Magnetically-responsive self assembled composites

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This *tutorial review* summarizes the recent advances on the self assembly of magnetic nanoparticles into one-, two-, and three-dimensional architectures using synthetic polymers and biopolymers. The materials have unique stimuli-responsive behavior that emerge in response to internal and external magnetic fields. For example, magnetic fields can be used to elicit a magnetic response from the materials, whether the material rearranges in response to the external field, or provides information regarding the local environment of the nanoparticles. These materials hold great promise for applications ranging from data storage to nanomedicine.

Introduction to MNP-polymer assemblies

Magnetic nanoparticles (MNPs) provide a set of building blocks for constructing stimuli-responsive nanoscale materials with properties that are unique to this scale. The size and the composition of MNPs are tunable to meet the requirements for a range of applications including magnetic fluids,[1] catalysis,[2] data storage media,[3] biomedicine,[4] and toxic waste remediation.[5] For example, superparamagnetic nanoparticles (SPMNP) are suitable for bio-related technologies such as magnetic resonance imaging contrast agents and biosensors, while ferrimagnetic or ferromagnetic nanoparticles (FMNP) are required for information storage technologies such as hard disk drives and magnetic tape. The literature is rich with methodologies for the synthesis of MNPs with defined composition, size, shape and magnetic properties.[6] As the controlled synthesis of these magnetic building blocks advances, the need for robust strategies to integrate them into composite materials increases. MNP-polymer composites, in particular, represent materials which enable MNPs to be employed as magnetically responsive materials. The MNPs are most commonly dispersed within a polymer in a random manner, as is the case for magnetic recording tape media. However, there is a growing interest in developing methods to create more ordered MNP-polymer composites wherein the nanoparticles are organized into defined geometries. Precise control over the spatial organization of MNPs within the polymer matrix enables one to generate magnetic devices with greater capabilities, such as improved areal densities for storage applications or higher sensitivity for biosensors. The ability to create organized MNP chains, arrays, and networks, however, depends on our ability to fully understand and control the assembly processes of these materials.

Nature inspires the use of self assembly in the "bottom up" fabrication and organization of nanoscale materials.[7] Understanding how chemically derived self assembly processes control the construction and organization of a variety of functional nanomaterials across extended and multiple length scales is of growing interest in many areas of materials research. Self assembly processes with nanoparticles enable the formation of one-, two-, and three-dimensional assemblies, but require an understanding of the interparticle and intermolecular forces at play. The processes that have been

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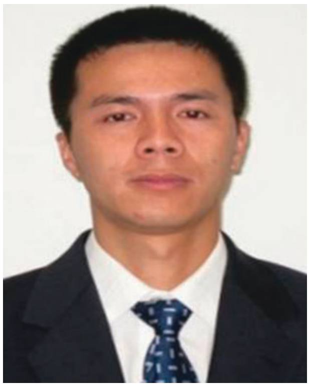

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developed for organizing non-magnetic nanoparticles into arrays may not be suitable for all MNPs.[8] For FMNPs, interparticle magnetic attractive forces may exist which can hamper the assembly of these particles into organized architectures as a consequence of the uncontrollable aggregation of the nanoparticles (magnetic fields decrease through space by a factor of $1/r^3$). SPMNPs, on the other hand, do not have a permanent magnetic dipole in the absence of an applied magnetic field and therefore are not prone to the same aggregation behavior as FMNPs.

The functionality present on the MNP surface also greatly impacts their assembly behavior. In most cases, the surface of the MNPs is passivated by an organic monolayer that protects them from aggregation and provides solubility in solvents. The particle surface also represents the interface at which the particle and polymer interact within the composite assembly. Self assembly processes require favorable interactions between the MNP building blocks and the polymer, such that stable equilibrium (or near equilibrium) structures are formed.[9] The types of intermolecular interactions include hydrogen bonding, metal coordination, electrostatic attraction, dipole–dipole interactions, Van der Waals forces, and hydrophobic interactions between MNPs and polymers.[10] The successful self assembly of MNPs into well defined nanostructures not only depends on the ability to control precisely their composition, shape, and size, but also on the modification of the MNP surface with the desired functionality that mediates interactions with the polymer.

Polymer-mediated self assembly of MNPs provides unique opportunities to tailor the physical and chemical properties of the composites by varying the polymer composition and chain length. The polymer not only serves as a scaffold to organize the MNP building blocks into well defined structures, but also acts as a structural element to control interparticle distances and provide mechanical integrity. Moreover, advances in synthetic polymer chemistry—particularly controlled living polymerizations—enable the synthesis of a variety of polymer compositions with defined molecular weight and low polydispersity.[11]

This review will highlight the utilization of polymer scaffolds for the controlled assembly of MNPs into well ordered nanostructures. The self assembly of MNP building blocks into one-, two-, and three-dimensional architectures using synthetic polymers or biopolymers will be summarized, in addition to their emerging applications.

Magnetic properties of MNPs

Generally speaking, all materials exhibit a response to magnetic fields to varying degrees. Magnetic materials can be classified by the value of their magnetic susceptibility (χ), which is indicative of the effectiveness of an applied field to induce a magnetic dipole.[12] Diamagnetic materials (most organic materials, for example) are weakly repulsive toward an externally applied field and exhibit a χ in the range of $10^{-5} \sim 10^{-6}$. The materials with a χ value in the range of 10^{-5} to 10^{-3} are weakly attractive toward an externally applied magnetic field and are defined as paramagnetic. Some materials show ordered magnetic states and are magnetic even without an external field and can be classified as ferromagnetic, ferrimagnetic, or antiferromagnetic depending on the nature of the coupling interaction between the electrons within the materials.

