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From One to Many: Dynamic Assembly and Collective Behavior of Self-Propelled Colloidal Motors

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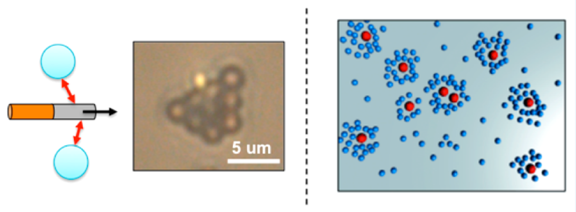
Ⓢ *Supporting Information*



CONSPECTUS: The assembly of complex structures from simpler, individual units is a hallmark of biology. Examples include the pairing of DNA strands, the assembly of protein chains into quaternary structures, the formation of tissues and organs from cells, and the self-organization of bacterial colonies, flocks of birds, and human beings in cities. While the individual behaviors of biomolecules, bacteria, birds, and humans are governed by relatively simple rules, groups assembled from many individuals exhibit complex collective behaviors and functions that do not exist in the absence of the hierarchically organized structure.

Self-assembly is a familiar concept to chemists who study the formation and properties of monolayers, crystals, and supramolecular structures. In chemical self-assembly, disorder evolves to order as the system approaches equilibrium. In contrast, living assemblies are typically characterized by two additional features: (1) the system constantly dissipates energy and is not at thermodynamic equilibrium; (2) the structure is dynamic and can transform or disassemble in response to stimuli or changing conditions. To distinguish them from equilibrium self-assembled structures, living (or nonliving) assemblies of objects with these characteristics are referred to as *active matter.*

In this Account, we focus on the powered assembly and collective behavior of *self-propelled colloids*. These nano- and microparticles, also called *nano-* and *micromotors* or *microswimmers*, autonomously convert energy available in the environment (in the form of chemical, electromagnetic, acoustic, or thermal energy) into mechanical motion. Collections of these colloids are a form of synthetic active matter. Because of the analogy to living swimmers of similar size such as bacteria, the dynamic interactions and collective behavior of self-propelled colloids are interesting in the context of understanding biological active matter and in the development of new applications. The progression from individual particle motion to pairwise interactions, and then to multiparticle behavior, can be studied systematically with colloidal particles. Colloidal particles are also amenable to designs (in terms of materials, shapes, and sizes) that are not readily available in, for example, microbial systems. We review here our efforts and those of other groups in studying these fundamental interactions and the collective behavior that emerges from them. Although this field is still very new, there are already unique and interesting applications in analysis, diagnostics, separations, and materials science that derive from our understanding of how powered colloids interact and assemble.

■ INTRODUCTION

Micromotors are tiny "engines" that move in fluids, powered by chemical reactions or by external energy in the form of light, heat, ultrasound, or magnetic induction (Figure 1).[1−5] Since the initial reports of synthetic micromotors in 2004−2005,[6−8] much work in this growing field has been devoted to understanding the mechanisms of motility and developing applications, especially in separations, chemical and biochemical analysis, environmental remediation, and drug delivery.[9,10]

One of the striking features of autonomous micromotors is the resemblance of their movement to that of living microorganisms. Synthetic micromotors and flagellar bacteria are micrometers long and swim at similar speeds. As a consequence of their small size, they are subject to random thermal forces (Brownian motion) and reorient as they move. They operate in the same regime of Reynolds number, which is the ratio of inertial force ($F = ma$) to viscous force. At a Reynolds number of 10^{-4}, bacteria and micromotors must both apply force continuously in order to continue to move (since their inertia is very small). As they plow through fluid, they create a "wake" over viscous lengths that are comparable to their size. In the case of chemically powered motors and bacteria, they also emit chemicals that can diffuse several body lengths away in the time it takes the motor to move one body length. Effectively, chemically powered motors are surrounded by a cloud of reactants and products that can "signal" their neighbors and thus influence their interactions.

Microscopic objects that move under their own power and interact with each other are interesting as active matter.[11]

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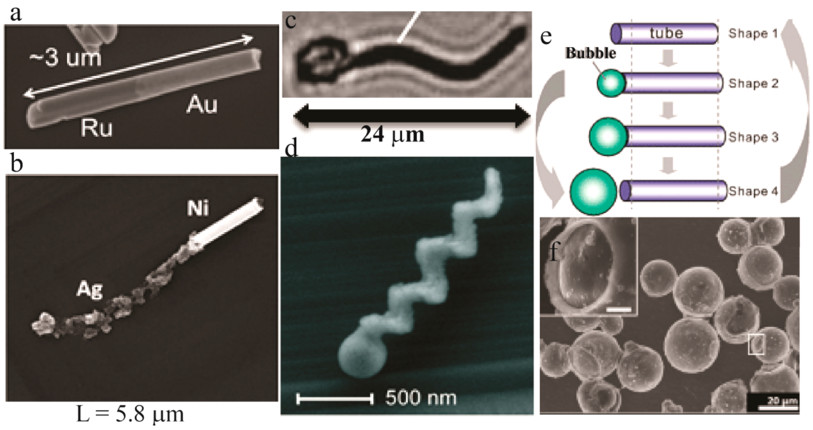

