

Macroscopic Arrays of Magnetic Nanostructures from Self-Assembled Nanosphere Templates

Shemaiah M. Weekes,* Feodor Y. Ogrin, William A. Murray, and Paul S. Keatley

School of Physics, University of Exeter, Exeter EX4 4QL, U.K.

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We have extended the widely used technique of nanosphere lithography to produce nanosphere templates with significantly improved long-range order. Single, ordered domains stretching over areas greater than 1 cm^2 have been achieved by assembling spheres with the correct surface chemistry on a water/air interface. Self-assembly over macroscopic areas is facilitated by a combination of electrostatic and capillary forces. The presented technique is easily implemented, and the assembled monolayers can be transferred onto almost any surface, thus making the procedure applicable to a broad range of nanoscale research. We demonstrate this through the fabrication of hexagonally ordered, macroscopic arrays of magnetic nanostructures with modified magnetic properties.

1. Introduction

Highly ordered arrays of nanostructures are expected to play a vital role in future photonic and magnetic devices.^{1–5} To facilitate progress in this area, new cost-effective fabrication techniques are urgently required. However, maintaining long-range order while achieving nanoscale resolution over macroscopic length scales is still a significant challenge.⁶ Where fabrication schemes do exist they are predominantly costly and time-consuming to implement. In contrast, the manipulation of natural self-assembly is an attractive route to creating large-area nanostructured arrays efficiently and cheaply.⁷ One such technique, nanosphere lithography, is a highly accessible, low cost, parallel fabrication process capable of producing nanostructured surfaces over large areas and with high resolution.⁸ In addition to dots, highly ordered sphere arrays can be used to create interstitial triangular structures⁹ metallic rings,¹⁰ nanopillars,¹¹ and multilayers with modified topography,¹² producing a rich variety of controllable properties. Currently, a major stumbling block in the application of this technology is the lack of long-range order present in self-assembled templates.¹³ Nanosphere arrays typically consist of numerous microscopic domains, with little or no correlation between them. Long-range order, though, is crucial to many technological applications, including magnetic recording where precise addressing of nanoscale magnetic “bits” is essential. In this work, we address the specific problem of macroscopic order and present a simple solution.

2. Experimental Section

Highly ordered nanosphere templates were fabricated using the following procedure. Commercially available (Duke Scientific Corporation, carboxylate-modified microspheres product) suspensions of monodisperse polystyrene nanospheres were obtained with diameters in the range of 120–950 nm. The hydrophilic spheres were terminated by carboxyl groups with parking areas (the average sphere surface area per carboxyl group) of $8\text{--}120 \text{ \AA}^2$ per group depending on the sphere diameter. The colloids were obtained as 4 wt % suspensions and further diluted in a 1:1 ratio in ethanol, which acted as a spreading agent. Self-assembly was accomplished on the surface of ultrapure water of resistivity $18 \text{ M}\Omega\cdot\text{cm}$ contained within a Teflon bath of dimensions $190 \times 45 \text{ mm}^2$. The bath was overfilled slightly to allow the use of Teflon sliders to compress and position the monolayer, the water being retained in the bath by surface tension.

The spheres were introduced to the water surface via a glass microscope slide placed at one end of the bath at an angle of $\sim 45^\circ$ with respect to the water surface. A $20 \mu\text{L}$ pipet was used to dispense the colloid slowly onto the hydrophilic slide at the interface between the slide and the surface of the water (Figure 1). On contact with the water, the spheres immediately form a monolayer and start to assemble. As the self-assembly proceeds, centimeter-sized ordered domains can be identified by their bright interference and uniform color. Scanning electron microscope (SEM) images confirm that these regions correspond to single domains where both the lattice direction and the hexagonal order are preserved over the whole area.

3. Results and Discussion

The physical process responsible for the ordering of spheres at a liquid interface has been studied by several groups.^{14,15} Recently, Nikolaidis¹⁵ et al. proposed that the mismatch in dielectric constants of adjacent fluids can result in an asymmetric charge distribution on a particle adsorbed at their interface. The resulting electric dipolar field has two effects: an electrostatic repulsion between adjacent spheres and an additional capillary attraction due to the deformation of the liquid meniscus by electrostatic stresses. This mechanism for the creation of an attractive capillary force is vital because spheres with diameters of less than $5 \mu\text{m}$ generally do not have sufficient weight to deform the liquid meniscus by means of gravity.¹⁶ From our preliminary investigation of the conditions leading to large-area,

* Corresponding author. E-mail: s.m.weekes@exeter.ac.uk.

