Pattern transfer nanomanufacturing using magnetic recording for programmed nanoparticle assembly

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Abstract. We report a novel nanomanufacturing technique that incorporates patterned arrays built entirely from Fe3O4 nanoparticles into a flexible and transparent polymer film. First, the nanoparticles are patterned using the enormous magnetic field gradients at the surface of commercial disk drive media, and then the resulting architecture is transferred to the surface of a polymer film by spin-coating and peeling. Since the particles are immobilized by the field gradients during the spin-coating process, the patterned array is preserved after peeling. To demonstrate the potential of this technology, we fabricated a 5 mm diameter all-nanoparticle diffraction grating capable of producing a white-light optical spectrum. We also demonstrate several extensions to this technology, where, by adding an external magnetic field during assembly, we created both periodic variations in topography, as well as a nanocomposite with two vertically and horizontally separated nanoparticle layers. As this technique leverages the nanometer resolution inherent in current magnetic recording technology, strong potential exists for low-cost nanomanufacturing of optical and electronic devices from a variety of nanomaterials with ~ 10 nm resolution.

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1. Introduction

The goal of nanomanufacturing is to develop practical methods for leveraging novel properties inherent in nanomaterials to yield viable new technologies. Realizing a practical and scalable platform for nanomanufacturing macroscopic materials and architectures via bottom-up self or directed assembly is a critical aspect of current nanotechnology research [1]. In particular, reprogrammable mechanisms for assembling and then transferring large area nanomaterial assemblies into application platforms are needed, where the "raw" material is a nanoparticle or similar nanoscale material, and the finished product is a designed, macroscopic structure built from the raw materials. One approach to nanomaterials assembly uses external electromagnetic forces to position and assemble arrays of nanoparticles [2]. Here magnetic-gradient force directed assembly was originally employed by Bitter to visualize domains and surface features in magnetic materials [3]. This "Bitter technique" has been applied for imaging the patterns created by magnetic recording on disk drive media [4], and for separating weakly magnetic and nonmagnetic particles through high gradient magnetic separation (HGMS) [5]. More recently, lithographed arrays of magnetic materials biased with external magnetic fields have been used to assemble magnetic particles in a fluidic environment [6, 7, 8, 9, 10, 11, 12, 13, 14], yielding techniques for particle transport for drug delivery [15, 16], masking for lithography [17], and stitched membrane assembly [18].

Hard disk drives using magnetic recording technology store much of the world’s information on Cobalt alloy magnetic media with grain sizes < 10 nm in diameter, bit lengths in the 30 nm range, and track widths < 100 nm, i.e. at significantly smaller length scales than the lithographed structures described above [19]. Driven by explosive growth in the market for storage capacity over the past decade, the disk drive industry has leveraged giant magnetoresistance (GMR), advanced materials, and scalability to drive the core technologies to nanoscale dimensions, and in terms of required critical dimensions for lithography, the data storage roadmap closely matches the semiconductor industry [20]. Presently, the industry is aiming toward a 1 Terabit/in² areal density target where bit lengths and track widths will be 11 nm and 38 nm respectively [21].

Enormous magnetic field gradients exist at recorded magnetization transitions in disk drive media, suggesting the application of magnetically recorded transitions for local magnetophoresis. From the conventional expressions describing the magnetic field of recorded transitions in disk media [19], we find the magnetic field gradient ranges from > $4 \times 10^6 \ T/m$ at 25 nm to $\sim 5000 \ T/m$ at 1 $\mu m$ above the surface (see Appendix). These field gradients are significantly higher than the $\leq 1000 \ T/m$ gradients typically employed in external field-driven magnetophoresis [22]. At 50 nm above the disk surface, the work done by this field gradient to move a 10 nm diameter nanoparticle (partially magnetized by the medium field at this height) one diameter toward the surface exceeds $k_B T$ [23], meaning that the magnetic gradient force will dominate over other transport mechanisms at this height for $\sim 10 \ nm$ and larger nanoparticles [22, 23, 5] (see Appendix). Therefore, these gradients allow for precision assembly of ferrite nanoparticles into large area
patterns, and we have previously employed AFM to determine a coating-to-coating repeatability for this process of $27 \pm 11 \text{ nm}$[24].

