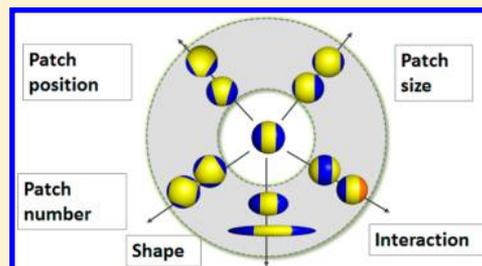


Janus and Multiblock Colloidal Particles

Qian Chen,[†] Jing Yan,[†] Jie Zhang,[†] Sung Chul Bae,[†] and Steve Granick^{*,†,‡,§}Departments of [†]Materials Science and Engineering, [‡]Chemistry, and [§]Physics, University of Illinois, Urbana, Illinois 61801, United States

ABSTRACT: We review recent developments in the synthesis and self-assembly of Janus and multiblock colloidal particles, highlighting new opportunities for colloid science and technology that are enabled by encoding orientational order between particles as they self-assemble. Emphasizing the concepts of molecular colloids and colloid valence unique to such colloids, we describe their rational self-assembly into colloidal clusters, taking monodisperse tetrahedra as an example. We also introduce a simple method to lock clusters into permanent shapes. Extending this to 2D lattices, we also review recent progress in assembling new open colloidal networks including the kagome lattice. In each application, areas of opportunity are emphasized.



■ INTRODUCTION

Janus particles have come a long way since their origin as a suggestion by de Gennes,^{1,2} who envisioned particles with two faces and their potential applications even at that time as surfactants and membrane applications, a “skin” that can “breathe”. Today, even more complex internal particle structures such as tailor-made clusters and extended lattices can be imagined and implemented. Although the original vision concerned Janus particles too large to display Brownian motion, this article concerns colloid-sized particles that are larger than molecules but small enough to diffuse by Brownian motion. An exciting variety of synthesis methods, assembled structures, and applications are under development. Especially when one considers that understanding has reached a high level of maturity concerning conventional particles whose interactions are isotropic,³ this is an exciting time in which to study such anisotropic particles, with Janus particles as the prototype system.

These particles possess different surface chemistry on two sides, for example, positive and negative domains of electric charge for dipolar particles⁴ or hydrophobic and hydrophilic domains for amphiphilic particles.⁵ Although Janus particles are named after the Roman god Janus with two faces, other ancient cultures also imagined two incompatible properties within a single unity. In Chinese philosophy, seemingly opposite forces are viewed as naturally interconnected, a concept known as Yin and Yang. Hence, Janus particles can also be viewed as Yin–Yang particles.

Although much activity so far in this field revolves around the synthesis of new types of Janus particles,^{6–9} here we emphasize their self-assembly, which produces aggregates superficially like micelles formed by surfactant molecules but with key differences discussed below. Going beyond the traditional two-faced Janus geometry,¹⁰ multiblock colloidal particles with more intricate, novel self-assembled structures^{11,12} are also discussed below.

Concerning potential applications, much guidance is provided by analogy to small surfactant molecules. Amphiphilic Janus particles stabilize emulsions, as surfactant molecules are known to do; such particles are expected to adsorb to interfaces and foam surfaces even more strongly than particles whose chemical makeup is isotropic.^{13–15} But applications go beyond this. Janus particles can also assist chemical catalysis, boosting catalytic activity.¹⁶ They find applications in drug delivery: into the same particle, a variety of drugs can be loaded and subsequently released either simultaneously to achieve synergy between them or in controlled sequence if demand changes with time.^{17,18} There also exist potential applications in display technology, as shown long ago by the controlled orientational switch between the dark and bright sides, by external magnetic or electric fields.¹⁹ In the field of polymer-filled composites, there exist potential applications to assemble stress networks and tailored pathways of electrical conductivity. In the field of template-directed synthesis, the unique structures formed from their self-assembly can serve as templates by growing chemicals conformally around these exotic structures and removing them afterward.

This article emphasizes the use of Janus and multiblock particles as building blocks for colloidal engineering, with an emphasis on the consequences of their unique anisotropy. In this scenario, Janus colloids are particles decorated with domains on the surface with properties distinct from those of the virgin surface. Those domains, usually mutually attractive, can serve as connection paths during the assembly process to direct individual building blocks into complex architectures. This approach requires the building blocks to be highly monodisperse, not only in the overall size but also in the patch size and property, to allow the rationalization of their behavior, which has been a big challenge for experimentalists. Until

Received: May 31, 2012

Revised: July 5, 2012

Published: July 6, 2012

recently, this synthesis challenge of high-quality Janus particles has resulted in a lack of quantitative self-assembly experiments. For a long time, computer simulations^{20–26} and experiments have competed to lead the way; many of the seminal proposals come from simulations.

■ SYNTHESIS OF JANUS PARTICLES

In the early days, methods to synthesize Janus particles were crude by today's standards. One approach² was to perform surface functionalization and then break the particle into fragments, giving automatic Janus character to the fragments. Although this generates heterogeneous particles without control over the shape, size, or purity, this remains an easy, low-cost approach.

Another early method, still used widely today, gives Janus particles of higher quality: this is directional coating onto a monolayer of homogeneous particles previously deposited on a flat substrate.^{27,28} With this approach, the size and polydispersity of the particles are determined solely by the starting particles. Directional coating generates Janus particles with one hemisphere coated perfectly, and a subsequent etching process can, in favorable cases, reduce the area coverage as desired.¹² This approach can also be used as a basis to study single-particle rotation in complex environments²⁸—the “MOON particle” approach introduced by Kopelman's group.²⁹ This finds applications in areas from physical sciences to biosensors because the rate of rotation is very sensitive not only to the environment but also to the particle size.

