A materials chemistry perspective on nanomagnetism†

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Nanomagnetism encompasses naturally occurring magnetic molecules and clusters as well as artificially structured low-dimensional magnetic materials. Basic research areas include the pursuit of novel interfacial magnetic coupling and spin-transport phenomena and creating new magnetic electronic architectures. In addition to the study of fundamental magnetic phenomena, nanomagnets may in the future form the basis of emerging technologies, such as in ultra-high density data storage media, ultra-strong permanent magnets, and biological and chemical sensing. Herein we highlight materials chemistry contributions to the quest for new magnetic functionalities, including the fabrication of surfactant-mediated magnetic particles and soft matter templates as platforms for hierarchically assembled hybrid magnetic materials. Nanomagnetism is positioned at the frontier between chemistry and magnetism. Devising methods to organize functional magnetic nanostructures draws on the unique strengths of a diverse materials chemistry community.

Introduction

Magnetism has been studied since the sixth century B.C. when the Greek philosopher Thales of Miletus noted the attraction of iron to lodestone; it is also at the vanguard of modern innovations in nanotechnology. Magnetism arises because electrons have the quantum mechanical property of spin.[1,2] Traditional magnets anchor applications as disparate as electricity generation, medical imaging, and information storage. The reduced dimensionality that comes with nanoscale magnetic structures, however, introduces abundant novel phenomena interesting on both a fundamental and an applied level.[3] The most obvious change that occurs when moving from bulk materials to nanomaterials is the reduction of coordination. In the bulk, most outer-shell electrons are occupied in bonding interactions; these electrons are often non-magnetic because, according to the Pauli principle, each bonding pair contains electrons with opposite spin.[4] As dimensionality, and hence coordination, is reduced, more electrons are available to lead to magnetism. One can also view this connection in a band picture. The Stoner criterion states that strong exchange interactions and a large density of states at the Fermi energy, $n(E_F)$, favor ferromagnetism. A wider bandwidth corresponds to a lower $n(E_F)$. Structures with reduced dimensionality have narrower bandwidths, *i.e.* larger $n(E_F)$, and consequently a greater propensity to exhibit magnetic behavior.

Nanomagnetism research often concentrates on confined hybrid materials. Confinement offers numerous opportunities for harnessing new functionalities built on the interplay of competing interactions. Hybrid nanostructures can be exploited for spin injection and to generate a spin-polarized current useful for novel magnetotransport studies.[5]

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Semiconductor–magnet hybrids and magnetic semiconductors can enable circuits where both the spin and the charge of the electron are manipulated for spintronic devices.[5,6] Films and nanoparticles that couple soft and hard ferromagnetic layers into composites offer the potential to transcend the limits of today's strongest commercial magnets.[7] Spin dynamics of lithographically patterned magnetic dots have revealed intriguing magnetic vortex behavior.[8,9] Magnetic fields at magnetic domain walls produce remarkable tunable interfacial patterns that can be imaged with magnetic force microscopy (MFM) and spin-polarized scanning tunneling microscopy (SP-STM).[10,11]

Materials chemistry and magnetism are in synergy because, in order to reveal the underlying physics of magnetic phenomena, the highest quality materials are required. Conversely, the best caliper of sample quality can be the physical measurement of magnetic properties. The synergy is well exemplified by complex systems such as molecular magnets,[12–16] catalysts,[17–21] magnetic perovskites,[22] and supramolecular organometallic magnetic compounds.[23] Chemical and physical diagnostic tools that merge the boundaries of chemistry and magnetism include magnetic spectroscopies and microscopies such as Mössbauer spectrometry,[24] neutron scattering,[25] photoelectron emission microscopy (PEEM),[26] SP-STM,[27] MFM,[28] magneto-optic Kerr effect (MOKE),[29] electron spin resonance (ESR), electron paramagnetic resonance (EPR), and nuclear magnetic resonance (NMR). Chemistry is a critical partner in the advancement of nanomagnetism. One area of potential future intersection is in the field of organic spintronics.[30] Traditional electronics use only the charge of the electron, whereas in spin electronics the quantum mechanical spin of the electron offers a number of potential advantages such as non-volatile memory.[31] Realizing spintronic devices will require materials through which spins can freely travel relatively large distances. The strong spin–orbit coupling inherent to many high-Z metals limits spin diffusion lengths,[32] thereby making fabrication of many purely inorganic spintronic devices challenging. Organic materials are low Z and hence have intrinsically weak spin–orbit coupling, suggesting the possibility of longer spin-coherence times and spin-diffusion lengths. Additionally, matching the impedance across disparate hybrid circuit structures is a looming challenge. The resistance of organic materials can be tuned to match that of other layers in multilayer structures thereby improving spin injection across interfaces.