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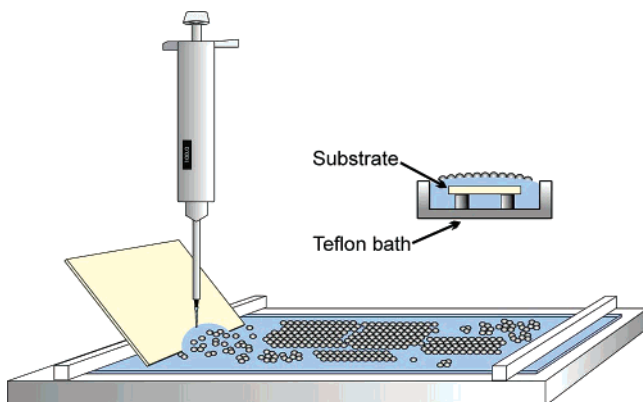


Figure 1. Self-assembly at a water/air interface. The water surface is used as a medium to facilitate the self-assembly. The inset shows a cross section of the bath, demonstrating the transfer of a monolayer onto a solid substrate.

ordered domains, we have found that the specific surface chemistry of the spheres is the major factor in obtaining a balance between the repulsive electrostatic force, which provides the spheres with mobility, and the attractive capillary force, which produces long-range order. In general, spheres that have a parking area (or effectively the surface area of the sphere per carboxyl group) that is significantly larger than 50 \AA^2 per group and hence reduced surface-charge density assemble immediately into a number of microscopic domains. It appears that they lack the flexibility to reassemble into large macroscopic domains as a result of their reduced electrostatic repulsion. Conversely, spheres that have a parking area that is significantly smaller than 50 \AA^2 per group and hence an increased surface-charge density do not assemble at all, likely because the electrostatic repulsion is greater than the attractive capillary force.

As an example, we have experimented with two types of spheres of similar size, 950 and 780 nm, but with significantly different parking areas of 8 and 51 \AA^2 per group, respectively. It was found that for the latter type, with a parking area close to 50 \AA^2 per group, the assembly of large, centimeter-sized domains was achieved easily once the sliders compressed the monolayer into an area of less than $50 \times 45 \text{ mm}^2$. In the case of the former type, no ordering could be achieved even after compression. The spheres had a tendency to spread or “flow”, avoiding any ordered formation. Another type of sphere, with a diameter of 120 nm and a parking area of 112 \AA^2 per group, showed a tendency to assemble instantly, even without compression. The spheres formed a close-packed monolayer that was very rigid and tended to “crack” into smaller formations once the monolayer was disturbed by movements of the water or sliders. A similar effect was observed when attempting to assemble carboxyl nanospheres that were 390 nm in diameter with a parking area of 102 \AA^2 per group. We understand this behavior to be a manifestation of the fact that the parking area, or surface charge density, plays a crucial role in balancing the attractive capillary forces between the spheres and thus can be used to manipulate order formation. Unfortunately, in our experiments it was not possible to study this effect systematically because the spheres are supplied with predetermined specifications. However, it may be possible to control this effect by modifying the chemistry of the water through the introduction of surfactants, for example, and further work is currently being undertaken to investigate this possibility.

After assembly, the highly ordered monolayers are transferred onto solid substrates by placing the substrates just below the water surface prior to the introduction of the spheres. After the sphere assembly is complete, the close-packed monolayer of

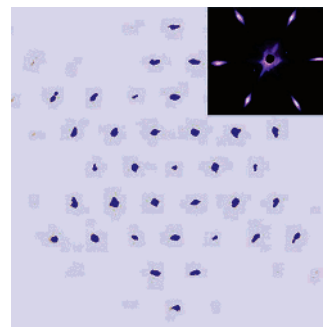


Figure 2. Composite modular Fourier transform obtained from a series of 25 SEM images of a close-packed monolayer taken over a length of 1 cm. The angular peak widths of the composite Fourier transform correspond to a maximum change in the lattice direction of 5° over the entire region. The Fourier image contains contributions from the hexagonal structure factor of the array and an additional form factor due to the hexagonal boundaries that the spheres acquire after metal evaporation. The inset shows the diffraction of a 3-mm-diameter laser beam from a monolayer of 390 nm spheres deposited on a glass substrate. (SEM imaging has been performed on the sample covered with a 3 nm layer of Cr to provide an electric discharge).

