

Directed Self-Assembly of Nanoparticles

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Self-assembly (SA) refers to the process by which nanoparticles or other discrete components spontaneously organize due to direct specific interactions and/or indirectly, through their environment.¹ Self-assembly is typically associated with thermodynamic equilibrium, the organized structures being characterized by a minimum in the system's free energy, although this definition is too broad.² Essential in SA is that the building blocks organize into ordered, macroscopic structures, either through direct interactions (*e.g.*, by interparticle forces), or indirectly using a template or an external field. In the present review article the recent advances are considered from the perspective that in order to successfully exploit nanoparticle self-assembly in technological applications and to ensure efficient scale-up, a high level of direction and control will be required. The thermodynamic forces that drive self-assembly may need to be modulated, either by rational use of chemistry or templating, or directed by means of external fields. Directed self-assembly (DSA) still employs the basic principles of self-assembly by carefully choosing and constructing the building blocks, yet facilitates the process by modulating the thermodynamic forces without going into advanced and intricate techniques. This may also give rise to novel ordered nonequilibrium structures, free from the constraints of entropy maximization, and hence these systems can “reside” in a state of local equilibrium within the global free energy with low entropy states often characterized by complex spatial or coherent spatiotemporal organization.

We thus present an overview and an assessment of the different methods and possible tools that have been proposed to di-

ABSTRACT Within the field of nanotechnology, nanoparticles are one of the most prominent and promising candidates for technological applications. Self-assembly of nanoparticles has been identified as an important process where the building blocks spontaneously organize into ordered structures by thermodynamic and other constraints. However, in order to successfully exploit nanoparticle self-assembly in technological applications and to ensure efficient scale-up, a high level of direction and control is required. The present review critically investigates to what extent self-assembly can be directed, enhanced, or controlled by either changing the energy or entropy landscapes, using templates or applying external fields.

KEYWORDS: self-assembly · directed assembly · nanoparticles · templates · electric fields · interfaces · flow

rect self-assembly. Chemistry is a first element in the toolbox: using concepts similar to those developed in supramolecular chemistry, molecular interactions can be tailored and used to create ordered assemblies. Recent advances in this area have focused on designing particles with stimuli responsive interparticle interactions and morphological or functional features that result in directional interactions. Alternatively, particles with specific physical properties can be designed to maximize their interactions with external directing fields (*e.g.*, magnetic, electric, and even flow), or directing surfaces (confined geometries, interfaces). Especially the latter areas of self-assembly and multiscale pattern formation of nanostructured materials under external fields are still poorly understood and offer great potential for further work. Given the breadth of the topic, and being conscious that it would have not been possible to make an exhaustive literature review including all the significant contributions in each area, we made a selection, which in our opinion highlights the major developments and the future directions.

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DIRECTING SELF-ASSEMBLY BY MOLECULAR INTERACTIONS

One of the fundamental aspects of research on the synthesis and morphological control of nanoparticles has traditionally been colloidal stabilization, with the aim to avoid aggregation and flocculation. However, we are now facing a stage toward the promises of bottom-up nanofabrication, in which the aggregation of nanoparticle building blocks, specifically mimicking nature in employing rather weak and often specific interaction forces, will be essential to achieve the desired structures and functionalities. However, this requires a high degree of control to direct the aggregation process. Chemistry can be seen as an obvious handle toward

this target, since it offers control through molecular interactions, which is often inspired from other fields, such as (stimuli-responsive) polymer science³ or supramolecular chemistry.⁴ However, because of the limited length scale of molecular forces within the colloidal interface and the advantages from having a large surface area with respect to particle volume, this will be mostly effective when particle sizes are maintained below 100 nm,⁵ and thus we shall restrict ourselves in this section to review the assembly of “nanoparticles”. Additionally, although research has been devoted to the self-assembly of nanoparticles made of a variety of materials,^{6–9} we

decided to focus primarily on gold nanoparticles, since their chemical stability, facile surface functionalization, and possible shape modulation, render them a canonical example to illustrate the various processes involved in chemistry-directed nanoparticle assembly.¹⁰ Hence, without any intention to highlight their importance over that of other nanoparticle systems, the major part of the recalled examples of self-assembly in this section will deal with gold nanoparticles.

In agreement with the definition of directed self-assembly (DSA), this discussion focuses on tools and ideas that permit the modulation of the forces responsible for triggering self-assembly. From the chemical point of view, this implies using stimuli to control the interactions between molecules located at the colloidal interfaces. The most usual stimuli in this respect include temperature, electromagnetic radiation (e.g., light), pH, solvent polarity, or redox activity, and they are employed to spatially distribute the particles, either *via* straightforward intermolecular interactions between capping agents or on top of predefined templates.

Moreover, the modulation of nanoparticle assembly is often related to either the reversibility of the process² or the control over interparticle spacing (periodicity). Therefore, these factors are major limiting criteria for chemically assisted DSA. Additionally, for the sake of simplicity, in the discussion of chemically assisted DSA we decided to omit the aspects related to the interplay between colloidal interactions¹¹ (e.g., van der Waals, electrostatic, steric, magnetic) which are obviously affected by the applied stimuli.

Templated DSA. In geometrical terms, templates can be considered as surface-modified substrates (in 1D, 2D, or 3D), containing active sites, which can selectively induce nanoparticle deposition. This intuitively entails the concept of a template that is significantly larger than the nanoparticles to be deposited. However, as we show here, the concept actually allows for template sizes that can range from below to well above the size of the nanoparticles (Figure 1e,f,g). Therefore, it is important to stress, that in the discussions that follow, the template is considered as *any* object serving as a scaffold onto which different particles can be arranged into a structure with a morphology that is complementary to that of the template. With this picture in mind, a variety of elements, such as single molecules (Figure 1e), microstructures (e.g., carbon nanotubes, Figure 1f), or block copolymers (Figure 1g), can become templates. Recently, an additional distinction between soft and hard templates has been proposed.¹² Soft templates possess a spatial distribution of specific reactive sites with affinity toward certain particles, resulting in a controlled periodicity of the assembled particles and eventual formation of hierarchical structures (e.g., DNA). On the contrary, for hard templates, even if they define the final structure of novel and interesting assemblies, the control that they can provide over periodicity within the assembly is rather poor. We start our review of template assisted DSA with the soft template approach, emphasizing on the use of small molecules, linear polymers, biomolecules, and copolymers as suitable templates. Carbon nanotubes are chosen as an example of a hard template with a surface that can be chemically modulated, and which are suitable substrates for directed nanoparticle assembly.