Figure 1. Synthetic micromotors that are powered by energy in different forms: (a) Bimetallic nanorods powered by ultrasound; (b−d) Flexible and helical nanopropellers powered by magnetic fields; (e) Rolled-up microengines powered by chemical fuels through release of bubbles; (f) Janus microswimmers powered by chemical fuels, scale bar 2 μm. Panel a reproduced with permission from ref 2. Copyright 2012 American Chemical Society. Panel b reproduced with permission from ref 3. Copyright 2011 Royal Society of Chemistry. Panel c reproduced with permission from ref 8. Copyright 2005 Nature Publishing Group. Panel d reproduced with permission from ref 10. Copyright 2009 American Chemical Society. Panel e reproduced with permission from ref 4. Copyright 2011 Royal Society of Chemistry. Panel f reproduced with permission from ref 5. Copyright 2013 John Wiley and Sons.

Living systems provide many interesting examples of active matter, for example, self-assembling actin filaments and microtubules, swarms of bacteria, and herds of animals. The organization and maintenance of these structure is dynamic, requiring input of energy, and interesting properties emerge. While most research has focused on living systems, the recent discovery of dynamic, self-assembled structures in collections of synthetic motors has opened new opportunities to exploit the tools of chemistry and microfabrication to study active matter and develop new applications.[12]

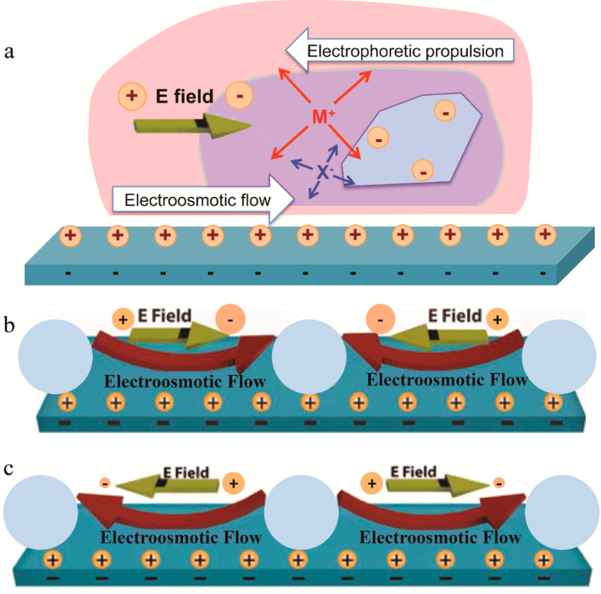

Figure 2. Colloid propulsion by diffusiophoresis. In panel a, a negatively charged, asymmetric particle (blue polygon) generates ions M^+ and X^-, predominantly on the left side of the particle. If the cation diffuses faster than the anion, the concentration gradients create an electric field that propels the charged particle and also generates osmotic flow along the negatively charged substrate. In panels b and c, the colloid (blue spheres) is symmetric or has low charge density relative to the substrate, so electroosmotic flow is the dominant effect. These flows can push the particles toward or away from each other depending on the relative diffusivities of the cations and anions. Reproduced with permission from ref 14. Copyright 2012 the American Chemical Society.