spheres remains surprisingly flexible. Because of their highly visible diffraction patterns, the ordered domains can be positioned directly over the substrate using the Teflon sliders. The water surface is then slowly lowered onto the substrate by draining the bath, and the substrate is dried. Successful transfer of ordered monolayers onto a variety of substrates including silica, polymers, and metal films has been achieved using this technique. This is in contrast to traditional methods of spin or drop coating where a highly uniform and hydrophilic surface is crucial to assembling the monolayer by means of immersion capillary forces.^{17,18}

To illustrate the outstanding long-range order that can be achieved, we have used two independent approaches: diffraction from a defocused laser beam and SEM imaging. In the first case, we have used a HeCd laser of wavelength 325 nm to observe the diffraction after reflection from a monolayer of 390 nm spheres deposited on a glass substrate. A 3-mm-diameter laser beam was used in conjunction with a fluorescent screen to produce the image shown in the inset of Figure 2. Any change in lattice direction results in a rotation of the diffraction pattern, causing a smearing of the diffraction maxima. Because a clear hexagonal diffraction pattern is observed with well-defined maxima, it can be concluded that directional order is preserved over the area illuminated by the laser beam. Subsequent scanning of the laser beam across the sample confirmed that directional order is preserved over an area of 1 cm^2 . It should be noted that when considering laser diffraction images one has to be careful in the correct interpretation of the intensity variation. Hypothetically, if the illuminated area of the array had a 5% “intrusion” area of uncorrelated domains then the diffraction pattern intensity would be affected in direct relation to the areas’ ratio. In other words, as well as the main hexagonal pattern, one would observe *low*-intensity peaks (or a ring, depending on the degree of polycrystallinity of the intrusion area) in between the main Bragg reflections. However, in our samples such a possibility is unlikely. SEM examination of large ($100 \times 100 \text{ \mu m}^2$) areas shows that the lattice does not have such intrusions. Instead, microscopic

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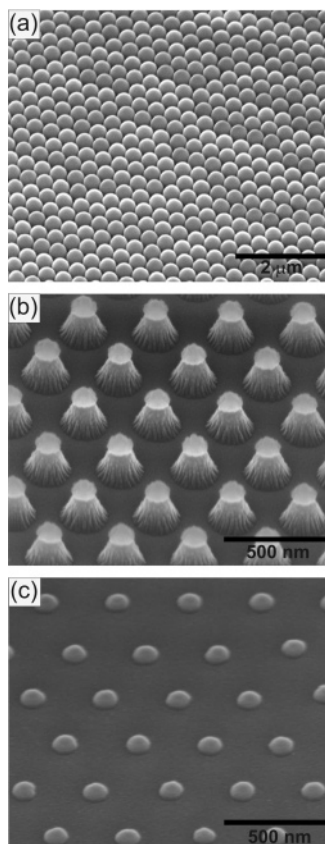


Figure 3. Example fabrication procedure utilizing a highly ordered nanosphere template. (a) Close-packed monolayer of 390-nm-diameter polystyrene spheres deposited on a 200-nm-thick polymer film and a 30-nm-thick NiFe underlayer. (b) Reactive ion etching used to create a template of polymer posts capped by spheres. (c) NiFe dots of 120 nm diameter formed after selective Ar ion milling through the sphere/polymer mask.

imperfections in the form of dislocations, mismatches, or defects normally result in *shallow* deviations of the principal axis of the lattice.

To quantify the maximum angular deviation over the sample area, we have employed the following procedure. A series of SEM images of size $25 \times 25 \mu\text{m}^2$ was obtained at $400 \mu\text{m}$ intervals over a total length of 1 cm. A modular Fourier transform of each image was extracted, and the series of 25 Fourier images was summed to produce the composite image shown in Figure 2. As expected, a distinct hexagonal diffraction pattern is seen with tightly focused spots. This composite image was analyzed to obtain the angular width of the diffraction maxima, which corresponds to the rotation of the lattice direction over the imaged region. The maximum deviation of the pattern in this series of images corresponds to a change in lattice direction of 5° . Although defects such as vacancies may still exist over this area, this analysis clearly demonstrates that excellent hexagonal order is achievable over domains of less than 0.1 mm typically achieved using conventional techniques.^{11,19,20} We also note that by comparing the two diffraction patterns one can see that the laser diffraction also has a broadening of the Bragg peaks in the radial direction. Normally, the broadening indicates the uncertainty in the correlation length between the Bragg planes in the chosen direction. Given that the SEM patterns do not exhibit such an

