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Review

A Practical Guide to Active Colloids: Choosing Synthetic Model Systems for Soft Matter Physics Research

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Synthetic active colloids that harvest energy stored in the environment and swim autonomously are a popular model system for active matter. This emerging field of research sits at the intersection of materials chemistry, soft matter physics, and engineering, and thus cross-talk among researchers from different backgrounds becomes critical yet difficult. To facilitate this interdisciplinary communication, and to help soft matter physicists with choosing the best model system for their research, we here present a tutorial review article that describes, in appropriate detail, six experimental systems of active colloids commonly found in the physics literature. For each type, we introduce their background, material synthesis, operating mechanisms, notable studies from the soft matter community, and comment on their respective advantages and limitations. In addition, the main features of each type of active colloid are summarized into two useful tables. As materials chemists and engineers, we intend for this article to serve as a practical guide, so those who are not familiar with the experimental aspects of active colloids can make more informed decisions and maximize their creativity.

1. Introduction

There has been mounting research interest over the last fifteen years or so in active colloids,[1-7] which are a special type of colloidal particle or microorganism that converts energy stored in the environment into autonomous motion ("swimming") in liquids. This definition covers a broad range of materials and systems that can be categorized into two varieties: natural active colloids and synthetic active colloids. The former includes bacteria, algae and many types of cells, each with unique propulsion mechanisms, metabolism, and dynamics.[1, 8, 9] The latter are human-made, most often inorganic, and lifeless, yet they also exhibit life-like motion, collective behaviours and mysteries that[10-17] resemble their natural counterparts.[18-20] Synthetic active colloids are also known as "synthetic microswimmers", "micromotors" or "colloidal motors" within various communities,[21] and will be referred to as "active colloids" in this article for the sake of simplicity.

It is arguably this similarity that fuels our imagination and gives rise to active colloids' popularity among researchers from a variety of disciplines. To materials chemists and chemical engineers (such as ourselves), the mere concept of injecting energy (and "life") into synthetic, microscopic particles is inherently fascinating, not to mention the tantalizing prospect of biomimetic, intelligent materials with unique properties. To a biomedical engineer, the movie *Fantastic Voyage* comes to mind (even though it's become a bit of a cliché after extensive references) and vistas of nanomachines roaming in blood vessels and killing cancer cells readily excite and inspire. Soft

matter physicists approach this topic from yet another angle. To them, active colloids become a useful, simple model system of active matter,[22-29] a key concept for understanding complex processes such as the formation of biofilms, metastasis of cancer, self-organization of cellular functions, and even flocks of birds, schools of fish and crowds of people. Soft matter is often considered an interdisciplinary subfield of physics covering a wide range of phenomena across many scales,[30-34] and active colloids are a vivid testimony to this interdisciplinarity.

With interdisciplinarity comes a cost of communication among disciplines, and sometimes formidable obstacles for scientists on either side. For example, Janus particles with special material properties or unique shapes are often a prerequisite for functional active colloids,[35-38] yet their chemical/physical synthesis can appear daunting to non-experts. By the same token, the physical analysis of colloidal dynamics and their assembly can be equally elusive to materials scientists and engineers (not to mention unfamiliar terms such as "Langevin equations" and "Onsager principles"!). As the research field of active colloids prospers and collaborations develop, this issue worsens, where a lack of effective communication between materials chemists and physicists can create barriers that undermine productivity.

This tutorial review is one step towards bridging this gap, by describing the experimental details of the synthesis and operation of six active colloid systems typically found in the literature: bimetallic rods or spheres, Pt-coated Janus microspheres, Janus colloids demixing water-lutidine, photochemically powered TiO_2 or Fe_2O_3, ICEP microswimmers and Quincke rollers (see later sections for detailed descriptions). These six types belong to two main categories: phoretic active colloids,[39-43] and those powered externally.[44-47] For each type,

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we describe their material synthesis, operating mechanisms, notable examples of physics studies, advantages and limitations. To assist readers unfamiliar with these designs, two tables are included that list important features of all these active colloid systems (Table 1) and rank each system (somewhat subjectively) from 1 to 3 stars based on qualities such as the simplicity of active colloid synthesis or degree of user control (Table 2). The goal of this article is to help soft matter physicists, experimentalists and theorists alike, learn the pros and cons of each active colloid system, and choose the system most suitable for their research.

