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Janus Particle Synthesis, Assembly, and Application

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ABSTRACT: Janus particles are colloidal particles with more than a single type of surface chemistry or composition, ranging in size from hundreds of nanometers to a few micrometers. Like traditional colloids, they are large enough to be observed under optical microscopy in real time and small enough to diffuse by Brownian motion, but their interesting and useful new properties of directional interaction bring new research opportunities to the fields of soft matter and fundamental materials research as well as to applications in other disciplines and in technologies such as electronic paper and other multiphase engineering. In this review, a variety of methods that have been used to synthesize Janus particles are introduced. Following this, we summarize the use of Janus particles as basic units that assemble into novel structures and tune important material properties. The concluding sections highlight some of the technological applications, including recent progress in using Janus particles as microprobes, micromotors, electronic paper, and solid surfactants.



1. INTRODUCTION

Colloidal particles are a unique type of material class defined by their size, usually hundreds of nanometers to a few micrometers in diameter. They are ubiquitous in our everyday life, dating back to ancient times, with examples including some that are useful (pigments, milk, modern personal care products, and the like) and others that are undesirable (soot and particle pollution, for example). From a scientific point of view, they bridge the realms of microscopic particles and macroscopic objects by capturing the essence of both: they are small enough to be agitated by thermal energy yet large and slow enough in their Brownian diffusion to be observed by optical microscopy in real time. Dominant interactions in colloidal systems, such as electrostatic, van der Waals, and dipolar interactions, govern the system behavior in a similar manner as they would do in atomic and molecular systems.

What is new regarding these materials, whose existence and usefulness have been known for so long? Colloidal particles have been used as model systems to study fundamental problems in condensed matter[1] because colloidal systems obey the same thermodynamic rules as do atomic and molecular systems, though at a conveniently longer time and length scale for observation. This is an advantage because it is very difficult to observe ultrafast dynamics in molecular systems. Janus particles, named after the Roman god Janus, present a relatively new concept in this field. It was first popularized by Pierre-Gilles de Gennes in his 1991 Nobel Prize lecture.[2] It did not attract much attention until roughly 15 years later, but since that time, interest has burgeoned, increasingly so from year to year. In the original vision, de Gennes imagined a new kind of surfactant: amphiphilic colloidal particles with two different faces, one polar and the other one nonpolar. Like any traditional surfactant that adsorbs to a liquid interface, the amphiphilicity would stabilize the interface yet allow the skin to "breathe" through interstices between these particles. Today, the science and engineering communities have broadened this vision and have proposed many additional interesting questions and potential applications. Because the definition of Janus particles captures a broad vision, many micro- and nanosized particles possessing anisotropic properties are labeled as Janus.

In this Instructional Review, we introduce the extended family of Janus particles, with a focus on the synthesis, self-assembly, directed assembly and applications of hard colloidal particles akin to the original definition of Janus particles with well-defined faces. Janus particles in this group can be amphiphilic (hydrophilic on one side and hydrophobic on the other) or dipolar (anionic on one side and cationic on the other), or they may possess other asymmetric properties. Within this framework, first we introduce a variety of techniques that have been used in the synthesis of Janus particles, discuss their merits and limitations, and then move on to the important role that Janus particles can play in the bottom-up engineering of new and smart materials as well as in studying nonequilibrium phenomena in soft matter physics. In a later section, we will briefly introduce other anisotropic and patchy particles and conclude this review with the potential applications of Janus and patchy particles in other fields of research and in applied technology. Theoretical and simulation developments in the field have also been fruitful[3−5] but are not a focus of this tutorial. More comprehensive[6−8] and more

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specialized[9−15] reviews of Janus and anisotropic particles are recommended to interested readers. Those reviews cover subjects not treated here, including but not limited to the synthesis of polymeric Janus and multicompartment particles, theoretical models for studying Janus particles, design rules of anisotropic colloidal assembly, and external field control of Janus and anisotropic particles.

2. SYNTHESIS OF JANUS PARTICLES

Since the first synthesis of Janus particles in 1988,[16,17] a large variety of synthetic methods have been developed to contribute to the thriving growth of Janus particle research. Regardless of the various materials and techniques that are employed, the synthesis of Janus particles can be classified into two categories: surface modification and compartmentalization. Surface modification methods render isotropic particles anisotropic on the surface, whereas compartmentalization methods build Janus particles from scratch and the synthesized particles are anisotropic in composition.

2.1. Surface Modification. Because so much is already known about the synthesis of nano- and colloidal particles with isotropic surface chemistry, Janus particles are derived from surface modification schemes of isotropic particles. The main idea in surface modification is to protect part of the initially homogeneous particle and modify the unprotected part. This is usually realized by using masks, templates, and geometric constraints imposed by neighboring particles, sometimes combined with the development of physical vapor deposition and lithographic techniques. An iconically perfect Janus particle would be strictly composed of two perfect hemispheres, but under many circumstances, it is desirable to have unequal areas of these two patches. With differing definitions when it comes to details of the definition, the anisotropy of Janus particles is often referred to as Janus balance.[18−21]

2.1.1. Controlled Modification at Interfaces. Two-phase interfaces, including air−liquid,[22] liquid−liquid,[23] and solid−liquid,[24] are the first generation of masks that enable the selective treatment of otherwise isotropic particles. In the first creation of amphiphilic Janus particles,[16] Casagrande and Veyssié protected one hemisphere of commercial glass beads with a cellulose varnish to keep it hydrophilic and treated the other side with octadecyltrichlorosilane so that it becomes hydrophobic as a result of the coverage of aliphatic chains. Over ensuing years, the reaction of the silica surface and silane has continued to be one popular surface modification option to generate the desired surface chemistry, especially when taking advantage of the versatility of incorporating different functional groups located at the terminus of the silane molecules. Other less general reactions can also be used to modify the surface if the particle surface itself houses certain reactive residues. For example, part of the particles can be deactivated so that only the rest of the particle with activated ester moieties reacts with IgG proteins.[25]

However, the two-phase interface can mask and expose only a single layer of particles for modification, which significantly limits the number of particles being treated. Therefore, this method was capable of generating only a small quantity of Janus particles, until the recent use of emulsions to generate interfaces for masking. Emulsions of two immiscible liquids increase the area of the interface greatly and open a door to synthesizing Janus particles in large quantities. This has been done at the liquid−liquid interface,[26] where spherical silica particles are dispersed in a mixture of water and immiscible organic solvent and are partially modified by the reaction of their surface hydroxyl groups with an alkylsilylation agent, which also has been done at the liquid−solid[24] and air−solid interfaces,[27] where a wax droplet with particles adsorbed to its interface can be separated by solidifying paraffin wax at an appropriate temperature, as shown in Figure 1. The fraction of the modified area can be further tuned by adding surfactants to the emulsion so that the contact angle of three phases (water/oil/particle) is controlled.[19]

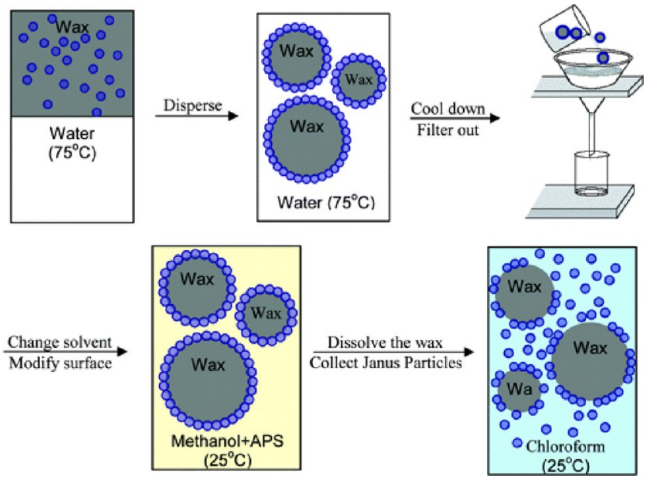


Figure 1. Controlled modification at interfaces. Schematic illustration showing Janus particle synthesis by functionalizing particles adsorbed to a solidified water−oil emulsion. Adapted with permission from ref 27.

