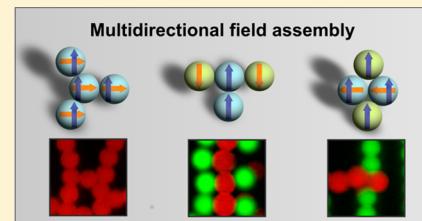


Assembly of Reconfigurable Colloidal Structures by Multidirectional Field-Induced Interactions

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ABSTRACT: Field-directed colloidal assembly has shown remarkable recent progress in increasing the complexity, degree of control, and multiscale organization of the structures. This has largely been achieved by using particles of complex shapes and polarizabilities (Janus, patchy, shaped, and faceted). We review the fundamentals of the interactions leading to the directed assembly of such structures, the ways to simulate the dynamics of the process, and the effect of particle size, shape, and properties on the type of structure obtained. We discuss how directional polarization interactions induced by external electric and magnetic fields can be used to assemble complex particles or particle mixtures into lattices of tailored structure. Examples of such systems include isotropic and anisotropic shaped particles with surface patches, which form networks and crystals of unusual symmetry by dipolar, quadrupolar, and multipolar interactions in external fields. The emerging trends in making reconfigurable and dynamic structures are discussed.



1. INTRODUCTION

A rich variety of soft materials can be formed by the assembly of building blocks on any length scale, from molecules to polymers to particles and even to living cells.^{1,2} Self-assembly is one of the major routes to organizing molecules into larger-scale structures such as cell membranes, crystals, and micelles.^{3,4} It is the result of the mutual attraction and orientation of the molecular building blocks, resulting into the formation of self-assembled aggregates of well-defined morphology whose structure can be tuned by modulating the intermolecular interactions.⁵ Such a level of precise, directional, and interactional reconfigurability has yet to be achieved for larger colloidal-scale particles.

Colloidal particles dispersed in a water medium are usually electrostatically stabilized, and an external force is needed to organize them into supracolloidal domains. Precise control over the interactions between the colloids can lead to their self-assembly into diverse morphologies such as colloidal clusters, chains, and 2D and 3D crystals.^{6,7} It is generally accepted that long-range particle structures assemble gradually via weakly attractive potentials near thermodynamic equilibrium, where the ensemble energy is minimized by spatial orientation. Hence, following this thermodynamically determined pathway, particles with weakly attractive spatially isotropic pair potentials acquire the equilibrium state of close-packed crystals.⁸ Similar “trivial” (at least from the perspective of this review) close-packed structures are formed by confining spherical particles in restricted volumes.⁹ Unlike the isotropic particles, patchy colloids preferentially self-assemble into open lattices when driven by the entropy gain associated with the vibrational and rotational modes of patch-to-patch assembly.^{10,11} On the other hand, colloidal particles isotropically interacting via strongly attractive potentials typically form kinetically trapped fractal-like agglomerates.¹² This strong interparticle attraction between

the colloids results in unusual interfacial and bulk rheological properties of the dispersions.¹³

The assembly of directionally oriented supracolloidal structures requires a spatially anisotropic interaction between the particles. An effective way to introduce such an asymmetric pair potential is through the application of external fields.⁶ External electric and magnetic fields are the most widely used tools for introducing an attractive potential between particles and assembling them into well-defined structures ranging from nano- to mesoscale. Moreover, external fields also introduce local and/or global intensity gradients resulting in additional body forces on the particles, which further direct the assembly process by effects relying on dielectrophoresis and magneto-phoresis.^{14,15} Examples of structures that have been assembled by external fields include crystals, nano- and microwires, electro- and magneto-rheological fluids, and other multi-responsive materials.¹⁶ Additional modification of the particle properties and field parameters enables the formation of a broad range of new classes of assemblies, which can further serve as precursors for fabricating advanced materials. We present here an overview of the developments and trends in the area of external-field-directed assembly of colloidal particles. We generalize the types of more complex multipolar interactions that can be induced by external fields and correlate the interactions with the structure of the assemblies formed. Concurrently, we provide our perspective on the forthcoming developments in this rapidly growing and evolving field of directed assembly.

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2. SPHERICAL ISOTROPIC PARTICLES IN EXTERNAL FIELDS

In the absence of external field, spherical particles without surface heterogeneity have spatially isotropic interparticle interactions. During entropically driven self-assembly under confinement, the colloidal spheres crystallize into face-centered-cubic or randomly stacked hexagonal structures.⁹ However, when such particles are subjected to external fields, the field-induced anisotropic interactions lead to their directional assembly in various aligned mesophases.¹⁷ In this section, we briefly summarize the origins of the field-induced particle polarization, the resulting interactions, and the types of structures formed.

The simplest pattern of polarization, typically present in symmetric particle systems such as dilute suspensions of spherical colloids in external fields, can be approximated by a dipole embedded in the particle. The polarized spheres interact with the applied field and the neighboring particles, resulting in directionally assembled chains and arrays.¹⁸ Although the chain assemblies formed by particles in external electric or magnetic fields are structurally similar, the physical origin of the induced dipolar attractions is different. Under the action of a magnetic field, the net dipole induced in the particle arises from the alignment of its local magnetic domains along the direction of the applied field, thus the dipole is embedded inside the particle. Conversely, in an external AC electric field the dipoles are induced by the combined polarization of the core material and the counterionic layer around the spheres.¹⁹ Hence, the overall length of the electric dipole can exceed the geometric size of the polarized body. The frequency-dependent complex permittivity ϵ^* of a material in an AC electric field is given by²⁰

$$\epsilon^*(\omega) = \epsilon - i \frac{\sigma}{\omega} \quad (1)$$

where ϵ is the permittivity, σ is the conductivity of the material, ω is the angular frequency of the applied electric field, and i is the imaginary unit. Depending upon the relative conductance of the material and the counterionic layer, the complex polarizability may change at high frequencies, effectively inverting the dipole orientation. This frequency dependence is much less pronounced for metallic particles at high frequencies where the polarization is dominated by their high bulk conductance.^{21,20} The net induced dipole moment (μ) in a spherical particle of radius r is given by²²

$$\vec{\mu} = 4\pi\epsilon_m K_{CM} r^3 \vec{E} \quad (2)$$

where E is the applied electric field intensity, $K_{CM} = (\epsilon_p - \epsilon_m)/(\epsilon_p + 2\epsilon_m)$ is the Clausius–Mossotti function, and ϵ_m and ϵ_p are the complex permittivities of the suspending medium and particle, respectively, as given by eq 1.