In this Application article, we focus on two areas in which materials chemistry and magnetism are inextricably linked: magnetic nanoparticle synthesis and polymeric templating of magnetic materials. Both research areas rest on the foundation of chemical self-assembly. In the quest for miniaturization, top-down lithographic approaches to create nanoscale magnetic structures are approaching fundamental limitations. Even cutting-edge electron beam lithography cannot create structures smaller than 10 nm. Furthermore, lithographic techniques are often serial and therefore expensive and slow. Advancing nanotechnology will necessitate innovations that allow parallel synthesis of hierarchical structures in the 1–100 nm size range. Bottom-up self-assembly approaches, predicated on chemical processes, offer a promising route to overcome the shortcomings of lithography. Self-assembly is a method of integration in which components, driven by weak interactions, spontaneously organize themselves *via* random motion until a stable structure is obtained. Components in self-assembled structures find their appropriate location based solely on their structural and chemical properties. Self-organizing systems, however, generally do not form a vast array of technologically significant structures on their own. Frequently, combining top-down and bottom-up methods into a unified approach that transcends the limitations of both is the optimal solution.

Colloidal magnetic nanoparticles

Monodispersed magnetic nanoparticles are of interest for both technological and fundamental reasons. From an applied standpoint, these materials are promising candidates to extend the density of data storage media into the Tbit in^{-2} regime,[33,34] for spin-dependent electron transport devices,[35] and for therapeutic or diagnostic medical functions.[36–38] From a basic research perspective, nanoparticles have large surface-to-volume ratios and serve as a link between atomic and solid state physics. More specifically, magnetic nanoparticles offer unique systems to study surface magnetism. Nanoparticles, often called "artificial atoms," may serve as building blocks of new materials composed of supercrystals with mixtures of metallic, semiconducting, and/or insulating units. Such composites could be tailored with desired physical properties. The promise of nanoparticle applications is broadened further by the introduction of core–shell systems, for example, having a magnetic core encapsulated in a protective, and perhaps even biocompatible, skin. Magnetic nanoparticles can be semiconducting, insulating, or metallic. They can be prepared by methods that range from mechanical to gas-phase to chemical. We focus on chemically synthesized metallic magnets, such as cobalt and iron–platinum, and their assembly into ordered arrays and we take a brief look at future opportunities.

Metal salt reduction is the most flexible method to produce magnetic nanoparticles. Using this scheme, metal ions are rapidly reduced in solution to create neutral species that grow into magnetic nanoparticles in the presence of stabilizing organic molecules:

$$\begin{aligned}&\text{metal salt} + \text{reducing agent} \xrightarrow{\text{heat}+\text{surfactants}}\\&\text{neutral nanoparticles}\end{aligned} \tag{1}$$