The composition of the nanoparticles directly impacts the magnetic properties and anisotropic behavior of the particles. A variety of synthetic routes, including thermal decomposition, metal reduction, microemulsion, and coprecipitation, have been established to prepare highly stable MNPs. The composition of the as-synthesized MNPs vary, but include metals particles, such as Fe[13] and Co,[14] iron oxides, such as Fe_3O_4,[15] spinel ferrimagnets, such as $CoFe_2O_4$ and $MnFe_2O_4$,[16] as well as alloys, $CoPt_3$[17] and FePt.[18] The chemical synthesis of magnetic nanomaterials has been discussed extensively in recent reviews,[6] and thus is not discussed within this tutorial.

The magnetic behavior of a material can be described by a hysteresis loop that measures the change in the magnetization (M) with the strength of an applied magnetic field (H). As shown in Fig. 1a, when an external magnetic field is applied, magnetic interaction induces alignment of the spins along the field direction. When the field is sufficiently large enough, the magnetization is said to be saturated. The corresponding maximum value of the magnetization achieved in this state is called the saturation magnetization (M_s). Reducing the strength of the field can lead to some loss of magnetization. When the applied magnetic field is reduced to zero, the materials still retain a considerable degree of magnetization with a net measureable moment, which is known as the remanent magnetization (M_r). The ratio of the remanent magnetization to the saturation magnetization (M_r/M_s) is called the squareness ratio and varies from zero to a maximum of one. The coercive field (H_c) is the magnitude of the field that must be applied in the reverse direction in order to bring the magnetization of the sample back to zero. In the ideal case, a reproducible symmetric hysteresis loop is achieved by cycling the applied field back and forth in opposite directions. In most cases, the hysteresis loop of a magnetic material can be experimentally measured using a vibrating sample magnetometer (VSM) or superconducting quantum interference device (SQUID) magnetometer. Materials with different magnetic properties have different shapes of hysteresis loops. The shape of the hysteresis loop is especially of interest for magnetic recording applications, which require a large remanent magnetization, moderate coercivity (≥ 2000 Oe), and ideally a square hysteresis loop.[3]

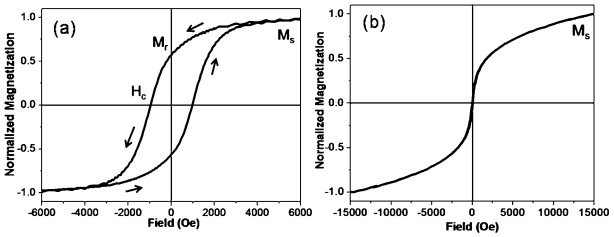

Fig. 1 Representative hysteresis loops for a magnetic sample that is (a) ferromagnetic, and (b) superparamagnetic; M_s, M_r, and H_c represent the saturation magnetization, remnant magnetization, and coercivity, respectively.

The shape of the *M*,*H* loop is strongly affected by the magnetic anisotropy of the material, which is defined as the dependence of the magnetic properties upon the direction in which they are measured. There are several kinds of anisotropy including magnetocrystalline, shape, stress, externally-induced, and exchange anisotropy.[19] Most nanoscale magnets derive their anisotropy from either crystallinity or shape. Magnetocrystalline anisotropy, which arises from spin–orbit coupling, is intrinsic to the material and independent of particle shape. The interaction between neighboring spins (associated with each atom) is strong, and keeps the spins parallel or antiparallel to one another. The alignment of the magnetization favors a specific crystallographic direction defined as the easy axis. In contrast, a polycrystalline sample that does not have a preferred grain orientation does not have magnetocrystalline anisotropy. If this particle were spherical, an applied field can magnetize the sample to the same extent in any direction. However, if the same particle were not spherical but rod-like, for example, then the sample is easier to magnetize along its long axis than the short axis. Thus, the magnetic particle now has shape anisotropy. Therefore, the ability to obtain high magnetic anisotropy not only depends on the crystal structures of MNPs, but also on their shapes. The shape induced magnetic anisotropy is usually larger than the magnetocrystalline anisotropy. A well-known example of shape anisotropy is the use of sub-micrometer needle-shaped iron particles for magnetic tape.

Bulk magnetic materials possess multiple domains, or groups of spins whose magnetic moments are oriented in the same direction. The decrease in size of the bulk materials down to the nanoscale ultimately affords single domain magnetic nanoparticles. The critical domain size ($D_{critical}$) for spherical particles largely depends upon the composition of the particle.[12,19] While single domain magnetic particles can maintain ferromagnetic or ferrimagnetic properties, the particles become superparamagnetic as their size continues to decrease. When the dimensions of a bulk ferromagnet are reduced to critical lengths on the nanoscale, the material is no longer capable of retaining a strong dipole moment at certain temperature in the absence of an external field. Due to the small size of MNPs, the reduced number of aligned spins is no longer sufficient to retain a net dipole moment that can compete with thermal fluctuations (*i.e.*, magnetic dipolar forces weaker than kT). Thus superparamagnetic materials do not exhibit a square hysteresis in the *M*,*H* loops. In the presence of an external field, the dipoles of a superparamagnetic material can be easily aligned and magnetized to a high M_s value as shown in Fig. 1b. However, when the field is removed, the magnetization goes to zero, leaving no remnant magnetization.

Superparamagnetic behavior of MNPs is dependent on the temperature. Below a critical temperature, referred to as the blocking temperature (T_B), the dipole moments in the MNPs are able to align and couple to generate a net remnant magnetization. Above T_B, thermal fluctuations dominate and the material rapidly loses coupling of unpaired spins. This superparamagnetism of magnetic materials is generally regarded as the fundamental density limit for recording media.[3,20] However, the magnetic nanomaterials with superparamagnetic properties are useful for biomedical applications, as they are not subject to strong interparticle magnetic interactions in solution and can be stable under physiological conditions.