■ PARTICLE INTERACTIONS INDUCED BY CHEMICAL GRADIENTS

Chemically powered microswimmers inevitably create local concentration gradients by consuming reactants and generating products. Concentration gradients can also be imposed externally, for example, by dissolution of a salt crystal near the particle. The resulting concentration gradients can drive particle motion through *diffusiophoresis*.[13,14] Figure 2 illustrates the mechanism of diffusiophoresis for ionic solutes, where electrostatic effects such as electrophoresis and electroosmosis dominate. M^+ and X^- ions are generated at the surface of the particle (blue polygon), and one of these ions diffuses faster than the other. For dense particles that float above a negatively charged glass surface, the up−down symmetry is broken by the glass substrate. Additional symmetry breaking occurs if the particles are irregularly shaped or fabricated as Janus particles. The electric field that results from differential ion diffusion drives both particle movement (through electrophoresis) and fluid flow along the charged substrate (through electroosmosis). Electroosmotic flow is typically dominant and causes particles (blue spheres) to move toward or away from each other along the surface, as illustrated in Figure 2b,c. For example, photolysis of silver chloride particles (AgCl) in water generates hydrochloric acid (HCl). Because H^+ ions diffuse away from the particles faster than Cl^- ions, inward flow along the glass substrate (Figures 2a,b) causes particles to move together, but they avoid contact with each other because of their negative surface charge.[15] In contrast, sparingly soluble $CaCO_3$ particles create outward flows because OH^- ions (formed by hydrolysis of CO_3^{2-} ions) diffuse faster than Ca^{2+} ions.[16] Although the movement is fastest with charged solutes, neutral molecule diffusiophoresis has also been predicted and observed in systems where there are no charged reactants or products.[17−21]

Because ion concentration gradients created by diffusion persist over long distances,[13,22] the electric fields illustrated in

Figure 2 are long-range compared with shorter-range viscous[23] and van der Waals forces[24,25] and can result in the collective behavior of large numbers of particles as discussed below.[15,24−32]

Modes of Collective Behavior Induced by Diffusiophoresis

Chemical signaling is a strategy universally used in biology for communication between cells, to regulate processes such as gene expression, and to coordinate population-wide behaviors of microorganisms. For example, in response to stimuli, bacteria secrete signaling chemicals to which their neighbors respond.[33] Similarly, synthetic colloids can release molecules such as oxygen or acids in response to chemical stimuli[24,27] or light.[15,26,31] The colloids respond to concentration gradients created by their neighbors, resulting in different modes of collective, biomimetic behavior as shown in Figure 3. These include the reversible, photochemically driven assembly and explosion of particle swarms (micro-“fireworks”),[26] dynamic clustering,[24,31] schooling, and predator−prey behavior (Video S1, Supporting Information),[15] all through diffusiophoretic interactions.

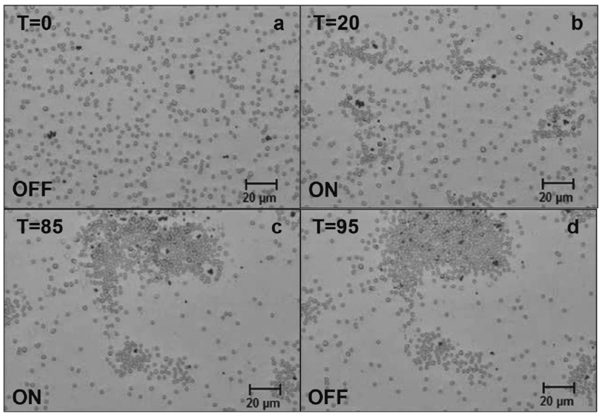

Figure 3. Predator−prey behavior between passive silica colloids (light gray) and active AgCl colloids (darker spheres): (a) No light is applied. (b, c) When illuminated with UV light, the silica spheres actively surround the AgCl particles. Under illumination, an exclusion zone forms around the AgCl particles. (d) This exclusion zone disappears when the light is turned off. Time stamps (in seconds) and the status of the light are given in the upper and lower left corners. Scale bars: 20 μm. Reproduced with permission from ref 15. Copyright 2009 John Wiley and Sons. Images are snapshot sequence from Video S1, Supporting Information.

The diffusion of protons in water is roughly 1 order of magnitude faster than that of anions such as Cl^-, Br^-, or $H_2PO_4^-$, so reactions that release protons have especially strong diffusiophoretic effects. Photolysis of AgCl colloids generates Cl_2 and Ag, and Cl_2 then rapidly disproportionates to HCl and HOCl. Dissociation of HCl molecules generates protons, driving the microscopic processes shown in Figure 2a. This chemical cascade is reversible, so when the light is switched off, the chemical gradients and flows run in the opposite direction. Similarly, irradiation of TiO_2 colloids with UV light, especially in the presence of electron donors such as methanol, releases protons and results in movement.[26] The flows also reverse in this system in the dark, resulting in a “fireworks” effect as the light is switched on and off.