A synthetic strategy to create a novel metastable phase of cobalt, ε-Co, has been reported by two different groups.[39,40] The significance of this development is that the synthesis yields monodisperse nanoparticles that can self-organize into superlattices. This phase can then be converted into common hcp or fcc phases *via* annealing at 300–350 °C or 450–500 °C, respectively, with control over the interparticle spacing obtained by tailoring the annealing conditions. The ε-Co is synthesized by injection of dioctyl ether superhydride solution into hot $CoCl_2$ solution in the presence of oleic acid and trialkylphosphine. Reduction occurs immediately, producing many small metal clusters that, in turn, serve as nuclei for the subsequent growth of nanoscale single crystals. The length of the hydrocarbon chains in the trialkylphosphine determines the resulting particle size by sterically controlling the growth rate. These nanoparticles are stabilized by organic surfactant capping molecules that also facilitate their dispersion in solvents, allowing their assembly onto solid substrates. Slow evaporation of a carrier solvent from a cobalt dispersion deposited on a flat surface permits highly ordered superlattice structures to form, driven by attractive van der Waals forces and dipolar magnetic interactions (Fig. 1a). Self-assembled films of Co nanoparticles exhibit an interesting magnetoresistivity effect due to spin-dependent tunneling.[35] Two-dimensional arrays of spin-dependent tunnel junctions may perform well as nonvolatile memory devices.[31]

FePt-based nanomaterials are promising candidates for future ultrahigh density recording media, as will be discussed in the next section. The primary synthetic goal is to synthesize monodisperse magnetic particles with uniform stoichiometry and diameters of 3–5 nm. Solution phase chemistry offers an attractive alternative to traditional vacuum deposition techniques. FePt nanoparticles can be synthesized by reduction of metal salts with $NaBH_4$ in reverse micelles of cetyltrimethylammonium bromide, by thermal decomposition of $Fe(CO)_5$ and polyol reduction of $Pt(acac)_2$ in the presence of oleyl amine and oleic acid, or by polyol reduction of both $Fe(acac)_2$ and $Pt(acac)_2$ in the presence of oleyl amine and oleic acid.[41–43] FePt particle size in the latter reactions can be controlled by first growing 3 nm seed particles and then adding additional reagents to mature the existing seeds to the desired diameter. The stoichiometry is tuned by adjusting the molar ratios of the iron and platinum salts.[44] As with Co arrays, slow solvent evaporation from FePt nanoparticle dispersions leads to well-ordered self-assembled superlattices (Fig. 1b).[34,45–48]

Applications for magnetic nanoparticles can be significantly expanded by increasing the complexity *via* the introduction of binary systems. Furthermore, fundamentally interesting coupling phenomena are expected to emerge in these materials. One tactic is to combine nanoparticles with different physical properties into composite structures. Another approach is to fabricate nanoparticles containing a core of one material and a shell of another. Indeed, the core–shell methodology is an area of enormous potential for future developments, as seen in areas as disparate as semiconductor luminescence,[49–51] biorecognition,[52] and environmental toxin adsorbents.[53]

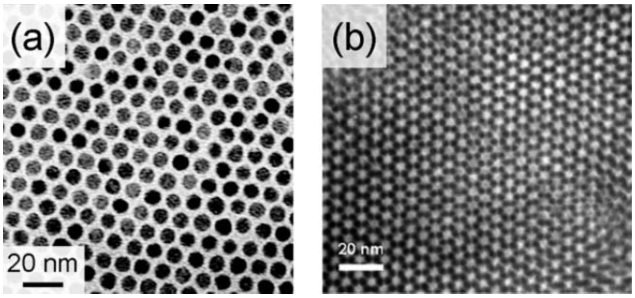

Fig. 1 (a) Transmission electron micrograph of self-assembled superlattice composed of 10 nm Co nanoparticles (image courtesy Shouheng Sun). (b) Transmission electron micrograph of self-assembled superlattice composed of 3 nm FePt nanoparticles (reprinted with permission from *J. Phys. Chem. B*, Copyright (2004) American Chemical Society).[43]