Small molecules are often easily available and inexpensive, but they contain a limited number of binding sites, so that they mostly result in irreversible nanoparticle aggregation and thus, their utilization in directed self-assembly is challenging. However, molecules that are sensitive to temperature¹³ or pH¹⁴ have been shown to indeed be applicable for DSA. With these concepts in mind, a controlled spatial distribution of nanoparticles can be achieved by applying rules and concepts that are well established in supramolecular chemistry. Weak and reversible interactions between molecular units (template) and nanoparticle capping agents provide unlimited possibilities toward control over macro-

VOCABULARY: **Self-assembly** – process by which nanoparticles or other discrete components spontaneously organize into ordered structures • **directed assembly** – process whereby an intrinsically self-assembling system is aided or modulated using directing agents, external fields, or templates • **templates** – any surface-modified object (1D, 2D, or 3D), which contains active sites, suitable for selective nanoparticle deposition • **directing fields** – externally imposed fields (in a broad sense), such as electric, magnetic, and flow fields, or combinations thereof, that modulate or enhance the thermodynamic forces that drive self-assembly • **capillarity or capillary action** – forces exerted by interfacial or surface tension effects that lead to a directed self-assembly at interfaces or in thin films

scopic assemblies. In an interesting recent example, the specific halogen bonding (XB), in a parallel fashion to hydrogen bonding, was applied for the first time to direct gold nanoparticle clustering.¹⁵ Gold nanoparticles functionalized with an XB donor were found to undergo progressive aggregation in the presence of a bifunctional XB acceptor. Modulation of the assembly time and template concentration resulted in the formation of either chainlike structures or large, dense assemblies. An alternative strategy to modulate nanoparticle assembly involves understanding and using the distribution and chemistry of the coordination sites in template molecules. As recently shown,¹⁶ the degree of assembly in gold nanoparticles increased with the number of functional groups (pyridyl) in the templates (between one and four). However, a more elegant approach was recently proposed for reversible clustering based on pseudorotaxane host–guest interactions¹⁷ (Figure 2a), in which geometrical control allowed the assembly into homodimers, trimers, and tetramers by simply varying the initial symmetry of the template molecule (Figure 1e). In this work, gold nanoparticles functionalized with molecules containing electrochemically active guest units (tetrathiafulvalene), were allowed to interact noncovalently with a template containing host units (tetracationic cyclophane), resulting in fully reversible assembly in solution, through cyclic reduction (assembly) and oxidation (disassembly). The pseudorotaxane concept was later extended by the same authors into a polypseudorotaxane system, where the host units were incorporated in a linear polymer,¹⁸ so that extended networks could be obtained, comprising nanoparticles cross-linked with the polymer. Such a selective “sponge” could capture or release nanoparticles of different types by reduction or oxidation processes, respectively. This concept of polymer-mediated assembly was already introduced in 2000, under the term “brick and mortar”,¹⁹ showing how modulation of solvent polarity (Figure 2b) or temperature could trigger the reversible hydrogen bonding between a linear polymer and gold nanoparticles.

Proposed in 1996, the concept of DNA controlled nanocrystal self-assembly,^{20,21} has gained extremely high popularity.^{22–30} Gold nanoparticles can be functionalized either by large numbers of DNA strands, leading to network materials,²⁰ or by discrete numbers of DNA strands, forming discrete assemblies.²¹ In this process, gold nanoparticles capped with noncDNA strands, were induced to assemble upon addition of a double-cDNA template. Interestingly, the nanoparticle aggregates could be easily disassembled upon heating (see the following section and Figure 2e). DNA can thus provide fine control over interparticle spacing within free-standing films, which can be used for instance to tune the plasmonic and mechanical properties over micrometer length scales.³¹ Additionally, the helical structure of DNA makes it a particularly interesting tem-

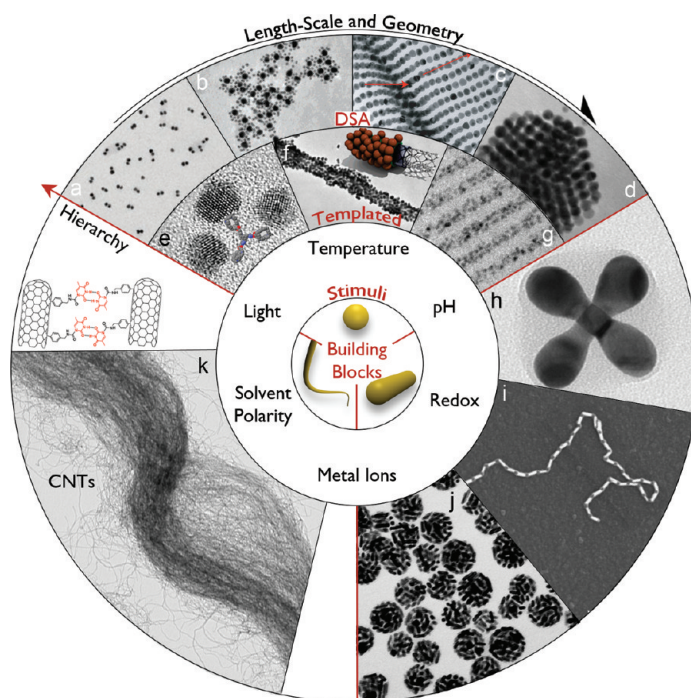


Figure 1. The universe of directed self-assembly by molecular interactions. Available building blocks are classified in terms of aspect ratio (AR), ranging from AR = 1 (isotropic, mostly spheres (a–g)) through $1 < AR < 15$ (rod-like (h–j)) to $AR > 15$ (wires (k)). Self-assembly of gold nanoparticles on templates (macromolecules¹⁷ (e); carbon nanotubes⁴⁰ (f); block-copolymers³⁸ (g)) can lead to geometries that are complementary to those of the templates. In template-free self-assembly, stimuli responsive molecules adsorbed on NPs surface induce controlled aggregation. Temperature-sensitive DNA can induce particles clustering^{28,29} (a, b) via H-bonding or induce formation of two-dimensional superlattices³¹ (c), whereas light sensitive azobenzenes induce formation of colloidal crystals⁵² (d) via molecular dipole–dipole interactions. Hydrophobic interactions can induce assembly of nanorods into low symmetry clusters;⁶⁶ (h) chainlike structures⁶³ (i) or spherical objects,⁶³ (j) by tuning the volume fraction of the different solvents. Similarly, highly anisotropic carbon nanotubes undergo assembly into bundles via H-bonding induced changes in the medium polarity⁶⁵ (k). Finally, hierarchical self-assembly can be achieved using preformed assemblies as building blocks. Images reprinted with permission from the references as indicated: (a) Copyright 2009 Nature Publishing Group; (b) Copyright 2006 American Chemical Society; (c) Copyright 2009 Nature Publishing Group; (d) Copyright 2007 National Academy of Sciences, U.S.A.; (e) Copyright 2009 American Chemical Society; (f) Copyright 2006 Royal Chemical Society; (g) Copyright 2009 Nature Publishing Group; (i, j) Copyright 2007 Nature Publishing Group; (k) Copyright 2009 Royal Chemical Society.

plate since it allows introducing chirality in the nanoparticles assembly,^{32–34} which has become of enormous interest in fields such as plasmonics and metamaterials.³⁵ Even though chiral properties have been only registered so far from gold nanostructures made by lithographic methods, solution phase assembly into chiral geometries would offer advantages such as larger scale production or reduced dimensionality that render it an extremely appealing prospective.