Formation of MNP-polymer assemblies

There are two primary approaches employed in the formation of MNP-polymer assemblies: (1) preformation of a polymeric template followed by nucleation and growth of MNPs within the polymer matrix (Fig. 2, Route (1), *versus* (2) preformation of the well-defined MNPs followed by its co-assembly with polymer scaffolds (Fig. 2, Route 2). The first strategy often utilizes block copolymers which self-assemble into a defined morphology (*i.e.*, spherical, cylindrical, or lamellar structures) by controlling the molecular weight and volume fractions of the individual blocks.[21] In this approach, chemical functionalities that bind metals is incorporated into one of the block segments in order to sequester MNP precursors within one of the domains of the self assembled template. The metal precursors are then transformed into MNP *via* thermal decomposition or chemical reduction. The polymer matrix not only acts as a nucleation template for particle growth, but also provides a barrier against agglomeration of the MNPs after they are formed. This approach can afford one-dimensional particle-containing micelles, two-dimensional thin films, or three-dimensional bulk assemblies with reasonable control over the size, shape, and uniformity of the MNPs.[22]

The second approach to the formation of MNP-polymer assemblies involves synthesizing the MNP prior to its assembly into a composite. This strategy takes advantage of advances in colloidal synthetic methods which allow the formation of well-defined particles with control over their size and shape. In addition, either a 'grafting to' approach wherein a preformed polymer of defined length and composition is attached to the nanoparticle surface, or a 'growing from' strategy wherein polymer growth is initiated from the nanoparticle surface, affords the formation of well defined

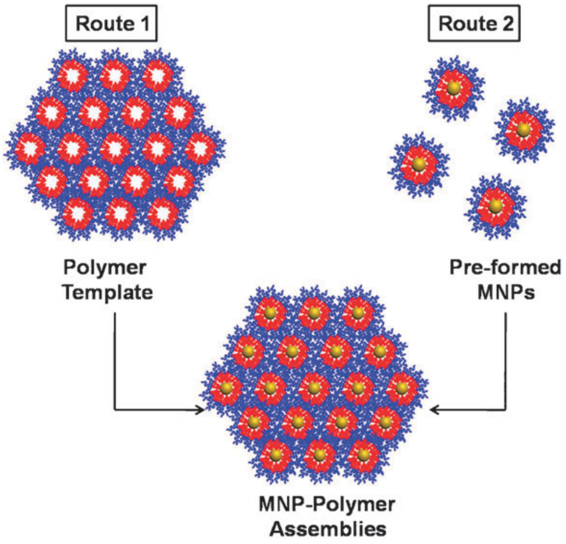

Fig. 2 Two general approaches for self assembling MNP-polymer composites.

MNP-polymer composites. Using this approach, uniform and well-defined MNPs and polymers are attainable, which may be beneficial to the consistency and quality of the samples. Therefore, the second approach has become an attractive and versatile alternative toward the fabrication of MNP-polymer assemblies with well defined nanostructures and controlled magnetic properties.

One-dimensional MNP-polymer assemblies

The synthesis of one-dimensional MNP-polymer assemblies is inspired by those observed in Nature, wherein chains of either single domain magnetite (Fe_3O_4) or greigite (Fe_3S_4) ubiquitously exist in all magnetotactic bacteria and eukaryotic algae.[23] These chain structures within the microbes result in permanent magnetic dipoles and performs as an orientation system for the microorganisms. MNP-polymer composites can be self assembled into linear magnetic wires that are one particle wide, and microns in length. The anisotropic formation of these assemblies is analogous to the polymerization of the MNP building blocks into chain-like structures. Moreover, the magnetic composition of the nanoparticles yields dynamic stimuli-responsive materials wherein an external magnetic field can (1) initiate the formation of the MNP-polymer chains, and/or (2) orient the chain in space to align with the field.

Stable MNP-polymer composite filaments can be formed in the presence of an applied magnetic field. Goubalt and co-workers reported the linking of maghemite (γ-Fe_2O_3) nanoparticles into chains using a high molecular weight poly(acrylic acid) which could span across the surfaces of two neighboring particles.[24] In these experiments, the formation of the linear aggregates was dependent upon both the concentration of the components and the strength of the applied magnetic field. Interestingly, the authors report that the strength and duration of the magnetic field determined the average length of the filaments. As opposed to synthetic components, Biswal *et al.* reported the synthesis of flexible paramagnetic NP chains utilizing streptavidin-coated MNP strung together by telechelic biotin-functionalized poly(ethylene glycol).[25] These materials are being investigated as micro-magnetic actuators and micromechanical sensors.

Polyelectrolytes are also useful for constructing linear MNP-polymer composites. Minko *et al.* utilized poly(2-vinyl-*N*-methylpyridinium iodide) to bind citric acid coated superparamagnetic Fe_3O_4 nanoparticles in the presence of an applied magnetic field (Fig. 3).[26] The wire-like composites were stable, and the irreversible assemblies could be manipulated in an external magnetic field. Recently, Hatton and coworkers demonstrated the formation of composite chains patterned within the channels of microfluidic devices (Fig. 4).[27] In contrast to the approaches described above wherein the core of the composite beads was magnetic and the shell was non-magnetic, the Hatton group utilized MNP composites comprised of a non-magnetic polystyrene core coated with polyelectrolyte layers and γ-Fe_2O_3 nanoparticles to form a magnetic shell. The glass surface of a microchannel was first patterned with an amine functionality by microcontact printing to enable selective localization of core–shell MNP composites onto the microchannel surface and their subsequent covalent attachment was enabled using an amidation reaction between the patterned amine functional groups and the carboxylic acid groups on the surface of MNPs. The MNPs form well defined chains across the channel in the presence of a magnetic field. Moreover, the crosslinked core–shell MNP chains proved to be mechanically flexible in the absence of an applied field, and more rod-like when the field was reapplied.