In a relatively dilute dispersion, where the interparticle separation is much larger than the particle diameter, each polarized particle can be approximated as a point dipole. The resulting dipole–dipole interaction potential is expressed by²³

$$U_{12} = \frac{1}{r_{12}^3} \left[\vec{\mu}_1 \cdot \vec{\mu}_2 - 3 \frac{(\vec{\mu}_1 \cdot \vec{r}_{12})(\vec{\mu}_2 \cdot \vec{r}_{12})}{r_{12}^2} \right] \quad (3)$$

where $\vec{\mu}_1$ and $\vec{\mu}_2$ are the dipole moment vectors of particles 1 and 2 and r_{12} is the distance between the particle pair. The polarized particles mutually attract and assemble along the direction of the applied field.²⁴ The typical structures formed by colloidal particles brought together by dipolar interactions are

linear chains, described in detail in section 3.1.¹⁸ Both particles that are more and less polarizable than the dispersing medium form chains colinear with the direction of the field.^{24,25} However, a mixture of two types of particles, one of which is more and the other of which is less polarizable than the medium, may result in the coassembly of linear mixed chains orthogonal to the direction of the applied field (details in section 3.3). The formation of particle chains in external fields is a nonequilibrium process. Secondary interactions between the chains lead to the formation of 2D and 3D crystals over extended times (details in section 3.1).²⁶

The natural evolution of this research field is toward the use of more complex particles and/or complex field configurations. For example, recent studies in the area of external-field-directed assembly has revealed that quadrupoles or multipoles can be induced in metalloelectric patchy particles (details of this assembly presented in section 3.2).^{27,28} For the purpose of exploring the rich variety of possible configurations that can form under the action of such complex interparticle interactions, we examine the cases of particles whose polarization pattern can be described with a pair of induced dipoles. The configurations attained by such particles would be governed by the interdipolar separation (δ) and relative angular orientation (ψ) of the two dipoles. Some of the possible configurations formed by pairs of double dipolar particles are summarized in Figure 1a.

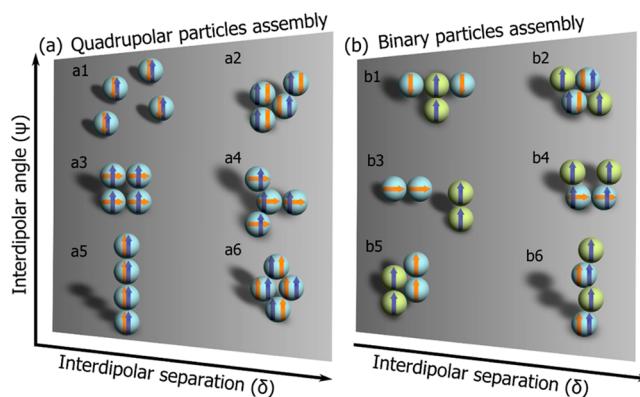


Figure 1. Generalized scheme of colloidal assemblies formed by induced multipolar interactions, including quadrupolar and a mixture of quadrupolar and dipolar particles. The dipoles (orange and blue) shown in the schematic can originate from electric and/or magnetic fields acting simultaneously in different directions or from different polarization modes in (anisotropic) particles. These dipoles can be cross-interacting or not, depending upon their phase and origin. (a) The change in the relative angular (ψ) and spatial orientation (δ) of the dipoles in quadrupolar particles leads to a difference in the motifs of particle assembly. (b) The polarization patterns also control the structure of particle assemblies in a mixture of dipolar–dipolar particles and dipolar–quadrupolar particles.

The net dipole moment is the vector sum of two dipole vectors. In the trivial case when one of the dipoles in the particle is inverted, i.e. $\psi = 180^\circ$ (Figure 1a, structure a1), the coupled dipoles will cancel each other and no assembly will take place. Another routine case is realized when the two dipole vectors are aligned and their centers coincide with the center of mass of the particle, i.e., $\delta = 0$ and $\psi = 0^\circ$, (Figure 1a, structure a5, section 3.1). This configuration is equivalent to a single dipole, and the particles would assemble into linear chains. Several interesting structures can be obtained when ψ attains

values of between 0 and 180° . In these asymmetric dipolar configurations, the effective interparticle interactions can be approximated as combinations of dipoles that will lead to distinct assembly patterns. For orthogonal dipoles, i.e., $\psi = 90^\circ$ (Figure 1a, structure a3), the particles will assemble into square lattices. In other cases where $\psi \neq 90^\circ, 0$, or 180° , particle crystals with oblique and rhombic symmetries would be formed. A precise tuning of the relative angular orientation ψ of dipoles in a particle can be achieved experimentally by changing the angle between bidirectional electric and/or magnetic fields applied independently or in a phase-synchronized sequence. The experimental methods for achieving such precise control over the electric and/or magnetic multipolar angles are discussed in section 3.2.²⁹

A second key parameter that can be controlled experimentally is the interdipolar separation, δ . It can be varied by changing the surface chemistry or polarizability patterns of the particles. In general, any deviation in δ ($\neq 0$) will lead to a spatially asymmetric multipolar pair potential and will result in more open particle networks in comparison to particles with centrally located dipoles. A summary of some of the representative structures that can be formed with $\delta \neq 0$ as a function of the interdipolar angle ψ is presented in Figure 1a. Two parallel dipoles ($\psi = 0^\circ$) at a distance δ apart (Figure 1a, structure a6) would guide particle assembly into a hexagonal close-packed 2D crystal, whereas antiparallel ($\psi = 180^\circ$; Figure 1a, structure a2, section 3.2) dipoles will form chains in directions parallel and perpendicular to the vector of applied fields. At intermediate angles, i.e., $0^\circ < \psi < 180^\circ$ $\delta \neq 0$, a bidirectionally percolated network will be formed. The fractal dimension of the assembled percolated networks would be determined by the relative angular orientation of the induced dipoles.

Another potentially powerful approach to assembling comprehensive colloidal structures is the coassembly of multiparticle dispersions, where each type of constituent particle A and B possesses distinct response to the applied external field. Schematics of a few representative assemblies that can be formed by a mixture of two dipolar particles are shown in Figure 1b. The relative angular orientation (ψ) in the particle mixture can be defined as the angle between the dipoles of A and B particles. Experimentally, this can be achieved by using multiple fields and particles that can be selectively polarized by one of the fields. Biparticle dispersions with parallel dipoles, i.e., $\psi = 0^\circ$ (Figure 1b, structure b5), will assemble into mixed composite chains and 2D hcp particle crystals.³⁰ This structure transforms into bidirectional chains when the induced dipoles in the two-component colloidal particles are antiparallel with $\psi = 180^\circ$ (Figure 1b, structure b1, section 3.3).³¹ At $\psi = 90^\circ$, the assembly of a mixture of A and B particles is likely to yield mostly independent chains of the particles (Figure 1b, structure b3). Further complexity in the assembled biparticle structures could be achieved by using a mixed dispersion of particles with one dipole (type A) and two induced dipoles (type B). Here, we will discuss the case where one dipole of particle type B is off-center by a fixed distance δ . The relative angular orientation ψ of the quadrupolar particles remains the second variable. For the case where all of the dipoles are parallel, staggered chain configurations will be assembled, whereas at $\psi = 90^\circ$, the formation of an open percolated structure could be expected (Figure 1b, structure b4). A further increase in ψ to 180° would result in the formation of an ABA-type mixed 2D hcp crystal. We believe that the change in the particle dispersion

composition, relative spatial dipolar orientation, and interdipolar angle are extremely efficient means of directing the assembly and reassembly of responsive structures. Concrete progress in the investigation of some of the systems discussed above is presented with research result examples in the next sections.