The restrictions of these interface modification methods include the limited number of reactions that are available for modification and the lack of precise control of the modification area due to the fluctuations of interfaces and diffusion of modifying reagents, especially for particles of smaller size. The particle shape is generally limited to spherical if one wishes to have controlled modification because the orientation of particles of other shapes at the interfaces may be hard to define. Although a solvent-free method has been described,[27] the clean separation of modified particles from the masks and modification reagents can still be improved.

2.1.2. Physical Deposition. As an alternative method of surface modification, physical deposition using electron beam evaporation or sputter coating allows more geometric freedom to design Janus particles. The geometry of modification is controlled by the nature of the deposition technique, with the use of real or virtual masks, including the mutual shadowing effects from nearby particles.[28] For example, with directional coating by electron beam evaporation of a monolayer of colloidal particles, Janus particles can be coated with metals or other materials in a precise half−half geometry.[29] A special case of directional coating is the so-called glancing angle deposition, usually aided by shadowing effects from neighboring particles. This allows the shape and area of the coating to be controlled by changing the incident angle of deposition,[30] as shown in Figure 2A. It also offers the possibility to synthesize particles with more than one patch by using sequential deposition[31] and/or elaborately designed masks.[28] To improve resolution, one masking technique has filtered the deposition beam through the interstices of different stackings of particles, improving the deposition spatial resolution to a fraction of the

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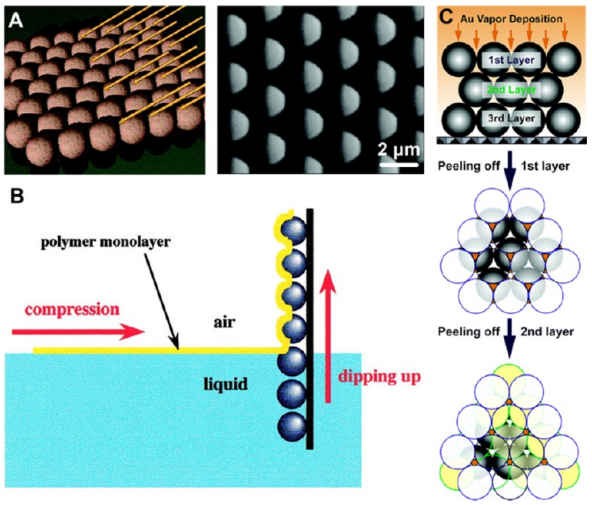


Figure 2. Synthesis of a Janus particle based on physical deposition. (A) Glancing-angle deposition based on the shadowing effect from neighboring particles. The patch size and shape depend on the incident angle of directional coating. Adapted with permission from ref 30. (B) Schematic procedure of asymmetrical microsphere preparation by the LB technique. The copolymer monolayers were transferred to the monolayer of microspheres to modify part of the particle surface. Adapted with permission from ref 22. (C) Schematic illustration of the procedure to create colloidal spheres with Au-patterned surfaces by the combination of Au vapor deposition and using the top mono- or bilayers of colloidal crystals as masks. The orange spots represent Au domains remaining on spheres after removing the first and second sphere layers. Adapted with permission from ref 32.

particle size. Very complicated patches can be deposited onto particles using this approach (Figure 2C).[32]

The deposition of conductive or magnetic materials onto particles renders them susceptible to electric and magnetic fields. On the other hand, coating can also enable further modification. If special surface chemistry properties are desired, then modifications often require more than one step in a sequence of procedures. With the defined geometry of single or multiple patches on particles, further modification toward site-specific interactions can be performed to render the particles functional at selected sites in various ways. This step requires the modification reaction to specifically occur only at selected sites. In addition to the widely used silane species that reacts exclusively with oxide surfaces, another versatile reaction for surface modification is the specific bonding between gold/silver and thiol-terminated molecules.[33] The availability of functional groups on thiol-terminated molecules is broader than for silane molecules; for example, there exist thiol-terminated DNA and thiol-terminated biotin/avidin, facilitating specific bonding reactions between modified particles so that particles interact only with their counterparts by design. Surface modification can also be performed using microcontact printing, in which case inks are transferred to substrates by selective contact with masks loaded with inks. For example, particles can be printed by picking up "polymer ink" using the Langmuir−Blodgett technique (Figure 2B)[22] or using a PDMS mask with ink that can be transferred to particles to which it adheres by either chemical or physical interactions.[34]

The physical deposition technique can be applied to particles of other shapes, ellipsoids or rods,[35] for example. Nevertheless, the main drawback of this method is still the limited quantities of particles produced because the deposition works only on particle monolayers. When one seeks to apply the method using multilayers of particles as masks, the separation of differently coated particles is a stiff challenge.

2.1.3. Electrochemical Deposition. Recently, a surface coating technique to produce Janus particles in the bulk using bipolar electrochemistry was developed by Kuhn et al.[36] In contrast to previous techniques, not only is the surface modification implemented in bulk rather than at the interface so the quantity of output is not limited but also there is no need for masks. The asymmetry in this method is introduced by the polarization of conductive particles generated by the applied electric field. With appropriate metal salts in aqueous solution, a sufficient potential difference drives the electrodeposition of metal onto the cathodic poles of the particles (Figure 3). With

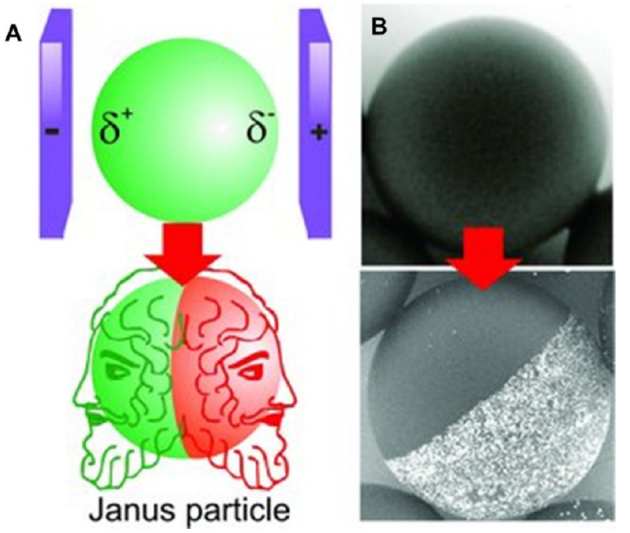


Figure 3. Bipolar electrodeposition for the synthesis of Janus particles. (A) Principle of bipolar electrochemistry: sufficient polarization of a conducting particle allows the geometrical symmetry to be broken. (B) SEM images of glassy carbon particles before and after bipolar electrodeposition. The particle diameter is around 20 μm. Adapted with permission from ref 36.

added gelating agents to increase the viscosity of the solution, particles are prevented from rotating during the reaction time so that electrodeposition takes place only on the cathodic side of the particle, thus rendering the particle Janus. This can also be used to modify particles of other shapes, and immobilization is not as strong a requirement as for spheres because particles of other shapes adopt a preferential orientation (usually the major axis) when polarized in the electric field.

This method produces large quantities of Janus particles with a precise two-face boundary and can deposit different materials, including gold, platinum, nickel, copper, and even inorganic and organic polymer layers[37] onto a wide range of particles of different sizes and shapes. One limitation is that the particles have to be made of conductive materials. Because of the difference in growth mechanisms, chemically deposited metal layers are not as smooth as for a physically deposited metal film. In fact, they are intrinsically flawed with copious defects and cracks. Discontinuous islands of metal can be seen in the SEM images in Figure 3 and have been discussed in a different context[38] in which the mechanism for active particle swimming in a solution containing fuel was differed according to whether

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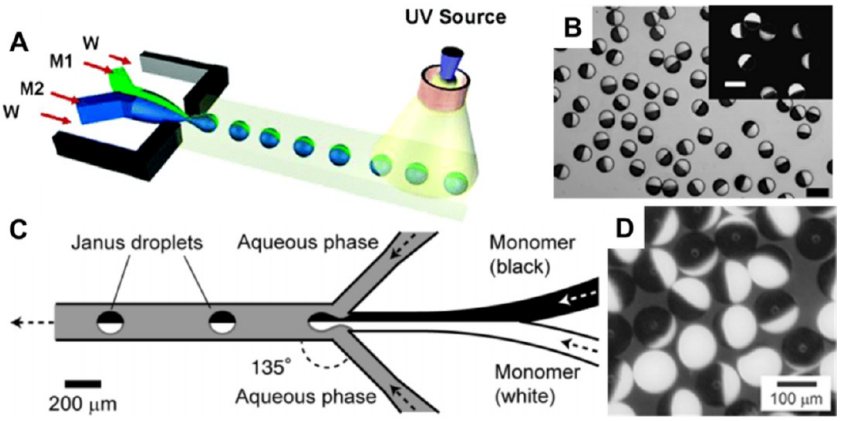


Figure 4. Synthesis of Janus particles with a microfluidic device. (A) Schematic illustration of the generation of Janus droplets from immiscible monomers M1 and M2, emulsified in an aqueous solution of SDS (W). The droplets are irradiated with UV light in the downstream channel. (B) Optical microscopy images of Janus particles. Bright and dark phases are polymers of M1 and M2, respectively. The scale bar is 100 μm. (A) and (B) are adapted with permission from ref 44. (C) Schematic illustration of the channel and flow configuration for bicolor Janus particle synthesis. (D) Monodisperse bicolored polymeric particles. (C) and (D) are adapted with permission from ref 45.