To scale up to larger quantities, it is necessary that each synthesis batch contains a higher surface area than a monolayer can provide. This requirement can be met by emulsions of oil in water, building on the fact that particles adsorb tightly to oil–water interfaces¹³ and cannot rotate when the oil is cooled to temperatures at which it is waxy. Each side of an adsorbed particle is then, by design, protected because it faces the other phase, and chemical modifications can be performed from either phase. This method can be scaled up simply because emulsions can offer huge amounts of interface in a small volume. By adjusting with cosurfactant how deeply particles penetrate the matrix phase, one can control the respective areas of the two Janus sides.^{15,30} Approaches of this sort are most appropriate to producing Janus particles from previously manufactured colloidal particles of homogeneous chemical makeup; in a different spirit, it is also possible to produce Janus particles based on the assembly of block copolymers.³¹

Even more recently, methods were developed to synthesize triblock Janus particles. The following simple strategy is particularly effective.¹¹ One begins by depositing, onto particles on a planar support, the traditional Janus geometry. Then with a stamp one lifts the coated particles off the support and turns them around, laying them back on a planar support but with the opposite side facing outward. Finally, one deposits a new coating layer. In this way, one can produce particles with north and south poles of symmetric or asymmetric surface areas, arranged either parallel to one another or off-axis. These methods are readily extended to particles of anisotropic shape, such as colloidal rods, cubes, and icosahedra.

Going beyond the traditional approaches of amphiphile-driven self-assembly, it is exciting to notice the other possibilities. There is electrostatically driven assembly⁴ and magnetically driven assembly. When magnetic Janus and multiblock colloids, the members of whose family are growing rapidly owing to emerging synthesis developments,^{32–36} are

subjected to magnetic or electric fields, concepts of self-assembly must be generalized beyond the principles of energy minimization for traditional thermal systems.

■ VISION OF MOLECULAR COLLOIDS

The vision of molecular colloids with structures formed by orientationally dependent potentials has become a goal in colloid science.^{20,37,38} Its experimental implementation should, in our view, meet the following criteria. First, directional interaction should prevent random aggregation into the unbounded shapes of crystal, glass, or fractal aggregates. Second, reversibility should ensure the equilibrated structure; the useful analogy to molecules is supramolecular self-assembly, not the covalent bond. Third, the idea should scale up to large quantities.

The Janus spheres introduced in the previous section offer a direction in which to design such materials. As building blocks, we have selected micrometer-sized spheres, hydrophobic on one surface domain and negatively charged elsewhere.^{10,39} They were visualized by epifluorescence microscopy. Our use of micrometer-size particles causes the range of interparticle forces, relative to particle size, to be much less than in some computer simulations;⁴⁰ this is considered to be a key aspect of the resulting self-assembly. Meanwhile, micrometer-sized particles present the advantage that they can be imaged directly.

For spheres whose hydrophobic domains are hemispheres, clusters grow with two constraints: first, particles must come close enough to experience hydrophobic attraction; second, the number of nearest neighbors does not exceed six. We find them to self-assemble to form a complex network with reversible growth can be categorized as falling into three major reaction mechanisms: addition of individual particles step by step, fusion of smaller clusters into a larger one, and isomerization.¹⁰

For these polymorphous clusters, the attractive hydrophobic patches can orient in different ways while keeping the same geometrical shape. This promotes dynamic interconversion between isomeric clusters. Similar structures exist for the depletion-induced assembly of homogeneous particles, but to observe them requires that they be kept isolated from one another to avoid aggregation.⁴¹ In the Janus particle approach, the cluster shapes are stabilized against aggregation, which is why clusters live in close proximity without fusing.

Moreover, clusters can elongate into wormlike chains, also called Bernal spirals or Boerdijk–Coxeter helices, composed of three twisting strands of particles arranged such that each particle, except those at the ends, has six neighbors.^{42,43} We observe their formation to be nearly always by the addition of clusters to other clusters, the reactive ends of two clusters fusing with one another, resulting in a linear catenation of face-sharing tetrahedra. Repulsion between the charged zones excludes branch points, which would require particles at the branch to have more than six nearest neighbors. This is why these Bernal spirals are stable up to the highest particle concentrations, unlike what is observed when homogeneous particles form Bernal spirals at lower particle concentration.⁴²

For perspective, molecular reaction dynamics occur on picosecond or faster time scales, requiring an ultrafast experiment or computer simulation for analysis. The merit of these colloidal transformations is that they occur on the time scale of seconds. They are visualized one-by-one without ensemble averaging. One such reaction dynamic is the switching of handedness of a Bernal spiral. The reaction occurs along a trajectory that minimizes the needed bond rearrange-

ments, which was again observed in another helix-formation system from dipolar dumbbells, seemingly different from our chemically anisotropic Janus colloids but sharing the same orientational dependence in mutual interaction.⁴⁴ The transformations of smaller colloidal clusters are reminiscent of the structural arrangements of their atomic analogues, atomic clusters,^{45,46} but now are observed in real time on a single-particle level.