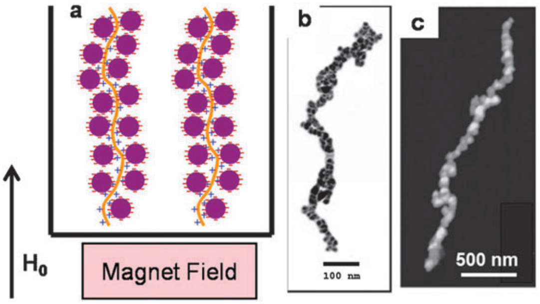

Fig. 3 (a) Representation of polyelectrolyte mediated magnetic nanowires in the presence of a magnetic field. (b) TEM image and (c) AFM image of the wire-like nanostructures. Reproduced from ref. 26 with permission from the American Chemical Society.

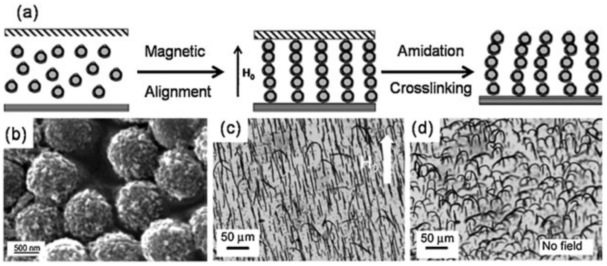

Fig. 4 (a) Schematic illustration of the formation of flexible magnetic chains. (b) SEM image of the magnetic beads; (c) optical image of the aligned magnetic chains under a magnetic field; (d) optical image of the permanently crosslinked magnetic chains in the absence of a magnetic field. Reproduced from ref. 27 with permission from the American Chemical Society.

In contrast to SPMNPs, FMNPs have a permanent magnetic dipole moment at a given temperature in the absence of a magnetic field. One-dimensional ferromagnetic MNP-polymer assemblies with a chain-like structure have been used as templates to build more complex nanoarchitectures with unique properties.[28] Pyun *et al.* reported the synthesis and assembly of polystyrene coated ferromagnetic cobalt nanoparticles with an inner diameter of 10 nm (Fig. 5).[29] The end functional polystyrene surfactants bearing an amine, carboxylic acid, or phosphine oxide were first synthesized using controlled radical polymerization, and then used as the protective layer in the synthesis of cobalt nanoparticles *via* the thermolysis of dicobalt octacarbonyl [$Co_2(CO)_8$]. TEM images of the core–shell structures show the polystyrene shell as a light corona around the dark cobalt cores which was 2 nm in thickness (Fig. 5a). Ferromagnetic particles are typically prone to irreversible aggregation as a consequence of the strong interparticle magnetic attractive interactions. However, these cobalt composites exhibited improved colloidal stability in a variety of nonpolar organic solvents (*e.g.*, toluene, THF,

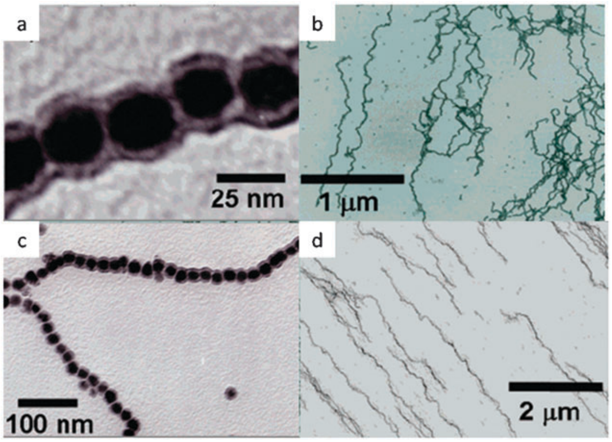

Fig. 5 TEM images of PS-coated Co nanoparticles; (a) image showing the Co colloidal core (dark center) and PS polymer shell (light halo); (b and c) sample deposited from toluene dispersions onto carbon coated copper grid resulted in self assembled single MNP-Polymer chains; (d) sample casted from toluene and aligned under a magnetic field (100 mT) while drying. Reproduced from ref. 30 with permission from the American Chemical Society.

hexane and dichloromethane) over a period of several months, which is attributed to the steric effects of the polymer coating. One dimensional magnetic assemblies of the polymer coated cobalt nanoparticles can be achieved readily by drop casting the particle dispersion onto a carbon coated copper grid. The individual polymer coated cobalt nanoparticles were organized into extended chain-like structures spanning several microns in length (Fig. 5b and c).[30] The formation of one-dimensional chain structures was attributed to the magnetic dipolar associations of individual cobalt nanoparticles. These chain-like nanoparticle assemblies can further be aligned using weak magnetic fields (100 mTesla) as shown in Fig. 5d.

While linear polymers of defined length and composition are useful for co-assembly with MNPs, other well-defined polymer architectures, such as dendrimers, are also useful for creating MNP-polymer assemblies. The Rotello group reported the self assembly of Fe_2O_3 nanoparticles with PAMAM dendrimers using electrostatic attraction and demonstrated direct control of interparticle spacing based on the dendrimer generation (Fig. 6).[31] Upon assembly, one can observe a decrease in blocking temperature (T_B) with an increase in dendrimer generation. Thus, the dendrimer mediated magnetic nanoparticle assemblies with controlled manipulation of interparticle spacing provide new dimensional influence to control magnetic properties beyond just the size and shape of the nanoparticles.

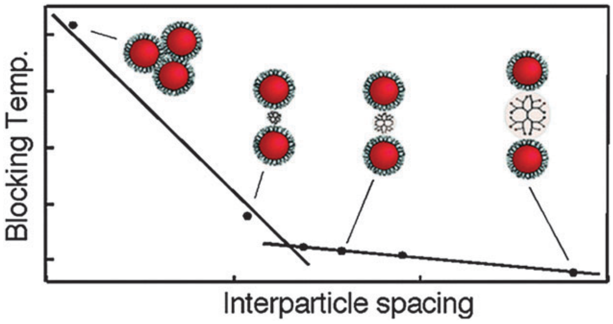

Fig. 6 PAMAM dendrimer mediated self assembly of Fe_2O_3 MNPs wherein the block temperature (T_B) decreases steady as the particles are spaced farther apart from one another by controlling the generation of PAMAM dendrimer. Reproduced from ref. 31 with permission from the American Chemical Society.