Perhaps the simplest examples of magnetic core–shell nanoparticles are those in which a magnetic core is surrounded by an oxide shell as a natural result of exposure to environmental oxygen. Oftentimes in these systems, the core material is ferromagnetic whereas the shell is antiferromagnetic, as in colloidal Co/CoO and CoNi/(CoNi)O schemes.[54–57] Exchange anisotropy can originate from the interfacial coupling between ferromagnetic and antiferromagnetic materials. It manifests itself in a shifted hysteresis loop, an effect known as exchange bias (Fig. 2a), which is used to control the magnetization of devices, such as spin valves that sense changing magnetic fields *via* the giant magnetoresistance effect.[58–61] Despite the fact that exchange bias was first described nearly fifty years ago, the microscopic mechanisms of exchange bias remain a topic of active research. Chemically synthesized core–shell nanoparticles, through the ability to tune the dimensions of both layers and the interface between them, present a novel approach to such research. The core–shell approach can also be used to thwart oxidation of magnetic nanoparticles by coating with protective barriers such as SiO_2,[62] or to isolate catalyst nanoparticles within oxide shells to minimize secondary reactions of the products.[63]

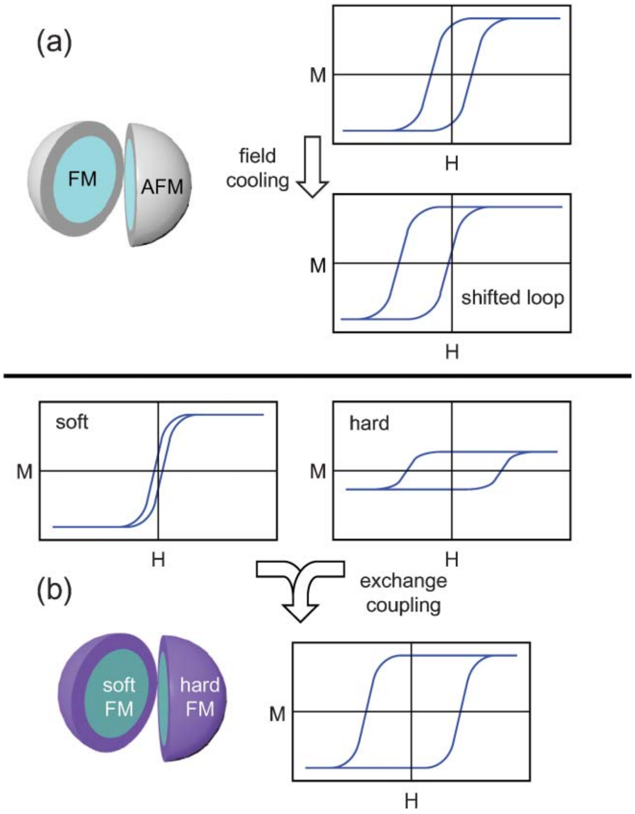

Fig. 2 (a) Schematic *M*–*H* hysteresis loops of an exchange bias system. The center of the loop is shifted to the side after field cooling from above the Néel temperature due to coupling between antiferromagnetic and ferromagnetic layers. (b) Schematic *M*–*H* hysteresis loops of an exchange spring system. Coupling of the soft and hard ferromagnets leads to an enhanced energy product with both large coercivity and large magnetization.

One can also imagine the growth of one ferromagnetic material onto another. An illustrative example is nanocomposites of magnetically hard and soft phases that interact by magnetic exchange coupling. Such systems aspire to push the envelope of advanced permanent magnet applications due to their combination of large coercive field and large magnetization. This combination forms an energy product that is an engineering measure of the overall strength of a ferromagnet (Fig. 2b). Model systems have already been created using mixtures of hard and soft magnetic nanoparticles.[64] The next step is to control the interphase coupling using chemically synthesized core–shell nanoparticles.[65,66] These materials, such as FePt/Fe_3O_4 nanoparticles, have intimate contact between the core and shell and, therefore, effective exchange coupling and cooperative magnetic switching. The tunability inherent to this approach suggests it can lead to permanent magnets stronger than those commercially available today.