We emphasize the multidimensional character of this problem and the requirement of having well-defined, precise control of the building blocks. The building blocks should be fully characterized by the same set of parameters, in experiment as well as in simulation, to enable high fidelity in experiments and a highly accurate comparison with simulations. Five parameters are proposed (Figure 1) as the pointer for

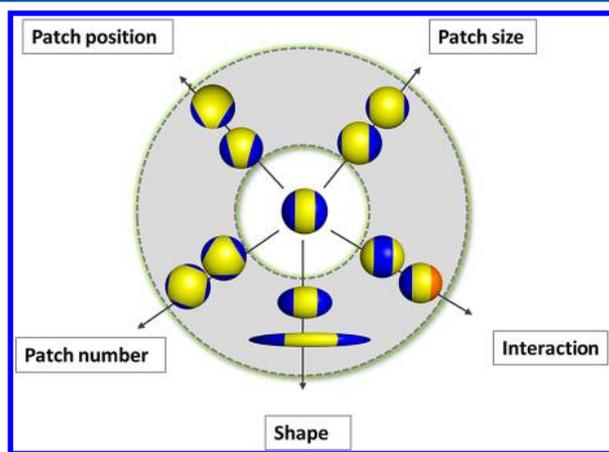


Figure 1. Various parameters to control the self-assembly of patchy colloids: size of patches, number of patches, shape of patches, position of patches, and patch–patch interactions determined by the surface chemical makeup of patches. Illustrated here for spheres, eggs, and needles (oblate spheroids), these parameters also generalize to other shapes such as rods, cubes, and other polyhedra.

laboratory synthesis. These include the patch size (determining the coordination number), patch position (determining the connection geometry), patch number (determining the focused coordination domains), patch interaction (determining the nature of the bond), and patch shape to accommodate the variety of building blocks required for directed assembly.

We call attention to an area of opportunity: analogies to chemical reaction dynamics can be explored, especially the distinction between diffusion-limited and reaction-limited chemical reactions. Direct visualization reveals that particles constantly jiggle about their mean positions, a process that may be analogous to highly excited vibrational motion in molecules, with the vibrations occasionally causing collective rearrangements. Making this concept quantitative presents an enticing prospect for future studies but may require method development because the images of 3D structures are projected into the 2D plane.

■ DESIGNING MONODISPERSE COLLOIDAL CLUSTERS

Valence is a useful concept by which to design colloidal superstructures. Although it might be tempting to design spheres with pointlike attractive domains, it is more realistic in practice to form extensive domains that can accommodate a

definite number of nearest neighbors, with this number being the valence. Hence the concept of colloidal valence has nothing to do with quantum mechanics but gives guidance for understanding how connection paths propagate from one colloidal particle, outward through the rest of the eventually self-assembled system.

This geometric rule applies when colloid–colloid attraction, whatever the form of the potential may be, is short-ranged relative to the particle size. Then interactions between attractive domains can be regarded as attraction contacts such that the greater the number of contacts, the lower the energy of the structure. Therefore, the number of attractive contacts is maximized at equilibrium, when energy dominates entropy.

Using the valence rule, we have designed colloidal tetrahedra that are symmetric structures with four indistinguishable constituent particles. This requires the valence to allow no more than three neighbors per particle. On the experimental side, we controlled the area of hydrophobic domains by etching Au coatings on spheres and determined the surface area using SEM (scanning electron microscopy) images of dry particles (Figure 2). The optimal valence was determined (caption of

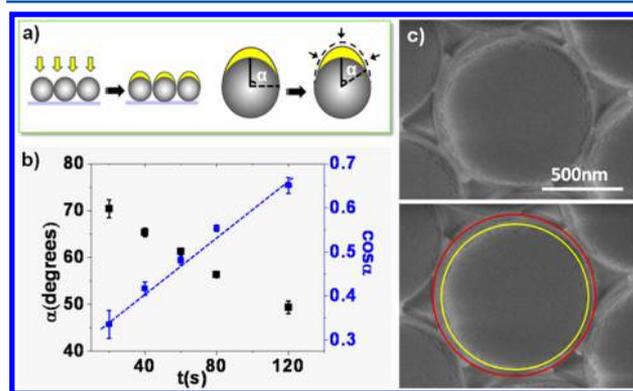


Figure 2. How to control the valence of Janus spheres. (a) A monolayer of polystyrene spheres was coated with 2 nm of Ti and then 15 nm of gold and then etched to shrink the size of the gold patch (defined as α , half the opening angle). (b) Working curve showing the decrease in the valence (black squares) vs the etching time. (c) SEM images of the final state. The lower image shows the size of the particle (red circle) and the size of the patch (yellow circle). The smaller area gives this particle a smaller valence than the initial full hemisphere of coating.

Figure 3). Figure 3b, a histogram of cluster size, demonstrates that nearly monodisperse tetrahedra resulted. Although it is true that polydisperse clusters including tetrahedra can in principle also be prepared by a top-down approach,⁴⁷ the novel point here is that these monodisperse clusters were prepared by spontaneous self-assembly.

When the valence was increased slightly, the size of the resulting colloidal clusters also increased (Figure 4), consistent with expectations from the valence rule. Note that these self-assembled structures in Figure 4 are polydisperse, indicating the presence of different structures whose energies are nearly degenerate. Hence, entropy can be neglected when a single structure dominates energetically as for tetrahedra formation but can be important when the building blocks can adopt multiple isoenergetic structures. Despite the simplicity of the valence rule, it can serve as a useful rule of thumb to anticipate possible new structures. Janus particles with attractive hemispheres can have, by this rule, at most six nearest neighbors.

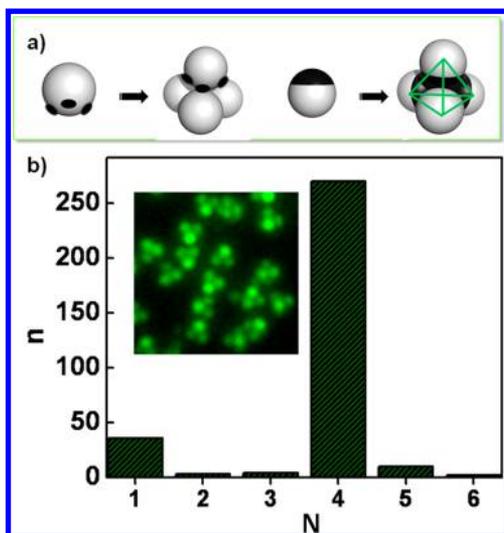


Figure 3. Self-assembly of a monodisperse tetramer from Janus spheres. A valence of 3 is produced after etching to yield a half-opening angle of $\alpha = 67^\circ$. (a) Two self-assembly routes are illustrated. (b) Histogram of the cluster size, illustrating the dominance of the tetrahedron structure, in equilibrium with monomers. The inset shows a fluorescent image of these tetrahedra in an aqueous suspension.