From the examples listed above, it is clear that nanoparticle self-assembly has been successfully achieved over distances of nanometers and micrometers. However, the need for real technological applications will require a controlled organization over much longer length-scales. Therefore, block-copolymers (BCP), which

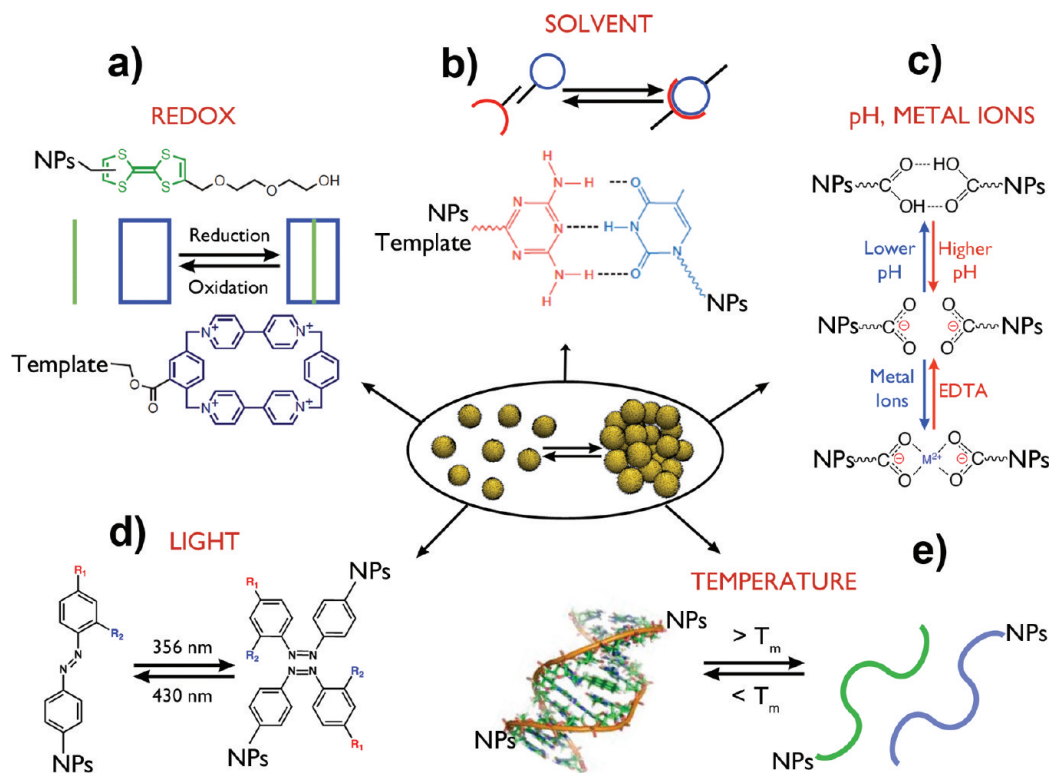


Figure 2. Molecular level of directed self-assembly. Colloidal interfaces with distributed stimuli-sensitive molecules are crucial for reversible self-assembly. (a) Electrochemically active host–guest complexes can induce clustering¹⁷ or aggregation into polymeric sponges¹⁸ via cooperative II–II and H-bonding. (b) Solvent mediated aggregation of particles by H-bonding.¹⁹ (c) Modulated concentration of H⁺ or metal ions induces reversible interparticle interactions by H-bonding⁵⁶ or metal-ion coordination.⁵⁸ (d) Photoisomerization of grafted molecules on the particles surface induces molecular dipole–dipole interactions.⁴⁷ (e) Temperature induced denaturation of the DNA strand allows keeping particles dispersed, while a decrease in temperature causes aggregation.²⁰ Note, that some molecular forces are common for different stimuli. For instance, H-bonding can be modulated by solvent nature, pH, or temperature. Such multistimuli response provides additional control in assembly by competitive/cooperative interaction. Panel a reprinted from ref 17. Copyright 2009 American Chemical Society. Panel d reprinted from ref 47. Copyright 2006 American Chemical Society. Panel b reprinted with permission from ref 19. Copyright 2000 Nature Publishing Group.

self-assemble into well-defined nanostructured arrays over macroscopic distances, constitute ideal platforms for directing the assembly of nanoparticles.^{36,37} However, this often requires modification of the capping ligands to make the nanoparticles compatible with a specific side of the copolymer, which can be synthetically challenging. Thus, external stimuli would hardly affect the assembly, once the particles have been incorporated within the matrix. However, some progress has been recently reported in this direction, through the incorporation of stimuli-responsive molecules, which interact with both the nanoparticle ligands and the polymer side chains in a noncovalent manner,³⁸ so that interparticle distance and spatial distribution could be modulated by temperature or light.

Although hard templates often provide no control over nanoparticle periodicity, they may offer novel properties when combined with nanoparticle units. Because of their particular morphology and chemical composition, one of the most prominent examples of hard templates are carbon nanotubes (CNT), in which surface chemistry plays an important role toward the incorporation of active sites for nanoparticle assembly.³⁹

One of the straightforward methods to achieve directional assembly directed by CNT structures is the simple electrostatic assembly driven by polyelectrolyte surface wrapping.⁴⁰ Although this process does not provide a handle over nanoparticle spacing or additional manipulation, it offers a degree of generality that can be exploited for subsequent DSA (Figure 1f). For example, incorporation of CNTs covered with gold nanorods into a thermosensitive polymer matrix (polyvinyl alcohol), followed by stretching, resulted in the directional assembly of the nanocomposites, providing interesting optical effects.⁴¹ On a different front, similar 1D orientation was achieved upon application of an external magnetic field to carbon nanotubes covered with magnetic nanoparticles.⁴² However, the functionalization of CNTs can also be achieved through specific recognition processes, involving for example temperature-dependent DNA duplexation/denaturation, which was proposed for reversible assembly/disassembly of Au nanoparticles.⁴³ Hybrid systems of gold nanoparticles and CNTs were also fabricated through photocontrolled host–guest interaction based on α -cyclodextrin and azobenzene derivatives,⁴⁴ so that Au nanoparticles

capped with α -CDs could be reversibly attached and detached from the surface of modified carbon nanotubes upon alternate UV irradiation and darkness periods.

Template-free DSA. In the previous section we highlighted the importance of templates in ultimately defining the final structure of nanoparticle assemblies. In this respect, we only dealt with stimuli, which could influence the spatial distribution of nanoparticles on predefined templates. In this section, we focus instead on systems in which capping molecules act not only to maintain a good dispersion of particles, but also to selectively respond toward external stimuli, thereby directing the assembly process with no need for additional template molecules. The distribution of capping molecules on the surface of the particles is highly relevant, since it can lead to patchiness when such distribution is not uniform, which in turn may lead to an additional means to control the arrangement of the nanoparticle building blocks within the assemblies. It should however be noted that also the self-assembly of patchy colloids (often related to so-called Janus particles) has been mostly implemented for large particle sizes and non-Brownian objects, whereas the self-assembly of patchy particles in the sub-100 nm range remains a challenging task.⁴⁵ In the template-free DSA, even if simple mixing of oppositely charged nanoparticles could lead to formation of colloidal crystals,⁴⁶ external stimuli can provide additional control, allowing us to modulate interparticle forces under equilibrium or nonequilibrium conditions.⁴⁷ Among the large number of stimuli easily accessible in nature or even in the chemistry lab, one can identify temperature, light, solvent polarity, or even ion concentration as suitable triggers for the assembly processes. The intermolecular forces involved, which can be modulated by the above listed stimuli, are related to hydrophobic interactions, hydrogen bonding, molecular dipole interactions, or π - π stacking.