3. FIELD-DRIVEN ASSEMBLY OF ISOTROPIC SPHERICAL PARTICLES

3.1. Dipolar Particles. In this section, we present examples of particle structures formed predominantly by induced dipolar interactions. Previous theoretical and simulation studies have shown that the equilibrium assembled state of the dipolar particles is governed by the particle volume fraction and interparticle attraction (effective temperature).^{33,34} One common type of particle that could be used to illustrate these assembly principles experimentally is the latex microspheres. An example of the assembly of polystyrene latex microbeads in an external ac electric field is shown in Figure 2a. The

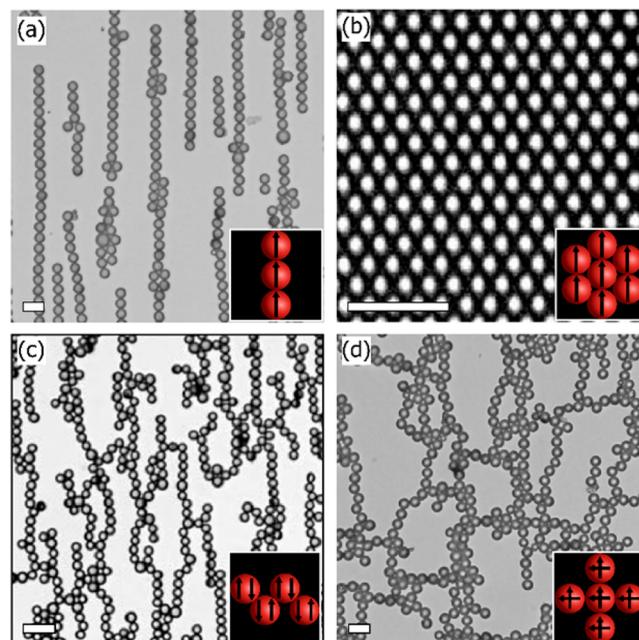


Figure 2. Examples of field-directed assembly of isotropic particles. (a) Microscope image showing the formation of linear necklace-bead type chains of latex particles upon the application of an external ac electric field. (b) Microspheres driven into a hexagonal close-packed equilibrium structure upon prolonged exposure of the ac electric field. (c) Electric-field-assembled 2D percolated network formed by quadrupolar metallocdielectric particles with antiparallel dipoles. (d) Bidirectional percolated particle network assembled by induced orthogonal magnetic and electric dipoles. The insets are indicative of the interparticle interactions responsible for structure formation in the respective cases. The scale bar in each image corresponds to $10 \mu\text{m}$. (b) and (c) respectively are reprinted with permission from references 32 and 45. Copyright 2004 and 2010 American Chemical Society and Royal Society of Chemistry.

experimental setup and procedural details have been described previously.³² The particles form linear chains aligned along the direction of the applied field (Figure 2a, here vertical). Such field-induced chaining of the particles in an external field is the basis of operation of magneto- and electrorheological fluids as dampers and shock absorbers.³⁵ In addition, this type of field-

driven particle chaining can be used in the assembly of metallic microwires and flexible microchains.^{17,36–38} The field-driven assembly is a multistage dynamic process where the initially rapidly formed chains mutually attract and hierarchically reassemble into 2D or 3D hexagonal crystals.²⁶ The 2D structure of latex microspheres assembled after longer exposure to the external ac electric field is exemplified in Figure 2b. The observed behavior is a combination of interparticle dipolar attraction and dielectrophoretic force confining the particles into a 2D plane (Figure 2b).³² According to point dipole interaction model eq 2, the dipole–dipole interaction remains attractive for $0^\circ < \theta < 54.09^\circ$, where θ is the angle between dipoles μ_i and μ_j with respect to the direction of the applied field. The interparticle attraction force transforms into a repulsive force when $54.09^\circ < \theta < 90^\circ$.²⁴ Such well-organized arrays of particles have been utilized as precursors in the making of photonic crystals, surface-enhanced Raman spectroscopy substrates, and antireflective coatings.^{26,39}

3.2. Quadrupolar Metallo-Dielectric Particles. The origins and implications of multipolar interactions of atoms with an electromagnetic field have been a topic of interest in quantum physics.⁴⁰ Recently, it has been shown that colloidal analogues to atoms can also have multipolar interactions, which govern the field-directed assembly.^{23,45} One such example is given by patchy metallocdielectric particles that can be assembled into percolated networks using a high-frequency ac electric field (Figure 2c).⁴⁵ The unusual symmetry of the assembled structure has been correlated to the frequency-dependent relative polarization of the metallic and polymer sections of the particle. At high frequency, the polarization of the counterionc layer around the polymer part of the single patched metallocdielectric particle is suppressed and the dielectric part reverses its polarization direction with respect to the metal. This reversal in the polarization leads to the induction of two antiparallel dipoles viz. a quadrupole in a particle.^{23,27} The resultant quadrupolar interactions between the particles lead to their chaining along and orthogonal to the direction of the applied ac electric field. Further changes in the number and size of patches on such metallocdielectric particles could control the multipolar interactions and in this way guide the pattern of particle assembly in the field.

The fabrication of patchy colloids and their bidirectional percolation are nontrivial experimental tasks that require advanced fabrication techniques. We have developed an alternative simple and robust approach to achieving two-directional percolation of simple microspheres by the coapplication of electric and magnetic fields.²⁹ We use a dispersion of latex spheres with magnetic nanoparticles embedded in their core that possess biresponsiveness toward external electric as well as magnetic fields. The particles are suspended in water and enclosed in a thin chamber. The fields driving the two-directional assembly are applied in mutually perpendicular directions by using a pair of electrodes inside the cell and a couple of collinear external electromagnets generating a uniform magnetic field in directions orthogonal to the electric one (though this direction can be arbitrary, as the external magnets outside the chamber can be placed at any orientation with regard to the electrodes inside). This setup gives us a facile means to induce electric and magnetic dipoles in each particle that further leads to the formation of an interconnected network (Figure 2d).²⁹ The relative orientation, i.e., the angle between the electric and magnetic dipoles induced in the microspheres and their strength, can be tuned independently by

changing the direction and intensity of the applied field. Although the two dipoles are independently induced in each particle, the percolated network formed by the particles with orthogonal dipoles is visually similar to the particle network formed by the quadrupolar metallocdielectric spheres mentioned above (Figure 1c,d).²³ However, the interparticle interactions driven by two independent fields could be controlled separately, and the time-dependent collapse and percolation transition can be modified.²⁹ The multidirectionally percolated particle networks can be used as the basis for fabricating novel materials with enhanced mechanical stability, directional conductivity, and unusual thermal and electrical transport properties.