In this article, we describe a successful proof-of-concept applying this magnetic recording "nanotechnology" for nanomanufacturing. After the particles have been assembled and the remaining colloid removed, we perform a polymer coating and peeling process[25, 26] that transfers the nanoparticles from the disk medium surface to a flexible, transparent film while maintaining the magnetically-recorded nanomaterial pattern. Thus we combine the disk drive’s $\sim 10 \text{ nm}$ spatial resolution and ability to pattern large surface areas with precisely-controlled fluidic deposition to create complex assemblies, employing individual nanoparticles in a colloidal solution as "raw materials".

2. Nanomanufacturing process

2.1. Disk drive medium used for nanoparticle coating

Figure 1 (A-D) gives a pictorial overview of our nanomanufacturing process, with the inset of Figure 1(A) outlining the entire process schematically. We employ pre-recorded, longitudinal magnetic recording media, using $\sim 1 \text{ cm}$ circular coupons cut from commercial recording "disks" as the assembly substrate (Figure 1A-inset). The thin film magnetic media are grown on Al substrates and have magnetizations of $\sim 450 \text{ kA/m}$, as determined using Vibrating Sample Magnetometry (VSM) on a Quantum Design Physical Property Measurement System (PPMS). Commercial disk drive media are patterned into sectors along the circumference of the disk prior to distribution through a process called servo-writing, which creates regions known as servo sectors between the data sectors [19]. These regions have magnetic field patterns which are used with a servo-algorithm to keep the recording heads accurately positioned over the data tracks. Figure1(A) shows both data and servo-patterned regions of the medium, with the servo sector comprising the varying width marks running diagonally from the left center to the lower right corner of Figure 1(A). In addition to using pre-written regions of media for nanoparticle assembly, we employ a contact recording tester[27] to magnetically-record desired transition patterns into the medium. A contact tester is a scanning probe tool that scans a magnetic recording head with nanometer precision while in contact with disk media, with electrical connections to the recording head providing for both programmed precision magnetic recording and transition field imaging with the GMR readback head [19]. Figure 1(A) shows 7 tracks written with our contact tester at different spacing offsets across the servo and data regions from the lower left to middle/upper right of the image. Each transition recorded into the medium emits a magnetic field into the space above the transition, with magnetic field lines directed to adjacent, oppositely magnetized transitions. These rapidly changing field lines create a large and spatially-localized magnetic field gradient as described in the appendix.
2.2. Nanoparticle deposition onto disk media

We employ commercial (Ferrotec, Nashua, NH - EMG-707) and in-house synthesized[28, 29] ferrofluid to create these assemblies on our disk coupons. First the coupons are sonicated in Perfluorosolv Fomblin (PFS-1 flushing fluid - Solvay Solexis, West Deptford, NJ) for 15-30 seconds to remove the hydrocarbon lubricant from the disk surface. Ferrofluid is diluted to \( \sim 0.01-0.05 \% \) of the stock solution in \( >10^{17} \) Ohm deionized water and deposited onto the coupons in a liquid cell (radius 7.5 mm) and covered to a depth of 3 mm. The superparamagnetic nanoparticles that are suspended in the ferrofluid just above the disk surface are magnetized by the transitions’ magnetic field, and are then attracted to the transitions by the field gradient, which is largest at the surface of the medium and at the location of the transition. After several minutes, phosphate buffer (pH 7.2, VWR, Inc.) is added to the liquid cell to modify the electrostatically-charged ligand on the nanoparticle surface that typically stabilize a colloidal solution[30, 31]. This step is critical for keeping the nanoparticles in place on the disk surface as the remaining ferrofluid solution is pumped away with a peristaltic pump. Samples which were not treated with buffer solution typically do not yield a complete coating of
ferrofluid on the disk surface, while treated samples are stable and easily imaged with an optical microscope. Bright and dark-field optical images of the coated disk surfaces are obtained using a Nikon instruments LV-200 microscope equipped with a Canon digital SLR.

