Magnetic Click Colloidal Assembly

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Ⓢ *Supporting Information*

ABSTRACT: We introduce a new class of spherical colloids that reversibly self-assemble into well-defined nonlinear structures by virtue of "magnetic patches". This assembly is driven by tunable magnetostatic binding forces that originate from microscopic permanent magnets embedded underneath the surface of the particles. The resulting clusters form spontaneously in the absence of external magnetizing fields, and their geometry is determined by an interplay between magnetic, steric, and electrostatic interactions. Imposing an external magnetic field enables the clusters to unbind or change their geometry allowing, in principle, the creation of materials with a reconfigurable structural arrangement.

The self-assembly of colloidal matter into target functional materials is of both practical and fundamental interest. In principle, increasingly complex superstructures can be created from elementary building blocks via a cascade of sequential interactions.[1] Instructions for assembly can be coded in the particle interaction landscape by altering the shape of the building blocks[2,3] and tuning strength and nature of the forces acting between them.[4–7] In particular, when building blocks interact by means of discrete binding sites on their surface, a "colloidal valence" emerges that enables the formation of stoichiometric assemblies[8] typical of atomic systems. Surprisingly, this idea has been explored almost exclusively using chemical surface patches.[7,9–12]

There is an important reason to investigate the magnetic self-assembly of colloidal superstructures: unlike electrostatic and chemical interactions, magnetic forces are not screened in solution and are virtually independent of changes in experimental conditions such as temperature, pH or solvent composition, thus, giving us significant experimental design freedom. To date, however, examples of colloidal self-assembly involving magnetic forces are either limited to simple linear or circular dipolar structures or rely on the induced magnetization of paramagnetic particles exposed to external magnetic fields.[2,5,13–15] Designing a rational assembly mechanism based on magnetostatic interactions requires particles with localized and well calibrated magnetic dipole moments. The resulting magnetic forces should be strong enough to bind particles together only when the magnetic patches are in close proximity to one another but are not sufficient to cause magnetic flocculation. Here we demonstrate that such a magnetic binding mechanism can be realized using iron oxide inclusions buried just below the particle surface to generate localized permanent magnetic dipoles.

Our most basic building block consists of an organosilica polymer sphere with a single hematite micromagnet embedded. Similar to colloidal Geomag toys, these spheres magnetically "click" forming directional bonds by means of their magnetic patches. The synthesis protocol, which is shown schematically in Figure 1A, starts with the preparation of hematite micro-
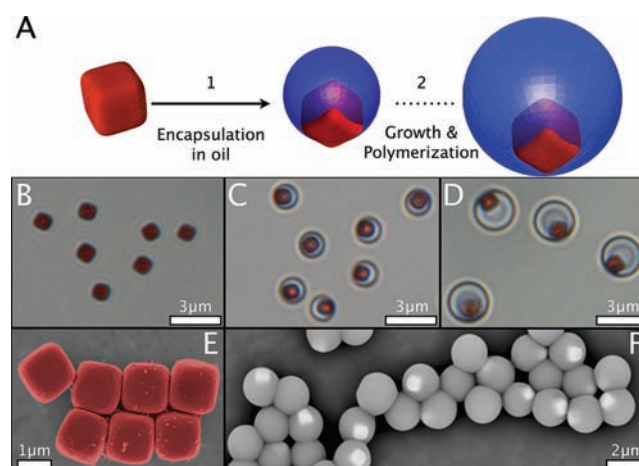
Figure 1. Particles fabrication. (A) Schematic diagram showing the synthetic steps involved in the preparation of particles with a single magnetic patch. First, monodisperse micromagnets are encapsulated into polymerizable oil droplets via a seeded dispersion polymerization. Next, the droplets are grown to the target size and polymerized. (B–D) Encapsulation and growth can be conveniently followed by optical microscopy. In the pictures, we show different stages during this process. (E) False-color SEM image showing the bare micromagnets; (F) SEM image of the final spherical particles carrying a single magnetic patch.