3.3. Binary Colloidal Assembly. In the previous sections, we discussed the external-field-directed assembly of colloidal dispersions where all of the particle are of same type and have homologous induced dipoles. In this section we show that several distinctive features can be introduced into the equilibrium assembled state by using a mixture of two or more types of particles interacting via dissimilar interaction potentials. In a multiparticle assembly process, complex interactions between the particles can arise from the difference in the relative polarizability of each component particle with respect to the dispersing medium. It has been demonstrated that multiparticle dispersions can be assembled into complex architectures following the dipolar and multipolar interaction pathways (Figure 3a).²⁵ A dispersion of paramagnetic and diamagnetic colloidal particles in a ferrofluid medium can exhibit axial quadrupoles, axial octupoles, linear quadrupoles, and mixed multipoles.²⁵ The interparticle interactions and the assembly pattern were regulated by the magnetic polarizability of the dispersing medium. Binary colloidal mixtures can also be assembled into complex superlattices of unusual symmetries and into multidirectional chains by the interplay of dipolar and ionic current-driven electrohydrodynamic interactions.⁴¹

Recently, we reported that at low ac electric field frequencies a similarly charged particle pair polarizes along the same direction and forms longitudinal composite particle chains in the direction of the applied field.³⁰ These longitudinal single chains reconfigure into chains from transversal triplets when the frequency was increased beyond a critical value (Figure 3b). The lateral attraction and alignment of the particles originate from the frequency-dependent change in their polarizability.³⁰ The transversal configuration of the particles was shown to be energetically favorable in a narrow frequency regime (100–200 kHz) of the applied ac electric field. In addition, we found that the size and number ratio of the dispersed particles play important roles in determining the equilibrium assembled configuration. In a binary particle dispersion of different sizes, an excess number of smaller particles leads to the formation of bidirectional chains whereas at equal particle concentrations well-defined triplets have been observed. It can be inferred that by an interplay between dipolar and stereoselective interactions, colloidal particles can be assembled into arrays of unusual symmetries and configurations.

Mixed particle systems can also be conducive to assembling permanently fixed structures. In aqueous colloidal dispersions, the particles are generally stabilized by surface charge repulsion. The assemblies formed by these particles under the action of an external field are impermanent and disintegrate in the absence of induced attractive forces upon switching off the field. On the other hand, oppositely charged colloids exhibit an attractive pair potential, resulting in irreversible snapping of the particles.

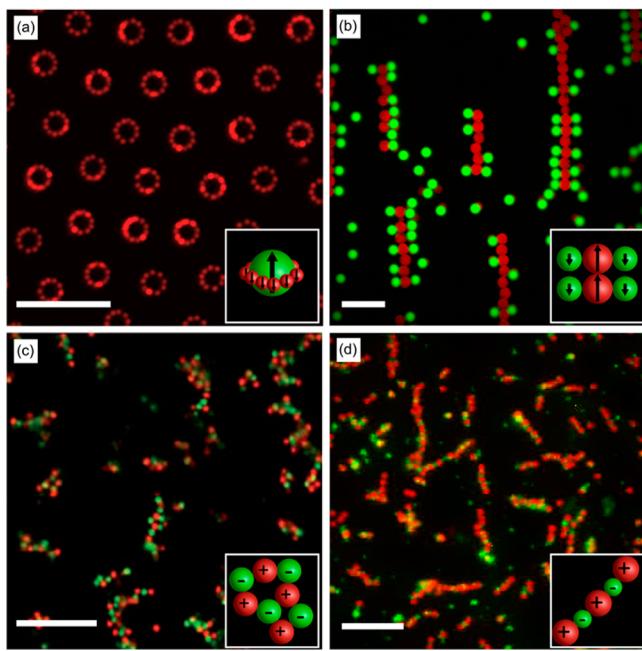


Figure 3. Examples of structures resulting from the directed assembly of interacting biparticle dispersions. (a) Microscope image of colloidal “flowers” formed in an external magnetic field by a mixture of oppositely polarized magnetic particles in a ferrofluid. (b) Colloidal triplets formed in an ac electric field by lateral attractive interaction between particles having different surface conductivities. (c) Confocal image of fractal aggregates formed in a binary dispersion of oppositely charged colloidal particles. (d) Permanent chains of oppositely charged particles formed by an initial application of an electric field. In all panels, the scale bar corresponds to a 20 μm length. (a), (c), and (d) are reprinted with permission from references 25, 12, and 22, respectively. Copyright 2009 Nature publishing Group, 2011 The Royal Society of Chemistry, and 2014 American Chemical Society.

Mixtures of strongly attractive oppositely charged particles are known to form random heteroaggregates.⁴² Figure 3c illustrates such fractal heteroaggregates formed by positive (red) and negative (green) microparticles.^{12,43} This irreversible binding of oppositely charged particle pairs can be used to assemble permanent structures. Recently, we demonstrated that heteroaggregating microparticles can be coassembled into permanent linear chains of alternating positive and negative particles.^{22,44} The method takes advantage of the much shorter time scale of the field-driven assembly (~ 10 s) in comparison to the characteristic time needed for electrostatically driven microparticle aggregation at this concentration ($\sim 10^3$ s). In an external ac electric field, the particles align into chains of a random sequence with regard to their surface charge. After the initial burst, the field is switched off and the assembled chains begin coming apart specifically at the junctions between similarly charged particles (where the particles repel each other). This partial disassembly leads to the formation of short permanent chains of alternating positive and negative particles, the average length of which can be interpreted on the basis of combinatorial models (Figure 3d).²² Permanent chain assemblies made of alternating oppositely charged particles can find multiple applications, including novel electrorheological and magnetorheological fluids, colloidal liquid crystals, microscaffolds for biological templating, and various responsive and optical materials.