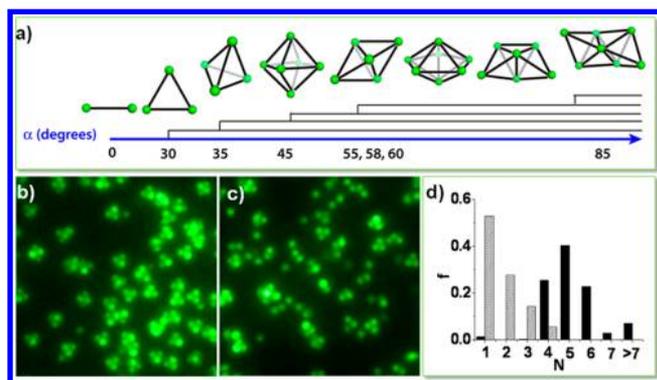


Figure 4. Relation between valence and cluster shape. (a) The required valence to form various indicated clusters. The valence is expressed in terms of the allowed range of the half-opening angle, α . (b, c) Examples of clusters assembled from $\alpha = 70^\circ$ (black columns in d) and $\alpha = 55^\circ$ (gray columns in d).

This was compared to experiment in a recent report from this laboratory,¹⁰ with the conclusion that the valence criterion correctly anticipated that spheres were assembled into a tubular structure, although to explain the selection among different possibilities of the observed chiral triple-helix option required additional considerations of relative entropy.

LOCKING JANUS CLUSTERS INTO PLACE

Paradoxically, one desires reversible attraction to generate designed equilibrated structures by self-assembly yet later on wishes these cluster shapes to become more robust to environmental disturbance. The strategy of “locking” structures into place allows one to harvest them and then to manipulate them as entities in their own right. For example, the usual colloidal clusters formed by Janus spheres (Figures 3 and 4) easily fall apart if placed in a different environment such as deionized water.

To lock particles into place so that their assemblies can later serve as secondary building blocks, the challenges are twofold.

First, irreversibility must be introduced in situ, within the suspension medium in which the clusters formed. Second, the transformation scheme needs to be orthogonal to the self-assembly process. Many of the potential locking mechanisms^{48–51} must be ruled out because they would risk perturbing or even collapsing the preassembled clusters.

One strategy focuses on clusters of amphiphilic spheres, all of which have their hydrophobic sides facing the interior. There is useful analogy to make with the DLVO theory, which is well known to predict a primary minimum of strong attraction from van der Waals forces in addition to the reversible shallow secondary minimum, provided that the ionic strength allows the particle–particle separation to be sufficiently small (Figure 5). The idea can be extended by analogy to the hydrophobic

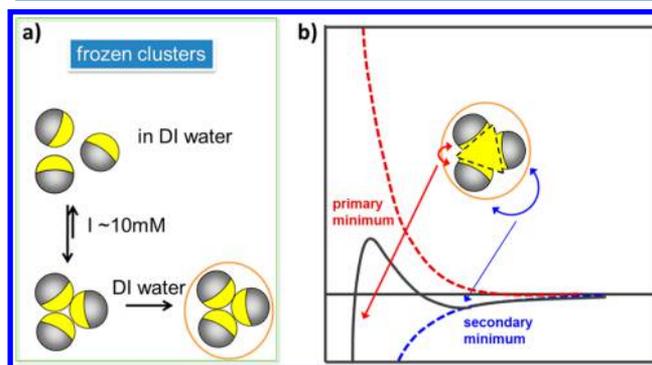


Figure 5. Strategy to lock clusters into place. (a) Individual Janus spheres (yellow side hydrophobic, gray side charged) form equilibrated clusters at 5 mM NaCl, fall into an attractive minimum at 10 mM NaCl, and maintain their shape after being redispersed in deionized water. (b) At 10 mM salt, the attractions between hydrophobic cores of the clusters fall into the primary minimum and maintain their cluster shapes after being redispersed in deionized water.

attraction as well. To capitalize upon this in experiments, we used larger amphiphilic Janus particles for a clear visualization of the hydrophobic side (black under the transmission microscope) and selected their makeup to be silica so that they would sediment into an easily imaged monolayer. The particles were made to have a valence of 2 and form dynamic colloidal clusters at 5 mM NaCl. Then an increase in ionic strength to 10 mM NaCl dampened the mutual reorientations of component colloids within a trimer, indicating the formation of permanent bonds between the hydrophobic contacts (Figure 6a). No disassociation of hydrophobic contacts was observed when the clusters were reimmersed in deionized water (Figure 6a), showing the permanence of this effect. The harvested colloidal clusters, though polydisperse in shape, repack into an ordered planar hexagonal lattice (Figure 6b).

Although it is true that this concept is generalizable and scalable, having better control over the locking process would be desirable. We consider the development of new synthesis strategies to lock Janus clusters into place to be an area of great opportunity.