cubes following the method described by Sugimoto.[16] The resulting cubes are uniform in size and shape, and posses a permanent magnetic moment[17] as demonstrated by the formation of dipolar structures in a zero external field (see Movie 1 and Figure S1 in Supporting Information). Next, the magnetic cubes are encapsulated into polymerizable silicon oil droplets as follows: an oil-in-water emulsion is synthesized in situ via a polycondensation reaction between metastable water-

soluble silanols to produce insoluble silsesquioxanes that phase separate nucleating monodisperse droplets as further described in Sacanna et al.[18] Each cube, initially suspended in the water phase, acts as a nucleation site for the formation of an oil droplet, thus, producing droplets with a single magnetic inclusion. A key feature of this encapsulation mechanism is that, during the phase transfer from water to oil, the cubes are trapped at the interface by surface tension, thus, leaving one face of the cube exposed to the water phase. We will refer to this surface inhomogeneity as "magnetic patch". In the final step of our synthesis, a radical polymerization hardens the oil phase, yielding patchy colloids as shown in Figure 1F. The nucleation and growth mechanism enables us to control the droplet's size with accuracy and produces monodisperse droplets (polydispersity <5%) which cannot be prepared with common homogenization methods.

Each magnetic patch has a permanent dipole moment m whose magnitude is proportional to the volume v of the embedded cube. Assuming a single domain particle behavior, m is expressed as $m = I_0 v$, where I_0 is the spontaneous magnetization per unit volume of the particle. The maximum magnetic interaction energy V_m, that two magnetic cubes can generate, is attained when their dipoles are in a head-to-tail configuration, and is given by:

$$V_m = -\mu_0 m^2 / (2\pi r^3) \tag{1}$$

where μ_0 is the magnetic permeability of vacuum, and r is the distance between the centers of two cubes. If we assume $I_0 = 2.2 \times 10^3$ Am^{-1} for hematite,[19] the maximum magnetic attraction that two patches can generate at contact can be estimated to be in the order of $400 k_B T$, where T is the temperature and k_B is Boltzmann's constant. To this attractive term, an electrostatic repulsion contribution must be added to account for the negative surface charge that the particles develop in water. For the simplest case of two flat patches interacting across a 1:1 electrolyte, we can use the expression for charged parallel plates:[20]

$$V_{el} = 64\rho\lambda A \tanh^2\left(\frac{ze\psi_0}{4k_B T}\right)e^{-h/\lambda} \tag{2}$$

where A is the area of the patch, ρ is the ionic strength, ψ_0 is the surface potential, λ is the Debye screening length, and h is the distance between the interacting surfaces. The total potential energy of two patchy particles was calculated as a function of the interaction distance at four different ionic strengths (1:1 electrolyte), and it is shown in the Supporting Information. Because of its short-range nature, the attractive magnetic term between two patchy particles is generally offset by the long-range repulsion of their electric double layers. This results in suspensions of particles that behave as purely repulsive colloids so the particles exist as singlets, as shown in Figure 2A. The particles' charge, however, can be partially screened by adding salt to the colloidal suspensions. This effectively activates the magnetic patches promoting the formation of magnetic bonds between interacting particles (see Movie 2 in the Supporting Information). Under such conditions, monodispersed clusters self-assemble in zero field as illustrated by the time-lapse image sequences of Figure 3A−C. Particle assemblies can be reversibly unbound by adjusting the salt concentration in the system, which effectively changes their binding energy (see Figure S2 in the Supporting Information).
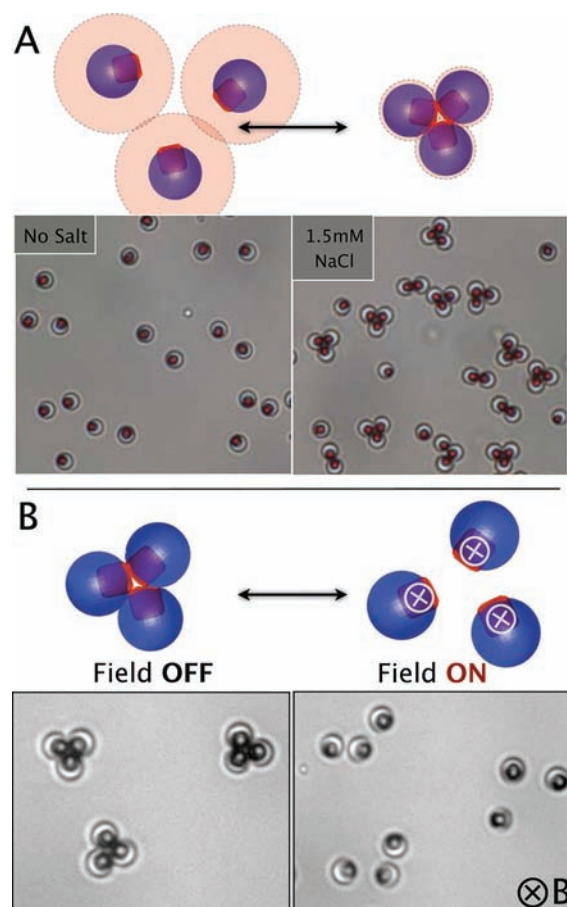
Figure 2. Reversible binding. (A) When suspended in deionized water, the magnetic patchy particles are purely repulsive and only singlets are observed. However, if the Debye screening length is reduced below 6 nm by means of added salt (here 1.5 mM NaCl), the patches become "sticky" and particle clusters start forming. (B) Clusters formed at high salt concentration in zero-field can be disassembled by imposing an external magnetic field. Here planar trimers diffusing on a glass slide are quickly exposed to a 30 G field perpendicular to the substrate. The resulting parallel-aligned dipoles repel each other, causing the clusters to unbind.