AgCl colloids, through the photochemically driven inward flows illustrated in Figure 2b, attract each other to form schools of colloids. These schools can grow over time by capturing nearby particles, and they also attract each other to merge into larger schools. Colloidal silica particles are not photochemically active, but they respond to the HCl released by AgCl particles and migrate toward them in a kind of predator (silica)−prey (AgCl) interaction (Figure 3 and Video S1 in Supporting Information). The propensity to exhibit these collective behaviors increases with colloid number density and chemical reactivity, as supported by both experimental data[24] and simulations.[12] This is similar to the prediction of bacterial clustering through chemotactic collapse in the Keller−Segel model (KS model),[34,35] which characterizes the role of chemical sensing in bacterial pattern formation. This model proposes that cluster formation by bacteria occurs only beyond a threshold population density (“Chandrasekhar” number) that is proportional to the reciprocal of the chemical production rate (i.e., chemical reactivity). Although this threshold has not yet been quantitatively identified in colloidal systems, the similarities in behavior are striking and the quantitative theory may help in the design of colloids that better mimic their living counterparts.

Transitions between Collective Behaviors via Orthogonal Stimuli

Colonies of living organisms such as ants can transition between modes of collective behavior (e.g., defense and foraging) in response to different stimuli (enemies and food). To mimic these transitions, we can design active colloids that are driven by two or more reactions that propel particles at different speeds or in different directions. By switching the dominant reaction through different stimuli, we can alter the collective behavior of the colloidal assembly.

An example of this switching occurs when H_2O_2 is added to the AgCl−UV light system, forming a “chemical clock” (Video S2, Supporting Information).[28] Two competing processes, the reduction of AgCl to Ag by UV light and the oxidation of Ag to AgCl by peroxide, produce and consume HCl, respectively. This competition and the associated gradient reversal lead to periodic attraction and repulsion between colloids. As a result, active AgCl colloids exhibit an oscillatory attach−release motion with neighboring silica spheres, as shown in Figure 4a.

Systems that exhibit sequential transitions between two modes of collective behavior can be designed by using a reversible chemical reaction. For example, Ag_3PO_4 microparticles in dilute ammonia rapidly reach an equilibrium state.[29] Addition or removal of ammonia shifts the equilibrium, producing or consuming ions that include fast-diffusing OH^-. The system is analogous to the photochemically driven AgCl system, in that Ag_3PO_4 colloids can be driven into clustering and dispersing states by the removal or addition of ammonia, as shown in Figure 4b. The attraction between active Ag_3PO_4 and passive silica colloids upon removal of ammonia leads to hierarchical clustering, whereas large Ag_3PO_4 particles can pump away tracer particles upon addition of ammonia (Video S3, Supporting Information). Ag_3PO_4 colloids also respond to a second stimulus, namely, UV light, and the decomposition of Ag_3PO_4 drives the colloids in the same way as the addition of ammonia. With two independent stimuli driving the Ag_3PO_4 colloids, a NOR gate can be designed with UV and ammonia as inputs (“present” means “1”), and collective behaviors of clustering and dispersion as output “1” and “0”, respectively, as shown in Figure 4c. When this NOR gate is in operation, the output “1” can be obtained only when both inputs are “0”. The

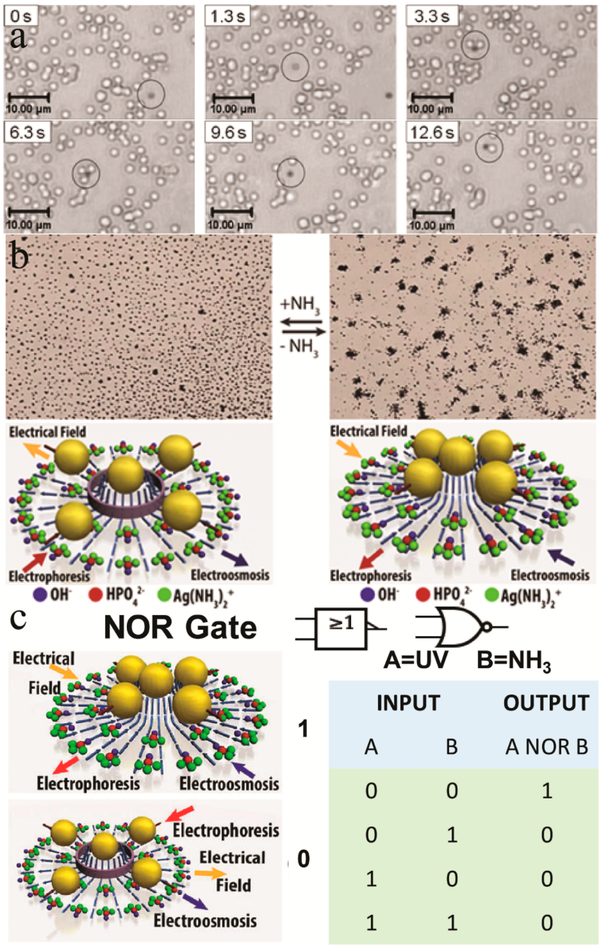

Figure 4. Transition between collective behaviors. (a) Oscillatory attach−release interactions between active AgCl colloids and nearby passive silica spheres due to the two competing processes sketched at the right (Video S2, Supporting Information). (b) Reversible transition between two collective behaviors through diffusiophoretic interactions and gradient reversal. Silver orthophosphate colloids disperse and cluster reversibly with addition and removal of ammonia. (c) The transition from dispersion to clustering in panel b can be halted by UV light, and the two different responses of the colloids under two orthogonal inputs enable the design of a "NOR" logic gate. Reproduced with permission from refs 28 (panel a) and 29 (panels b and c). Copyright 2010 and 2013 the American Chemical Society.