Generalizing the relevance of magnetic nanoparticles to chemical and biological systems will require the synthesis of particle shells with functional chemistry. By coating a magnetic core with a thin gold shell,[67] Au-thiol chemistry can be used as a platform for introducing ligands with functionality to manipulate aggregation, solubility, and reactivity—all the while maintaining the magnetic utility of the core. Biomedical applications demand stringent surface presentations that make the particles invisible to (or at least stable to) the body's major defence machinery, the reticulo-endothelial system, and to prevent aggregation that would inhibit the transport of particles through the body. Prospects include improving magnetic resonance imaging, site-specific drug delivery, manipulation of cell membranes, and hyperthermic treatment for cancerous cells. Moderate successes have been achieved using iron oxide nanoparticles capped with dextran, polyethylene glycol, polyethylene oxide, and other brush polymer coatings;[68,69] complete elusion of the reticulo-endothelial system, however, is an ongoing challenge.

There are numerous opportunities for materials chemistry to contribute to colloidal magnetic nanoparticle research. On the synthetic side, key topics include improving stability, preventing aggregation, developing greener methods, and scaling up processes for industrial applications. While there are still myriad issues to address in single-component and basic core–shell systems, a largely unexplored research area is the synthesis and characterization of particles composed of many layers, or ''onion'' particles. It is reasonable to assume that systems of this nature will lead to novel coupling phenomena—and perhaps to novel applications. Work in the assembly of magnetic nanoparticles into functional assemblies will be discussed next, including the utilization of polymers as structural or chemical templates for nanomagnetic materials.

Polymeric templating of magnetic materials

Self-assembly of nanostructures is emerging as a supplement to, and perhaps even a replacement for, high resolution lithography in nanotechnological applications. In particular, block copolymers films have garnered significant attention as templating agents owing to their tunable domain size and shape.[70,71] Diblock copolymers are composed of two covalently linked but chemically dissimilar polymer chains (A and B). They naturally self-assemble into nanoscale ordered domains. The specific geometry of the ordering depends upon several factors: the total length of the chain (N), the fraction of the polymer that is component A (f_A), and the A–B interaction parameter (χ). When the product χN is sufficiently large, increasing f_A leads sequentially to self-organized microdomains of spheres, cylinders, gyroids, and lamellae of A surrounded by a matrix of B. Manipulating N while keeping f_A constant scales the domain size. The structural versatility of block copolymers derives from this ability to tune the size and shape of self-assembling domains. Microdomains within polymer films have been used both as masks for the deposition of functional materials, taking advantage of the differential etching rates of the polymer blocks, and as direct templates for functional materials, taking advantage of the disparate chemical nature of the polymer blocks. A challenging problem in block copolymer research is to gain arbitrary control over microdomain location, orientation, and defect density. Achieving this control involves the manipulation of one or more external fields—typically electrical or mechanical—during preparation of the polymer film. Only with such combinations of top-down and bottom-up approaches can one achieve arbitrary long-range-ordered systems.

Magnetic data storage may be able to take advantage of block copolymer templating in the future. First, we examine where the magnetic recording technology is today. Magnetic recording density of hard disk drives has been doubling annually and high end commercial media today stores almost 100 Gbit in^{-2}. The media are manufactured using sputtered granular films. These films consist of continuous active magnetic layers that are magnetized in the film plane. Shortcomings of granular media are that the grain size and grain size distribution are approaching fundamental limits and that the bits can potentially interact with each other because the film is continuous. Patterned media, *i.e.* media with discrete isolated bits, offer a number of possible advantages to enter the Tbit in^{-2} storage realm. Inherent isolation from direct coupling and the ability to sustain perpendicular magnetization, which is likely to be more stable against demagnetization, are clear benefits. (From a technical engineering level, one might also expect lower media transition noise, track edge noise, and nonlinear bit shift effects while allowing precise servo information to be inserted into the media itself.[72])

Researchers are beginning to explore the viability of diblock copolymers as templates for patterned magnetic media. One such approach uses electric field alignment, utilizing the shape anisotropy of the dielectric polymer domains and the associated orientation-dependent polarization energy to align the domains parallel to the field lines.[73,74] This phenomenon has been used to create self-assembled templates for high density magnetic nanowire arrays with aspect ratios of ~ 35 (Fig. 3a).[75,76] Diblock copolymer cylinders are coaxed into aligning perpendicular to the substrate using an electric field, and then the cylinders are selectively etched using deep UV light. Electrodeposition is used to fill the resulting cavities with cobalt. Such arrays exhibit coercivity (H_c) parallel to the wire axis that is significantly larger than that for a continuous