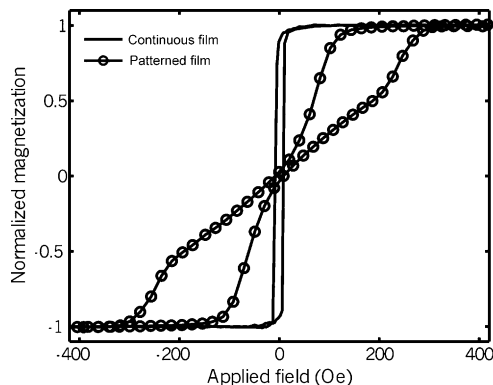


Figure 4. Magnetization reversal of a 30-nm-thick NiFe film before and after patterning. An obvious change in reversal behavior is observed after the film is patterned into a hexagonal array of 120-nm-diameter dots. The loop shape of the patterned film is characteristic of reversal via the formation and annihilation of magnetic vortices.

effect, we believe that in this case it may result from the three-dimensional nature of the diffractive objects (i.e., because of the depth variation of the spheres).

Once deposited, the highly ordered monolayers can be further processed to produce a range of nanostructures. As an example, we have fabricated arrays of NiFe dots using a combination of reactive ion etching (RIE) and Ar ion milling, as shown in Figure 3. A silica substrate was coated with a 30 nm NiFe film by sputtering, followed by a 200-nm-thick spin-coated polymer buffer layer of antireflective coating (Brewer Science Inc., WiDE-15) and finally an ordered monolayer of 390 nm spheres. Once assembled, RIE in an O_2 atmosphere was used to reduce the diameter of the spheres. Because the polymer layer is also susceptible to the O_2 plasma, a structure of conical polymer posts capped by polystyrene spheres results. This template structure was then exposed to an Ar ion plasma that mills the NiFe film by physical sputtering. The material beneath the posts is protected and remains unaffected by the milling, resulting in an array of 120 nm NiFe dots. The diameter of the dots can be controlled by varying the O_2 etching time and the polymer thickness.

It is well known that the patterning of magnetic films can be used to manipulate the magnetization reversal mechanism leading to technologically important applications.⁶ To demonstrate this, Figure 4 compares the magnetic switching of the NiFe film before and after patterning. The magnetization loops were obtained by a longitudinal magneto-optical Kerr effect (MOKE) using a HeNe laser with a $400 \mu\text{m}$ spot size. After patterning, the magnetization loop acquires a steplike structure indicating a significant change in reversal behavior. The steplike magnetization reversal of the patterned film is characteristic of vortex²¹ formation and annihilation, a phenomenon that may have applications in high-density magnetic random access memory²² (MRAM). Because such dots can be produced with excellent order over centimeter length scales, the presented technique provides a route to creating technologically important media over macroscopic areas. This will allow the use of powerful characterization techniques including X-ray resonant scattering and neutron scattering where large-area, highly ordered arrays are vital.

In addition to the periodicity, another appreciable advantage of this technique is the flexibility of the materials that could be

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patterned. In contrast to conventional methods, with this technique the ordered templates of nanospheres can be applied to a broad range of surfaces. In our experiments, we have successfully used different materials, including metals, dielectrics, glasses, and polymers, although certain care should be taken when transferring the templates onto surfaces. The patterning in this case can be limited by the ability to mill the material. However, milling is not the only option for patterning, and a number of other fabrication techniques are available to transfer the template structure into the chosen material (e.g., etching and plating¹¹). The uniformity of the patterns and their resolution will depend mainly on the corresponding parameters of the chosen spheres. It is expected that with the correct choice of surface chemistry the methodology suggested here should be applicable even for spheres in the sub-100-nm range; however, the increased dispersion of the sphere dimensions and nonuniformity of the selective etching/milling processes will likely result in a reduction of the ordered domain size and uniformity of the pattern.

4. Conclusions

The ability to produce nanostructured surfaces over macroscopic areas is likely to be of crucial importance to the integration of nanotechnology into commercial devices. In this work, we have shown that macroscopically ordered nanostructures can be created with directional order preserved over areas of 1 cm² using a simple and widely accessible technique. We have applied SEM/Fourier imaging and laser diffraction to demonstrate that the lattice direction is preserved to within 5° over this macroscopic area. The technique has been demonstrated in practice through the fabrication of highly ordered arrays of magnetic dots. In addition to dots, highly ordered sphere arrays can be used to create a broad range of nanostructures with modified topography, producing a rich variety of controllable properties. It is thus expected that the presented advances in nanosphere lithography will be of value to those working in a variety of fields, including magnetism, photonics, and nanoelectronics, facilitating wider access to large-area nanostructured surfaces.

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