KAGOME LATTICE AND POLYHEDRAL PARTICLES

Periodically ordered arrangements of colloidal particles have long been of interest. Large enough to be seen under the optical microscope, they serve as model systems for studying the crystallization dynamics and phase behavior of atomic crystals, and it is usual to observe close packing when gel states

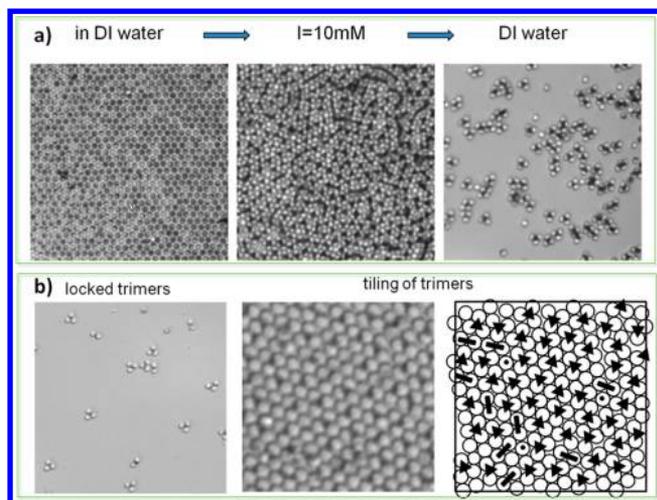


Figure 6. Bright-field optical microscope images of locked clusters. (a) Experiments following the strategy in Figure 4. The Janus particles are 2 μm silica particles with a Au coating (black, the hydrophobic domain). (Left to right) Deionized water, 10 mM NaCl, deionized water. (b) The use of locked trimers as secondary building blocks to tile into a “disordered” hexagonal lattice. (Left to right) Locked trimers, a hexagonal lattice of locked trimers, a schematic diagram of the hexagonal lattice in which the triangles and lines denote locked trimers, and coexistent locked dimers of a smaller fraction, respectively.

do not intervene. Occasionally by patterning the wall upon which the crystal grows or by introducing multiple-length-scaled interparticle potentials, less closely packed structures such as body-centered lattices can be fabricated.⁵² However, the engineering of even more complicated crystals requires a preference for a particular connectivity.

The kagome lattice (Figure 7) has been intensively sought by theorists for its importance both as a typical type of isostatic

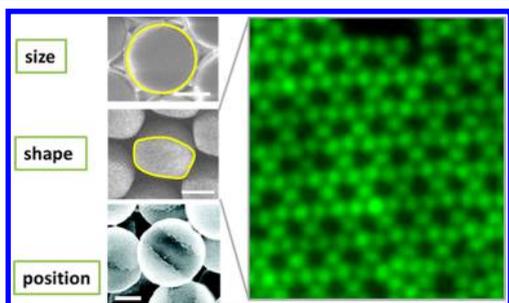


Figure 7. (Left) SEM images (scale bar: 500 nm) showing different design elements of a patch: the patch size in a Janus sphere (top), the patch shape in a triblock sphere employed to form the kagome lattice in the left panel (middle), and the patch position in a triblock sphere (bottom). (Right) Fluorescent image of a kagome lattice.¹¹ Each of the constituent spheres has a diameter of 1 μm .

lattice⁵³ and as the most geometrically frustrated magnetic material.⁵⁴ The 2D kagome lattice in particular is composed of interlaced triangles whose vertices have four contacting neighbors each. Although this structure has been obtained using molecular assemblies on metal surfaces through metal–organic coordination,⁵⁵ this surface-templating approach differs from the spontaneous assembly described below.

We designed triblock Janus spheres that could be imaged directly by epifluorescence microscopy and coated them at two poles with gold to render them hydrophobic with a self-

assembled monolayer of *n*-octadecanethiol. In this way, the colloids are attractive at their poles but repulsive elsewhere. Although attraction between hydrophobic poles is insensitive to the ionic strength of the aqueous particle suspension, their repulsion can be tuned by simply adding NaCl to change the screening length. Meanwhile, the area and shape of the hydrophobic patches on the colloids can be tuned, which determines their valency and consequently their final self-assembled structure. The formation of a 2D kagome lattice was observed when the hydrophobic patch at each pole allowed two neighbors—a valence of 2—on each pole of the sphere. Two aspects are worth emphasizing. First, particles in lattices of this kind, formed by reversible assembly, are agitated by thermal fluctuations. In principle, there is much to be learned from measuring their vibrational modes and the associated phonon spectra. Second, because the self-assembly is not onto a surface template, one can envision even more structures when triblock spheres are constructed with an asymmetric valence on the two poles or with a valence that fails to be collinear. We have outlined some of these possibilities elsewhere.¹² Others are illustrated in the right panel of Figure 8.

When spheres self-assemble with reversible attraction between them, they are apt to wobble and even deform spontaneously just from Brownian motion because attraction can be satisfied at multiple points where the spheres come together. The connection network of the assembled structures is degenerate, subject to distortion to multiple states without the need to break or reform bonds. To investigate the consequences, we have employed triblock Janus colloids for the convenient visualization of their connection network using optical microscopy and have selected silica particles because they sediment into monolayers. They were prepared with a Y-shaped bonding geometry, in other words, a valence of 2 on one pole and a valence of 1 on the other pole. As they self-assemble, they pack into condensed alternating layers forming the geometric shapes of triangles and squares (Figure 8) to maximize hydrophobic contacts as suggested by the valence rule. Because even domains with valence equal to unity are extended beyond a pointlike region, the layers can slide over each other while maintaining all of the energy-relevant connections (Figure 8b). Interestingly, such sliding motions present more than just the mathematical curiosity of a floppy mode; they assist the insertion of new, free clusters into existing layers, as shown in Figure 9. We envision that if structures of this kind were exposed to other varieties of structural units, then sliding motions might similarly incorporate them into the final assemblies. This demonstrates an essential feature of these reconfigurable materials: freedom and flexibility to reshape. In this case, it originates from the inherent floppiness of the assembled structure.