Temperature-sensitive and weak molecular interactions are often applied toward directed self-assembly. An obvious example is related to DNA duplexes, where DNA melting temperature (T_m) can be used as a switch to turn “on” and “off” the interactions between complementary strands (Figure 2e). In terms of an assembly process, upon mixing different batches of nanoparticle solutions, capped with cDNA strands, aggregation will take place. However, when the mixed solution is heated up, denaturation of duplexes will result in disassembly of the aggregates back into separate particles. This interesting feature has been applied not only toward the controlled, reversible aggregation of spherical^{22,23} or rodlike²⁴ gold nanoparticles, but also for carbon nanotubes.²⁵ Additionally, it has been shown that careful temperature modulation of the solution containing spherical nanoparticles coated with DNA, can lead to the formation of micrometer-sized crystalline aggregates,

with a body-centered-cubic lattice structure.^{26,27} In such supracrystals, nanoparticles play the role of artificial atoms, in which the interacting molecules are homogeneously distributed on their surface. Interestingly, the distribution of DNA on the particle surface can also be asymmetric, leading to “patchy” particles,²⁸ which can interact with each other *via* their cDNA strands, forming gold homodimers²⁹ (Figure 1a) or colloidal clusters with exotic shapes^{30,28} (Figure 1b). Also from prior knowledge in supramolecular chemistry, π - π interactions⁴⁸ have found application in the controlled aggregation of nanoparticles.⁴⁹ Hybrid materials containing inorganic nanoparticles and π -conjugated polymers have been used for preparation of dendron-like aggregates,⁴⁹ where the assembly takes place at room temperature, while disassembly can be induced at elevated temperatures (~ 80 °C). Note, that π -conjugated capping agents are also sensitive to solvent polarity, which will be discussed below. These hybrid materials, even though their preparation requires elaborated organic molecules with specific functional groups, have been considered for application in optoelectronic devices or organic transistors technology.⁵⁰

Optical switching phenomena in organic molecules have been the subject of great interest due to their possible application in energy storage systems or in photochemical devices. Therefore, an increased focus on light-induced self-assembly of nanoparticles was only a matter of time.⁴⁷ Certain organic molecules change their physical properties when irradiated with light of a specific wavelength. For example, the initially nonpolar organic compounds azobenzene or spiropyran become polar under UV light irradiation, while in the dark or under visible light they return to the initial state (Figure 2d). Such behavior was explained by their ability to undergo photoisomerization. Basically, UV light can induce the transition from a more stable trans state into the cis isomer, thereby facilitating intermolecular attractions. Thus, combining this photoswitchable feature with their ability to chemisorb on gold surfaces (*via* a thiol group), these molecules can drive nanoparticles into assemblies stabilized by dipole-dipole interactions (Figure 1d) or H-bonding, while irradiated with UV light.^{51,52} Light sensitive molecules have also found application in controlling interparticle distances within gold⁵³ and silver⁵⁴ aggregates. By photoisomerization between the trans and cis states of an azobenzene dithiol linker, electromagnetic coupling between particles could be readily controlled.

As discussed above, temperature changes or light irradiation can affect weak interparticle interactions or induce changes in the conformation of the capping agent, thereby promoting an attraction or repulsion between the particles. However, one can also consider modifying the capping molecules but still be insufficient to cause global flocculation, and thus provide opportunities to devise DSA. In general, the self-assembly

process can be modulated through the concentration of certain additives (ions) or of nanoparticles themselves. Let us consider the concentration of protons in solution, that is, pH. The colloidal stability of metal nanoparticles functionalized with hydrogen bonding ligands (e.g., carboxylic groups) is highly dependent on the pH of the surrounding solution and can thus be modulated by strong hydrogen-bond interactions at low pH and repulsive electrostatic interactions at high pH (Figure 2c). This concept has been applied for reversible assembly of spherical⁵⁵ and rodlike nanoparticles.^{14,56} pH has also strong effect on the structural conformation of polypeptides, which are often used as stabilizers but can also drive the self-assembly of particles *via* peptide folding at certain pH values. This concept has been extensively reported and very recently reviewed.⁵⁷ Note, that polypeptides can also fold in the presence of metal ions (Figure 2c) (M^{2+}),⁵⁸ which makes such systems good candidates in colorimetric sensing of heavy metals.⁵⁹ Since the pH of the solution can be modulated under equilibrium or nonequilibrium conditions, the self-assembly by this stimulus appears promising toward the production of self-adapting systems.^{47,60} For instance, it was shown that pH oscillators induce cyclic DNA aggregation.⁶¹ A chemical clock producing periodic pH changes (each hour) directly affected DNA conformation by modulated hydrogen bonding. Obviously, more examples in this direction are needed for a better understanding of the complexity of the self-assembly under equilibrium or nonequilibrium conditions.

Solvent polarity can play a crucial role in the self-assembly process. For instance, when solvent polarity of a methanol–toluene mixture is increased by increasing the methanol fraction, gold nanoparticles covered with aromatic ligands experience increased π – π interactions.⁶² This leads to formation of the hexagonal and 1D structures when the mixture is drop-casted on the surface as measured by fluorescence spectroscopy and TEM imaging. Solvent mixtures can also modulate hydrophobic^{63,64} forces and hydrogen bonding.⁶⁵ Gold nanorods have been self-assembled from DMF/THF–water mixtures through a hydrophobic interaction caused by changing water volume fraction, leading to dimer, chainlike structures (Figure 1i) or spherical aggregates (Figure 1j). Shape anisotropy can also be exploited in conjunction with solvent, as in the cross structures shown in Figure 1h, formed from gold nanodumbbells upon the addition of water to the THF/DMF mixture.⁶⁶ A broad range of materials are subject to solvent effects. For example, carbon nanotubes functionalized with thymine groups have been reversibly assembled upon suspension in solvents that do not interfere with the H-bond formation (Figure 1k).

We have thus seen that, in template-free DSA, there is a compositional simplicity and no need for additional binding molecules (templates) to drive the assembly.

Obviously, there is still plenty of room to explore new stimuli, which are so creatively exploited by nature. Moreover, facing the challenges of multistimuli-responsive systems will require building blocks with multifunctional features of the kind recently reported for magnetic Janus particles containing separate temperature and pH sensitive sites.⁶⁷ Combining the sensitivity toward multiple stimuli within a single particle will open new possibilities for the modulation of molecular forces in terms of cooperative/competitive interactions, leading to self-adapting structures with dynamic rearrangement of building blocks.

EXTERNALLY DIRECTED SELF-ASSEMBLY

The use of external influences and fields to control particle suspensions has long been a powerful means for tailoring the mechanical, optical, and electronic properties of materials in applications ranging from electro-mechanical systems over nanocomposites to electronic inks. More recently, external fields have emerged as key methods to direct the assembly of colloidal and nanoparticles. Electric or magnetic fields are obvious candidates for field-directed assembly, but assembly in fluid flows and even electromagnetic fields in the form of spatially patterned optical traps have been demonstrated to hold promise for scale-up. Yet, perhaps the greatest power of field-directed assembly lies in *combinations* of effects, particularly when used with particles that are tailored to be intrinsically responsive, for example, having anisotropic, anisometric, or asymmetric properties as discussed in the previous section. For these reasons, field-directed assembly promises to be a key paradigm in the bottom-up fabrication of novel functional nanostructures that will enable new materials and devices.

