembled architectures. In this direction, it is important to search for a relatively simpler approach to synthesize high quality monodisperse nanoparticles. For the past few decades, thermal decomposition of organometallic compounds has been extensively investigated for the synthesis of good quality, highly monodisperse magnetic nanoparticles [21–23]. Although thermal

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decomposition method is a well accepted and widely used synthetic route, it suffers from severe drawbacks regarding industrial feasibility, especially with respect to the need for large scale chemical synthesis of highly monodisperse nanoparticles. Therefore, the synthesis needs to be scaled up in order to obtain high yield nanoparticles. Until now, the most widely used economical way to synthesize large quantity ferrite nanoparticles are coprecipitation [24] and hydrothermal/solvothermal routes [25–28]. The experimental challenges in the synthesis of homogeneous magnetic nanoparticles by coprecipitation route lies in maintaining the appropriate reaction conditions such as pH, temperature, ionic strength and the concentration of the salts. Also, the particles obtained by coprecipitation route tend to be polydisperse in nature [29]. On the other hand, solution mediated solvothermal reaction enhances the interparticle diffusion of the reagents resulting in the rapid and direct crystallization of single phase materials [30–33]. In the last few years, as the understanding in the formation mechanism of nanoparticles grew, synthetic reaction conditions have been successfully scaled-up to synthesize good quality nanoparticles in large scale [30,31].

In the present investigation, we introduced N-methyl 2-Pyrrolidone (NMP) as a high boiling solvent for the solvothermal route to synthesize large-scale, nearly monodisperse $CoFe_2O_4$ nanoparticles. An equimolar mixture of oleic acid and oleyl amine was used to make the particles hydrophobic. The present study describes the formation of a suitably compressed monolayer of $CoFe_2O_4$ nanoparticles at the air/water interface and its subsequent transfer to cadmium arachidate modified glass substrate at controlled rates. 2D organization and packing of the individual magnetic oxide nanoparticles were also studied by TEM at different surface pressures. We propose an approach to form a long range stable LB monolayer of magnetic nanoparticles on the cadmium arachidate treated glass substrate. This strategy to obtain stable magnetic LB films on glass substrate is not specific to our system but it could be employed for any similar systems.

2. Experimental section

2.1. Synthesis of oleic acid stabilized magnetic nanoparticles

The chemicals iron acetylacetonate, cobalt acetylacetonate, oleic acid, oleylamine, cadmium chloride and arachidic acid (99% pure) were purchased from Aldrich chemicals. N-methyl 2-prrrolidone (NMP) was purchased from Merck chemicals. All the chemicals were of analytical grade or better. Iron acetylacetonate (0.10 M) and cobalt acetylacetonate (0.05 M) was mixed with 0.10 M oleic acid and 0.10 M oleylamine in 35 ml NMP. The mixture was heated to about 50 °C to form a homogeneous solution. The mixture was stirred for a while and transferred into a 50 ml of autoclave with Teflon lining. The autoclave was heated to 200 °C in a preheated oven for 3 h. After cooling to room temperature, a black–brown precipitate was precipitated after the addition of 50 ml of ethanol. The black–brown precipitate was centrifuged for 15 min at a speed of 10, 000 rpm. The product was dispersed in hexane. Excess surfactants were washed out by repeating the precipitation and centrifugation thrice. The precipitate was further dried at 60 °C in a vacuum oven. In a typical scale-up solvothermal reaction, similar workup procedures were followed with 0.25 M iron acetylacetonate, 0.125 M cobalt acetylacetonate, 0.15 M oleic acid and 0.15 M oleylamine in 35 ml NMP. The final yield of the samples was found to increase from ~0.25 g to ~0.50 g per solvothermal reaction, as we scale-up the amount of iron acetylacetonate and cobalt acetylacetonate from 0.10 M:0.05 M to 0.25 M:0.125 M. The samples were characterized for their phase purity and crystallinity by powder X-ray diffraction (XRD) measurements (Panalytical Xpert Pro) with Cu Kα radiation using a Ni filter. Further measurements were performed on the scaled-up $CoFe_2O_4$ nanoparticles. Particle sizes were investigated by transmission electron microscope (TEM), model JEOL 1200 EX, on a carbon coated TEM copper grid after dispersing the powder in toluene. HRTEM analyses were done on model FEI Technai 30 system operated at 300 kV. The fringes were generated by subtracting the noise of the original selected area with a Digital Micrograph (TM) 3.71 for GMS 1.2 Build 22. HRTEM samples were prepared by dispersing the sample in toluene. The Fourier transform infrared (FTIR) spectra of surfactant coated magnetic nanoparticles were recorded in the 400–4000 cm^{-1} ranges (Perkin–Elmer system, spectrum One B) by preparing KBr (Merck, spectroscopy grade) pellets (0.1 wt.% sample). Magnetic measurements were carried out using a Quantum Design MPMS system. The measurements were made between 5 and 300 K using zero-field-cooling (ZFC) and field-cooling (FC) protocols at 50 Oe, and the hysteresis loops were obtained in a magnetic field varied from +4 to −4 T. In ZFC magnetization, the sample is cooled from room temperature to 5 K, without any external magnetic field, and the magnetization is measured while warming the sample in an applied field of 50 Oe. In FC magnetization, the sample is cooled from room temperature to 5 K under a magnetic field of 50 Oe and the magnetization is measured while warming the sample, in the presence of a field.

