

Polymer Mediated Self-Assembly of Magnetic Nanoparticles

Shouheng Sun,^{*,†} Simone Anders,[‡] Hendrik F. Hamann,[†] Jan-U. Thiele,[‡] J. E. E. Baglin,[‡]
Thomas Thomson,[‡] Eric E. Fullerton,[‡] C. B. Murray,[†] and Bruce D. Terris[‡]IBM T. J. Watson Research Center, Yorktown Heights, New York 10598, and IBM Almaden Research Center,
650 Harry Road, San Jose, California 95120

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In nanoparticle dispersions, each particle is stabilized against aggregation with a layer of organic/inorganic coating. Such nanoparticles can be used as building blocks to fabricate functional nanostructures via self-assembly. This nanoparticle-based self-assembly is governed by particle–particle and particle–substrate interactions. Controlled self-assembly of magnetic nanoparticles has stimulated great interest recently as it may offer a convenient tool for magnetic nanodevice fabrication. A tightly packed assembly of exchange-decoupled magnetic nanoparticles may serve as future ultrahigh-density data storage media.¹ Magnetic nanoparticles buried in a dielectric or nonmagnetic metal matrix may exhibit novel giant magneto-resistive properties.² Controlled assembly of small magnetic nanoparticles on the end of a sharp tip, such as an AFM probe, is expected to yield high sensitivity for magnetic force sensing at high spatial resolution.³ Selective combination of biomolecules with magnetic nanoparticles may enhance the ability for biomolecule recognition⁴ and magnetic field-assisted drug delivery.⁵

We report on a polymer-mediated self-assembly of magnetic nanoparticles into smooth magnetic nanoparticle-containing films with control of assembly dimension and thickness. Solution-phase synthesis has been proved to be an efficient way of making monodisperse magnetic nanoparticles, including elemental Co,⁶ Fe,⁷ and binary FePt⁸ and CoPt⁹ nanoparticles. Self-assembly of these monodisperse nanoparticles via solvent evaporation yields magnetic nanoparticle arrays that exhibit high local ordering. However, at present time, such regular arrays are difficult to form over an extended area with controlled assembly structure and thickness, and generally, various gaps among groups of regular arrays exist. For the application in ultrahigh density magnetic recording, the magnetic nanoparticles need to be assembled uniformly over a large area in only two to three nanoparticle layers.^{1a} Unfortunately, current self-assembly approaches fail to gain such precise control. The reported polymer-mediated nanoparticle assembly has the advantage of highly controlled assembly thickness and dimension and shows great potential for magnetic recording applications.

The assembly process involves exchanging oleic acid/oleyl amine around each magnetic nanoparticle with a functional polymer that is previously deposited on a substrate. The ligand-exchange experiments show that various functional polymers, such as poly(vinylpyrrolidone) (PVP) and poly(ethylenimine) (PEI) can replace oleic acid/oleylamine around these nanoparticles to give polymer-protected nanoparticles. For example, mixing a hexane dispersion of cobalt nanoparticles and a dichloromethane solution of PVP at room temperature can lead to PVP-protected cobalt nanoparticles that dissolve readily in methanol, ethanol, and dichloromethane solvent. It occurs to us that exchanging the stabilizers bound to the particles with multifunctional polymers that attach to a substrate

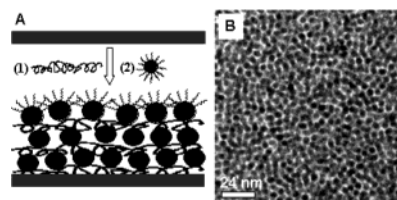


Figure 1. (A) Schematic illustration of polymer-mediated self-assembly of nanoparticles by alternatively absorbing polymer and nanoparticles on a solid surface. (B) A TEM bright field image of three layers of 6 nm Fe₅₀Pt₅₀ nanoparticles assembled on PEI.

may help the controlled assembly of magnetic nanoparticles. The general principle of this process is based on polymer-assisted layer-by-layer assembly,¹⁰ and is applied first here to assemble metal-based magnetic nanoparticles. We focus on the assembly of FePt nanoparticles, as such an assembly might be suitable for future ultrahigh-density data storage media.