addition of either component shifts the chemical equilibrium that disperses Ag_3PO_4 clusters and consequently produces an output of "0".

Applications of Diffusiophoretic Propulsion

The study of colloid propulsion and collective behavior by diffusiophoresis already suggests several new applications. Diffusiophoretic transport can recruit particles to source zones of ions, allowing one to both detect (with fluorescent markers) and repair cracks in materials. For example, scratches in glass and cracks in bone, in contact with aqueous solutions, release ions locally at a much higher rate than smooth surfaces. This effect has been used to recruit polymerization agents to scratches in plastics[36] and growth factors to damaged bones.[37] Diffusiophoretic pumping induced by salt concentration gradients can enhance oil recovery by driving electroosmotic fluid flow in dead-end pores that contain trapped oil.[38] Salt concentration gradients at the surface of electrodialysis membranes actively drive negatively charged colloids, such as clays, to the membrane. This effect has only recently been recognized as a major contributor to membrane fouling.[39] By placing $CaCO_3$ particles at the membrane surface, one can reverse the direction of colloid propulsion. This may represent a solution to fouling in desalination and other membrane-based technologies. These new approaches to long-standing problems derive from the understanding gained in the study of active colloids and suggest that many more applications are possible.

■ SHORT-RANGE INTERACTIONS BETWEEN ACTIVE COLLOIDS

Although chemical gradients that act over long distances are sufficient to drive the collective behavior of colloids, short-range interactions, acting on length scales comparable to the dimensions of the particles themselves, are also important, especially at high particle density. Short-range forces include electrostatic interactions, van der Waals attraction, viscous forces, and steric repulsion, among others. The specific interplay between the moving colloids and their environment thus depends on their composition, shape, size, and surface charge. This is especially true for active colloids that do not release chemicals, such as those propelled by electromagnetic fields or ultrasound. Even for colloids propelled by chemical gradients, short-range effects can lead to behaviors that cannot easily be explained by diffusiophoresis alone.

Interplay between Chemical and Nonchemical Effects

Short-range forces often result in specific pairwise interactions between particles (Figure 5). One example is the assembly of bimetallic microrods moving in H_2O_2 solutions, which transiently form staggered pairs as shown in Figure 5a (Video S4, Supporting Information).[40] The electrocatalytic decomposition of H_2O_2 generates protons at one end of the Pt−Au rod and consumes them at the other. The most favorable electrostatic interaction occurs when the region of negative charge in the solution surrounding the end of one rod is close to the region of positive charge around the other. The attractive force is on the same order as the drag force that can separate the rods, so catalytic doublets (and some triplets) form and dissociate over a time scale of seconds.

Shorter range van der Waals attractions have been invoked to explain particle dimers formed by tadpole-shaped Pt−SiO_2 microparticles in H_2O_2 (Figure 5b).[41] Hydrodynamic interactions at low Reynolds number can also generate attractive or repulsive forces between particles.[42−44] Indeed, rod-shaped bacteria align into organized aggregates predominantly because of these hydrodynamic effects.[45] Thus, pairwise interactions can arise from several kinds of forces, which become complicated when chemical reactions are also involved in driving the motion.

Multiple effects lead to dynamic interactions in catalytically powered microrotors (Figure 5c, Video S5, Supporting Information),[46] which can rotate as fast as 400 rpm. Interestingly, the pairwise attraction or repulsion depends on the relative sense of rotation of the two particles. The mechanism is not understood but may involve both electrostatic and hydrodynamic interactions.