2.3. Nanoparticle pattern transfer to flexible, polymer film

After imaging the nanoparticles assembled on the disk drive surface, the coupon is spin-coated with a liquid polymer (Diskcoat 4220 - General Chemical Co., Brighton, MI). Undiluted Diskcoat spun at 2600 rpm for 30 seconds yields a \( \sim 200 \) nm thick film, as determined using both stylus and optical profilometry. After curing for 15-30 minutes in air at room temperature, the polymer-nanoparticle assembly is peeled from the medium with adhesive tape to yield a suspended film over a 5 mm diameter circular window (arrows in Figure 1(B)). By adjusting the spin speed, spin time, and by diluting the Diskcoat in DI water, a variety of polymer thicknesses can be obtained, ranging from 100 nm to several \( \mu \)m. However, we found that only films thicker than 200 nm yield an intact film after peeling, and the films discussed here have thicknesses that range from 200-500 nm. These nanomanufactured materials are flexible, transparent, and contain programmed arrays of nanoparticles[25, 26]. Figure 1(C) shows a reflection optical diffraction spectrum created by sending collimated white light through the assembled nanoparticle layer in the central 5 mm region in figure 1(B). Figure 1(D) also shows that the polymer film itself is not completely defect free, with some unpatterned bubbles remaining in the polymer layer after curing. However, these random defects do not contribute to the diffracted spectrum, as there is no spectrum visible from peeled films without nanoparticles. The peeled films are generally stable, but can be made to repeatably change shape in response to a temporary increase in humidity/temperature (i.e. by breathing on the polymer film), as observed by distortion in a reflected white light spot that returns to a non-distorted shape when the environment returns to ambient.

In addition to optically imaging the nanoparticle-containing polymer films (figure 1(D)), we load them into the VSM and determine their magnetic state. As expected for superparamagnetic nanoparticles, our peeled films show zero remanent magnetization, meaning that the assembled arrays do not remain magnetized without an applied magnetic field. Visual inspection of the coupon surface after peeling shows no remaining nanoparticles, and AFM measurements of coupons after peeling likewise show no particles in several locally-imaged regions. After the initial film peel, second and third films were deposited, cured, and peeled. VSM measurements of these subsequent films are indistinguishable from measurements of films that do not contain nanoparticles. Our VSM’s rms sensitivity \( \sim 1 \times 10^{-6} \) emu is \( \sim 2 \% \) of the total moment measured from first-peel films that contain the patterned, transferred nanoparticles. These observations suggest that at minimum 98 \% of the nanoparticles are transferred to the film during the initial peeling step.
2.4. Nanomanufacturing process metrology

Atomic and Magnetic Force Microscopy (AFM/MFM) images of nanoparticles both on the disk surface and as embedded in the polymer were obtained with an Agilent PicoPlus SPM operating in non-contact (AC) mode. For AFM, we employed BudgetSensors Tap300 300 kHz tips having 40 N/m force constants and < 10 nm tip radius for AFM, while for MFM we used 75 kHz High Resolution MFM tips with < 25 nm radius, coated with Co alloy and Al on the backside of the cantilever (Nanoscan Ltd., Dubendorf, Switzerland). To study the repeatability and aid in AFM imaging of assembled nanoparticles, we used optical photolithography to place a series of numbered frames on top of the disk coupon[32]. These 30 nm thick Cu frames were sputter-deposited onto patterned photoresist followed by lift-off, and enable us to find the same exact region of the disk with our AFM to study the assembled pattern as a function of coating process for repeatability and thickness testing. Figure 2(A-D) show a series of images of the servo marks on a coupon taken with (A) MFM, (B) Dark-field microscopy, (C) AFM of the coupon surface after assembly, and (D) AFM of the peeled film. Figure 2(A-C) demonstrate that the nanoparticle assembly (imaged both optically and with AFM) closely matches the magnetic force gradients as imaged with MFM. Further, figure 2(C-D) shows that the nanoparticles maintain their pattern after transfer to the polymer film[25]. The striations observed in figure 2(C-D) are ∼ 10 nm high polishing marks left from the disk manufacturing process, and since they do not change from coating to coating, make an excellent reference for image correlation to determine the repeatability of our assembly process, which is presently 27 ± 11 nm [24]. Figures 1 - 2 demonstrate our nanomanufacturing process along with a metrology for assessing repeatability of repeated coatings, before and after transfer to the polymer film.