4. ANISOTROPIC PARTICLE ASSEMBLY

Particle packing and assembly into ordered lattices are driven by interparticle interactions and the entropy change during the assembly process. In the previous sections, we discussed the assembly of spherical isotropic particles only, where anisometric surface interactions and entropic packing effects are absent. In this section, we show how deviations from spherical shape and nonuniform surface functionality of the particles introduces new interaction components, which then determine the morphology of the resulting assemblies. In the past decade, multiple experimental and theoretical studies have been performed to predict and understand the assembly of anisotropic particles.^{45–47} The colloidal particle anisotropy can be categorized into two groups: (a) surface anisotropy and (b) shape anisotropy (Figure 4). These two types of

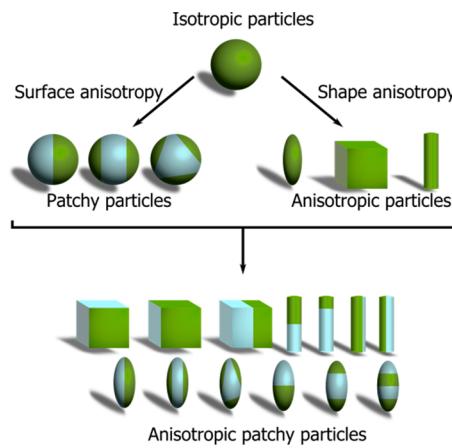


Figure 4. Scheme illustrating the general classification of the shape- and surface-chemistry-dependent anisotropies, where spherical particles with stereoselective surface modification are termed patchy particles and the particles of nonspherical shape are termed anisotropic particles. Multiple classes of anisotropic patchy particles can be defined on the basis of a combination of the shape and surface anisotropy.

anisotropies can be further combined into new classes of particles incorporating both shape and surface anisotropy.⁴⁸ Shape-anisotropic particles of well-defined morphology can be experimentally fabricated using techniques such as particle stretching,⁴⁹ soft lithography, micromolding, and microfluidics.^{14,46,49} The surface anisotropy of these particles can be a result of directional partial metal deposition,²⁸ microcontact printing,⁵⁰ selective surface wetting,⁵¹ side-selective precipitation polymerization,⁵² or fusing of clusters of particles of varying compositions.^{7,53} In the following section, we discuss the implication of the surface and shape anisotropies of these colloidal particles on the external field-directed assembly.

4.1. Field-Driven Assembly of Surface-Anisotropic Spherical Particles. The deviation from spatially isotropic interactions in surface-anisotropic spheres arises from patches of dissimilar charges, “stickiness”, polarization, or other functionality differing from the rest of their surface. The surface anisotropy may be introduced by methods such as selective metal vapor deposition, or any of the other methods for synthesizing anisotropic particles listed in the previous section. The size and shape of the patches define the net interparticle interactions and during field-driven assembly guide the formation of specific motifs and hence establish the structure of the resulting multiparticle assemblies.^{51,56,57}

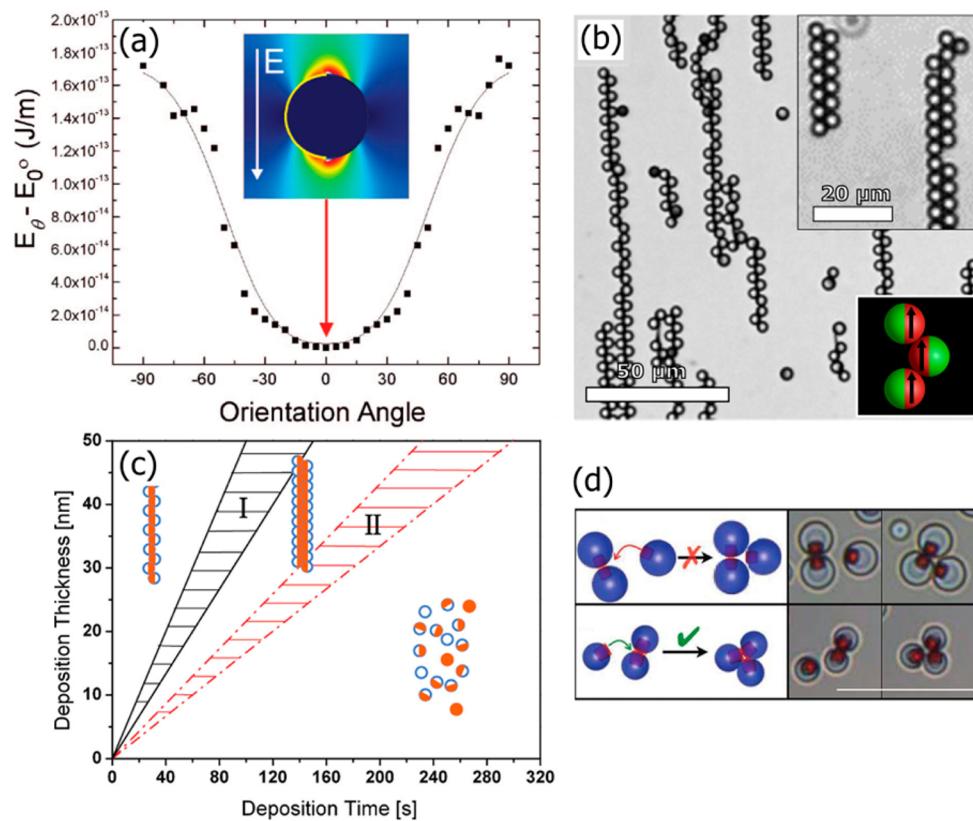


Figure 5. Examples of the directed assembly of Janus and patchy particles. (a) Change in the electrical energy of a Janus particle at different angular orientations with respect to the applied ac electric field. The energies were calculated by the surface integration of 2D COMSOL simulations (inset). (b) Micrograph of metallo-dielectric Janus spheres forming staggered chains along the direction of the applied external magnetic field. The inset shows the assembly of Janus particles into double chains. (c) Phase plot of magnetic-field-directed assemblies formed as a function of metal deposition time and thickness. (d) Polymer spheres with embedded micromagnets assembled selectively into dimers or trimers by the application of an external magnetic field. (a–d) Reprinted with permission from references 27, 19, 54, and 55, respectively. Copyright 2008, 2012, and 2013 American Chemical Society and 2009 The Royal Society of Chemistry.