When the particles are confined to a flat surface, their assembly can also be regulated by means of an external magnetic field, as illustrated in Figure 2B. In the absence of an applied field, the particles self-assemble into clusters driven by magnetostatic interactions between their patches (in Figure 2B, planar trimers are shown). However, a sufficiently strong external field, which in Figure 2B is applied perpendicular to the field of view, can force the magnetic dipoles to change their orientation via a solid rotation of the whole particle. This results in adjacent parallel dipoles that repel each other causing the clusters to unbind. This sudden dipole−dipole repulsion, as well as the particles rotation that follows the exposure to the field, is qualitatively captured by Movie 3 in the Supporting Information.

Because the particles can form magnetic bonds only when their patches are in a close proximity, steric constraints dictate the number of particles in a cluster and the cluster shape. We can define a steric hindrance parameter $s = A_c/A_p$ as the ratio between the total particle surface area A_c and the active magnetic patch area A_p. Experimentally, we found that for $s > 28$ the patchy particles self-assemble exclusively into dimers
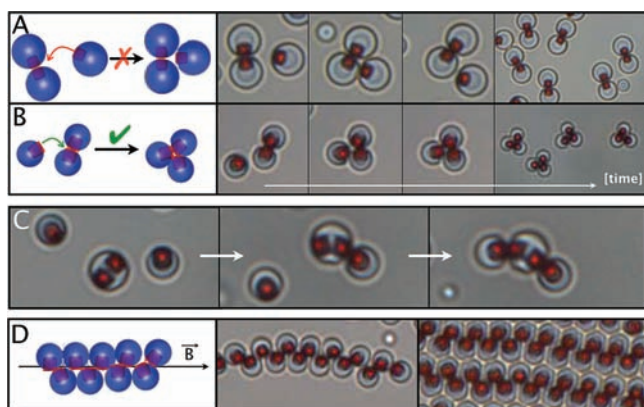
Figure 3. Magnetic-click colloidal assembly of monodisperse clusters, colloidal molecules and linear chains. (A and B) By varying their size, particles with a single magnetic patch (monovalent) can selectively form dimers or trimers depending on their steric hindrance parameter s (see also Figure S3 in the Supporting Information). (C) Time sequence showing the self-assembly of a colloidal molecule by means of directional magnetic bonds between a divalent and two monovalent particles. (D) When an external magnetic field is imposed, the clusters can be forced to rearrange into long linear structures or, at high particle volume fractions, into layered packings.