Two- and three-dimensional composite films

Several techniques have emerged for creating more ordered two- and three-dimensional assemblies of nanoparticles including Langmuir–Blodgett transfer, layer-by-layer assembly, and diblock copolymer lithography. A complete discussion of these techniques is beyond the scope of this tutorial, but this topic has been extensively reviewed.[32] These techniques can also suitable for assembling magnetic nanoparticles with well ordered nanostructures.

Sun and co-workers developed a polymer mediated layer-by-layer process to assemble 4 nm superparamagnetic FePt nanoparticles into large scale two-dimensional arrays (Fig. 7).[33] A silicon substrate was first functionalized with polyethylenimine (PEI) using a spin coating process. The modified substrate was subsequently dipped into a solution containing FePt nanoparticles where the amine groups of the PEI exchanged with the oleic acid surfactants to bind a monolayer of nanoparticles onto the substrate surface. The total thickness of the two-dimensional nanoparticle assemblies can be tuned by alternately dipping into a solution of FePt nanoparticles and a solution of PEI. The authors further demonstrated the transformation of the superparamagnetic composite assembly into a ferromagnetic one *via* thermal annealing. During this process the internal particle crystal structure transforms from chemically disordered fcc to chemically ordered fct. Moreover, by inducing the transformation into ferromagnetic particles post self-assembly, this approach avoids the random aggregation associated ferromagnetic particles as a result of the strong interparticle magnetic interactions. This method provides a convenient process of fabricating

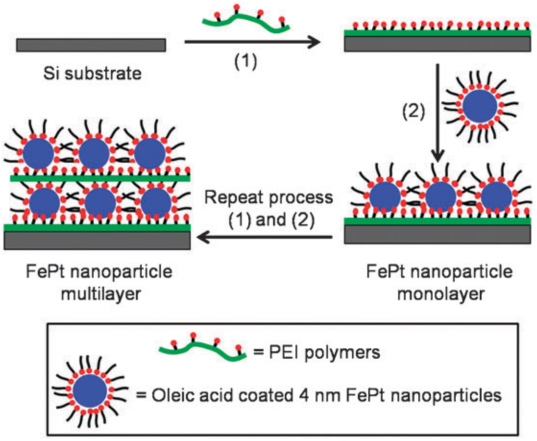

Fig. 7 Schematic representation of polymer mediated layer-by-layer assembly of a two-dimensional array using 4 nm FePt nanoparticles and PEI. Process 1: PEI polymer deposition; Process 2: FePt nanoparticle deposition. Reproduced from ref. 33 with permission from the American Chemical Society.

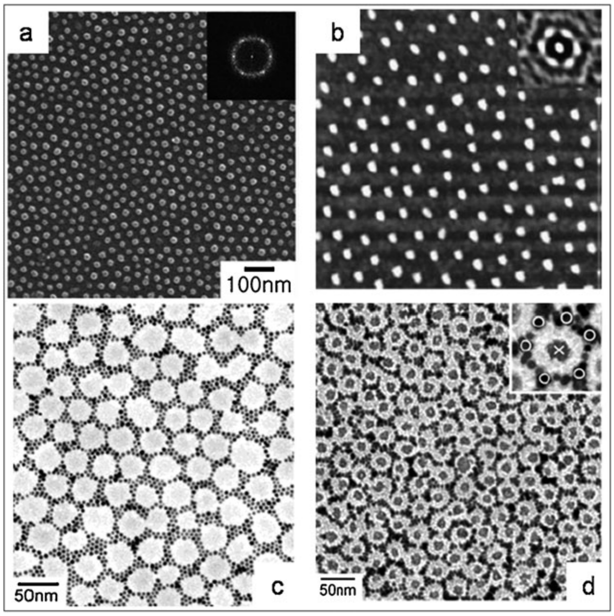

Fig. 8 Diblock copolymer micelle mediated two dimensional MNP assemblies. Arrays containing (a) iron oxide nanoparticles, (b) Co nanoparticles, (c) gold nanoparticles, and (d) iron oxide nanoparticles (inside) surrounded with gold nanoparticles (outside). Reproduced from ref. 34 and 35 with permission from the American Chemical Society and Wiley Publishing Group.

two-dimensional ferromagnetic nanoparticle assemblies that may be suitable in the future for magnetic recording applications that require high areal densities. However, this method requires a thermal annealing process which can unavoidably cause the coalescence of FePt nanoparticles and the deterioration of the particle monodispersity.

Micelles that are self-assembled on a surface are useful as templates for controlling both the size and the spacing of MNPs. Boyen and coworkers have utilized micelles comprised of polystyrene-*b*-poly(2-vinylpyridine) (PS-*b*-PVP) for the synthesis of cobalt nanoparticles (Fig. 8).[34] The core of the micelle can encapsulate cobalt salts that bind to the pyridyl units of the polymer. Upon transfer onto a flat surface, the micelles containing the cobalt salts assemble into a hexagonal packing arrangement. Treating the sample with oxygen plasma to remove the organic polymer followed by hydrogen plasma to reduce the cobalt precursors, afforded a highly ordered cobalt nanoparticle array. Simply changing the amount of cobalt precursor within the micelle allows one to obtain particle sizes ranging from 2 nm to 10 nm, whereas changing the length of the polymer blocks allows one to adjust the interparticle distance from 30 nm to 100 nm. Such MNP arrays with ferromagnetic-antiferromagnetic compositions (Co/CoO) can be useful in the exchange-biased magnetic systems. A similar method has been reported to directly assemble two different nanoparticle compositions (gold and iron oxide nanoparticles) simultaneously into a monolayer film using diblock copolymer micelles as shown Fig. 8d.[35]