The most widely studied class of “patchy” particles of specific fundamental and practical interest is the Janus particles where the physical and/or chemical properties of one hemisphere of the spherical particle are different from those of the other. Janus spheres can be fabricated by a number of experimental techniques.⁷ In our previous studies, we have shown that the assembly motif of the metallocodielectric Janus colloids in external electric or magnetic fields is primarily governed by the interactions between the strongly polarized metal halves of the spheres.^{19,27} These particles form staggered and double chains in external electric and magnetic field, respectively.¹⁹ The energetics of the different angular orientations and the assembly of various staggered chains from metallocodielectric Janus particles in an external electric field can be conveniently evaluated by 2D COMSOL simulations.²⁷ One example of a simple calculation is shown in Figure 5a as a plot of the change in the total electric energy of the particle in the range of $-90^\circ < \theta < 90^\circ$, where θ is the angle between the metal hemispherical patch and the ac electric field. It confirms that the energetically most favorable rotational orientation of a Janus particle is one where the metal hemisphere is collinear with the applied external field (Figure 5a). This orientation occurs rapidly when the field is switched on and facilitates the further staggered chain assembly.²⁷

Janus particle assembly into special symmetry chains oriented along the direction of the applied field is reported in multiple studies.^{19,27,54,58} Two common patterns of the assembly of

magnetic Janus particles into staggered chains in the presence of an external magnetic field are shown in Figure 5b.¹⁹ The role of the type of Fe_{1-x}O coating of such Janus particles in the formation of staggered chains has been investigated, and it has been found that Fe_3O_4 -capped particles assembled into double chains, while no assembly was observed for $\alpha\text{-Fe}_2\text{O}_3$ -capped Janus particles (Figure 5c).⁵⁴ The change in the metal deposition conditions alters the oxidation states of iron in the surface coating and thus leads to different assembled symmetries (Figure 5c), highlighting the critical role of patch properties in field-driven assembly.

Several other studies on the external-field-assisted assembly of multipatch particles have demonstrated the formation of multiple classes of one-, two-, and three-dimensional structures.^{28,55} The size, shape, and orientation of the surface patches modify the interparticle interactions and control the morphology of the assemblies. In addition to assembling these patchy particles into long-range-ordered structures, external fields have also been used to transport the particle to specific target sites. For example, particles with magnetic surface patches can be directed to target sites on a patterned substrate.⁵⁵ In the bulk, the magnetic patch-to-patch attraction combined with the spatial steric hindrance of the particles can lead to their assembly into doublet and triplet clusters (Figure 5d). In a more general analogy, the patchy colloids and their assembled structures can be considered to be colloidal analogues of atoms and molecules.⁵⁶ The directed assembly

of these colloids into higher-ordered domains mimics and in some cases models the nature of molecular processes such as polymerization and molecular reaction kinetics.⁵⁹

4.2. Shape Anisotropic Particles. The field-directed assembly becomes an especially useful and precise tool when used to make structures from nonspherical particles. The spatial anisotropy introduces additional steric and entropic components to the pair potential and directs the structure and symmetry of the assemblies. Several theoretical studies have highlighted the role of entropy in the self-assembly of anisotropic particles into ordered crystals of unusual symmetries.^{11,47,62} The shape anisotropy introduces directional entropic forces between the particles and directs their assembly into ordered structures.⁵⁵ The recent advancements in microfabrication techniques made it possible to construct a wide range of anisotropic particles with well-defined shapes.⁵⁵ The ability to synthesize such particles (albeit sometimes in limited quantities) has now opened a wide range of opportunities for their directed assembly, which is becoming a topic of study.^{60,61,63–65}

In the presence of external fields, the assembly is governed by two major factors: (a) polarization of particles in the direction of the applied field and (b) entropic interactions, i.e., interparticle packing factors. In general, external fields impart an additional torque component on the nonspherical particles, which typically aligns the particle's major polarization axis along the direction of the applied field.²⁰ The interplay of the induced dipole–dipole interaction and the torque acting on the anisotropic particles determines the structure and orientation of the assemblies. In addition to the field torque, the assembly kinetics also plays a crucial role in determining the resulting morphology. Particles of anisotropic shape may form kinetically trapped metastable structures, which otherwise would not be observable in spherical particles. Figure 6a illustrates the assembly of polymer microcubes (at low number density) into linear chains in an external electric field. The microcubes minimize their center-to-center distance and maximize their contact area by assembling via edge-to-edge overlap rather than vertex-to-vertex attachment. Fluorescence microscopy images of the electric-field-driven chaining of fenestrated hexagon (hexnut) and rods are shown in Figure 6b,c, respectively.⁶⁰ More recently, linear arrays of metal organic framework (MOF) polyhedra have been assembled in an external electric field (Figure 6d).⁶¹ Similar to the microcube assembly, the spatial orientation of the polyhedra has been such that the induced dipolar attraction minimized the interparticle separation by preferential facet-to-facet attachment. The facets promote particle interlocking, and the chain structure persists after switching off the external electric field.⁶¹ The assembled particles in Figure 6 had only one major polarization axis, which directed their assembly. However, particles with two major axes (boomerang-type particles) have shown no preferred orientation and have attained ill-defined kinetically trapped configurations in the external field.⁶⁰

Anisotropic particles subjected to external fields form unusual crystal structures with tunable packing density. The research on this topic is still in its initial stages, and various exciting opportunities are waiting exploration. We expect that in addition to enriching our fundamental scientific understanding, directed and spontaneous assembly of these anisotropic particles will lead to the development of novel multifunctional materials.⁴⁶ Even more diverse tools and

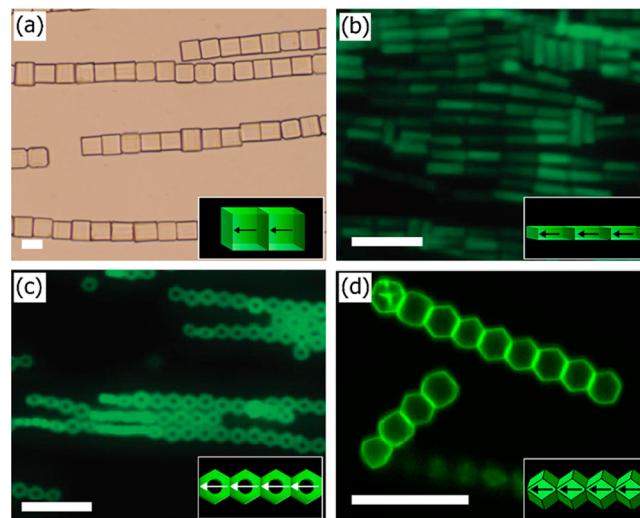


Figure 6. Examples of assemblies from anisotropically shaped particles in external fields. (a) Bright-field microscope image of polymer microcubes assembled into linear chains upon the application of an external ac electric field. (b) Fluorescence micrographs of the linear assembly of hexnuts and (c) rodlike polymer microparticles in an ac electric field. (d) Confocal image of the linear chains formed by MOF rhombic dodecahedra after the initial application of an electric field. The scale bar in each case corresponds to 10 μm . (b–d) Reprinted with permission from references 60 and 61, respectively. Copyright 2008 and 2013 American Chemical Society.

opportunities are offered by combining shape anisotropy with patchiness as described in the following section.