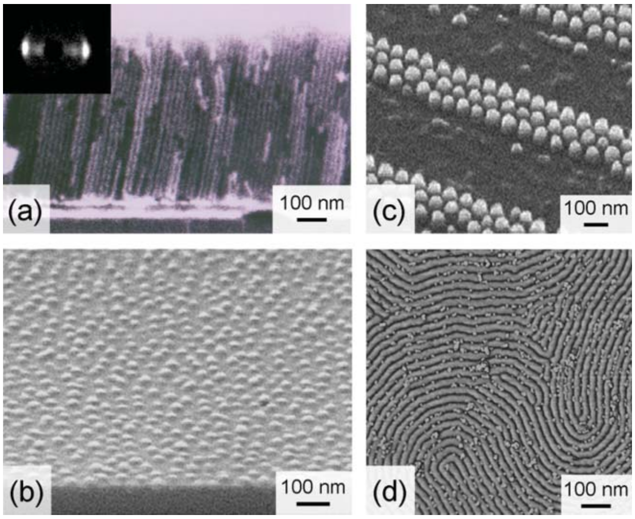

Fig. 3 (a) Cross-sectional scanning electron micrograph of electroplated cobalt nanowires in a diblock copolymer template. SAXS data displayed in inset (reprinted with permission from *Appl. Phys. Lett.*, Copyright (2002) AIP).[76] (b) Scanning electron micrograph of tungsten-capped cobalt nanodot array produced by block copolymer lithography (reprinted with permission from *Adv. Mater.*, Copyright (2001) Wiley-VCH Verlag GmbH).[78] (c) Scanning electron micrograph of nanopatterned CoPtCr magnetic dots prepared by graphoepitaxy and block copolymer lithography on 2.5 inch hard disk drive glass plate (reprinted with permission from *IEEE Trans. Mag.*, © 1949–1951 IEEE).[86] (d) Phase-mode atomic force micrograph of FePt nanoparticles selectively decorated on a diblock copolymer template.[93]

cobalt film of equal thickness. Single-domain behavior is the source of this enhancement; it is enabled by the fact that the diameter of the nanowires (14 nm) is much smaller than the critical single-domain diameter (50 nm) thereby avoiding the formation of magnetic domain walls that decrease the magnetization.[77] One can use a related approach to generate arrays of cobalt dots rather than cylinders. This change is desirable because it eliminates the need for electric field processing. Cheng *et al.* used a sphere-forming diblock copolymer as an etch mask in which the matrix surrounding the spheres is selectively removed *via* reactive ion etching.[78,79] In this manner, they were able to produce single-domain magnetic dots with densities of $\sim 7 \times 10^9$ in^{-2}, or about one-tenth the areal bit density of current state-of-the-art hard disks (Fig. 3b).

Spheres are not subject to orientation-dependent electric polarization. Hence, obtaining long-range two-dimensional order within dot arrays is not readily achievable using electric fields. An alternative route to this end is to use substrate relief structure to guide the epitaxial growth of the overlying polymer film—a technique known as graphoepitaxy. A key advantage of this approach is that the length scale of the relief structure can be much larger than the film's lattice parameter. This approach has been successfully applied, using photolithography for top-down surface patterning, to films of spherical phase diblock copolymers.[80,81] Recently, graphoepitaxy has also been extended to cylindrical phase polymer films. Such films inherently exhibit a far broader variety of defect structures on flat surfaces,[82] thereby opening up a wider range of potential applications for graphoepitaxy of diblock copolymer films.[83,84] Sundrani *et al.* also exploited the increased resolution capabilities of electron beam lithography to extend the length-scale envelope to smaller sizes than those achievable with light. Li and Huck have shown that nanoimprint lithography can also accomplish this goal.[85]