Measurement of a 50 µm long section of the regular pattern that creates the spectrum in Figure 1(C) yields 66 lines of nanoparticles as assembled on the disk media, but the same 50 µm scale bar yields 68 lines of nanoparticles on the polymer film (1360 lines per mm). Assuming equal spacing for these features, the nanoparticle line spacing decreases from 760 nm on the coupon to 735 nm in the polymer after peeling (the equal spacing assumption enables us to measure a 25 nm difference per line that is significantly smaller than our actual optical resolution). A similar analysis on the features in Figure 2(C-D) suggests that the 1.2 µm feature spacing decreases by ∼ 50-100 nm after transfer to the polymer film. Therefore, the net result is that the nanoparticle pattern shrinks by ∼ 5%. Even though the polymer may expand during curing, we expect the nanoparticles at the surface will remain fixed by the magnetic force, and thus when the polymer relaxes after peeling, the nanoparticle feature spacing decreases slightly.
3. Nanomanufacturing process extensions using external magnetic field

3.1. Controlling intra-layer assembly

Figure 2(A,C) demonstrate that the nanoparticle topography correlates precisely with the magnetic field spatial variation. We can further control the nanoparticle assembly process by applying a uniform external field over the fluid cell during assembly[33]. Figure 3(A-B) show optical images of the same region of media coated in zero external field (A) and with an external field, $H_{ext}=1.5 \text{kOe}$, directed toward the medium surface (B). In contrast to the zero field assembly process, the superposition of this 1.5 kOe field with the transition field (calculated from the equations in the Appendix) yields $H_{net} = 0 \sim 20 \text{ nm}$ above the surface. Therefore, the external field will exceed the medium field for $z > 20 \text{ nm}$ and magnetize the nanoparticles along the external field direction. These pre-magnetized nanoparticles will therefore be repelled from transitions with oppositely directed local field (with $H = 0$ at $z = 20 \text{ nm}$), while still being attracted to transitions whose local field constructively superposes with the external field. Thus in Figure 3(A) every transition is coated, while in (B) only every-other transition is coated. Close inspection of Figure 3 shows the similarities in the features between the two images, with spatially modulated features in the upper part of (B) that were horizontal lines in the upper part of (A), and gaps in (A)’s enclosed block-
Figure 3: A) Dark field optical image of disk media servo pattern coated without an external field. Here every transition magnetizes and then attracts nanoparticles. (B) Dark field optical image of the same disk region as (A), only coated in a 1.5 kOe external field (directed toward the surface). Note the staggered pattern in the upper section, and the gaps that have opened up in the rectangular block regions. At 1.5 kOe, the superposition of the alternating upward-directed transition and external field yields $H_{\text{net}}=0$ at a height of $\sim 20$ nm above the disk surface, and nanoparticles above this height are magnetized in the direction of the external field (which exceeds the transition field for $z>20$ nm). Particles magnetized by the external field should therefore be repelled from every other transition, and a comparison of panels (A) and (B) confirms that while all the transitions are coated in zero field (A), only half are coated in $H=1.5$ kOe (B).