4.3. Directed Assembly of Shape-Anisotropic Patchy Particles. The assembly of structures with more elaborate multifield responses requires the means to achieve directionality in both their surface and core interactions. In the previous section, we discussed the assembly of nonspherical particles having isotropic surfaces, which are guided by their packing orientation at close range. On the other hand, in section 4.1 we showed that patchy spherical particles have spatially anisotropic interactions determined by the mutual orientation and potentially long-range alignment of the surface patterns. One way to introduce even more sophisticated interactions is to combine the anisotropy in the particle shape with the anisotropic surface/bulk polarizability. The application of multiple fields (electric and magnetic) to these complex particles leads to the assembly of new types of long-range-ordered structures.

Recently, we showed that polymer microcubes selectively coated with metal on one side can serve as a model for understanding such complex interactions.⁴⁸ These patchy particles adopt linear configurations in external electric or magnetic fields. However, the local orientation of particles in the chains depends on the mutual interactions between the metal and polymer parts, which in turn can be controlled by the external field used for assembly. Axially aligned linear chains with metal on the same side were obtained in an electric field, whereas the preferred assembly pattern in a magnetic field is the staggered cube configuration (Figure 7a,b).⁴⁸ Similar configurations were observed for Janus polymer cylinders where one-half (along the major axis) was selectively metal-coated (Figure 7c,d). The formation of these distinct patterns of organization can be explained on the basis of the difference in the origin of magnetic and electric dipoles in the particles. In

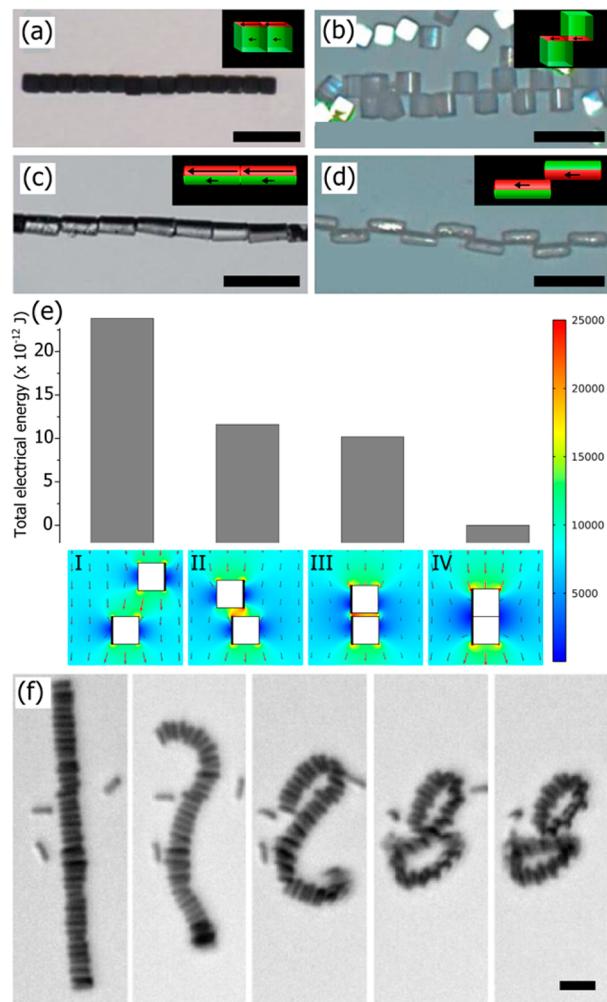


Figure 7. (a) Assembly of anisotropic patchy particles in electric (a, c) and magnetic fields (b, d). One-side-coated cubes (a) and Janus cylinders (b) form linear chains with metal on the same side in an ac electric field, whereas staggered chains are observed in the magnetic field (c, d). (e) The energy pathways of the ac electric field assembly of a pair of one-side-coated microcubes as calculated by COMSOL simulations. The axially aligned configuration is achieved by energetically favorable out-of-plane microcube rotation (II → III) during the assembly process. (f) Optical microscopy images of ribbons formed by the staggered assembly of Janus rods. Note that the ribbon reconfigures itself into daughter rings upon reversing the direction of the applied magnetic field. The scale bars in (a–d) and (f) correspond to 50 and 4 μm , respectively. (a–d) and (f) are reprinted with permission from references 48 and 66, respectively. Copyright 2013 Royal Society of Chemistry and 2013 Nature Publishing Group.

an external electric field, two distinct dipoles are induced into the polymer half and metal patch of the particles. Analogous to the case of spherical Janus particles, when two patchy microcubes approach each other, the total energy is minimized by axially aligning the metal patches along the direction of the applied field. This has been shown by our COMSOL simulation of patchy microcubes (Figure 7e).⁴⁸ The simulation confirms the origin of the experimental observation that a pair of microcubes with nonaligned metal patches (I and II, Figure 7e) self-reorient in the field to attain an axially symmetric configuration. This transformation may involve an out-of-plane microcube rotation (II → III, Figure 7e), and the energy required for this reorientation is compensated by polymer-to-

polymer and metal-to-metal dipolar alignment, which leads to a preference of linear over staggered symmetry.

When the metallo-dielectric cubes are subjected to an external magnetic field in an aqueous medium, the polymer part of the particles has no induced dipole and the assembly process is solely governed by the magnetic metal patch. The relative polarizability and the contribution of the interactions between the polymer domains can be further tuned by adding a ferrofluid component to the dispersion medium.²⁵ However, in the magnetic field assembly of patchy particles in pure water, the equilibrium assembled configuration is determined predominantly by the size and strength of the dipoles induced in the magnetically polarizable facets.

Overall, our study shows that the metal-coated sides of the cubes could readily serve as directors of the angular and mutual orientation of the microcubes in the resulting complex structures. Another notable study has been focused on the magnetic assembly of Janus dipolar rods of silica coated with a hemicylindrical magnetic layer. The rods assemble in ribbons and cyclic rings in an external magnetic field while aligning with their major axis orthogonal to the field, suggesting that the induced dipole is pointing along the short axis of the rod.⁶⁶ Thus, the polarization-induced alignment of these rods is different from the field-driven response of polymer Janus cylinders.^{48,66} Silica-magnetic Janus rods assemble in a side-by-side zigzag configuration, forming ribbonlike structures on a larger scale. These ribbons can be considered to be two-dimensional analogues of the staggered chains formed by spherical Janus particle chains.^{27,54,66} In the presence of a magnetic field, the ribbons are aligned linearly along the direction of the applied field. Upon reversing the field direction, the misalignment of the particles triggers their reconfiguration. The attraction between the ends of the ribbon dominates its bending energy, which results in the separation of aligned particles in the form of individual rings. The phenomenon was observed to be reversible with the application and removal of the external magnetic field.⁶⁶ Such processes of reversible reconfiguration reveal the further potential of making dynamically reconfigurable assemblies, which is discussed in the next section.