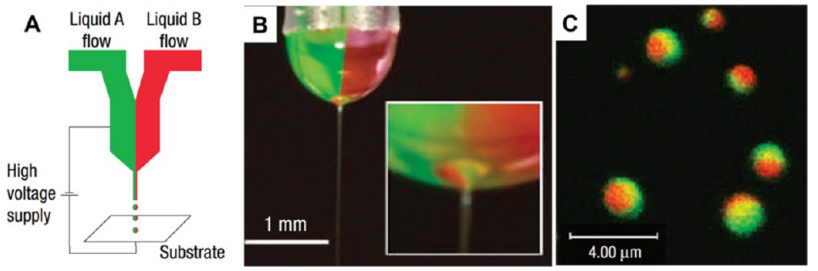


Figure 5. Biphasic electrified jetting using side-by-side dual capillaries. (A) Schematic diagram of the experimental setup used for electrohydrodynamic processing. (B) Digital image of a typical biphasic Taylor cone with a jet of PEO solution. (C) Confocal micrographs of biphasic particles shown in the fluorescence emission range of FITC and rhodamine B. Adapted with permission from ref 40.

Janus particles were produced by chemical or physical deposition.

2.2. Compartmentalization. In addition to the surface modification method, in which only part of the surface of otherwise isotropic particles is selectively modified, efforts have been made to synthesize particles with two or more compartments. These particles are Janus not only on the exterior but also in the interior. Depending on the synthesis technique, a wide range of combinations of different compartments are available, broadening the potential function and application of these particles. Various methods to synthesize Janus particles with more than one phase have been developed, including microfluidic[39] and electrohydrodynamic[40] cojetting, chemical synthesis,[41,42] and polymer self-assembly.[43] These methods may have fundamentally different mechanisms and foci, with their own merits and drawbacks, unified only by the fact that multiple separated compartments are contained in a single particle.

2.2.1. Microfluidic Coflow. Janus particles or biphasic particles can be synthesized using microfluidic coflow systems, in which two different liquids are forced to flow side by side without mixing and then are jetted to form droplets containing two distinct sections, which are then polymerized or cross-linked into solid particles upon UV radiation[44] (Figure 4A) or thermal polymerization,[45] as seen in Figure 4. It is important to keep the two different phases separated. This is usually done by controlling the fluid flow to remain in the laminar regime so that they flow in parallel and retain a sharp boundary.

Developed by Takizawa et al.,[45] the microfluidic channel used to produce Janus particles is a coflow system with a Y-shaped channel to construct a two-phase monomer stream and a sheath-flow geometry to form a neck so that the organic stream penetrates the coflowing aqueous stream and discharges Janus droplets (Figure 4). To obtain bicolored particles, black and white monomers are prepared by dispersing carbon black and titanium oxide pigments, respectively, in isobornyl acrylate (IBA). The two-color stream is introduced into the Y junction, and the aqueous stream surrounding it is loaded with steric stabilizer poly(vinyl alcohol) (PVA). Other surfactants such as sodium dodecyl sulfate (SDS) are also used for different monomers.[44]

After the droplet forms, rapid polymerization is necessary to minimize the mixing of two phases by diffusion. In ref 45, this is done by pouring the generated droplet solution into a hot bath and allowing the droplet to solidify in 20 s. Alternatively, the monomers can be preloaded with photoinitiator so that the droplet can be rapidly polymerized by exposure to UV light.[44] Microfluidic reactors have been shown to be a new way to synthesize a variety of versatile Janus or multiphase particles with good monodispersity, unique properties, and potential applications. The functionalization of these particles can be realized by loading conductive or magnetic nanoparticles for specialized applications.[46] So far, however, Janus particles prepared with this method are relatively large, around 100 μm in size. Low yield is another problem because the flow rate is slow to avoid mixing different phases by convection.

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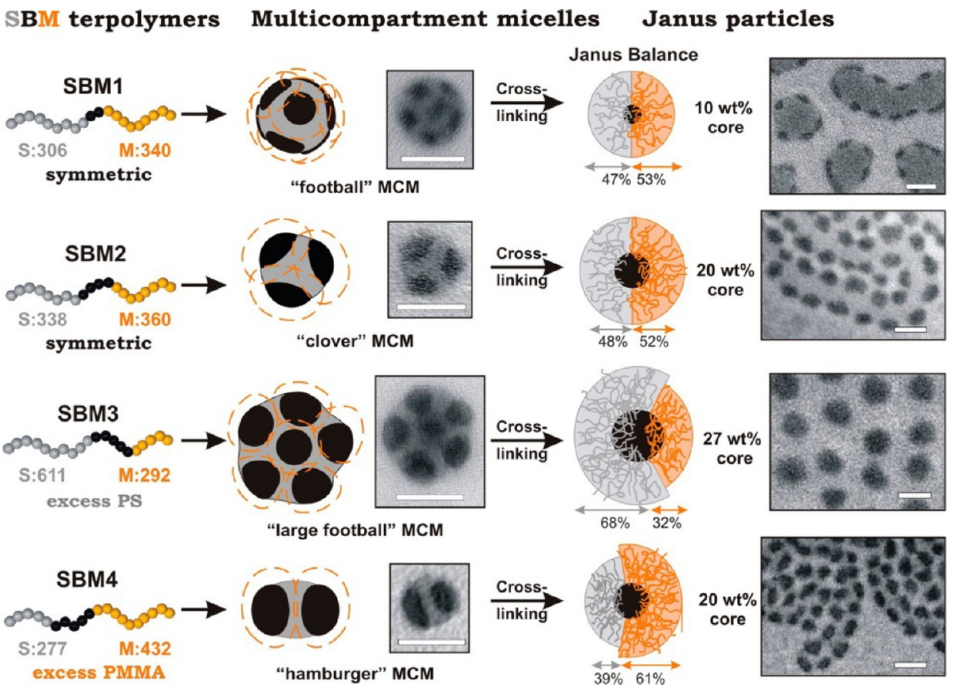


Figure 6. Synthesis of Janus particles with tunable core size and Janus balance from multicompartment micelles, with illustrations and TEM images. Scale bars are 50 nm. Adapted with permission from ref 18.

2.2.2. Electrohydrodynamic Cojetting. Similar to the microfluidic reactor, droplets of more than one composition can also be obtained by electrohydrodynamic cojetting, a process in which electrohydrodynamic forces are involved to manipulate polymer solutions.[40] When exposed to a strong electric field, the shape of a small volume of electrically conductive liquid starts to deviate from its natural shape determined by surface tension alone and forms a cone shape with a rounded tip. The cone is further deformed and emits a jet of fluid when the electric field is increased to pass a certain threshold. If the voltage increases further, then additional modes of droplet disintegration can be observed.[47]

The essence of the experimental setup is to generate Janus particles in side-by-side laminar flow of two or more different polymer solutions passing through a modified nozzle opening,[40] as shown in Figure 5A. With a high voltage (5−15 kV depending on the jetting conditions) applied, liquid jets of submicrometer size are emitted from the Taylor cone at the tip of the nozzle due to the electrohydrodynamic forces. Discontinuous droplets or continuous fibers can form depending on the surface tension and viscosity of the fluid. During the stretching process, if the solvent evaporates completely, then only particles of nanometer to micrometer size are left on the collecting electrode; with poly(ethylene oxide) (PEO) and poly(acrylic acid) (PAA), particles as small as 170 nm can be obtained. The stable droplet shape can be predicted according to the criterion of minimization of surface tension, but an intermediate unstable shape may be fixated if solidification starts before the droplet reaches its final shape. The solvent loss and fluid relaxation during the electrohydrodynamic processing further complicate the final result.