Like open spaces appearing in (B). Generally, there are half as many coated features in (B) as in (A). These changes from (A) to (B) are all caused the repulsion of pre-magnetized particles from opposing, spatially alternating transitions. While $H_{\text{ext}}=1.5$ kOe is sufficient to prevent nanoparticle coating on opposing transitions, for weaker external fields, $H_{\text{ext}} \sim 800-900$ Oe, we have observed partial coating of opposing transitions. Since the external field magnitude controls the height where $H_{\text{net}} = 0$ above opposing transitions, as well as enhancing the magnetization of nanoparticles above aligned transitions, transitions with constructive field superposition can yield thicker nanoparticle layers than the zero external field case, while transitions which oppose the external field produce a thinner layer than the zero field case. We have achieved such multiple topographies in our external field coatings, suggesting potential for creating assemblies with varying nanoparticle layer thicknesses controlled by applying a spatially varying external magnetic field template during assembly.
3.2. 3D Assembly: Controlling interlayer assembly

We can employ external fields to further extend our technique and create two vertically-separated, horizontally-interleaved layers of nanoparticles, with the layers assembled in oppositely-directed fields and separated by a polymer layer. Figure 4(A-B) show this process, with the left panel (A) demonstrating external field assembly at "positive" field transitions. After removing the ferrofluid, the layer is spin-coated with polymer, only instead of peeling the polymer, we expose the surface again to ferrofluid, this time in a "negative" field (right panel, B), and thus the particles assemble on "negative" field transitions. After this second coating, the film is further coated with a second layer of polymer and then peeled from the coupon. The dark field image in figure 4(A) shows alternating brighter and dimmer features. The dimmer interleaved features are the "negative" field transitions, which are still slightly coated at the intermediate external field used here, $H_{ext}=900$ Oe. The dark field image in figure 4(B) (two layers of nanoparticles) shows bright nanoparticle lines at the locations in figure 4(A) that were dim and weakly coated. Thus figure 4 A-B clearly display a horizontal single-transition width offset in the nanoparticles between the lower and upper layers, demonstrating the potential for nanomanufacturing 3D composites with both inter- and intra-layer control over the assembled topography and feature spacing.

4. Discussion and conclusions

Control over field-gradient driven magnetophoresis is typically limited by random thermo-fluidic effects including particle diffusion and Brownian motion, as observed in nanoparticle magnetophoresis experiments conducted at significantly weaker field gradients [22, 5, 34, 11]. The boundary between diffusive and driven nanoparticle transport is often derived under the assumption that the nanoparticles are moving at their terminal velocity, i.e. the inertial term in Newton’s 2nd law is presumed negligible. For recorded transitions at the medium surface, the field gradient changes strongly with height and is a maximum at the medium surface. Therefore, a nanoparticle trapped in the transition field experiences an ever-increasing acceleration with decreasing height and thus will not reach a terminal velocity. While diffusive effects may modify a nanoparticle’s trajectory, given the repeatability of the coatings, these effects are perturbative instead of dominant in these large field gradients. Since the transitions effectively remove nanoparticles from the fluid at lower heights, a concentration gradient could be created that enables diffusive transport (at large heights where the gradients are weaker) to drive nanoparticles toward the disk surface. Concentrating nanoparticles on a surface in the extreme gradient limit is clearly different than concentrating them via weaker field gradients in fluid [34, 22], and requires additional study. In particular, a new figure of merit for identifying transport regimes may be needed to properly explain the physics of the assembly process. Efforts are currently underway to understand how the total assembled magnetic moment experimentally determined via magnetometry
Figure 4: Schematic (top) and experimental demonstration (bottom) of directed assembly to nanomanufacture a patterned two-layer composite material. (A) Lower layer: Magnetic nanoparticles (directly above magnetic transitions) are assembled in a upward-directed external field ($H_{\text{ext}}=800$ Oe) and spin-coated with polymer (here the 'particles' correspond to bright marks in the dark-field image (lower panel, left). Note the magnetic field was not strong enough in this case to completely prevent assembly on the opposite transition, which appear as relatively darker, interleaved features between the bright features in the image. (B) A second layer of nanoparticles (on top of the polymer film in the upper right panel schematic) are assembled in a downward directed external field ($H_{\text{ext}}=800$ Oe) on top of the polymer film that covers the first layer of nanoparticles. In this dark field image (lower panel, right), the upper nanoparticle layer is now slightly brighter than the spatially-offset lower nanoparticle layer (see callout). The lower right image is somewhat blurry because the microscope is focusing through two layers of polymer film.

depends on both coating time and nanoparticle concentration. Finally, additional studies are needed to fully understand changes in the polymer film after peeling and extend this technique for large area applications, for example, by adding a second layer of stiffer polymer on top of the first layer prior to peeling.