In this section, we review a number of methods in which external fields have been used to create structures from a solution phase of precursor particles. A significant amount of this work has been performed with particles of micrometer dimensions, but the lower boundary of particle size is currently being extended into the nanoparticle regime. We therefore paid special attention to the mechanisms of field-directed assembly and how they scale as the particle size approaches nanometer dimensions.

Electric and Magnetic Fields. Colloidal and nanoparticle assembly in electric fields occurs due to induced interactions. Such field-induced interactions in suspensions have been studied in detail for both magnetically and electrically polarizable colloids, due to their importance to magneto- and electrorheology. The polarization mechanisms have been reviewed extensively in the past.⁶⁸ Briefly, most particles will polarize in electric fields, typically because their dielectric properties are mismatched to the surrounding medium.⁶⁹ Mobile charges, such as those in an electrostatic double layer also respond to applied fields and can contribute to the

polarization as well.⁷⁰ In the far-field, the *induced* field surrounding a polarized particle takes the form of a dipole and leads to a strong, anisotropic dipole–dipole interaction between particles. When the interaction is sufficiently strong to overcome Brownian motion, particles will initially form dipolar chains, then, over longer times, coarsen as chains laterally coalesce. Ideally, the coarsening proceeds *ad infinitum* to form the lowest energy structure, a body-centered tetragonal (bct), hexagonally close-packed (hcp), or face centered cubic (fcc) lattice, depending on the particle concentration and field.^{71–73} In practice, however, kinetically jammed states of percolated chains often result instead, due to interaction energies that are significantly greater than the thermal energy, kT . Indeed, this is the very mechanism underlying the field-responsive liquid-to-solid transition of electrorheological and magnetorheological fluids.⁷⁴

At weaker interaction strengths, electric field-induced dipolar interactions lead to ordered phases of two- and three-dimensional colloidal crystals. Alternating current (AC) fields are favored to avoid electroosmotic and electrochemical effects present when direct current (DC) is used. The field strengths are typically modest, on the order of $E \approx O(100)$ V/cm with frequencies ranging between 100 and 10^6 Hz. Lumsdon *et al.* demonstrated the assembly of micrometer-sized polymer latex particles into two-dimensional crystalline arrays upon the application of an AC electric field using coplanar electrodes⁷⁵ (Figure 3a). The coplanar electrode geometry exploits both dielectrophoresis, the movement of polarized particles along a field gradient, and the induced particle interactions to cause the self-assembly of these colloidal crystals from a dilute colloidal suspension. A key strength of field-assembly is the reversibility of the interactions, which leads to a rapid return to the disordered state when the field is removed. Such effects are useful for reconfigurable and switchable assemblies, but could also be exploited to quickly anneal defects in structures by rapidly cycling the field on and off. When exposed to such “pulsed” fields for long times, suspensions of polarizable particles form low-energy structures even when the field strengths are high enough that the structures in a continuous field would be dynamically arrested.^{76,77}

In addition to dipolar interactions, AC electric fields can also generate local electrohydrodynamic flows that mediate particle interactions and assembly, leading to two-dimensional superlattices and other complex planar assemblies, particularly when particles are near electrode surfaces and the electric field is oriented normal to the plane (in contrast to the coplanar geometry described above, where the field is parallel to the interface).^{78,79} Similarly, when suspensions are confined, particles assemble into fluid, 2D crystals, and worm-like and “honeycomb” arrangements depending on the degree of confinement.⁸⁰ This points to rather

complex interactions that are likely caused by a superposition of hydrodynamic interactions and a repulsive dipolar interaction, since the induced dipoles should be oriented orthogonal to the assembly plane. Because both the polarization and electrohydrodynamic flows are complex functions of the field frequency, the dominant mechanism driving assembly, and ultimately the structures that form, are highly tunable and diverse. Local flows can also be driven by the rotation of particles caused by the phase lag of the polarization with the applied electric field.^{81,82}

Most studies of directed self-assembly in electric and magnetic fields have used spherical particles. However, recent work has shown that particle shape can have a surprising and potentially powerful influence on the spatial organization of particles in external fields. Fields can be used to control both the translational and orientational order of anisotropic particles, and lead to structures that are otherwise unattainable using spherical particles. For instance, “peanut” hematite particles with *permanent* transverse dipole moments self-assemble into kinked chains in two-dimensions and, at higher concentrations, crystals with an oblique geometry of the $p2$ plane group.⁸³ In electric fields, polarizable ellipsoids have been shown to form similar zig-zag chains at low density but centered rectangular structures belonging to the $c2mm$ plane group⁸⁴ when a monolayer coverage is reached (Figure 3a). For rodlike fd-virus nanoparticles at frequencies where the double layers are polarized, a rich variety of phases and dynamical states have been found including a nematic phase, a striped phase, and a remarkable dynamic state where domains continuously form and remelt.⁸⁵ As fabrication methods for more complex particle shapes are being developed,⁸⁶ electric fields will continue to be an important method of directed assembly.

One of the key challenges of exploiting the field-induced interactions described above to direct the assembly of nanoparticles is the magnitude of the dipolar interaction relative to thermal forces. The dipole strength, which characterizes the maximum dipole–dipole interaction between particles relative to thermal energy, is

$$\lambda = \frac{\pi\epsilon_0\epsilon_s|C|^2a^3E^2}{kT} \quad (1)$$

where C is the complex particle polarizability (or dipole coefficient), a is the particle radius, E is the field amplitude, and ϵ_s and ϵ_0 are the solvent dielectric constant and permittivity of free space, respectively. Thus, the dipole–dipole interaction diminishes quickly as the particle dimensions approach the nanoscale. Nonetheless, some success has been reported using electric fields and nanoparticles. Gong and co-workers employed polymer latex particles with diameters ranging between 200 and 450 nm to grow three-dimensional

colloidal crystals from solution.⁸⁷ Crystals were observed to nucleate from interfaces, such as air bubbles, which suggests that strong field gradients arising from the interface of high and low dielectric materials play an important role. One advantage of this is that such interfaces can be patterned, further directing the nucleation and growth of colloidal crystals from solution. Because metallic particles have a much stronger response to fields than their lower dielectric constant counterparts, directing the assembly of such particles with nanometer dimensions by means of electric fields is more straightforward. Hermanson and co-workers exploited this effect to fabricate micrometer diameter wires from solutions of gold nanoparticles with diameters between 30–45 nm.⁸⁸ The gold particles were drawn to the electrodes by strong dielectrophoresis in an AC electric field. As they concentrate, the particles self-assemble to form stable microwires (Figure 3a). These wires in turn alter the local electric field such that growth occurs at the wire tip. Much smaller gold nanorods have also been oriented using AC electric fields, which was reflected in the possibility of selectively exciting their longitudinal or transverse plasmon modes.⁸⁹