This experimental setup can be easily adapted to more than two capillaries running in parallel at the laminar flow rate, and using this approach, particles with additional distinct compartments can be obtained.[48] Important parameters include the applied electric field, polymer molecular weight, polymer concentration, flow rate, viscosity, and conductivity. A large variety of particle shapes, sizes, and properties can be achieved. Surface and bulk functionalization are readily accessible by using polymers with different functional groups and by mixing other molecules in the polymer solution. Because the bulk property is asymmetric, particles prepared in this way can undergo shape change in response to external stimuli. This attractive feature, not possible for particles prepared by surface modification, has been demonstrated by Lahann et al.[49]

Nonetheless, this technique does prefer the use of aqueous solution because the spontaneous formation of vortices is difficult to avoid with organic solvents that have lower viscosity and conductivity. This not only limits the choice of polymers but also demands further cross-linking because the polymer particles are mostly water-soluble. As for most other techniques, shape control and monodispersity are inevitably compromised if smaller particles are desired.

2.2.3. Direct Bulk Synthesis. Janus particles with two distinct parts can also be synthesized in bulk solution from molecular or polymeric precursors such as heterodimers[23,41] and Janus micelles,[50] either through selective nucleation or polymer self-assembly. Many are on the lower end of particle size, on the order of 100 nm, and can be observed only under electron microscopy (SEM or TEM). Au-SiO_2 heterodimers have been synthesized by Chen et al.[41] with silica selectively grown on part of the gold nanosphere as a nucleation site. This worked as follows: the competitive coordination of the two incompatible ligands (PAA and MPAA) in a propanol−water solution created asymmetric functionalization on the surfaces of gold nanocrystals as a result of the segregation of different ligands. Because silica nucleation was inhibited by PAA, subsequent silica growth takes place only on the surface of gold spheres covered by MPAA.

Block copolymers with segments displaying dissimilar properties are able to self-assemble into nanoparticles with defined compartmentalization driven by the thermodynamics of

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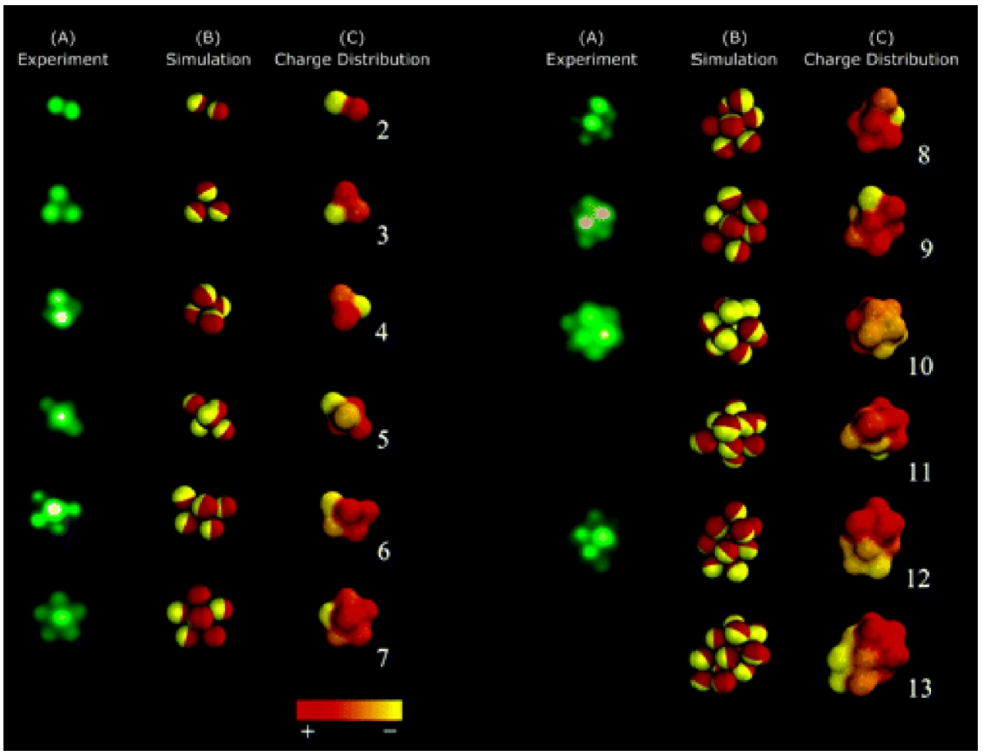


Figure 7. Comparison of experimental epifluorescence images and Monte Carlo computer simulations of the self-assembled structures of particles with nearly equal positive and negative charges on the two hemispheres. Adapted with permission from ref 29.

polymer mixtures. Soft Janus nanoparticles with a tunable Janus balance can be produced upon cross-linking of compartments within precisely defined multicompartment micelles that are self-assembled from triblock copolymers. As shown in Figure 6, M blocks serve as a stabilizing corona radiating from B compartments, riding on the core composed of S. Janus particles with two phase-separated hemispheres of S and M and a core of cross-linked B are obtained. Parameters such as the molecular weight, concentration, temperature, and ionic strength in some cases have different effects on different blocks, thus allowing one to control the synthesis of these soft Janus and multiblock particles.[18,51]

Using these methods just described, Janus particles of less than 100 nm in size can be synthesized with good scope to tune the particle composition and resulting properties. In addition, nearly spherical Janus particles and peanut-shape Janus particles, up to a few micrometers in size, can be synthesized with good uniformity in the bulk using dispersion and seeding polymerization methods. These approaches usually go through a two-step process: first the seed particles are synthesized by dispersion polymerization, and then the seed particles are swollen by a different[52,53] (or the same[54]) type of monomer so that they phase separate and can be polymerized to form a second lobe. This method also offers attractive flexibility regarding choices and the intentional design of the materials and properties of the two lobes.[52−54]

3. SELF-ASSEMBLY AND DIRECTED ASSEMBLY OF JANUS PARTICLES

Janus particles are useful in self-assembly because their interactions are more complex than for two isotropic particles: interactions depend not only on the separation in distance but also on mutual orientation. These considerations demand that one confronts a new problem of particle assembly: even at the same overall particle−particle separation, two particles have options of how to interact, depending on how they orientate relative to each other. For example, amphiphilic molecules such as soap molecules and phospholipids are Janus when one bears in mind that their polar hydrophilic headgroups and nonpolar hydrophobic tails are fated to remain part of the same molecule. This leads to the assembly of micelles and membranes that are vital for cells and numerous biological functions in the aqueous environment. In a similar spirit, the two faces of a Janus particle respond to external fields differently when they are placed in an electric field, magnetic field, chemical gradient, or temperature gradient. This leads to surprisingly rich emergent behavior and allows one to tune the properties and functions of materials assembled from these building blocks. Such spontaneous assembly of small elements into larger-scale structures is an important bottom-up approach to designing new materials with desired properties. In this section, we will focus on how colloidal Janus particles that are large enough to be observed with optical microscopy assemble into superstructures driven by interactions or external fields.