We call attention to opportunities. The purposeful design of other open colloidal lattices is considered to be within reach because there are many possibilities still to explore. Beyond the simple kagome lattice that has been demonstrated,¹¹ more important is the design rule: encoded with different information from the distribution, size, and shape of patches, colloids assemble as different small modules and organize into higher-order materials. For example, if the two hydrophobic poles in the current system were asymmetric and thus had a different valence, then we would be able to harvest colloidal dendrimers. Or if four patches are distributed with tetrahedral angles, a diamond structure would be artificially designed.²⁶

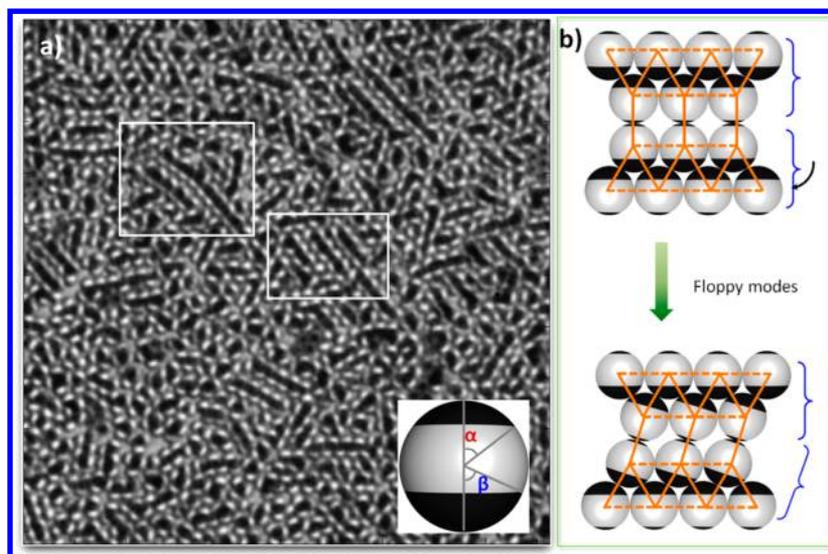


Figure 8. Assembled 2D (monolayer) structures of silica triblock Janus spheres with Y-shaped bonding geometry, a valence of 2 on one pole, and a valence of 1 on the other pole. (a) Bright-field optical microscope images of assembly from 2 μm silica triblock Janus spheres ($\alpha = 25^\circ$ and $\beta = 58^\circ$ as indicated in the inset). The two white boxes highlight alternating parallel layers of triangles and squares. (b) Schematic illustration of the floppiness of these structures.

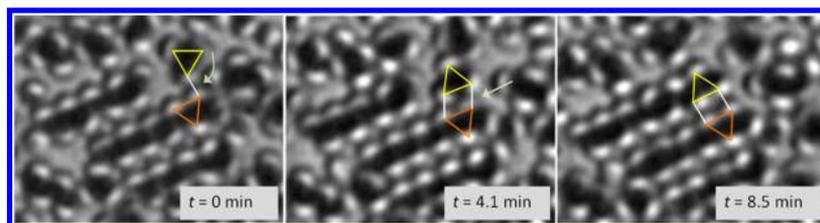


Figure 9. Refers to the system introduced in Figure 8. (Left to right) The panels show microscope images of the self-assembly process at successive times indicated in each panel, enabled by the floppiness of the structure. Zero time refers to when 10 mM salt was added to deionized water.

The emerging use of mesocrystals in which crystallographic axes are aligned holds other exciting possibilities.^{56,57} The important approach of learning to exploit the anisotropic interaction in self-assembly can indeed be generalized to the study of nanometer-sized particles, but we note two limitations: first, that this is a rather special case as the range of interparticle interaction in suspensions is typically likewise nanometric in size, and second, that the diffraction limit precludes visualizing adjacent nanometer-sized particles optically at the single-particle level.

Furthermore, metal–organic frameworks (MOFs) or porous coordination polymers (PCPs), prepared by the cocrystallization of metal ions and bridging organic ligands display colloidal-sized polyhedral shapes with an interesting potential for anisotropic self-assembly.⁵⁸

AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We thank Angelo Cacciuto, Shan Jiang, Hong Liang, Erik Luijten, and Jonathan K. Whitmer for collaborations. This work was supported at the University of Illinois by the U.S. Department of Energy, Division of Materials Science, under award DE-FG02-07ER46471 through the Frederick Seitz Materials Research Laboratory at the University of Illinois at Urbana–Champaign.

REFERENCES

- (1) de Gennes, P. G. Soft Matter (Nobel Lecture). *Angew. Chem. Int. Ed.* **1992**, *31*, 842.
- (2) Casagrande, C.; Veyssie, M. Janus Beads-Realization and 1st Observation of Interfacial Properties. *C. R. Acad. Sci.* **1988**, *306*, 1423.
- (3) Israelachvili, J. N. *Intermolecular and Surface Forces*, 3rd ed.; Academic Press: New York, 2011.
- (4) Hong, L.; Cacciuto, A.; Luijten, E.; Granick, S. Clusters of Charged Janus Spheres. *Nano Lett.* **2006**, *6*, 2510.
- (5) Hong, L.; Jiang, S.; Granick, S. A Simple Method to Produce Janus Colloidal Particles in Large Quantity. *Langmuir* **2006**, *22*, 9495.
- (6) Perro, A.; Reculusab, S.; Ravaine, S.; Bourgeat-Lamic, E.; Duguet, E. Design and Synthesis of Janus Micro- and Nanoparticles. *J. Mater. Chem.* **2005**, *15*, 3745.
- (7) Nie, Z.; Li, W.; Seo, M.; Xu, S.; Kumacheva, E. Janus and Ternary Particles Generated by Microfluidic Synthesis: Design, Synthesis, and Self-Assembly. *J. Am. Chem. Soc.* **2006**, *128*, 9408.
- (8) Dendukuri, D.; Pregibon, D. C.; Collins, J.; Hatton, T. A.; Doyle, P. S. Continuous-Flow Lithography for High-Throughput Micro-particle Synthesis. *Nat. Mater.* **2006**, *5*, 365.
- (9) Nisisako, T.; Torii, T.; Takahashi, T.; Takizawa, Y. Synthesis of Monodisperse Bicolored Janus Particles with Electrical Anisotropy Using a Microfluidic Co-Flow System. *Adv. Mater.* **2006**, *18*, 1152.
- (10) Chen, Q.; Whitmer, J. K.; Jiang, S.; Bae, S. C.; Luijten, E.; Granick, S. Supracolloidal Reaction Kinetics of Janus Spheres. *Science* **2011**, *331*, 199.
- (11) Chen, Q.; Bae, S. C.; Granick, S. Directed Self-Assembly of a Colloidal Kagome Lattice. *Nature* **2011**, *469*, 381.