In conclusion, we demonstrate a nanomanufacturing proof-of-concept by transferring magnetic-field assembled nanoparticles to the surface of a polymer film and verifying that the pattern is maintained after peeling. We have successfully employed this technique to nanomanufacture a stand-alone all-nanoparticle diffraction grating. By extending our assembly process to include external control of in-layer feature topography, as well as bilayer assembly with precision vertical and horizontal spacing, we suggest that commercial magnetic recording offers a novel and practical approach for creating large-area nanomanufactured composite materials.
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Appendix

To illustrate the enormity of the field gradients present at the recorded "bits" in disk drive media, Figure A1 plots the perpendicular magnetic field (A) and the perpendicular component of the magnetic field gradient (B) as a function of height above the disk medium surface (centered on the transition at x=0 in Figure A1 (A) inset), with the perpendicular (z-direction) magnetic field emitted from an in-plane recorded transition (infinite in y-direction) given by

\[ H_z = \frac{M_r}{2\pi} \log \left( \frac{(a + z - \frac{\delta}{2})^2 + x^2}{(a + z + \frac{\delta}{2})^2 + x^2} \right), \]  

\[ (A.1) \]

where \( M_r \) is the remanent magnetization of the disk medium, \( a \) is the medium transition parameter [19], \( \delta \) is the medium film thickness, \( z \) is the perpendicular distance away from the medium surface, and \( x \) is the horizontal distance away from the transition center. The dot product of the nanoparticle magnetization and the gradient of this field, (i.e. the z-component plotted in A1(B)), gives the downward force on a magnetic nanoparticle

\[ \vec{F} = \vec{M} \cdot \nabla \vec{H}. \]

\[ (A.2) \]

Using \( M_r = 450 \text{ kA/m} \), \( a = 10 \text{ nm} \), and \( \delta = 30 \text{ nm} \) (conventional values for the recording system we employ [19]), Figure A1(B) shows that the gradient varies from \( > 4 \times 10^6 \text{ T/m} \) at 25 nm to \( \sim 5000 \text{ T/m} \) at 1 \( \mu \text{m} \) above the surface.

As discussed in the text above, the field gradient near the surface is \( \sim 3 \) orders of magnitude larger than gradients traditionally used for magnetophoretic nanoparticle transport. By integrating Eq. A.2 over height, using the field gradient given in Eq. A.1, for a 10 nm diameter particle from \( z = 50 \text{ nm} \) to \( z = 40 \text{ nm} \), we obtain \( 3 \times 10^{-21} \text{ J} \) for the work done by the magnetic field, which is \( k_BT \) at \( T = 295 \text{ K} \). Thus at 5 nanoparticle diameters above the surface or below, the work done by the magnetic field exceeds the thermal energy that drives Brownian motion. In addition, even though the work done by the field is less than \( k_BT \) for \( z > 50 \text{ nm} \), it is always directed toward the surface, while Brownian forces are randomly oriented. This anisotropy likely assists recorded transitions in capturing nanoparticles from even greater heights and pulling them to the medium surface.
Figure A1: (A) Perpendicular magnetic field directed toward the surface of a magnetic recording medium centered on the medium magnetization transition between opposite directed local magnetizations (inset). The transition magnetic field ranges from 1000 Oe 50 nm above the disk to about 125 Oe 500 nm above the disk. (B) Absolute value of the perpendicular magnetic field gradient in Tesla/meter, showing that 25 nm above the disk, the gradient is more than 4 million T/m, decreasing to several thousand T/m 500 nm above the surface.

References


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