We have seen that, a large number of parameters can be used to control and tune particle interactions and subsequent self-assembly in AC electric fields, including field strength and frequency, particle shape, particle and solvent dielectric properties, and surface chemistry of the particles. Interactions can also be “programmed” more directly, by introducing patchiness in the particles or on their surfaces. Gangwal and co-workers recently described the assembly of metallodielectric janus particles in ac electric fields.⁹⁰ The particles consist of a polymer latex sphere with a hemispherical coating of gold. In the presence of an AC electric field, these metallodielectric particles assemble into unique chain structures, where the metallized halves of neighboring particles align in the direction of the applied electric field, while the dielectric halves alternate in the orthogonal direction, like an alternating pinnate leaf (Figure 3a). These staggered chains then assemble in various orientations to form two-dimensional metallodielectric crystals with structures that resemble an antiferroelectric phase. In a recent extension of this work, the same group demonstrated a stunning example of reconfigurable self-assembly using external fields.⁹¹ Substituting the gold layer with iron, the electric field assembly described above can be locked in by the permanent *magnetic* moment of the iron layer. Upon exposure to a demagnetizing field, the structure disassembles.

Overall, the use of external electric and magnetic fields remains of great promise and interest for directing the assembly of nanoparticles. The potential difficulty of using external fields to direct the assembly of particles as they reach nanoscale dimensions may be overstated. Note that eq 1 can be misleading to an

extent—the polarization mechanism determines the magnitude and frequency dependence of the dipole coefficient, C . In cases in which the polarization is dominated by the distortion of the electrostatic double layer surrounding the particles, the magnitude of C can become large because the charge separation length scale is no longer the particle radius, but instead on the order of the Debye screening length, which is large at low ionic strengths.⁹² This could potentially be exploited to drive the assembly of particles much smaller than eq 1 would lead one to believe. Finally, fields are easy to incorporate along with other forms of directed assembly, such as flows.

Flow Fields. Macroscopic viscous flows can be used to direct the assembly of a disordered suspension of particles into ordered crystals. A large body of work spanning nearly two decades shows that the application of a large amplitude oscillatory shear (LAOS) is particularly useful at ordering particles ranging in sizes from 100 nm to 1 μm .^{93–97} Similar to their repulsive and hard-sphere relatives, soft spheres also order in steady shear. Work with diblock copolymer micelles demonstrates the great promise for generating ordered structures of nanoparticles in the bulk.^{98,99} Shear rate and shear strain, particle volume fraction, particle interaction potentials, and polydispersity are factors that affect flow-induced ordering, and mechanistic insights have, for example, come from experiments on 2D monolayers.^{100,101} We refer the reader to the review by Solomon and Vermant,¹⁰² which discusses these factors in detail, as well as the proposed mechanisms of shear ordering from theory and simulation.

A significant disadvantage of steady or oscillatory shear to order nanoparticles is that high flow strengths are typically required, and once the flow is removed crystals melt back into disorder unless the concentration exceeds the equilibrium fluid-crystal phase boundary. For hard spheres, the particle concentration must exceed a volume fraction $\phi > 0.54$. In steady shear in particular, the ordered structure is dynamic and flowing, and therefore difficult to freeze in its crystalline state. However, the use of shear flows has been particularly effective for ordering glassy or jammed suspensions, when the particle volume fraction approaches the hard sphere glass limit ($\phi \approx 0.58$) or random close packing ($\phi \approx 0.64$). In these highly nonequilibrium and dynamically arrested states, flow provides an important mechanism for relaxation toward the equilibrium (ordered) structure.

Often nanoparticles are dispersed in a medium which has in itself a complex rheological behavior, for example, a polymeric matrix or a concentrated surfactant matrix. In those cases, flow will also induce anisotropic viscoelastic stresses which can in turn be used to direct self-assembly and lead to surprising features. For example, the presence of substantial normal stress differences in the sheared suspending media can lead

to the formation of both 1-D stringlike structures¹⁰³ and 2D-crystalline sheets¹⁰⁴ inside the matrix. For nonspherical particles, the presence of these anisotropic stresses in the sheared matrix fluids will lead to a complex cascade of orientational transitions,¹⁰⁵ which is for example important in CNT suspensions.¹⁰⁶ It is notable that flow does not always orient anisotropic objects in the flow direction, and for dilute systems the most uniform alignment is often found in the log-rolling state, with particles oriented orthogonal to the flow direction. The directed self-assembly of particles in complex fluids is an area which will need to be addressed in more detail in the future, as most industrial processes use (at least) a step where nanoparticle suspensions in a complex matrix are subject to flow and this may be exploited to generate specific structures.

Most flows encountered during processing are also more complex than the simple shear flows generated in the lab. For example, coating flows have become increasingly common means for directing the assembly of particles from dilute suspensions. Such flows generate ordered structures by way of the capillary, shear and elongational stresses that the suspension experiences, identical to ordering in bulk flows, but the concurrent process of solvent evaporation leaves an ordered intact structure deposited on the substrate. In its simplest form, “coffee ring” structures of particles remain when a drop of suspension is evaporated.¹⁰⁷ Coating methods that employ solvent evaporation are best suited to suspensions of hard or glassy particles, since soft particles form uniform (and potentially disordered) films as the solvent is removed, analogous to film formation from latex paints. However, even relatively soft particles, such as lattices below their glass transition temperature, can be deposited and used as a template. For instance, “inverse opals” can be created by using sol–gel chemistry or even nanoparticle dispersions, to fill the interstitial space between particles in a colloidal crystal of polymer latex spheres. Common methods include dip coating, flow coating (also referred to as convective self-assembly) and spin coating. Dip coating resembles the Langmuir–Blodgett deposition, and during vertical deposition particles are forced into ordered structures under the influence of the capillary forces leading for example to facile production methods for inverse opals¹⁰⁸ or, when aided by evaporation, the production of thin yet crystalline zeolite films.¹⁰⁹ More generally, the use of capillary-force-induced convective flows can be used to assemble particles in a variety of flow geometries.^{110–112} For example, a thin film can be generated by a thin blade, and the subsequent assembly of particles depends on an interplay between the driving capillary forces, solvent evaporation (to a smaller extent), and the suspensions properties (such as size distributions) (Figure 3b). The dominant parameters in convective self-assembly seem to be the deposition speed and the particle volume fraction.¹¹³ It has been

nicely demonstrated how these techniques can be combined with lithographic templates to achieve directed self-assembly of particles as small as 2 nm.¹¹⁴ An interesting route for the future is clearly to combine the specific features of the capillary interaction between nonspherical or chemically heterogeneous nanoparticles and the effects of convective assembly, which may be related to the recently reported assembly of gold¹¹⁵ or semiconductor nanorods,¹¹⁶ by evaporation of rather dilute dispersions.

Finally, classical techniques such as spin coating do offer the potential for creating ordered structures. Although this is an unsteady, nonuniform shear-dominated flow, large-scale fabrication of colloidal crystal/polymer nanocomposites has been reported.¹¹⁷ Shereda *et al.*¹¹⁸ showed that spin coating can be used to produce a spatiotemporal variation in the crystal order which is a universal function of the local reduced critical stress and the macroscopic strain. This should enable one to use spin-coating techniques in a predictive manner.

