

Patterned Langmuir–Blodgett Films of Monodisperse Nanoparticles of Iron Oxide Using Soft Lithography

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Recently monodisperse magnetic nanoparticle systems such as FePt, Co, Fe, Fe₃O₄, and γ -Fe₂O₃ have been made through solution-phase syntheses.¹ It becomes increasingly important to develop strategies to fabricate these nanoparticles into patterned thin films to explore their collective properties and the potential applications, such as ultrahigh-density magnetic storage media and magneto-optical devices.^{1–6} The unmediated self-assembly of monodisperse nanoparticles can only offer limited packing orders with almost no controls of the domain structure, packing density, and number of layers deposited. Among the techniques for the deposition of thin films of nanoparticles on solid substrates, layer-by-layer (LbL) deposition and Langmuir–Blodgett (LB, vertical lift) technique are some of the most promising methods because they enable fine control of the thickness and homogeneity of the monolayer, and ease for multilayer deposition.^{3,6–8} Recently, Sun et al. have succeeded in making poly(ethylenimine)–PtFe nanoparticle thin films using ligand exchange and the LbL deposition method.³ Werts et al. have showed that it was possible to pattern LB films of gold nanoparticles using electron beam lithography.⁹ Although several methods have been explored in patterning, a predefined organic layer on a substrate is typically required to deposit nanoparticles in certain regions.^{10,11} The approach is not ideally suitable for generating highly ordered and close-packed homogeneous patterns of nanoparticles, which is potentially important for applications.³

In this communication, we describe a method to make patterned LB films of iron oxide nanoparticles and to transfer these patterned films onto solid substrates using a soft lithographic technique.¹¹ We used oleic acid-stabilized ~ 11 and ~ 13 nm γ -Fe₂O₃ nanoparticles (see Supporting Information for synthesis and characterization) dispersed in hexane (~ 1 mg/mL) as the spreading solution.

LB films of γ -Fe₂O₃ nanoparticles were made using a KSV 3000 Langmuir trough in a Class 10000 clean room. The surface pressure was monitored using the Wilhelmy plate method. Nanoparticle suspension in hexane (800–1000 μ L) was spread at the air–water (Barnstead Nanopure II, 16.7 M Ω) interface using a microsyringe. Compression of the film was done at a rate of 10 mN/(m min) after the hexane evaporated (< 5 min). LB films were prepared at surface pressures ranging from 30 to ~ 65 mN/m and lifted onto solid substrates such as silicon wafer or poly(dimethylsiloxane) stamp (PDMS) at a rate of 5 mm/min. For transmission electron microscopy (TEM) characterization, LB films were directly transferred onto carbon-coated copper grids at a rate of 1 mm/min. For monolayer deposition, substrates were submerged in water prior to spreading.

A surface pressure versus area (π – A) isotherm for γ -Fe₂O₃ nanoparticles is shown in Figure 1. Insets of Figure 1 show representative TEM images of the LB films at different compression pressures. At low surface pressure (~ 15 mN/m), the nanoparticles

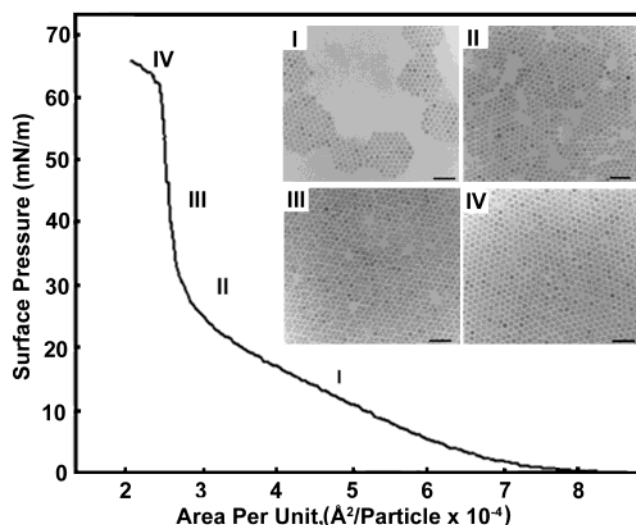


Figure 1. π – A isotherm diagram of monodisperse γ -Fe₂O₃ nanoparticles (~ 11 nm). Insets are TEM images for LB films made at four different surface pressures: (I) 15, (II) 30, (III) 45, and (IV) 62 mN/m. Scale bars are 50 nm.

are packed in patches connected randomly with large spaces. In each individual patch nanoparticles were highly ordered and formed hexagonal close-packed (hcp) structure. This ordered structure was very different from those LB films made of polydisperse particles and most likely due to the monodispersity of the nanoparticles. The Langmuir film was compressed into close-packed domains with diminishing void spaces at increasing surface pressure. We found that the γ -Fe₂O₃ monolayer could be compressed up to a pressure of ~ 65 mN/m (IV), which was much higher than those for thiolate-stabilized silver and gold nanoparticles.⁸ The images show rather uniform structures of nanoparticles, although defects could be observed even at high compression pressures. To achieve complete coverage of the substrate, a double layered LB film was sufficient. Figure 2 shows the first and second layer of a LB film of γ -Fe₂O₃ nanoparticles obtained at a pressure of ~ 40 mN/m. The monolayer region was essentially close-packed but with some visible defects as expected. It was interesting to note that the boundary line for the second layer could have accuracy within the size scale comparable to a single particle.