In addition to serving as thin film templates, polymers can serve as dispersion media for MNPs, provided that the MNPs and the polymers are mutually compatible. Combining this property with the periodic structures afforded by block copolymers allows polymer induced organization of MNPs. High affinity of the MNPs to a specific domain type will lead to a selective dispersion of the nanoparticles within the corresponding domains, which can spatially organize the MNPs. Ignacio and coworkers demonstrated that ultrathin films of microphase separated diblock polymers, poly (styrene-*b*-butadiene-*b*-styrene), could be utilized as templates for the incorporation of magnetic iron oxide nanoparticles (with near complete selectivity) within the PS domains.[36] The iron oxide nanoparticles were first modified with polystyrene brushes by atom transfer radical polymerization to improve both the dispersion and the affinity of nanoparticles for the PS domain. The segregation of iron oxide nanoparticles into PS domains was systemically investigated using differential scanning calorimetry, dynamical mechanical analysis, and atomic force microscopy. Other diblock copolymers, such as polystyrene-*b*-poly(methyl methacrylate) (PS-*b*-PMMA), have also been used to assemble oleic acid/oleyl amine-coated iron oxide nanoparticles into ordered arrays.[37] Thin films were prepared from a mixture of chemically modified superparamagnetic nanoparticle and diblock polymer solution. The MNPs arrange themselves within upright cylindrical PMMA domains due to the selective affinity to the minority phase. The incorporation of the nanoparticles inside the cylindrical domains increases the diameter of the cylindrical domains, as well as the distance between two neighboring domains. A spatially ordered arrangement of MNPs was observed when the MNP concentration was below 0.2 vol%.

Recently, our group developed a novel method to self assemble polymer modified ferrimagnetic $CoFe_2O_4$ nanoparticles into well-packed arrays.[38] The surface of the $CoFe_2O_4$ nanoparticles (average diameter = 18 nm, M_s = 80 emu/g, H_c = 1000 Oe), were modified with poly(acrylic acid-*b*-styrene) *via* a ligand exchange process as shown in Fig. 9. The short PAA block was used as the surface binding ligands for the MNPs, and the PS block was used as a protective layer for improving the stability and solubility of the MNP-polymer complex in organic solvents. The polymers were well suited for sterically stabilizing the ferrimagnetic nanoparticles, which otherwise agglomerate when stabilized by small molecule surfactants. The polymer modified $CoFe_2O_4$ nanoparticles exhibited improved colloidal stability in a variety of organic solvents. As shown in Fig. 10a and b, the ferrimagnetic $CoFe_2O_4$ nanoparticles remain monodisperse in size without obvious shape change after polymer modification. The polymer-modified $CoFe_2O_4$ nanoparticles were further spin-coated onto a silicon wafer to form close-packed assemblies of an MNP-polymer composite film (Fig. 11a).

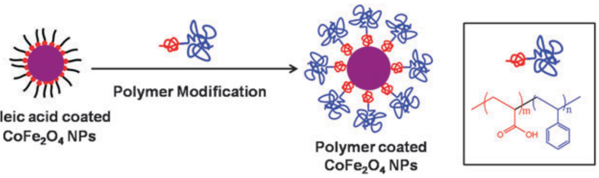

Fig. 9 PAA-*b*-PS block copolymer modified ferrimagnetic $CoFe_2O_4$ NPs with a diameter of 18 nm.

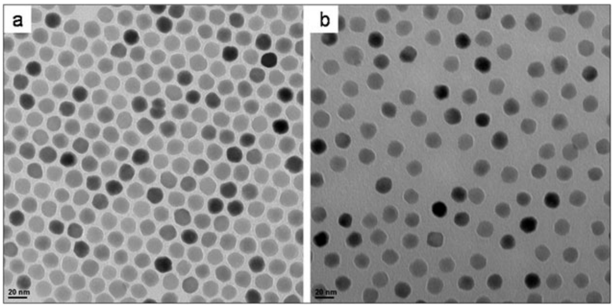

Fig. 10 TEM images of 18 nm $CoFe_2O_4$ NPs (a) before and (b) after modification with PAA-*b*-PS.

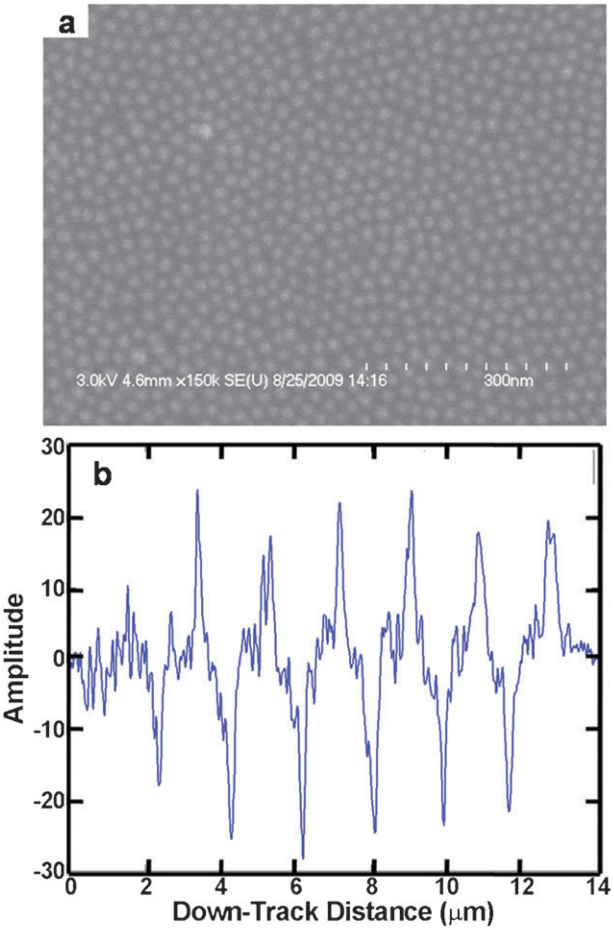

Fig. 11 (a) Top-down SEM image of the self assembled $CoFe_2O_4$ NP thin film; (b) Demonstration of magnetic write/read on the self assembled $CoFe_2O_4$ NP thin film.