(Figure 3A). When s falls between 19 and 26, however, there is enough room to accommodate a third particle in the cluster and establish a stable three-body interaction between the patches. At these values of s, trimers self-assemble with yields as high as 80% (Figure 3B). For a smaller value of s, selectivity drops significantly and only mixtures of different type of clusters are observed (some examples are shown in the Supporting Information). This is partially due to the small gravitational height of the colloids used in our experiment, which confine them in a quasi 2D system and favors the formation of rings instead of three-dimensional clusters.

Colloids with multiple magnetic patches, and thus higher valence number, enable the assembly of more complex stoichiometric aggregates. In Figure 3C, for example, a divalent particle embedding two micromagnets is mixed with two monovalent particles to form a colloidal molecule (see also Movie 5 in the Supporting Information). The absence of chemical bonds at the magnetic junctions allows the particles to reversibly unbind the assemblies or to reconfigure them into different structural arrangements. In Figure 3D, an homogeneous magnetic field is applied to force the clusters to reorganize themselves into linear chains of particles, while a weaker field gradient packs them into a dense layered sediment.

The same mechanism of recognition and binding that we have thus far demonstrated among colloidal particles in suspension can be easily adapted to bind particles on magnetically patterned surfaces. In Figure 4, for example, we show particles with a single magnetic patch that are streamed above a flat surface with embedded magnetic dots sandwiched between a glass substrate and a polystyrene coating layer. As the colloids diffuse in the vicinity of the surface, magnetic interactions guide them to land precisely on each magnetic target (see also Movie 4 in Supporting Information). This is of potential interest for drug delivery application where a particle with its cargo of active material has to be delivered to a specific location.

Finally, recent computer simulations have shown that magnetic particles in which the dipole moment is shifted
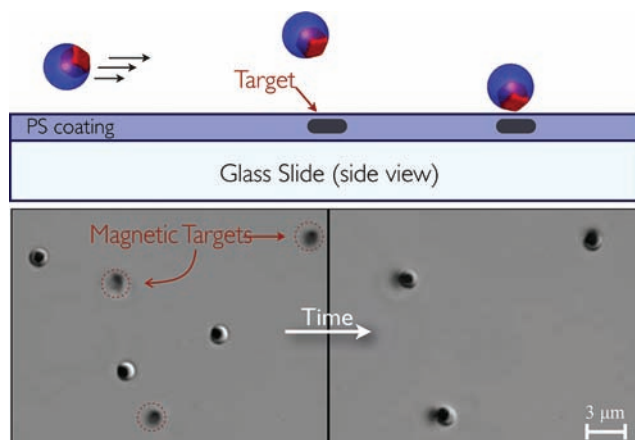
Figure 4. Binding to magnetic targets. Magnetic substrates were prepared by electrostatically trapping negatively charged micromagnets on positively charged glass slides that were previously cleaned by oxygen plasma etching and functionalized by silanization using 3-aminopropyltriethoxysilane. The slides with the attached magnets were then spin-coated with a layer of polystyrene (MW = 2 000 000 from Pressure Chemical) to obtain flat and homogeneous surfaces. The binding experiments were performed by simply flowing suspensions of patchy magnetic colloids on top of the substrates (see also Movie 4 in Supporting Information).

from the center of mass toward the particles' surface result in suspensions with new and peculiar micro- and macroscopic structures.[21] To this end, our colloidal system represent an ideal model system to experimentally investigate on the properties of ferrofluids with shifted dipoles.

In conclusion, we have described a novel recognition and binding mechanism between colloidal particles, based on simple magnetostatic interactions. This has been demonstrated by means of specially designed composite colloidal spheres with embedded monodispersed micromagnets. These magnets are located underneath the surface of the particles, generating localized permanent magnetic dipoles (magnetic patches). The resulting building blocks can be synthesized in bulk with a new and simple technique that enables us to control both the size of the particle as well as the size of the magnetic patch. In the absence of external fields, the particles can self-organize into well-defined clusters or bind at specific magnetic targets on a substrate. The magnetic bonds that are established among interacting particles are directional, reversible, and form regardless of the chemical environment surrounding it.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures, and figures and movies as noted in text. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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