Self-Assembly at Liquid Interfaces. A number of routes are available to exploit liquid–liquid interfaces as templates for nanoparticle assembly. The dominating driving force for getting the particles to assemble at the interface is the reduction in interfacial energy, and the assembly is further controlled by lateral interface-mediated capillary forces of varying origin. Especially when the particles are nonspherical, dressed with specific ligands, or when using Janus-type particles, this has proven to be a very versatile tool for assembly. A recent review by Böker *et al.*¹¹⁹ gives a complete overview of the field, here we will only highlight a few aspects and point toward some more recent developments. Trapping particles at liquid–liquid interfaces has been known for over a century in so-called Pickering–Ramsden emulsions.¹²⁰ Even nanoparticles can become essentially irreversibly trapped at interfaces, with larger-sized particles being driven most effectively to the interface, as has been shown for specifically coated CdSe nanoparticles.¹²¹ Nonspherical particles, both prolate and oblate, will typically be forced to lay flat on the interface and only at high surface pressures will the particles be forced to “flip up”.^{122,123} Different orientation and packing structures of nanorods at the liquid–liquid interface can hence be generated by controlling the aspect ratio, surface properties, concentration, and solvent evaporation rates.¹¹⁹ For nonspherical particles at interfaces the shape also plays an important role, the undulations of the contact line give rise to a spatially dependent and shape-dependent interface mediated capillary force, which even for nanoparticles will dominate the interparticle interactions.^{124,125} These interactions drive assembly in preferred orientations, for example rodlike articles achieve an end-to-end registry of particle faces,¹²⁶ whereas charged ellipsoids can assemble into complex

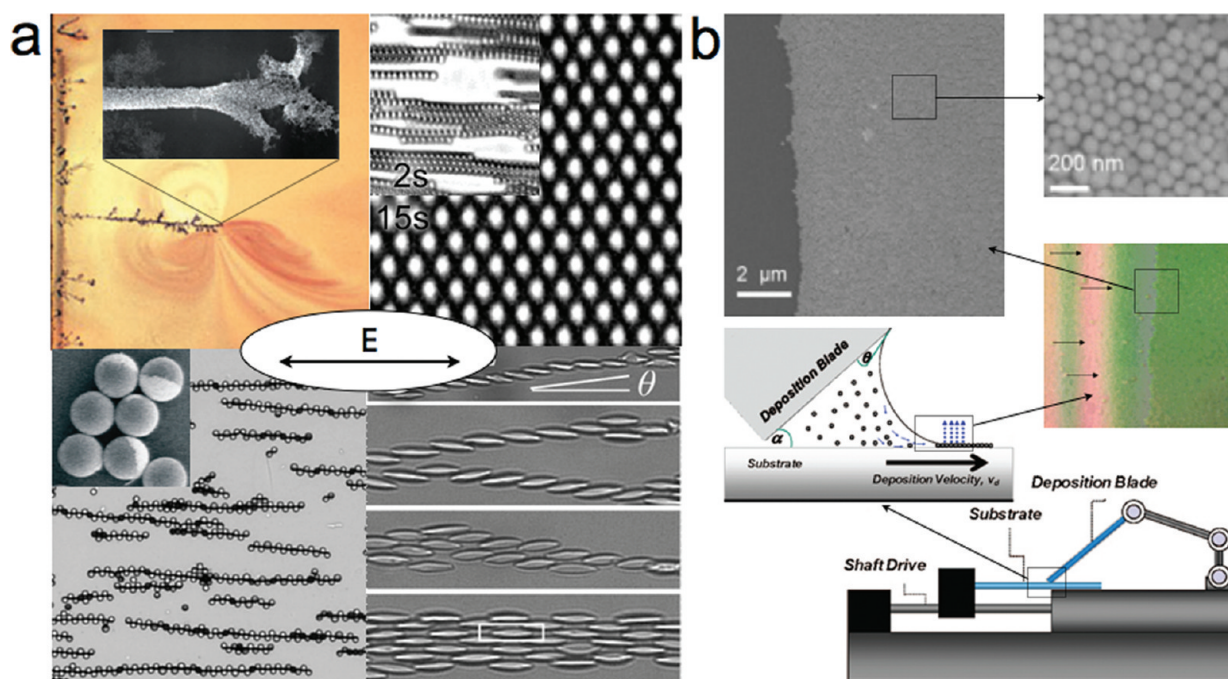


Figure 3. Directed assembly of particles in external fields (a), including the growth of microwires from gold nanoparticles,⁸⁸ assembly of micrometer-diameter colloidal particles into hexagonally close-packed arrays in AC electric fields,⁷⁵ assembly of metallo-dielectric janus particles,⁹⁰ and ellipsoidal particles.⁸⁴ (b) Flow-field induced self-assembly.^{110,111} Images reprinted with permission from the references as indicated. (a) Copyright 2001 AAAS; 2004 American Chemical Society; 2007 American Chemical Society; 2008 American Chemical Society; 2009 American Physical Society; (b) 2007 American Chemical Society; 2008 American Chemical Society.

triangular lattices as shown in Figure 4.¹²⁷ Self-assembly of bionanoparticles, such as rodlike viruses also reveals a complex interplay between electrostatic and capillary forces, with the easy formation of ordered structures with a variety of orientations.¹²⁸ These examples show how directed interfacial assembly is a versatile approach to achieve highly stable self-assembled structures. Mechanically stable membranes and capsules can be fabricated from such planar assemblies, by linking the particles through reactive organic molecules.¹²⁹ These nanoparticle membranes can actually retain their integrity when removed from the interface.

Several exciting developments in materials science exploit the self-assembly at interfaces in more complex designs. A clever method to generate novel materials is to induce phase separation in a solution or melt containing nanoparticles, with the newly created inter-phase sweeping up and assembling the nanoparticles. These materials, called “bicontinuous interfacially jammed emulsion gels” (Bijels)¹³¹ were originally proposed in simulations, but then also realized in the laboratory, and offer potential applications as scaffolds for novel gel materials¹³² and in polymeric matrices.¹³³ In particular, when Bijels are used with nonspherical particles, very interesting novel materials could be designed.

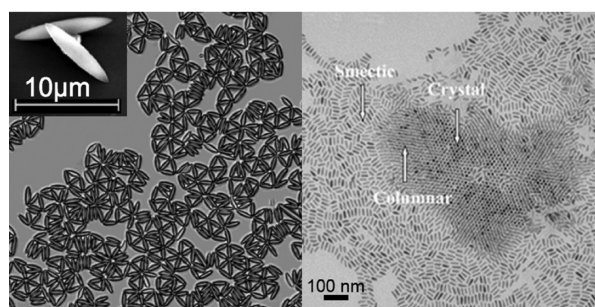


Figure 4. Two recent examples of capillary force driven self-assembly at liquid-liquid interfaces. (Left) Charged ellipsoidal particles assembling by shape-induced capillary interactions (see ref 127, image courtesy of Dr. D. Madivala). (Right) TEM image of a CdSe nanorod-stabilized water droplet after drying on a carbon-coated copper grid, revealing a hierarchy of ordered structures induced by the capillary forces that compress the interface during drying.¹³⁰ Copyright 2007 Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission. Wiley-VCH.