The magnetic recording industry is exploring the feasibility of using graphoepitaxy to create products containing magnetic nanostructures. Toshiba has reported the manufacture of a 2.5 inch disk suitable for ultrahigh bit density media containing circumferential CoPt or CoCrPt nanodots prepared using a polymer template.[86] The magnetic dots in this example are $\sim$40 nm in diameter (Fig. 3c). As the dots become even smaller, however, the thermal stability of the magnetization orientation decreases. The superparamagnetic limit, as it is known, refers to the particle size at which the thermal energy at room temperature will cause fluctuations of the magnetization orientation of a bit. Magnetic anisotropies such as the magnetocrystalline anisotropy energy (K_u), which aligns the easy magnetization axis of a ferromagnet along a preferred crystallographic axis, stabilize the magnetization against thermal fluctuations. The anisotropy determines how strongly a particle can hold onto its magnetic information. CoCrPt-based material, presently used in hard disks, has a moderate K_u and reaches its superparamagnetic limit around 10 nm. Smaller bits in next generation devices will require a change in material to one with a larger K_u, and fct-FePt has been identified by the recording industry as perhaps the best option currently available.[42] Top-down approaches are not a feasible route to produce production-scale quantities of sub-10 nm particles. One way to obtain ferromagnetic nanoclusters from the bottom-up is to perform thermal decomposition of organometallic complexes within bulk diblock copolymer films, which, *via* selective sequestration within one of the domains, leads to nanoscale patterns of polydisperse particles.[87,88] As discussed in the previous section, however, bottom-up colloidal synthetic techniques can be used to make significant quantities of nearly monodispersed 3–5 nm FePt nanocrystals. These particles are capped with surfactant molecules, typically oleic acid, that present a hydrophobic interface to the external environment. Diblock copolymers, often composed of alternating hydrophobic and hydrophilic domains, may serve as highly selective templates for deposition of these nanoparticles. This could result in self-organized structures with feature sizes smaller than those achievable with lithographic processes. There are reports in the literature of selective decoration using passivated metallic nanoparticles,[89,90] semiconducting nanoparticles,[91] bio-nanoparticles,[91] and even binary mixtures of nanoparticles.[92] However, directly depositing oleic acid-coated FePt nanoparticles onto a diblock copolymer film does not lead to a robust structure with a sufficiently high level of selectivity. Recently, this problem was overcome by introducing an additional template preparation stage in which the surface cylindrical domains within a polymer film are etched away with vacuum ultraviolet light.[93] The resulting corrugated film exhibits $\sim$99% adsorption selectivity for isolated oleic acid-coated FePt nanoparticles (Fig. 3d). Hopefully, advances of this type will help extend the historical growth of recording media areal bit density in the future.

There are, however, numerous significant challenges that remain. Materials chemists are well situated to address these issues. Foremost, standard polyol synthesis of FePt nanoparticles produces a chemically disordered fcc phase that is not ferromagnetic at room temperature. These particles must then be annealed above 530 °C to achieve the high-K_u ($L1_0$) fct phase—a process that leads to unwanted particle coalescence.[94] Chemistry may be able to circumvent this problem either by manipulating the capping molecules, incorporating a protective oxide coating, or by the direct synthesis of the fct phase.[95–98] Other challenges include obtaining higher density coverage of nanoparticles on the polymeric templates without particle aggregation and inducing order among the nanoparticles themselves rather than having a random spatial distribution within the selective polymer domains. Achieving both of these goals will require the rational design of appropriate chemical interactions between the nanoparticles and the template, as well as between the nanoparticles themselves. In addition, obtaining precise control over the geometrical arrangement of nanomagnetic materials in general, and thereby gaining precise control over the exchange interactions, is a challenge well suited to materials chemists. Thus, it is clear that the future of nanomagnetism is multidisciplinary and irrevocably linked to advances in chemistry and chemical processing with its historical bottom-up strategic methods.

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