- (12) Chen, Q.; Diesel, E.; Whitmer, J.; Bae, S. C.; Luijten, E.; Granick, S. Triblock Colloids for Directed Self-Assembly. *J. Am. Chem. Soc.* **2011**, *133*, 7725.
- (13) Binks, B. P.; Fletcher, P. D. I. Particles Adsorbed at the Oil–Water Interface: A Theoretical Comparison between Spheres of Uniform Wettability and “Janus” Particles. *Langmuir* **2001**, *17*, 4708.
- (14) Jiang, S.; Chen, Q.; Tripathy, M.; Luijten, E.; Schweizer, K. S.; Granick, S. Janus Particle Synthesis and Assembly. *Adv. Mater.* **2010**, *22*, 1060.
- (15) Jiang, S.; Granick, S. Controlling the Geometry (Janus Balance) of Amphiphilic Colloidal Particles. *Langmuir* **2008**, *24*, 2438.
- (16) Faria, J.; Pilar Ruiz, M.; Resasco, D. E. Phase-Selective Catalysis in Emulsions Stabilized by Janus Silica-Nanoparticles. *Adv. Synth. Catal.* **2010**, *352*, 2359.
- (17) Hwang, S.; Lahann, J. Differentially Degradable Janus Particles for Controlled Release Applications. *Macromol. Rapid Commun.* **2012**, early view, DOI: 10.1002/marc.201200054.
- (18) Champion, J. A.; Katare, Y. K.; Mitragotri, S. Particle Ashape: A New Design Parameter for Micro- and Nanoscale Drug Delivery Carriers. *J. Controlled Release* **2007**, *121*, 3.
- (19) Crowley, J. M.; Sheridan, N. K.; Romano, L. Dipole Moments of Gyron Balls. *J. Electrostat.* **2002**, *55*, 247.
- (20) Glotzer, S. C.; Solomon, M. J. Anisotropy of Building Blocks and Their Assembly into Complex Structures. *Nat. Mater.* **2007**, *6*, 557.
- (21) Doye, J. P. K.; Miller, M. A.; Mortenson, P. N.; Walsh, T. R. Energy Landscapes: From Clusters to Biomolecules. *Adv. Chem. Phys.* **2000**, *115*, 1.
- (22) Wales, D. J. Exploring the Energy Landscape. *Int. J. Mod. Phys. B* **2005**, *19*, 2877.
- (23) Zhang, Z.; Glotzer, S. C. Self-Assembly of Patchy Particles. *Nano Lett.* **2004**, *4*, 1407.
- (24) De Michele, C.; Gabrielli, S.; Tartaglia, P.; Sciortino, F. Dynamics in the Presence of Attractive Patchy Interactions. *J. Phys. Chem. B* **2006**, *110*, 8064.
- (25) Romano, F.; Sanz, E.; Tartaglia, P.; Sciortino, F. Phase Diagram of Trivalent and Pentavalent Patchy Particles. *J. Phys.: Condens. Matter* **2012**, *24*, 064113.
- (26) Munao, G.; Costa, D.; Sciortino, F.; Caccamo, C. Simulation and Theory of a Model for Tetrahedral Colloidal Particles. *J. Chem. Phys.* **2011**, *134*, 194502.
- (27) Petit, L.; Manaud, J. P.; Mingotaud, C.; Ravaine, S.; Duguet, E. Sub-Micrometer Silica Spheres Dissymmetrically Decorated with Gold Nanoclusters. *Mater. Lett.* **2001**, *51*, 478.
- (28) Anthony, S. M.; Kim, M.; Granick, S. Single-Particle Tracking of Janus Colloids in Close Proximity. *Langmuir* **2008**, *24*, 6557.
- (29) Behrend, C. J.; Anker, J. N.; McNaughton, B. H.; Brasuel, M.; Philbert, M. A.; Kopelman, R. Metal-Capped Brownian and Magnetically Modulated Optical Nanoprobes (MOONs): Micromechanics in Chemical and Biological Microenvironments. *J. Phys. Chem. B* **2004**, *108*, 10408.
- (30) Jiang, S.; Schultz, M. J.; Chen, Q.; Moore, J. S.; Granick, S. Solvent-Free Synthesis of Janus Colloidal Particles. *Langmuir* **2008**, *24*, 10073.
- (31) Walther, A.; Muller, A. H. E. Janus Particles. *Soft Matter* **2008**, *4*, 663.
- (32) Teo, B. M.; Suh, S. K.; Hatton, T. A.; Ashokkumar, M.; Grieser, F. Sonochemical Synthesis of Magnetic Janus Nanoparticles. *Langmuir* **2011**, *27*, 30.
- (33) Yang, S.; Guo, F.; Kiraly, B.; Mao, X.; Lu, M.; Leong, K. W.; Huang, T. J. Microfluidic Synthesis of Multifunctional Janus Particles for Biomedical Applications. *Lab Chip* **2012**, *12*, 2097.
- (34) Li, Y.; Zhang, W.; Hsieh, I.; Zhang, G.; Cao, Y.; Li, X.; Wesdemiotis, C.; Lotz, B.; Xiong, H.; Cheng, S. Z. D. Breaking Symmetry toward Nonspherical Janus Particles Based on Polyhedral Oligomeric Silsesquioxanes: Molecular Design, “Click” Synthesis, and Hierarchical Structure. *J. Am. Chem. Soc.* **2011**, *133*, 10712.