3.1. Self-Assembly. To emulate the assembly of atoms into molecules but without the intricacies of chemical bonds, the community of colloid scientists is interested in colloidal molecules. In this context, computer simulations of colloids with anisotropic interactions show the potential of working with particles whose surfaces have more complex patch structures than just hemispheres. For example, particles with four patches could emulate the tetravalent bonding of carbon atoms, which hold the potential to assemble into photonic bandgap materials.[55]

3.1.1. Assembly of Oppositely Charged Dipolar Janus Particles. A particle with two hemispheres possessing opposite charges can be seen as a dipolar Janus particle. In one early

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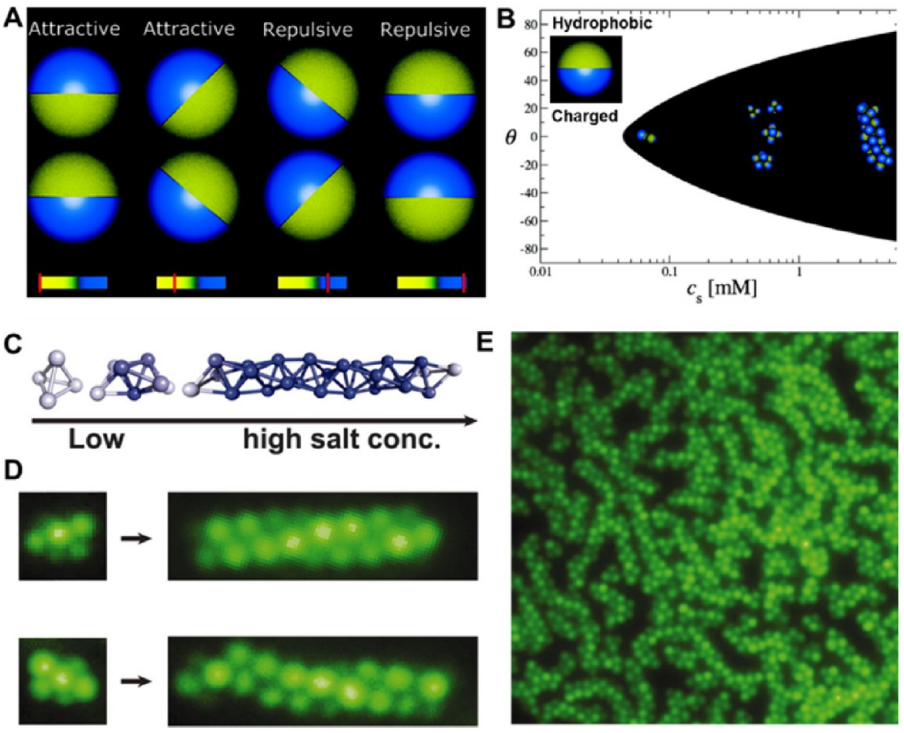


Figure 8. Self-assembly of amphiphilic Janus particles. (A) Pairs of Janus particles in water, each hydrophobic on one hemisphere and charged on the other. The interaction potential switches from attractive to repulsive at different relative orientations. (B) Region of permitted tilt angles between two charged hemispheres with 1 μm diameter held at a center-to-center distance of 1.02 μm, plotted as a function of the concentration of monovalent salt. (A) and (B) are adapted with permission from ref 33. (C) Geometric representation of helix growth by face-sharing tetrahedra. (D) Comparison of a small chiral cluster (3.8 mM NaCl) and a longer helical cluster (5 mM NaCl). (E) Fluorescent image illustrating the stability of wormlike structures at high volume fraction. (C)−(E) are adapted with permission from ref 56.

study,[29] Janus particles were synthesized by the directional coating of carboxylate-modified polystyrene particles by electron beam evaporation such that one hemisphere of the particle was coated with 2 nm of Ti as an adhesion layer and subsequently 15 nm of Au. Further functionalization using thiols with positively charged amine groups rendered the Au-coated hemisphere positive, and the uncoated hemisphere remained negatively charged. The positive and negative charges were almost balanced in magnitude, as confirmed by the nearly zero ζ-potential. The assembly experiments were conducted in PBS buffer (pH 6) at 1 mM ionic strength, in which the Debye screening length was approximately 10 nm, much less than the particle size (1 μm or larger). This ensured short-range interaction so that there was no large aggregation due to long-range attraction.

The assembled structures were mainly clusters in a dilute particle suspension, as illustrated in Figure 7. This differs from the chain and ring structures characteristic of magnetic and electric dipoles, partly because the dipole approximation is poor for large particles whose charges reside only on the surface. Because of the reduced symmetry in these Janus particles, the structure of larger clusters (for particle number N = 6, 11, 12, and 13) was highly asymmetric and different from that of the stable clusters predicted mathematically for densely packed isotropic particles. For N = 2, 5, 7, dipolar Janus particles assembled into the same cluster shapes as did isotropic particles. With the advantage of monitoring the kinetic process using real-time imaging, it was shown that dipolar particles first assemble into clusters and then the clusters tend to merge on the time scale of seconds to minutes. In addition, the defects in structures can be self-corrected during this annealing process. This indicates that the interactions involved are relatively weak, on the order of 5−10 k_BT (k_B is Boltzmann's constant) as estimated from simulations.

This bipolar functionality may be generalized to other shapes and extended to multipolar particles with more than two patches. In addition, it is intriguing to note that asymmetric charge distribution has been proposed, on the basis of experiments, to explain the aggregation of some proteins. Thus, these model particle systems may have some relevance to proteins and other more complex particles where the surface charge distribution is similarly patchy.

3.1.2. Assembly of Amphiphilic Janus Particles. Janus particles can also be amphiphilic: hydrophobic on one face and charged (thus hydrophilic) on the other. These Janus particles were synthesized by octadecanethiol modification after gold coating on one hemisphere, so the alkyl chains on one hemisphere rendered the surface hydrophobic.[33,56]

The anisotropic geometry of amphiphilic Janus particles is similar to that of dipolar particles, with different interactions that lead to distinctly new varieties of assembly. In water, the interactions between particles are dominated by hydrophobic attraction when the hydrophobic hemispheres face each other and by electrostatic repulsion when two charged hemispheres face one another, as shown in Figure 8A,B. Because the hydrophobic interaction is entropic in origin and insensitive to or weakly dependent on the ionic strength, whereas electrostatic interaction depends strongly on ionic strength, the interaction governing the assembly in this case can be seen as follows: at very low ionic strength, electrostatic repulsion is so strong that the particles strongly repel each other regardless of the orientation, but repulsion weakens significantly when the

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Debye length (electrostatic screening length) becomes smaller at high ionic strength so the particles can attract each other via hydrophobic interactions. In a dilute suspension, with increasing ionic strength, two Janus particles first orient in a strictly opposite direction (head to head) so that their hydrophobic faces are in close contact, and then the orientational freedom allows additional particles to be attracted. For this half−half geometry, the assembly of Janus particles follows two constraints: first, particles must approach sufficiently close to experience hydrophobic attraction; second, the maximum number of nearest neighbors is six because of the reduced symmetry of having attraction at one hemisphere only.

Observed under an epifluorescence microscope,[56] the use of particles with 1 μm diameter allowed individual particles to be resolved. At a relatively low salt concentration, the clusters were similar to those formed for homogeneous particles, with a size range of $N = 2-7$. Aggregation of these clusters was prevented by electrostatic repulsion between the charged surface regions, allowing clusters to reside in close proximity without coalescence. Long-range repulsion was reduced further by increasing the salt concentration, which allowed the growth of striking Boerdijk-Coxeter helical structures (Figure 8D).

Controlling the Janus balance, which is the size of the interacting patch, is a method to tune the interaction and the structures produced. The size of the hydrophobic patch determines the number of nearest neighbors that one particle can have by analogy with the bonding of atoms into molecules, and it can be interpreted as the "valence" of Janus particles. In this sense, the valence is 12 for an isotropic particle, 6 for a half−half Janus particle, and even less for a Janus particle with a smaller hydrophobic patch. Moreover, this geometric rule may be generalized to colloidal attractions that are short-ranged relative to the particle size, regardless of the form of the potential, provided that the same geometric constraints are ensured. Using this valence rule, monodisperse colloidal tetrahedra can be designed to have symmetric structures with four indistinguishable constituent particles, and the design is much simpler than if one were to base the synthesis strategy on pointlike interacting sites. This can be achieved by reducing the area of the hydrophobic patch to allow no more than three neighbors for any single particle.[57] This interaction and valence rule can also be generalized to triblock Janus particles, based on which Kagome lattice pattern was realized.[58]

3.1.3. Assembly by Depletion Interaction. As discussed above, when the interaction is short-ranged, the geometry rules of designing Janus particle assembly generally apply. Attraction leading to colloidal micelles can be achieved not only by the hydrophobic interaction of traditional colloid science but also by the depletion interactions. Depletion attraction is observed between large colloidal particles suspended in a solution of depletants, usually nonabsorbing polymers of much smaller size that are preferentially excluded from the vicinity of the large particles because geometrically they do not fit into the space between the larger particles.[59]