Combinations of Fields. Perhaps one of the most promising evolutions in the area of field-directed assembly is the way in which fields can be combined to guide nanoparticle self-organization. This retains the benefits of self-assembly—including scalability and elegant simplicity—while providing control over the ultimate structures that form, including orientation and defect density. An example of combined electric and magnetic fields was discussed earlier in the context of Janus particles, but several groups have also reported advances in the use of electric and magnetic fields combined with flow-directed assembly, such as dip coating or controlled evaporation. These studies make use of the external fields to control the orientation of anisotropic particles independent of the flow direction. For instance, Ding and co-workers recently demonstrated the fabrication of photonic crystals from magnetic ellip-

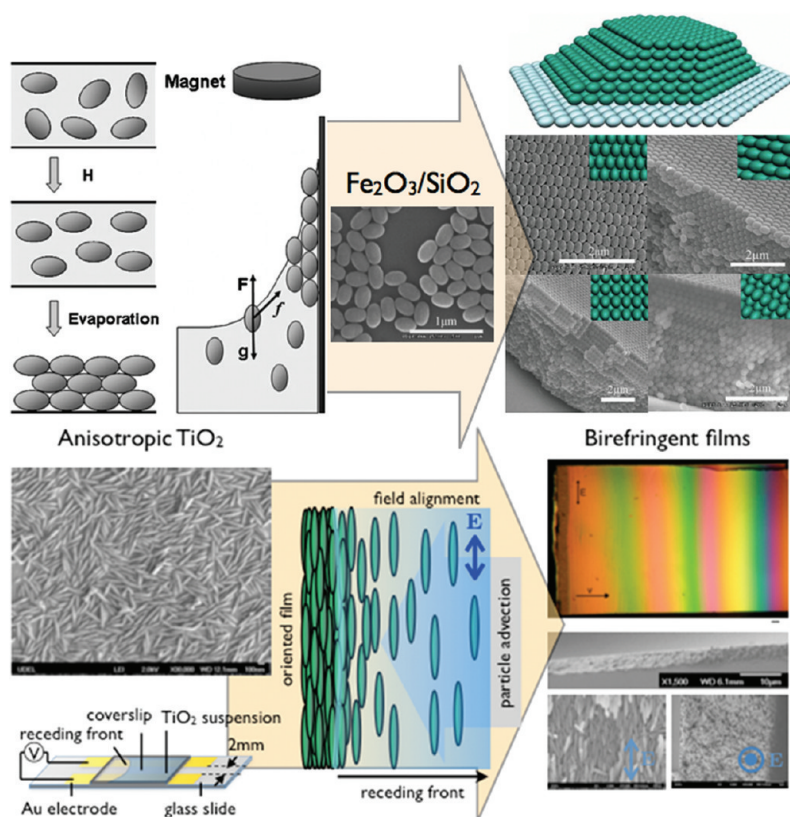


Figure 5. Two recent examples from ref 134 and 135 where the assembly of anisotropic particles was directed through the combination of fields and flows. Such ordered structures have novel photonic and mechanical properties. Reprinted with permission. Copyright 2009 Wiley-VCH Verlag GmbH & Co. KGaA.

soids with micrometer and submicrometer dimensions.¹³⁴ The ellipsoid orientation is controlled during the deposition by an external magnetic field, thus preventing particles from packing with random orientations as they are convected toward the drying front (Figure 5). Similarly, Mittal *et al.* recently used AC electric fields to orient ellipsoidal titania nanoparticles during a controlled evaporation deposition between two parallel plates.¹³⁵ The titania particles pack with a uniform orientation in the final film; furthermore, the orientation can be controlled not only by the field direction, but also the field *frequency* (Figure 5). This makes use of a well-known property that anisotropic particles with lossy polarizabilities exhibit several stable orientations in an external AC field due to multiple relaxation time scales set by the different characteristic particle dimensions (in this case, the equatorial and polar radii).¹³⁶ The effect is probably more prominent for electric fields, since the characteristic time scales of double layer polarization are significantly longer than the atomic-scale magnetization of magnetically active materials. A distinct advantage of controlling particle orientation by the field frequency is that the electrode geometry can remain fixed.

Overall, directed assembly by external fields enables precise control over the thermodynamics of assembly through a tunable order–disorder transition. Furthermore, the ability to pulse fields, and thus rap-

idly change the particle interactions, potentially leads to annealing methods that can be used to avoid jammed or kinetically frustrated states.

OUTLOOK AND CONCLUSIONS

In the preceding review, we broadly outlined several principal areas of directed self-assembly as they apply to nanoparticles. Self-assembly of nanoparticles refers to the process by which these material building blocks spontaneously self-organize, essentially through thermodynamic driving forces inherent to the system. The aim of this review has been to set the stage for what we define to be directed self-assembly of nanoparticles, a term which at first may be considered to be at odds with the concept of self-organization. However, a review of the literature demonstrates that directed self-assembly provides new tools for a tailored, bottom up approach to material design. Two key ideas emerge: first, that self-assembly of nanoparticles can be guided by tailoring the intrinsic characteristics of nanoparticles. Such “internally” directed self-assembly includes altering the particle interactions such that they are directional, for example, changing the particle shape, providing, for instance, a tendency toward localized structuring, or by introducing “patches” that focus interactions between particles. The other distinct concept of directed self-assembly of nanoparticles comes in the form of external direction, which utilizes electric

fields, magnetic fields, or macroscopic deformation (flow) to induce and guide self-assembly. In all, the power of directed self-assembly increases when these modes are combined. Internal and external directed self-assembly use changes in particle characteristics to exploit or enhance field responsiveness. For instance, anisotropic particles couple to external fields to align them at concentrations that would thermodynamically exist as isotropic solutions, while janus or patchy particles can be synthesized that tailor polarization interactions. Similarly, external fields can be combined, especially flow and fields; for instance, whereas capillary-driven assembly would lead to the formation of isotropic assemblies of anisotropic particles, an electric field can be used to guide the assembly into oriented, and ultimately transitionally ordered structures.

Looking forward, a major challenge for nanoparticle assembly is the lack of metrology to characterize the kinetics and structures *in situ* during the assembly process. The majority of work to date, particularly in field-driven assembly, has used micrometer-sized particles, partly due to the relative ease in which the developing and final structures can be monitored and quantified (for instance, using bright-field or confocal microscopy.) Although optical properties, such as birefringence, can provide limited structural information, *in situ* metrology of nanostructured materials formed by directed self-assembly will likely require fast subdiffraction microscopy techniques or time-resolved neutron or synchrotron X-ray scattering resources to be further developed. Such resources have proven highly effective in areas such as flow-induced crystallization of suspensions, by enabling researchers to characterize the effects of shear strain and shear rate on the disorder-to-order transition, for example. An important aspect that is reflected in this review is the convergence of techniques and concepts from both below and above toward the nanoscale, which can be implemented as soon as one understands the changes in the forces involved at each size regime. Therefore, multidisciplinary efforts will be required to fully implement these techniques and achieve a real control over the assembly and functionality of nanoparticles, for integration in devices.

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