- (35) Bao, H.; Butz, B.; Zhou, Z.; Spiecker, E.; Hartmann, M.; Taylor, R. N. K. Silver-Assisted Colloidal Synthesis of Stable, Plasmon Resonant Gold Patches on Silica Nanospheres. *Langmuir* **2012**, *28*, 8971.
- (36) Kaufmann, T.; Gokmen, M. T.; Rinnen, S.; Arlinghaus, H. F.; Prez, F. D.; Ravoo, B. J. Bifunctional Janus Beads Made by “Sandwich” Microcontact Printing Using Click Chemistry. *J. Mater. Chem.* **2012**, *22*, 6190.
- (37) Duguet, E.; Désert, A.; Perro, A.; Ravaine, S. Design and Elaboration of Colloidal Molecules: an Overview. *Chem. Soc. Rev.* **2011**, *40*, 941.
- (38) van Blaaderen, A. Materials Science: Colloids Get Complex. *Nature* **2006**, *439*, 927.
- (39) Hong, L.; Cacciuto, A.; Luijten, E.; Granick, S. Clusters of Amphiphilic Colloid Spheres. *Langmuir* **2008**, *24*, 621.
- (40) Sciortino, F.; Giacometti, A.; Pastore, G. Phase Diagram of Janus Particles. *Phys. Rev. Lett.* **2009**, *103*, 237801.
- (41) Meng, G. N.; Arkus, N.; Brenner, M. P.; Manoharan, V. N. The Free-Energy Landscape of Clusters of Attractive Hard Spheres. *Science* **2010**, *327*, 560.
- (42) Campbell, A. I.; Anderson, V. J.; van Duijneveldt, J. S.; Bartlett, P. Dynamical Arrest in Attractive Colloids: The Effect of Long-Range Repulsion. *Phys. Rev. Lett.* **2005**, *94*, 208301.
- (43) Sciortino, F.; Tartaglia, P.; Zaccarelli, E. One-Dimensional Cluster Growth and Branching Gels in Colloidal Systems with Short-Range Depletion Attraction and Screened Electrostatic Repulsion. *J. Phys. Chem. B* **2005**, *109*, 21942.
- (44) Chakrabarti, D.; Wales, D. J. Coupled Linear and Rotary Motion in Supramolecular Helix Handedness Inversion. *Soft Matter* **2011**, *7*, 2325.
- (45) Wales, D. J. Energy Landscapes of Clusters Bound by Short-Ranged Potentials. *ChemPhysChem* **2010**, *11*, 2491.
- (46) Calvo, F.; Doye, J. P. K.; Wales, D. J. Energy Landscapes of Colloidal Clusters: Thermodynamics and Rearrangement Mechanisms. *Nanoscale* **2012**, *4*, 1085.
- (47) Haes, A. J.; Haynes, C. L.; McFarland, A. D.; Schatz, G. C.; van Duyne, R. R.; Zou, S. L. Plasmonic Materials for Surface-Enhanced Sensing and Spectroscopy. *MRS Bull.* **2005**, *30*, 368.
- (48) Weissman, J. M.; Sunkara, H. B.; Tse, A. S.; Asher, S. A. Thermally Switchable Periodicities and Diffraction from Mesoscopically Ordered Materials. *Science* **1996**, *274*, 959.
- (49) Pan, G.; Sood, A. K.; Asher, S. A. Polarization Dependence of Crystalline Colloidal Array Diffraction. *J. Appl. Phys.* **1998**, *84*, 83.
- (50) Pan, G.; Tse, A. S.; Kesavamoorthy, R.; Asher, S. A. Synthesis of Highly Fluorinated Monodisperse Colloids for Low Refractive Index Crystalline Colloidal Arrays. *J. Am. Chem. Soc.* **1998**, *120*, 6518.
- (51) Ito, K.; Nakamura, H.; Ise, N. Ordered Structure in Dilute Suspensions of Charged Polymer Lattices as Observed in the Vertical Planes and in Mixtures of Heavy and Light Waters. *J. Chem. Phys.* **1986**, *85*, 6136.
- (52) Macfarlane, R. J.; Lee, B.; Jones, M. R.; Harris, N.; Schatz, G. C.; Mirkin, C. A. Nanoparticle Superlattice Engineering with DNA. *Science* **2011**, *334*, 204.
- (53) Souslov, A.; Liu, A. J.; Lubensky, T. C. Elasticity and Response in Nearly Isostatic Periodic Lattices. *Phys. Rev. Lett.* **2009**, *103*, 205503.
- (54) Atwood, J. L. Kagome Lattice: A Molecular Toolkit for Magnetism. *Nat. Mater.* **2002**, *1*, 91.
- (55) Mohan, P.; Nakajima, F.; Akabori, M.; Motohisa, J.; Fukui, T. Fabrication of Semiconductor Kagome Lattice Structure by Selective Area Metalorganic Vapor Phase Epitaxy. *Appl. Phys. Lett.* **2003**, *83*, 689.
- (56) Yasui, K.; Kato, K. Dipole–Dipole Interaction Model for Oriented Attachment of BaTiO₃ Nanocrystals: A Route to Mesocrystal Formation. *J. Phys. Chem. C* **2012**, *116*, 319.
- (57) Coelfen, H.; Antonietti, M. *Mesocrystals and Nonclassical Crystallization*; Wiley: Chichester, U.K., 2008.
- (58) Yanai, N.; Granick, S. Directional Self-Assembly of a Colloidal Metal–Organic Framework. *Angew. Chem., Int. Ed.* **2012**, *51*, 5368.