Anisotropic depletion interaction is realized by having different surface roughnesses on different surface portions of a particle,[54] for example, using a particle with a dumbbell shape, one smooth lobe, and one rough lobe (Figure 9A). When nonabsorbing polymer (depletant) is added to the particle suspension, there is a certain volume around each colloidal particle that is not available to the depletant because of the size of the depletant. Close contact of two smooth surfaces offers more additional volume to the depletant than the contact of

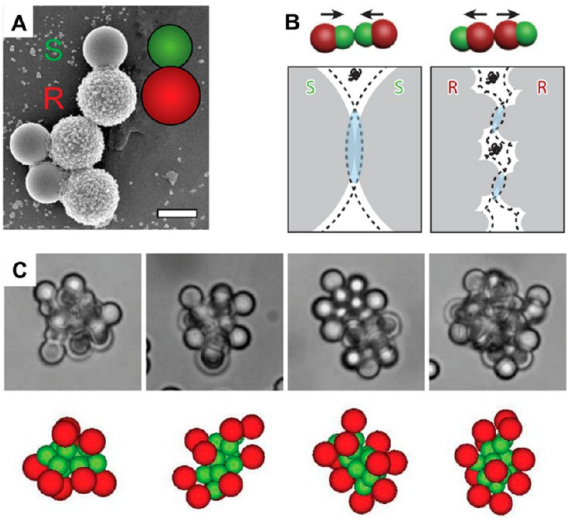


Figure 9. Self-assembly of patchy particles by roughness-specific depletion interactions. (A) SEM image of colloidal dumbbell particles with small and rough lobes. The scale bar is 2 μm. (B) The colloidal particles are surrounded by a region that is inaccessible to the depletant. When particles overlap, more additional volume is made accessible to the depletant. (C) Colloidal micelles assembled from 9 to 12 colloids with small smooth and large rough lobes. Adapted with permission from ref 54.

rough surfaces (Figure 9B), which is entropically favorable for the depletants and gives rise to the so-called depletion attraction. When the depletant concentration is high to make the attraction strong, Janus dumbbells with a small smooth patch organize into clusters, with the smooth and attractive parts facing into the interior. This resembles the geometry of surfactant micelles, where likewise the hydrophobic portions of surfactants attract each other (Figure 9C). The larger, rougher sides of the particles point outward from the clusters, resembling in this respect the hydrophilic headgroups of surfactant micelles composed of molecules. In spite of the difference in building blocks, clusters assembled from amphiphilic Janus particles[33,56] and smooth−rough dumbbells[54] share certain similar micellelike features and show the power of Janus colloidal particle systems as a useful tool.

3.2. Field-Assisted Assembly. Electric, magnetic, and flow fields can be used to assemble colloidal particles. Among them, electric and magnetic fields are most sensitive to anisotropic particle properties and are outstanding for their capability to operate from remote locations as well as for their convenience to be switched on and off. For these reasons, they are widely used to assist the assembly of Janus particles with different field responses on the two faces.

3.2.1. Electric Field. Here we focus on the assembly behavior of Janus particles coated on one hemisphere with metal via physical vapor deposition because the Janus boundary is better-defined than other modification methods in which the interfaces suffer from large fluctuations, such as the air−liquid interface. Orientation change in response to an electric field and asymmetric electrokinetic phenomena will be discussed later. This experiment can be tricky because relevant variables are numerous and sometimes hard to control; they include the electrode configuration, particle surface charge, particle conductivity, solvent conductivity, and flow fields associated with ion migration in electric fields. Despite potential pitfalls if an experimentalist is insensitive to these complications, the

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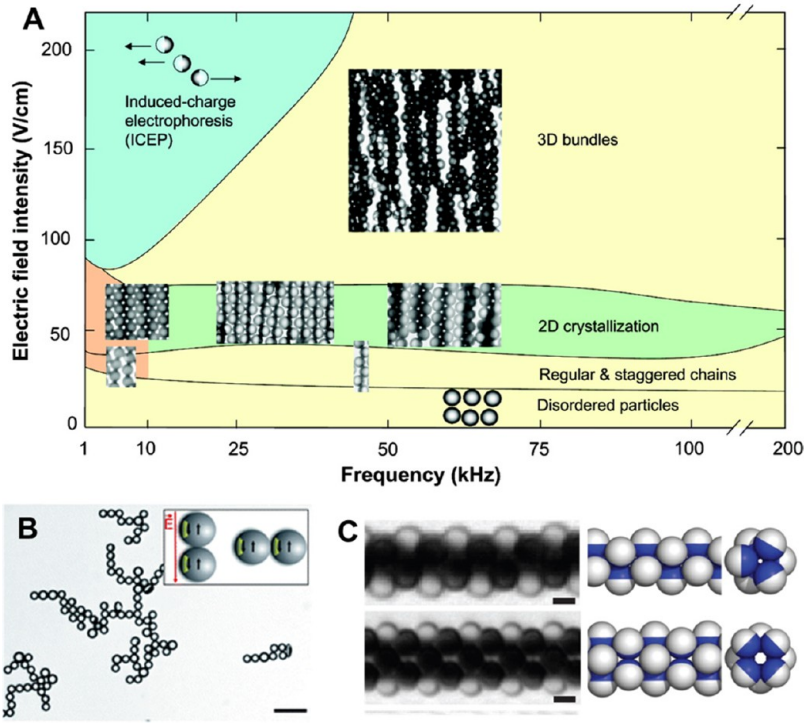


Figure 10. Janus particle assembly under electric and magnetic fields. (A) Dynamic and structural response of Janus particles to the ac electric field intensity plotted against field frequency in a thin experimental cell. The electric field direction is between the top and bottom of the optical images. Adapted with permission from ref 60. (B) The 11% single-patch particles form perpendicular, parallel, and staggered chains in an ac electric field. Adapted with permission from ref 61. (C) Observed images (left) and corresponding models of microtubes parallel to the precession axis. Adapted with permission from ref 63.

application of electric fields is one of the most useful methods of controlling particle assembly and even particle flow.

As reported by Velev and co-workers,[60] polystyrene Janus particles coated with gold on one hemisphere form zigzag chains (low concentration) and 2D crystals (high concentration) in water upon application of a high-frequency ac electric field. The authors explained that as particles tend to align in the direction of the electric field, but with stronger dielectric response at the metal-coated hemisphere, this arranges the particles into zigzag chains to maximize the alignment of induced dipoles. The zigzag angle is related not only to the frequency of the electric field but also to the geometry and thickness of the coating. Chains can even assemble perpendicular to the electric field direction. Figure 10A shows the phase diagram of assembly as a function of the electric field strength and frequency. There is no notable assembly at low fields; at medium field strength, particles form almost straight chains at low frequencies (<10 kHz); particles form zigzag chains at high frequency. Further increases in the field strength lead to the formation of 2D crystals and 3D bundles of chains.

Other work[61] using patchy particles, with various patch areas of less than a full hemisphere, showed a dependence on patch position and number of patches. Polystyrene colloids with a 25% gold-patch coverage showed staggered chain formation but a smaller zigzag angle than for a full hemisphere. Linear chains both parallel and perpendicular to the field directions were observed for the smallest patch areas (Figure 10B).

3.2.2. Magnetic Field. The response to a magnetic field can be programmed into colloids in two major ways. First, a magnetic coating can be deposited onto a portion of its surface area; second, magnetic nanoparticles can be embedded into a large particle that itself lacks response to magnetic fields.