2.2. Preparation of Langmuir–Blodgett film of arachidic acid and cadmium arachidate

LB films were deposited on 20 × 20 mm glass substrate. Before deposition, the substrates were cleaned, rinsed and treated with piranha solution (3:1 sulphuric acid to hydrogen peroxide). The substrate was put in a boiling piranha solution for half an hour and was subsequently rinsed thoroughly with Millipore water. The substrate was stored in Millipore water till the time of deposition. Arachidic acid monolayer was spread from a 1 mg/mL (50 μL) toluene solution in a NIMA LB trough (Model 312 D). The isotherm of arachidic acid was obtained by compressing the monolayer at a barrier speed of 50 cm^2/min. Arachidic acid was deposited on piranha treated glass slide at a target pressure of 45 mN/m at a constant speed of deposition of 2 mm/min with a wait interval of 100 s between each dip. The surface pressure was monitored using Wilhelmy plate. In order to study the isotherm of cadmium arachidate, 1 mg/ml (50 μL) arachidic acid (Aldrich, 99%) was spread from chloroform (HPLC grade) onto an aqueous sub phase with 1 mM Cadmium Chloride (Merck, AR). The pH of the water sub phase containing cadmium chloride was adjusted to pH 5.5 and 7 by adding 0.4 M NaOH solution. After the solvent got evaporated, the isotherm was taken by compressing the barriers. The LB films of cadmium arachidate, deposited on the piranha treated substrate were of Y type i.e. with adjacent layers stacked head to head or tail to tail [20]. Three layers of cadmium arachidate were deposited by a multistep creep method at a surface pressure of 45 mN/m with the barriers moving at a speed of 50 cm^2/min, and at a dipping speed of 2 mm/min with a wait interval of 50 s. Topography of the LB films was studied by Atomic Force Microscopy (AFM), a few days after deposition. AFM measurements of cadmium arachidate LB films were performed with Nano Wizard II (JPK company) in air at room temperature using a 1 μm scanner and a silicon AFM probe with <10 nm tip radius (on a cantilever-Tap 300E-G). Imaging was mostly done either in tapping or intermittent contact mode to minimize silicon tip induced damage of the LB films.

2.3. Preparation of Langmuir–Blodgett films of oleic acid stabilized cobalt ferrite nanoparticles

Oleic acid stabilized cobalt ferrite nanoparticles were dispersed in toluene and sonicated for 15 min. Nanoparticles suspension (1 mg/ml) was spread at the water–air (Milli-Q, 0.054 μS, Millipore) interface using a micro syringe. The compression of the film was done at a speed of 50 cm^2/min after the evaporation of the solvent. The monolayer deposition of cobalt ferrite nanoparticles on cadmium arachidate stabilized glass substrate was done at a surface pressure of 30 mN/m. The schematic representation of the deposition of $CoFe_2O_4$ nanoparticles on the modified glass substrate after depositing three layers of cadmium arachidate is shown in Fig. 1. Phase purity of the Langmuir film was further characterized by XRD after depositing 20 layers of cobalt ferrite nanoparticles. The topography of the films was studied by AFM. The 2D organization of the LB film was also studied by TEM after depositing two layers of $CoFe_2O_4$ nanoparticles on carbon coated copper grids at different surface pressures of 5 mN/m, 10 mN/m, 15 mN/m and 25 mN/m, at a dipper speed of 2 mm/min. All the grids were dried in air before characterization.

3. Results and discussion

Fig. 2 illustrates the powder X-ray diffraction pattern of the oleic acid coated $CoFe_2O_4$ nanoparticles. The XRD peak positions and the relative intensity of all diffraction peaks match well with the simulated pattern of bulk $CoFe_2O_4$ (a = 8.3919 Å, JCPDS No. 22-1086). The Bragg reflection peaks are clearly broadened, which could be because of the extremely small size of the ferrite formed. The average crystallite sizes were calculated using the Scherrer equation, $d = (0.9\lambda/\beta\cos\theta)$, where d is the diameter in Ångstroms, β is the half-maximum line width, and λ is the wavelength of X-rays. The average crystallite size is estimated to be about 4.0 ± 1 nm. The calculated cubic lattice parameter, a, is 8.392 ± 0.005 Å, which is comparable to that obtained for the bulk samples [34].

Fig. 3A represents the TEM micrograph of the $CoFe_2O_4$ nanoparticles. The formation of nearly monodisperse spherical particles is clearly seen. The particle size distribution, obtained from the TEM micrograph is shown in the inset (ii) of Fig. 3A. The histogram