Self-propelled particles that have hydrophobic surfaces can spontaneously form an organized structure in water via hydrophobic and capillary effects. For example, millimeter sized poly(dimethylsiloxane) disks coated with Pt autonomously move and self-assemble into rotating dimers through

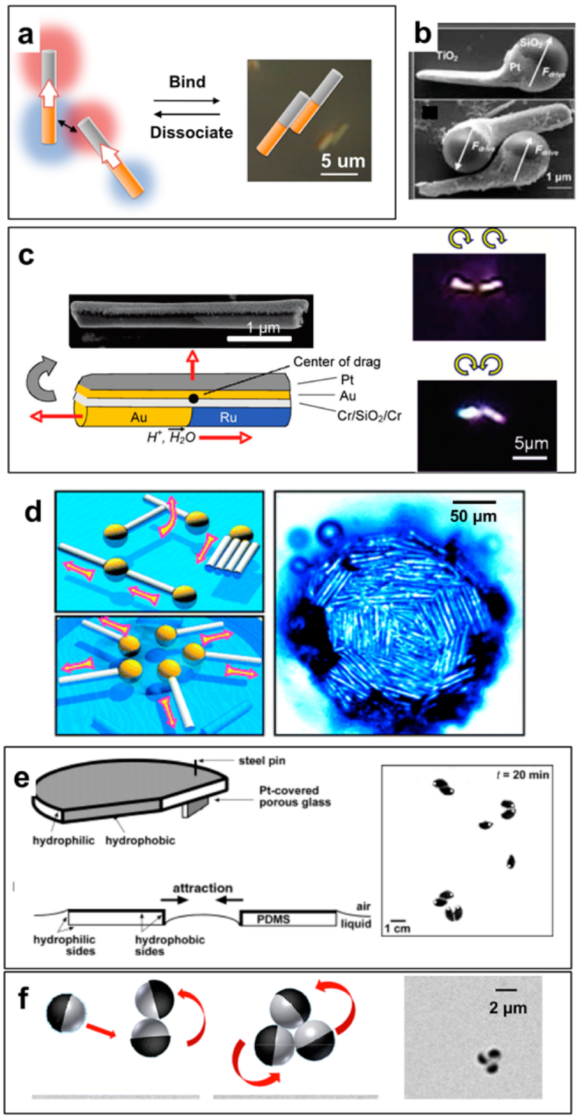

Figure 5. Dynamic assembly of chemically propelled colloids under the influence of nonchemical effects. (a) The reversible binding and dissociation of pairs of bimetallic rods propelled by the electrocatalytic decomposition of H_2O_2. The colors represent proton concentrations (red = high; blue = low). (b) The dimer formed by two tadpole shaped catalytic motors. (c) Two catalytic rotors dynamically interact with each other. (d, e) Assembly induced by capillary forces between bubble-propelled microtubes (d) or autonomously moving microdisks (e). (f) Janus microspheres with hydrophobic surfaces dynamically assemble in aqueous H_2O_2 solutions. Panel a reproduced with permission from ref 40. Copyright 2013 the National Academy of Sciences. Panel b reproduced with permission from ref 41. Copyright 2010 John Wiley and Sons. Panel c reproduced with permission from ref 46. Copyright 2009 American Chemical Society. Panel d reproduced with permission from ref 48. Copyright 2013 Royal Society of Chemistry. Panel e reproduced with permission from ref 47. Copyright 2002 John Wiley and Sons. Panel f reproduced with permission from ref 49. Copyright 2013 the American Chemical Society.

capillary forces (Figure 5e).[47] At the microscale, similar capillary effects induce swarming and dynamic clustering of microjets propelled by bubble ejection (Figure 5d).[48] Hydrophobic octadecyltrichlorosilane-modified silica microspheres capped with a catalytic Pt hemisphere patch dynamically aggregate into small clusters in H_2O_2 solutions, most likely by association of the hydrophobic surfaces of the self-propelled Janus spheres (Figure 5f).[49] In all three systems the same chemical reaction (catalytic decomposition of H_2O_2) occurs, and it is possible that diffusiophoretic or osmotic interactions also contribute to particle assembly.

Assembly without Chemical Reactions

Self-propelled colloids can also dynamically assemble in the absence of chemical propulsion. One example is the fast axial movement and rotation of metallic microrods in an acoustic field.[2,50,51] Rapidly spinning rods spontaneously assemble into polar chains that are only one particle wide (Figure 6a, Video S6, Supporting Information). Microrods shuttle in both directions along these chains while maintaining their alignment. Janus rods align in a head-to-tail manner (e.g., AuRu rods form a chain of AuRu|AuRu|AuRu...). Once the acoustic energy is