5. DYNAMICALLY RECONFIGURED ASSEMBLY AND ACTIVE COLLOIDS POWERED BY EXTERNAL FIELDS

As the science of field-induced interactions continues to grow and evolve, one of the next frontiers is the design and characterization of dynamically moving and reconfiguring assemblies actuated and controlled by external fields.^{67,68} One example is the collective dynamics of the particles in concentrated dispersions subjected to external fields, which leads to uncommon particle structuring.³⁹ In a biparticle dispersion of opposite charges, the particles driven by the applied field migrate toward opposite directions. This motion of the particles in two directions induces a dynamic segregation or demixing of the microspheres into positive and negative particle-rich domains or bands.^{8,69} These bands of charged particles are self-organized perpendicular to the direction of the applied electric field and exist as long as the field is present. A complete random remixing of the particles occurs upon switching the field off.⁶⁹

This dynamic reconfigurability of the colloidal assemblies is not limited only to their collective response. Small assemblies formed by colloidal building blocks can be switched between

distinct configurations by reversing the applied field direction or tuning its frequency. Recently, it has been shown that a preprogrammed assembly of Fe_3O_4 -capped Janus particles can lead to actuating staggered chains (Figure 8a).⁵⁸ For example,

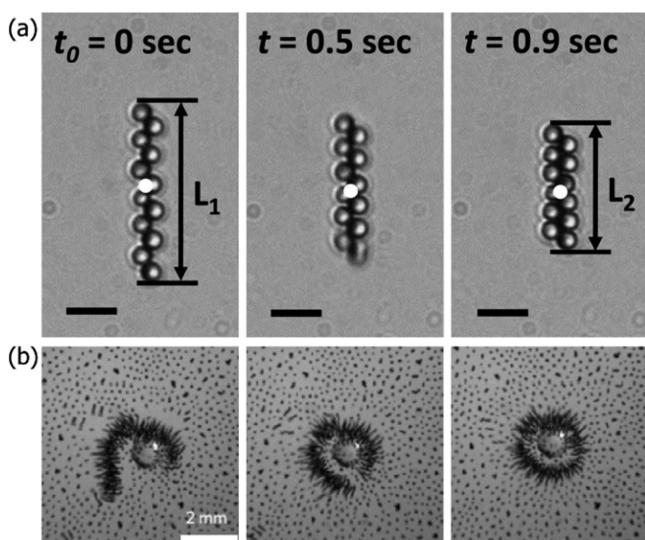


Figure 8. Examples of reversibly reconfigurable multiparticle assemblies. (a) Microscope images showing the compressive rearrangement of an Fe_3O_4 -capped Janus particle chain upon the application of parallel electric and magnetic fields. The scale bar corresponds to $10 \mu\text{m}$. (b) Colloidal aster maneuvered using an in-plane magnetic field to grab a spherical glass bead. (a, b) Reprinted with permission from references 58 and 70. Copyright 2013 American Chemical Society and 2013 Nature Publishing Group.

the application of parallel electric and magnetic fields can be used for the reconfiguration of the Janus particle staggered chains. In an external ac electric field, owing to the dipole–dipole interaction, the particles form staggered chains. A subsequent application of a static magnetic field in the direction parallel to the applied ac electric field results into additional attraction between the Fe_3O_4 caps and reconfigures them into double-chain structures. Although the mechanism of the process is still not well understood and is a topic of ongoing research, the dynamics of the contraction process can be used to determine the local bulk viscosity of the dispersing medium.⁵⁸ Another example of reconfiguration, coupled with motility, is the dynamic assembly of magnetic colloids into asters energized by the ac magnetic field at the liquid–liquid interface. The asters formed were the result of interfacial excitation by the applied field and the dipolar interactions between the magnetic particles. The assembled structures were shown to self-reconfigure and perform gripping and transportation of model objects (Figure 8b).⁷⁰

Colloidal particles in dispersions undergo random Brownian motion even in thermal equilibrium. More special particles that can convert internal energy into directed non-Brownian motion are termed “active colloids”.⁷¹ The best natural examples of such active colloids are motile bacteria, where the chemical energy produced by the cell is converted to bacterial motion.⁷² In colloids, external fields can act as a source of energy provided remotely to the particles in a dispersion.^{68,73} The combination of these active colloids with the programmable assembly and reassembly of colloidal matter is opening new frontiers in fundamental and applied research. One of the most intriguing

and futuristic applications of the dynamic reconfigurability of the colloidal structures is in the field of microrobotics.^{67,74} It has already been demonstrated that external fields can serve as effective means of supplying continuous energy to remotely operated motile nano- or microbots.⁷⁵ We expect that in addition to serving as a remote energy source, external fields can be used to trigger an on-demand assembly and disassembly of microrobots in the *in-vivo* environments.⁷⁴ The making of motile particle assemblies and “active colloids” is a rapidly emerging research area of both fundamental interest and inspired by the potential capabilities of these structures.⁷⁴ The assembled configurations and their subsequent actuation can be tuned further by introducing multipolar interactions between anisotropic particles. Thus, the combination of active colloids and field-directed self-assembly is likely to form the basis of principally new types of reconfigurable and morphing assembled structures in the future.

6. CHALLENGES AND PERSPECTIVES

The multipolar interactions presented here could help in programming the short- and long-range organization of particle structures assembled in external fields. They allow precise control of the properties of and responsiveness of the resulting precursors to new materials. It can be expected that the focus on the applications of such particle assemblies will shift from the presently investigated crystal lattices of various symmetries to more open, multidirectionally interconnected particle networks similar to the ones described in sections 3 and 4. Such particle networks can be integrated into new materials with unusual transport properties, such as having one-dimensional electrical and/or thermal conductance, anisotropic magnetic polarization, or polarized light transmittance. Other applications of material-embedded particle networks include making composites with preprogrammed responses to mechanical stress, shear, magnetic, and thermal fields, and depositing coatings with unusual tribology or controlled wetting properties.

In the longer term, the complex interactions, residual polarization, and self-reconfiguration of the assemblies from multipolar particles discussed here are also likely to shift research priorities from the assembly of simple static structures to the design and fabrication of complex dynamic ones. These new materials may include, for example, stimuli-responsive switchable composites that can be reversibly reconfigured from (a) ultrasoft to hard, (b) conductors to semiconductors to insulators, and (c) radiation absorbers to perfect reflectors. Thus, the examples we present here are just a prelude to a vast field of structures that could be made possible by multifield directed assembly. Other future technologies where directed assembly could play a key role include micro- and nanorobotics, supramolecular recognition, and materials self-regeneration. We believe that the efficient use of programmed interactions, combined with scaled-up assembly processes, could pave the way for the nanomanufacturing of advanced future materials.

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Notes

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