Janus particles coated with magnetic metal caps assemble into zigzag chains, similar to what is observed for metal-dielectric Janus particles in an electric field, except that in the case of sufficiently strong magnetic susceptibility the resulting structures remain intact after switching off the magnetic field. This is due to magnetization of the particles. Velev and co-workers[62] compared the behavior of 4 μm Janus particles with 8- and 34-nm-thick ferromagnetic iron caps. When a 0.15 T magnetic field was used, particles with a thicker coating formed zigzag chains with large angles and remained intact after the removal of the field, whereas particles with thinner metal coatings formed more compact zigzag chains that disassembled after the magnetic field was switched off. These observations appear to be general for magnetic Janus particles.[63] Note that remnant chains could be disassembled by demagnetizing the metal coils using an ac coil, however. Because the formation of zigzag chains results from aligning the effective magnetic dipoles in the direction of the magnetic field, the observation of different geometrical structures depending on the coating thickness shows that the effective magnetic dipole shifts differently according to the coating thickness, probably because deposited material is not uniformly distributed on the particle surfaces.[64] Janus particles with two compartments, only one of them magnetic, show similar zigzag chainlike structures in a magnetic field.[46] It has also been shown that Janus particles form crystal-like structures with large particle−particle separations if the magnetic field is directed perpendicular to the plane of the magnetic coating. This results from parallel dipole repulsion between particles.[46]

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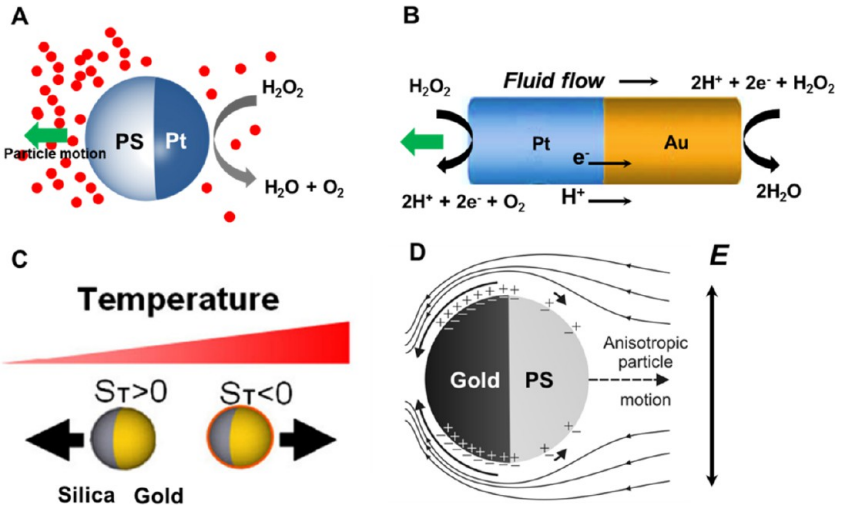


Figure 11. Janus micromotors. (A) A Janus particle driven by self-diffusiophoresis moves toward the nonreacting side in H_2O_2 fuel solution. Adapted with permission from ref 73. (B) A Pt−Au Janus rod is driven by self-electrophoresis to the Pt side in a H_2O_2 fuel solution. Adapted with permission from ref 78. (C) The direction of particle motion driven by self-thermophoresis differs for a Janus particle in water (positive Soret coefficient) and in Triton X-100 solution (negative Soret coefficient). Adapted with permission from ref 76. (D) A Janus particle driven by ICEP swims toward the dielectric side. Adapted with permission from ref 74.

With carefully designed time-varying magnetic fields, dynamic structures result. For example, magnetic Janus particles assembled into tubular structures when subjected to a precessive magnetic field. The magnetically responsive (nickel) coatings experienced a torque with two orthogonal components driving the particles to rotate around the precessing axis and oscillate perpendicular to the rotating plane simultaneously. To form stable tube structures, particles within the microtube must maintain their orientation within the rotating microtube while both rotate at the same time. Thus, the structure is controlled by dynamic synchronization criteria rather than static energy minimization as would be the case for equilibrium self-assembly and field-induced assembly.

4. APPLICATIONS

Numerous potential applications follow from the fact that Janus particles possess two distinguishable faces. They can be used as microprobes or sensors: this is because translational and rotational diffusion can reveal information about the local environment.[65] The two faces can respond to external stimuli differently. Because they represent two different states of the particle, a collection of them can carry much information and possibly be used as a display; this application has already been achieved in electronic ink technology.[66] The broken symmetry can allow particles to undergo active transport, which opens possibilities to design micromotors.[67,68] Finally, as foreseen by de Gennes,[2] Janus particles can be used as solid surfactants.

4.1. Microprobes for Microrheology and Bioimaging. Janus particles with distinct optical properties on two hemispheres can be used as tracers to probe the rheological properties of their local environment. Their optical properties are modulated by rotational diffusion to provide information in addition to the position of the tracers provided by conventional tracer particles.[69] This generates useful new information in complex environments where translational and rotational diffusion are not proportional, such as glassy materials and materials under shear.[70] The most interesting scenarios are when they are decoupled, for example, colloids' transport on a patterned surface[71] and shape-dependent diffusion.[72] To avoid artifacts, the two optically different faces should have the same physical interactions with their environment, which may be tricky experimentally.

4.2. Micromotors. When designed carefully, Janus particles suspended in a proper fuel solution will swim autonomously as a result of the anisotropic response of their chemical makeup to the environment. Over the past decade, synthetic micromotors have been developed on the basis of different mechanisms, most of which require broken symmetry on each particle. These include self-diffusiophoresis (chemotactic),[73] bubble propulsion,[38] induced charge electrophoresis (ICEP),[74] self-thermophoresis,[75,76] and self-electrophoresis,[77,78] all of which involve creating a local gradient or field associated with the particles themselves to drive their motion.[79]

When a polystyrene sphere with a platinum cap is placed in hydrogen peroxide solution, platinum catalyzes the local decomposition of hydrogen peroxide into water and oxygen. The resulting asymmetric distribution of reaction products propels the particle by self-diffusiophoresis (Figure 11A). This model of propulsion at low Reynolds number was proposed theoretically in 2005 and realized experimentally in 2007 by Golestanian and co-workers.[73,80] Because gas is generated during this catalytic reaction, bubble propulsion can compete with self-diffusiophoresis. Wu and co-workers recently compared the swimming behavior of physically deposited and chemically deposited platinum-dielectric particles and concluded that self-diffusiophoresis usually dominated for Janus particles with smooth metal films that were deposited by physical methods, whereas bubble propulsion dominates for chemically deposited coatings with rough metal surfaces whose defects provided nucleation sites for bubbles.[38] In the bimetal nanomotor system, the dominant mechanism is believed to be an electrochemical reaction of H_2O_2 fuel solutions that generate self-electrophoresis (Figure 11B).[77]

A similar propulsion mechanism can be achieved by self-thermophoresis when a half-metal coated colloidal particle is placed under laser irradiation.[75,76] The metal-coated hemisphere absorbs and heats up more than the uncoated portion, and the resulting local temperature gradient propels these

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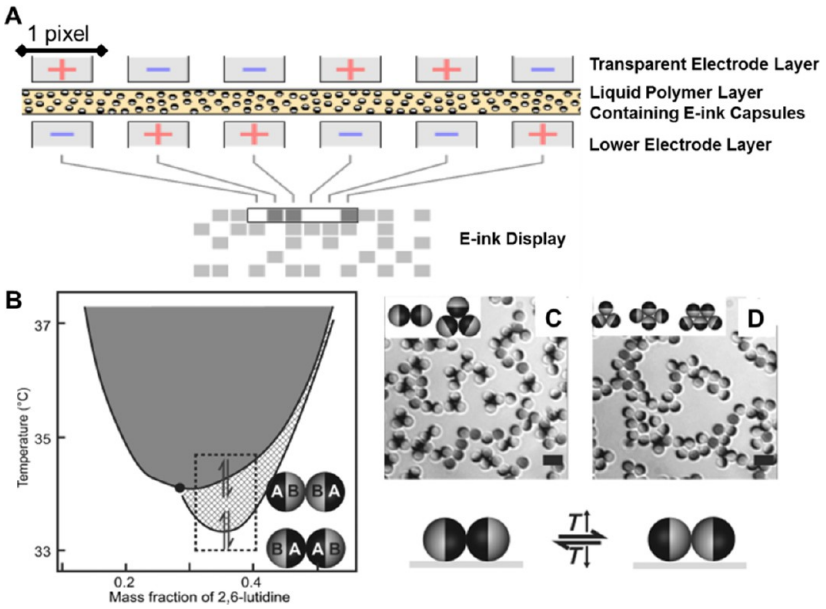


Figure 12. Janus particle as reconfigurable materials. (A) Structure of electronic paper with Janus particles embedded in polymer solution between electrodes. Adapted with permission from ref 66. (B) Scheme of switchable bonding between Janus particles in the context of the phase diagram of water/2,6-lutidine mixtures. A and B denote gold and silica hemispheres and arrows represent increasing and decreasing temperature. In the highlighted region, a transition between A–A bonding and B–B bonding occurs upon the change of temperature. (C) Gold–gold bonded clusters. (D) Silica–silica bonded clusters. (B)–(D) are adapted with permission from ref 84.

particles. The direction of particle motion depends on the Soret coefficient (Figure 11C), which may change sign with different suspending media.