The assembly of FePt nanoparticles into a macroscopic two-dimensional array on a polymer-functionalized substrate is depicted in Figure 1A. The assembly process includes: (1) surface functionalization with a layer of polymer coating and (2) replacement of the particle stabilizers with a pendant functional group of the polymer. The pendant functional group extends out in the solution. By dipping the polymer-derivative substrate into the particle dispersion, ligand exchange occurs and a strong monolayer particle assembly is formed. A PEI/FePt assembly is fabricated as follows: a HO-terminated substrate is immersed into chloroform solution of PEI for 30 s, then rinsed with ethanol and dried; subsequently, the dried substrate is immersed into hexane dispersion of the FePt nanoparticles for 30 s, followed by rinsing with hexane and drying. This gives one layer of FePt nanoparticle assembly. By repeating this simple two-step process in a cyclic fashion, a PEI/FePt multilayer assembly can be obtained. Figure 1B shows a TEM image of three layers of 6 nm Fe₅₀Pt₅₀ nanoparticles self-assembled on a PEI-modified silicon oxide surface. The assembly was annealed for further characterization.¹¹

Rutherford backscattering spectrometry (RBS) was used to measure the thickness of the assembly. For a series of three-, five-, seven-layered FePt nanoparticle assemblies, the assembly thickness measured by RBS is consistent with that predicted from the actual number of layers of FePt nanoparticles, indicating that smooth thin FePt nanoparticle assemblies are formed. X-ray photoelectron spectroscopy (XPS) measurements of the Fe 2p_{3/2} core level line of these assemblies reveal a layer or layers of iron oxides around FePt nanoparticles.¹² Angle-dependent XPS measurements seem to show a slight enrichment of the iron oxides at the surface of the films. Near edge X-ray absorption fine structure spectroscopy (NEXAFS) data on these thin nanoparticle assemblies indicate that all assemblies contain metallic iron and iron oxide(s). Different from thick (> 100 nm) FePt nanoparticle assemblies, these thin (< 10

* Corresponding author. E-mail: ssun@us.ibm.com.

[†] IBM T. J. Watson Research Center.

[‡] IBM Almaden Research Center.

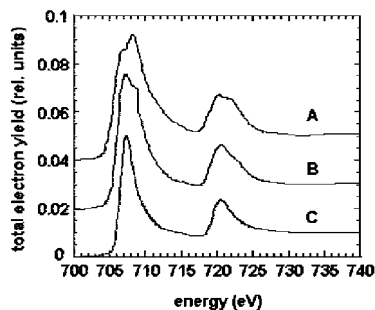


Figure 2. NEXAFS spectra for one- (A) and seven- (B) layer assemblies of 8 nm $\text{Fe}_{52}\text{Pt}_{48}$ nanoparticles annealed at 580 °C in N_2 for 30 min, together with a metallic Fe reference spectrum (C).

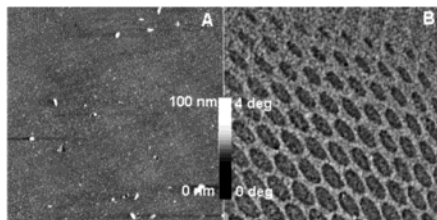


Figure 3. (A) AFM image ($17.4 \times 17.4 \mu\text{m}^2$) of a three-layer 4 nm $\text{Fe}_{58}\text{Pt}_{42}$ nanoparticle assembly annealed at 530 °C under $\text{Ar} + \text{H}_2$ (5%) for 30 min and treated with a focused pulsing laser (93 ns) under a perpendicular magnetic bias field (2.5 kOe). (B) MFM image of the film in (A).

particle layers) ones show various iron/iron oxide(s) fractions that are dependent on FePt nanoparticle size and FePt particle assembly thickness. Figure 2 shows the NEXAFS spectra for one- and seven-layer films of 8 nm $\text{Fe}_{52}\text{Pt}_{48}$ particles together with a metallic Fe reference spectrum. It can be seen that more metallic Fe exists in a seven-layer film than in a one-layer film.¹³ These iron and iron oxide variations directly affect the magnetic properties of the FePt assemblies.