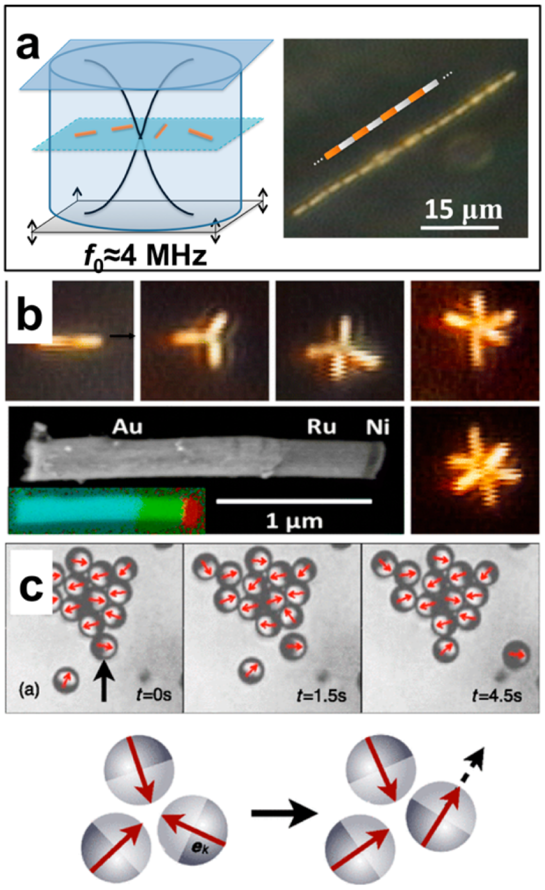

Figure 6. Assembly of self-propelled colloids without chemical propulsion. (a) Metallic microrods levitated in water by ultrasonic standing waves (left) assemble into rapidly spinning chains at the nodal plane of an acoustic cell (right, cartoons of gold–ruthenium microrods are superimposed on the optical micrograph of a chain formed by such rods). (b) Metallic microrods with ferromagnetic tips (bottom left, an SEM image and the elemental mapping false color of one Au/Ru/Ni rod) dynamically assemble into dimers, trimers, and multimers (optical micrographs). (c) Janus microspheres (2 μm radius SiO_2 half-coated with graphite) propelled by demixing of water–lutidine solutions form dynamic clusters by a self-locking mechanism. Panel a reproduced with permission from ref 2. Copyright 2012 American Chemical Society. Panel b reproduced with permission from ref 54. Copyright 2014 American Chemical Society. Panel c reproduced with permission from ref 55. Copyright 2013 the American Physical Society.

removed, the chain rapidly dissociates and the particles resume their individual Brownian motion. This assembly−dispersion−assembly process is completely reversible and can also be driven chemically,[52] demonstrating that the self-assembly process is dynamic. Although the rotation of these metallic rods is not well understood,[53] the respective contributions of electrostatic interactions, van der Waals forces, hydrodynamic interactions and primary and secondary acoustic forces between moving metallic rods in their assembly into chains has been studied.[2,67] In particular, since a vortex forms in the fluid around the rapidly spinning rods, hydrodynamic interactions are likely to be a major factor in the assembly process.

Acoustic levitation of metallic microrods in water provides a convenient way to study their collective behavior while providing an axial propulsion force. The kinetic energy imparted by ultrasound is analogous to temperature in the system and can be adjusted continuously by adjusting the acoustic power.[54] Interestingly, metallic microrods containing a nickel stripe at one end condense into geometrically regular dimers, trimers, and higher multimers (Figure 6b). The assembly of these colloid "molecules" is driven by attractive dipolar interactions between the ferromagnetic nickel stripes. The propulsion of the rods brings the fast moving rods together, where on close approach or collision they "bind." The propulsive force also serves to overcome the magnetic attraction between rods, preventing their irreversible aggregation and establishing equilibrium distributions of monomers, dimers, trimers, and higher multimers. Arrhenius and van't Hoff analyses determined the "bonding energy" between individual colloidal particles, which corresponded closely to the calculated magnetic dipole energy. This study illustrates that the ultrasonic cell is a useful test bed for measuring the strength of interparticle forces and also for assembling colloid multimers with complex shapes.

Self-locking was recently found by Speck et al. to be another viable mechanism by which self-propelled colloids could achieve dynamic self-assembly.[55] They fabricated Janus microspheres half-coated with carbon, which could be propelled autonomously by thermally induced local demixing of water and lutidine. Janus spheres that moved at ∼1 μm/s formed dynamic clusters, and the mean cluster size increased with motor speed. In order to explain the clustering behavior, the authors proposed a self-locking mechanism, in which the motor moves at a speed that is fast relative to rotational diffusion. As a result, particles that collide head-on remain "locked" in an aggregate, and the aggregation increases with increasing particle speed. The assembly is dynamic because particles continuously merge with and detach from the clusters. Importantly, this assembly mechanism appears to be generically applicable to any propulsion mechanism, independent of van der Waals forces, chemical gradients, and hydrodynamic effects.