The sample was then heated above the glass transition temperature (Tg) of polystyrene in the presence of a magnetic field in order to orient the magnetic moments of the particle parallel to the substrate. The polymer chains soften above its glass transition temperature, which provided mobility to the MNPs in the presence of an applied field. The vibrating sample magnetometry studies showed an increase in the squareness ratio of the MNP-polymer composite which indicated that the particles were oriented in the same direction. In a control experiment, VSM studies of samples that were placed in a magnetic field while heating at temperatures below the Tg of polystyrene did not exhibit a change in the remanence squareness. Similar results have been observed on the increase of remanence squareness of Co NPs under magnetic alignment.[39] These self assembled $CoFe_2O_4$ NP thin films with increased squareness ratio after magnetic alignment have potential applications in magnetic recording media. A contact test recorder and a giant magnetoresistance read and write head with a track width of 160 nm was used for magnetic recording demonstrations. Fig. 11b shows the magnetoresistive (MR) signals that are read back from the transitions by the MR sensor, which demonstrates that the self assembled MNP-polymer composite represents a prototype magnetic recording media with the potential of improved area bit densities over current technologies including magnetic tape.

Biopolymers

Biomolecules, including DNA, proteins, polypeptides and viruses, are rapidly becoming useful templates for the synthesis of MNP assemblies.[40] These complex biopolymers represent building blocks with a well defined shape and size, which is useful for more precise alteration of MNP composites. For example, DNA has frequently been used as a biotemplate owing to its strong electrostatic and coordination interactions with MNPs surfaces. MNPs varying in composition (such as Co, FtPt, Fe_2O_3, and $CoFe_2O_4$ nanoparticles) have been assembled using this approach.[41,42] Srivastava *et al.* reported DNA-mediated FePt nanoparticle assemblies using strong electrostatic interactions between cationic FePt nanoparticles and anionic DNA (Fig. 12).[43] In this case, the shape and size of the resulting aggregates could not be controlled. However, Ivanesic *et al.* utilized double-stranded DNA to guide the assembly of pyrrolidinone-capped Fe_2O_3 and $CoFe_2O_4$ nanoparticles.[41] Electrostatic interactions between the positively charged MNPs and the negatively charged backbone of DNA were employed to drive the assembly of MNPs to form nanowire composites. MFM images showed that DNA-templated MNP structures were strongly magnetic at room temperature after being deposited onto a silicon oxide substrate. In addition, the MNP-coated DNA assembly was digested using a restriction endonuclease, which demonstrated that the DNA was still biochemically active.[44] These linear DNA-mediated MNP assemblies may have potential applications as magnetic resonance imaging (MRI) contrast agents for cancer diagnosis and magnetic biosensors.[45]

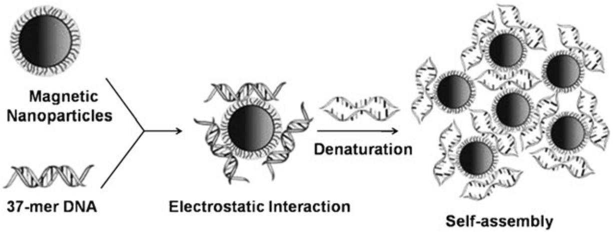

Fig. 12 Schematic representation of DNA mediated self assembly of FePt nanoparticles. Reproduced from ref. 43 with permission from Royal Chemical Society.

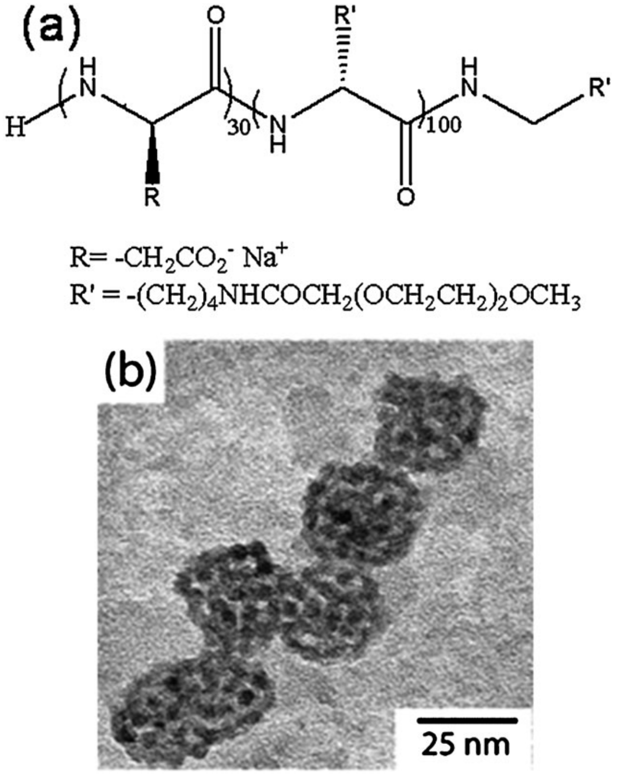

Fig. 13 (a) Polypeptide used for co assembly with Fe_2O_3 NPs, and (b) a TEM image of the resulting MNP-polypeptide assemblies. Reproduced from ref. 46 with permission from the American Chemical Society.