Because the widely studied metal-dielectric Janus particles are asymmetric in their electrical conductivity, this renders induced-charge electrophoresis (ICEP) as another powerful way to achieve self-propulsion. Flows resulting from the induced diffuse charge near a polarizable surface are referred to as induced-charge electro-osmosis (ICEO). If the induced charge around a particle is asymmetric, then the particle tends to be propelled. This phenomenon was predicted theoretically by Squires and Bazant using the standard low-voltage model for thin double layers[81] and realized experimentally by Velev and co-workers.[74] Upon applying an electric field, particles coated on one hemisphere with metal orient themselves so that their Janus interface is parallel to the field direction. They are initially shown to migrate toward the dielectric side perpendicular to the electric field (Figure 11D), but motion toward the metal side at higher electric field frequency has also been explored, which gives rise to interesting collective behavior of these particles.[67,68,82,83]

4.3. Reconfigurable Materials. If a particle is coated black on one side and white on the other and an externally applied electric field can make it flip, then it can act as a switchable optical element that can be used as a pixel in a display. The first electronic paper (Gyricon) was developed at Xerox's Palo Alto Research center by Nick Sheridon in the 1970s: it is composed of polyethylene Janus spheres of order 100 μm diameter that are white on one side and black on the other, carrying opposite charges.[66] These particles are embedded in a transparent silicone sheet, and each particle is dispersed in a bubble of oil so that it can rotate freely. The text or pattern displayed can be altered by the presence of an electric field, with the particles facing up or down (Figure 12A). Each pixel may contain several particles. The anisotropic surface properties of Janus particles and their resulting potential to respond to external stimuli make them an ideal candidate for reconfigurable materials more generally.

The reconfigurability of Janus particles can also be explored in self-assembly: not only single-particle behavior but also assembled structures can be responsive to external stimuli. Our group[84] showed that by placing the system at a tipping point, dramatic changes in assembled structure can be triggered by small, reversible environmental changes such as temperature. This relies on the exquisitely sensitive temperature dependence of wetting in a suitable mixture of two fluids. As an example, the binary mixture of water/2,6-lutidine was studied to cause critical Casimir attraction between colloids whose surface chemistry is isotropic.[85] As shown in Figure 12B, when Janus particles with one hydrophilic silica hemisphere and one hydrophobic gold hemisphere were dispersed in water/2,6-lutidine mixtures below the preferential wetting temperature, the charged silica surfaces repelled one another whereas the hydrophobicity of the gold-coated hemispheres caused them to attract.

Capitalizing creatively upon the reconfigurability of Janus particle assembly, Janus emulsions have been used to detect the concentration of bacteria. These Janus droplets contain surfactants with mannose on one side, which serves as a binding site for lectin, a protein produced by bacteria. Below the detection limit of lectin, the density difference of the two Janus hemispheres orients droplets with their equators parallel to the sample plane, but when lectin produced by bacteria passes a critical concentration, agglutination and titled geometry result from binding to mannose. The distinctly new optical properties of these naturally aligned droplets can be detected quantitatively. The Janus emulsion assays have been shown to bind to *E. coli* with sensitivity and selectivity, and they can be prepared with long time stability.[86]

4.4. Solid Surfactant. The inspiration for the Janus particle concept was de Gennes' vision that they should reside at a liquid–liquid or liquid–air interface.[2] In this respect, they can

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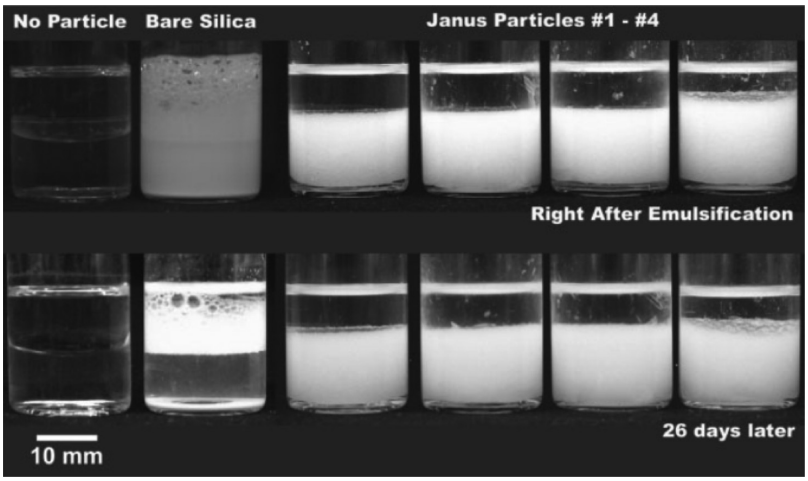


Figure 13. Photographs of emulsions. Emulsification was performed by the dispersing element running under 18 000 rpm for 1 min. Particles were 500 nm in diameter. The relative portion of hydrophobic and charged regions was parametrized by an angle α, the inclination angle corresponding to the radian from the center of the hydrophobic part to its edge. Janus particles #1−#4 had α = 45, 47, 57, and 72°, respectively. The emulsions stabilized by Janus particles could be dispersed in toluene but not water, thereby indicating that the emulsion type is water in oil. Adapted with permission from ref 10.

act as monolayers. Beyond this, structures assembled from Janus particles resemble micelles formed by surfactant molecules.[56] Moreover, Janus particles can be employed as emulsion stabilization agents because they adsorb strongly at the liquid−liquid interface.[26,29] Calculations show that proper surface chemistry improves the adsorption energy up to 3-fold.[87]

Janus particles synthesized by the wax emulsion method[27] have been used to investigate the ability of Janus amphiphilic particles to stabilize emulsions, and it was demonstrated that the area of the hydrophobic patches can be controlled using surfactant. Janus particles dispersed in toluene were then mixed with water. After emulsification, the emulsion was held at room temperature and immediately photographed to capture the state of the phase separation so that the emulsion stability could be evaluated by monitoring the changes in the suspension with time. For emulsions stabilized by Janus particles of different geometry, no changes were observed even after 3 weeks. In a control experiment, particles were harvested from the wax droplets before surface modification with silane. As shown in Figure 13, particles without chemical modification cannot stabilize the emulsions, which confirmed the need for Janus functionalization.[10]

5. CONCLUSIONS AND OUTLOOK

Taking stock today of where the field stands more than a quarter century after the vision of Janus particles was enunciated,[16] this instructional review has surveyed the many useful and imaginative ways to synthesize Janus particles, ranging from surface chemistry modification to compartmentalization and from the production of small amounts for academic study to the bulk synthesis of large amounts suited for industrial use. The appeal of the Janus concept goes far beyond synthesis. Unprecedented new self- and directed-assembly structures are possible, and unconventional design rules for novel materials start to reveal themselves when one uses Janus particles as building blocks. With the usually weak attraction (a few k_BT) encountered in self-assembly experiments and simulations, many equilibrium thermodynamic principles apply in systems where, in an optical microscope, one can visualize each structure individually with one's own eyes.

The scientific and technological opportunities offered by going beyond equilibrium excites many researchers currently. Janus particles also fit well into these interests because Janus particle motors are capable of converting chemical and electrical energy into mechanical energy using a versatile variety of scenarios. These active particles constitute model systems in which to study out-of-equilibrium materials[79,88,89] including active matter.[68,90] Janus and multiblock patchy particles likewise show great potential to contribute to the next generations of smart materials when one uses the proper design of their interactions and their abilities to sense external stimuli. We conclude with confidence that Janus and other anisotropic particles will continue to promote our understanding of the physical world, from equilibrium to out-of-equilibrium, and contribute to the development of novel smart materials using the approaches outlined in this tutorial review.

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Notes

The authors declare no competing financial interest.

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