CHEMOTAXIS OF ACTIVE COLLOIDS

In concentration gradients of chemical fuels, active colloids can undergo biased diffusion along the gradient, a phenomenon known as chemotaxis. Chemotaxis is important in the directional movement of cells such bacteria.[56] Recently chemotactic effects have been observed with bimetallic nanorods and Janus colloids, which move up externally imposed gradients of fuels and accumulate in regions of high concentration (Figure 7).[57−60] In gradients of their substrates, individual enzyme molecules such as catalase, urease, and RNA and DNA polymerase also chemotax toward higher substrate concentration.[61−63] This effect concentrates catalytic particles or enzyme molecules in regions of high substrate concentration, as illustrated in Figure 7. By placing a mixture of enzyme molecules in one channel of a microfluidic device and the substrate for one enzyme in the other, it is possible to separate the active and inactive catalysts based on their motility.[64]

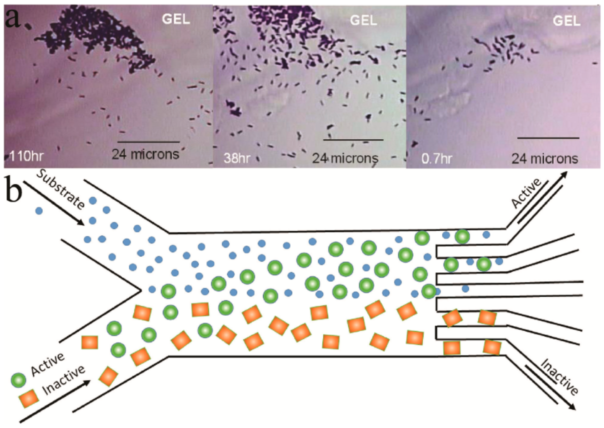

Figure 7. (a) Chemotaxis of Au−Pt microrods toward a gel containing H_2O_2. Reproduced with permission from ref 57. Copyright 2007 the American Physical Society. (b) Separation of active and inactive enzyme molecules based on chemotaxis in a gradient of the enzyme substrate. Reproduced with permission from ref 64. Copyright 2014 American Chemical Society.

Bacterial chemotaxis typically involves timing and memory effects that are not operative in colloidal systems. In contrast, the chemotactic behavior in synthetic systems can originate from a simple enhanced diffusion mechanism. Since the catalytic particles (colloids or enzymes) exhibit higher diffusivities with higher fuel/substrate concentrations,[58,65] the diffusion rate increases on moving up the gradient and decreases on moving down the gradient. Faster diffusion leads to a greater spread of the particles toward higher fuel/substrate concentration and thus movement of the "center of gravity" up the concentration gradient. This mechanism does not require temporal memory[56] and is supported by a finite element simulation of convection−diffusion in microfluidic channels.[63] Other mechanisms, including orientation in chemical gradients,[66] have been suggested as possibilities for colloidal chemotaxis.

In addition to chemotaxis in externally applied fuel gradients, active colloids can respond to the gradients produced by other colloidal particles and diffuse toward or away from them. This local chemotaxis introduces an effective attractive or repulsive interaction between active colloids that is substrate-specific. Evidence of this localized chemotaxis is observable with colloids that are functionalized with enzyme molecules, or at the molecular level when enzyme cascades are introduced into microfluidic channels. For example, catalase is an enzyme that undergoes faster diffusion at higher concentration of its substrate, H_2O_2. H_2O_2 is generated by glucose oxidase, which catalyzes oxidation of glucose. The net effect of this catalytic cascade is the enhanced diffusion of catalase toward glucose oxidase in the presence of glucose.[61]

OUTLOOK AND CONCLUSIONS

Although synthetic micromotors are now entering into their second decade,[6−8] the study of colloids as active matter is still just beginning. Colloids can be powered by chemical reactions and by other sources of energy, and there are many possible contributors to their long- and short-range interactions. We have focused here on some of the best-understood interactions that drive particle assembly and collective behavior, but other behaviors (for example, enzymatic chemotaxis) remain poorly understood.

Although we have not emphasized the applications of colloidal active matter, there are already several promising ones that are emerging in biochemical analysis,[67] drug delivery,[68] separations,[69] and materials science.[16,70] The practical side of this field will continue to develop as new collective phenomena are discovered and their mechanisms are better understood. Self-propelled autonomous motors make their own decisions based on the local environment. This ability to respond and move imparts versatility and is the foundation of collective behaviors such as swarming and schooling. For many future applications, it will be useful to have motors that can independently carry out operations such as sensing and reporting, with different populations of interacting motors performing different tasks.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Descriptions of supporting video files and videos in avi format. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.accounts.5b00025.

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