Engineered interactions between polypeptides and MNPs have also been utilized to generate highly organized assemblies. Euliss *et al.* reported a method to assemble Fe_2O_3 nanoparticles using the block copolypeptide, poly(diethylene glycol-lysine)$_{100}$-*b*-poly(aspartic acid)$_{30}$.[46] The surface of the hydrophobic Fe_2O_3 nanoparticles were first modified using tetramethylammonium hydroxide, in order to render the particles soluble in aqueous solution without the loss of structural and magnetic properties (Fig. 13). The modified Fe_2O_3 nanoparticles were combined with the block copolypeptides to form nanoparticle clusters. The authors proposed that the aspartic acid residues bind electrostatically to the nanoparticle surface, which further assembled into micellar structures, wherein approximately 20 MNPs comprised the core. Interestingly, the resulting clusters had a magnetic moment 20 times that of the single nanoparticle.

Viruses have also been investigated as templates for producing linear MNP nanostructured assemblies. Belcher and co-workers utilized a bacteriophage, which has the shape of a linear tube, for generating CoPt and FePt assemblies (Fig. 14).[47] The M13 bacteriophage was first modified by fusing either the CP7 CoPt-specific or FP12 FePt-specific peptide into the virus capsid, followed by nucleation of the CoPt and FePt nanoparticles *via* chemical reduction of a metal precursor in the presence of gP8-modified viruses. After annealing at 350 °C (to remove the virus template), uniform CoPt and FePt chains with 10 nm diameters was observed.

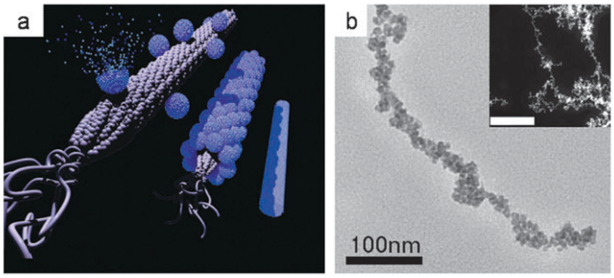

Fig. 14 (a) M13 bacteriophage virus mediated self assembly of magnetic CoPt and FePt nanoparticles; (b) TEM image of the unannealed virus-CoPt nanoparticle assemblies, (inset): STEM image of unannealed CoPt nanowires, Scale bar: 100 nm. Reproduced from ref. 47 with permission from Science Publishing Group.

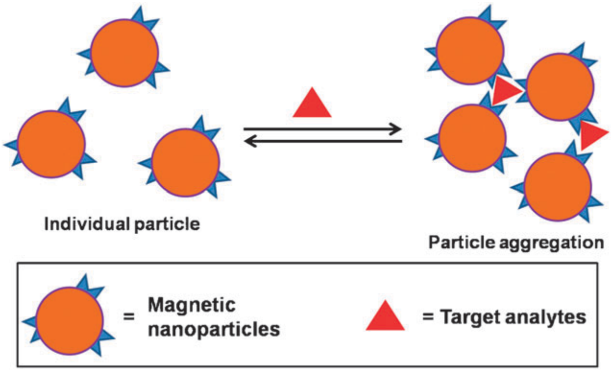

Fig. 15 Biomolecule detection using magnetic relxation switches. The analyte-induced aggregation of MNPs dephases the spins of the surrounding water protons more efficiently than MNPs present in the individual state. The effect is observed as a decrease in spin–spin relaxation time (T2).

Biosensors that are based on magnetic relaxation switches (MRS) exemplify exciting prospects for MNP-biomacromolecule composites. Superparamagnetic Fe_2O_3 MNP assemblies have been used as the sensitive probe to monitor DNA hybridization and protein binding.[48] When the MNPs were functionalized with 12-base pair oligonucleotides, the MNPs could be reversibly assembled in the presence of a complementary target sequence. The assembled Fe_2O_3 MNPs were more efficient at dephasing the spins of surrounding water protons (enhancing spin–spin relaxation times (T2)), relative to the non-hybridized MNPs (Fig. 15). This unique magnetic phenomenon associated with the MNP assembly was the basis for developing a sensor suitable for detecting DNA-base pair mismatches during hybridization.[49] In addition, magnetic relaxation switch technology can be used to detect biomolecular interactions with high efficiency and sensitivity. Weissleder *et al.* further reported the application of this technique to detect both the herpes simplex virus (HSV) and adenovirus (ADV) in serum samples by simply measuring the changes in T2 relaxation time during virus mediated self assembly of iron oxide nanoparticles.[50] The technique was able to detect as few as five viral particles in 10 μL of a 25% protein solution without an additional amplification step.

Conclusions

In this *tutorial review*, we highlighted one-, two-, and three-dimensional MNP-polymer composite assemblies, which show promise for developing devices for a broad range of applications with greater capabilities. Self assembly techniques provide pathways to afford nanostructured composite materials, wherein individual (or groups of) MNPs are organized in a well-defined manner. The magnetic characteristics of the polymer composites are dependent upon MNP size, shape, and composition. These variations allow one to tune the desired properties of the material for specific applications. Polymers and biopolymers differing in composition and architecture have been employed for creating magnetic composite materials, and play a critical role in the assembly behavior of the nanoparticles. These self assembled materials are attractive for their stimuli-responsive behavior. Magnetic fields can be used to elicit a magnetic response from the materials, whether the material rearranges in response to the external field, or provides information regarding the local environment of the nanoparticles. Moreover, the magnetic fields can be exerted through space, including human tissue, which makes these materials appealing for future biomedical applications.[51] Other applications include high density information storage,[3,52,53] wherein MNP-polymer composites have a long history in magnetic storage media that will continue with improvements in areal density, spacial order, and placement of particles. MNP-polymer composites provide a versatile set of stimuli responsive materials with exciting possibilities for future developments and applications.

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