We examined the deposition of Langmuir films of γ -Fe₂O₃ nanoparticles on patterned substrates using PDMS stamps. The PDMS stamp of microdot patterns (μ -dots, 1.0–1.5 μ m in diameter) used in this work was a negative copy of a PDMS stamp of a microwell array that was replicated from the original master of photoresist on silicon wafer made by using a standard photolithographic procedure.^{11,12} Double layers of γ -Fe₂O₃ nanoparticles were deposited onto the μ -dot patterned PDMS stamp at a surface pressure of ~ 40 mN/m. This patterned LB film was transferred

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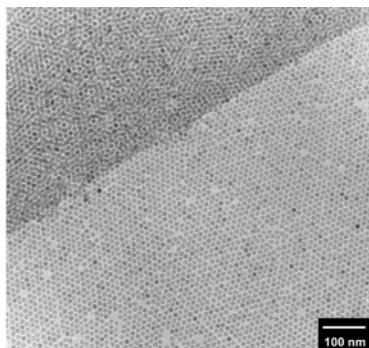


Figure 2. TEM image of a LB film of ~ 11 nm γ - Fe_2O_3 particles deposited onto a carbon-coated TEM grid at a surface pressure ~ 40 mN/m showing regions of the monolayer and double layer.

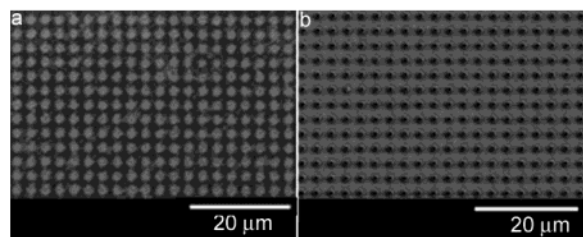


Figure 3. SEM images of (a) patterned μ -dot arrays of γ - Fe_2O_3 nanoparticle LB film on a silicon wafer, and (b) the original photoresist pattern of μ -dots.

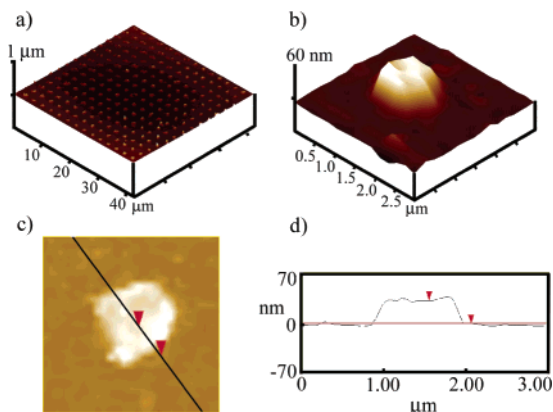


Figure 4. AFM images of μ -dot arrays of γ - Fe_2O_3 nanoparticle (~ 13 nm) LB films in (a) a large area; (b) a three-dimensional presentation, and (c) a top view of a single μ -dot; and (d) the cross section analysis.

onto a silicon wafer, freshly cleaned with acetone and methanol in a sonication bath and dried with a stream of N_2 , using microcontact printing (μ -CP). The light-brownish printed LB film could be directly observed by the naked eye. Figure 3a is a field emission scanning electron microscopy (SEM) image of the μ -dot patterned film of γ - Fe_2O_3 nanoparticles on a piece of silicon wafer. The quality of the original photo master (Figure 3b), the replicated PDMS stamps, and the applied pressure are some of the key factors that can affect the shapes of the printed μ -dots of nanoparticles. Tapping mode atomic force microscopy (AFM, Digital Instrument Multi Mode Nanoscope III) images show the average height of the dots is 40 ± 5 nm (Figure 4). The dots are not always perfectly round, which could be due to the imperfectness of the original master and deformation of the PDMS stamp¹³ when pressure was applied during the μ -CP process. The freshly prepared nanoparticle

LB films could be transferred onto both hydrophobic and hydrophilic substrates (see Supporting Information Figure S-3). The LB films on PDMS stamps left overnight or dried in an oven at 60°C for ~ 5 min, however, could not be transferred effectively onto either hydrophobic or hydrophilic substrates. This observation suggested that the freshness of the deposited LB films on PDMS stamps played an important role in the transfer process. Although we used oleic acid-stabilized monodisperse γ - Fe_2O_3 nanoparticles to demonstrate the deposition of LB films on PDMS stamps and the pattern transfer using μ -CP, this approach could be used to make different patterned structures of both magnetic and nonmagnetic monodisperse nanoparticles.

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Supporting Information Available: Synthesis, PXRD, XPS analysis of nanoparticles of iron oxide, and AFM images of LB films of these nanoparticles transferred onto hydrophobic and hydrophilic surfaces (PDF). This material is available free of charge via the Internet at <http://pub.acs.org>.

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