Superconducting quantum interference device (SQUID) (50 kOe field) measurements show that the high temperature annealed thin FePt particle assemblies are ferromagnetic, as annealing induces the particle structure transformation from chemically disordered *fcc* to chemically ordered *fcc*.⁸ Similar to that of thick (> 100 nm) FePt assemblies, the coercivity of the annealed thin films increases with annealing time and temperature. But the coercivity of these thin films is also dependent on assembly thickness. This is likely due to the iron/iron oxide ratio variation with the assembly thickness, as observed in NEXAFS. Preliminary studies show that the existence of iron oxide around FePt particles could destruct the *fcc* phase of these particles, resulting in an assembly with softer magnetic properties.¹⁴

To demonstrate that the magnetization pattern of the magnetic FePt particles can be controlled, we treated the annealed assembly further with a sharply focused laser diode beam (beam diameter 1 μm , wavelength 660 nm) with fast pulses (< 100 ns) under a magnetic field. The temperature introduced by this layer can reach from 200 up to 600 °C. The coercivity of the nanoparticles is reduced at these temperatures and allows for thermally assisted magnetization reversal of the particles by a weak magnetic bias field. Figure 3 shows the corresponding atomic force microscope (AFM) image (Figure 3A) and magnetic force microscope (MFM) image (Figure 3B) of a three-layer 4 nm $\text{Fe}_{58}\text{Pt}_{42}$ assembly that was annealed first at 530 °C under $\text{Ar} + \text{H}_2$ (5%) for 30 min, then treated with a focused pulsing laser (93 ns) under a perpendicular magnetic field (2.5 kOe). The AFM image shows that the smooth FePt nanoparticle assembly is intact after the laser treatment. The black spots in Figure 3B indicate the magnetization pointing to the

out-of-particle-assembly plane. The egg-like shape of the spots is due to the shape of the laser diode beam. We also found that reduced laser power resulted in smaller bits, as shown in Figure 3B, suggesting that it is possible to use a pulsing laser to write magnetic patterns in various packing densities on a thin FePt nanoparticle assembly.

We have described a simple chemical process of assembling FePt nanoparticles with control on assembly thickness and dimension. The process can be applied to any sized and shaped substrate, thus offering a great potential for FePt-based nanodevice fabrication. Such polymer-mediated assembly is not limited to FePt nanoparticles, and PVP and PEI polymers, but can be extended to many other magnetic or nonmagnetic nanoparticle and macromolecule systems as well. In a layer-by-layer assembled nanoparticle film, the nanoparticles from layer to layer can be the same, or they may be varied. Such control suggests that various functional nanostructures can be produced.

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- (12) Chambers S. A.; Joyce, S. A. *Surf. Sci.* **1999**, *420*, 111. We are unable to identify three iron oxides, FeO , Fe_2O_3 , and Fe_3O_4 , with XPS as binding energy of these iron oxides falls in a very narrow range, from 708 to 711 eV. Little metallic Fe is detected by XPS. This is easily understandable as particles are coated with a layer of polymeric hydrocarbon materials (~ 2 nm) and the electron escape depth at the photon energy of 1486.6 eV used here is less than 2 nm.
- (13) Due to the surface sensitivity of NEXAFS, the accurate iron/iron oxide ratio averaged over the FePt assembly is not available. Assuming a metallic FePt core with an iron oxide shell, an oxide thickness of only 0.2 to 0.3 nm is sufficient to explain the observed NEXAFS spectra.
- (14) Detailed magnetic studies on these thin nanoparticle assemblies are underway.

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