Before we begin, it is important to note a few caveats. First, we presume that readers have basic knowledge of colloidal physics and general chemistry. In particular, for readers unfamiliar with "active colloids" or new to this field, a recent tutorial review from us is highly recommended,[12] particularly for understanding various phoretic mechanisms ("phoretic" refers to motion of colloidal particles due to a gradient in a particular quantity, such as concentration or electric potential) mentioned in the following discussions (ref. 40 is also useful in this regard). The current review serves as a natural extension to our earlier review. Second, this article is not intended to educate the reader about soft matter physics or the physics of microswimmers, nor do we intend to list all the possible research topics one can engage by using active colloids. Rather, this article is like a detailed brochure for picking the right car model without reiterating how engines work, and where to drive the car is entirely up to the driver. Third, emphasis is placed on collective behaviours and dynamics in complex environments, in light of recent research trends. Finally, we have chosen to focus on six tractable experimental systems that are relatively clean, understandable and popularly used by soft matter physicists as models of active matter. As a result, we must unfortunately leave aside many important realizations of active colloids such as various modular microswimmers[48] and ferromagnetic colloidal microswimmers,[49, 50] which have not been discussed in the present article. Much of the following commentary comes from our direct experience over the past decade. Many of our comments are thus inevitably subjective and should be read with a proper amount of doubt and criticism.

Type of colloids		Mechanism	Major advantages	Shortcomings	Ref
Phoretic microswimmers	Bimetallic rods/spheres (2.1.1)	Self-electrophoresis	1. Mechanism (relatively) well-understood 2. Relatively fast (typically a few tens of μm/s)	1. Synthesis not easy 2. Poor sample uniformity 3. Bubbles appear in field of view at long times, high particle densities	51-54
	Pt-coated microspheres (2.1.2)	Understanding incomplete (Neutral or ionic diffusiophoresis, self-electrophoresis?)	1. Very simple synthesis 2. Simple experiment setup 3. Able to visualize orientation	1. Controversial mechanism 2. Bubbles appear in field of view at long times, high particle densities 3. Not very fast (typically ~ 10 μm/s)	55-57
	Water-lutidine demixers (2.2.1)	Neutral diffusiophoresis (with controversy)	1. Very simple synthesis 2. Clean, no chemical reaction 3. Can be externally modulated 4. Able to visualize orientation	1. Difficult to precisely control temperature or composition 2. Require a slightly more sophisticated experimental setup	58
	Photochemical Janus particles (2.2.2)	Self-electrophoresis (metal-coated TiO₂ microspheres). Others are unclear, suspected to be ionic diffusiophoresis	1. Particles of tuneable sizes, shapes and material properties 2. Chemical interactions give rise to interesting collective behaviours	1. Difficult to synthesize 2. Poor sample uniformity 3. Exact nature of chemical reactions or chemical species are often unknown	59-61
Externally powered	ICEP swimmers (2.3.1)	Induced charge electrophoresis (ICEP) under AC electric fields	1. Very simple synthesis 2. Mechanism well-understood 3. Clean, no chemical reaction 4. Both the magnitude and the nature of pair-wise interactions can be externally modulated 5. Able to visualize orientation	1. Require a slightly more sophisticated experimental setup 2. Experiments can be sensitive to additives or contaminants	62
	Quincke rollers (2.3.2)	Spontaneous rotation of dielectric microspheres under DC electric fields (Quincke effect)	1. Very simple synthesis 2. Mechanism well-understood 3. Clean, no chemical reaction 4. Can be externally modulated 5. Able to visualize orientation	1. Require a slightly more sophisticated experimental setup 2. High voltages required 3. Pair-wise interaction is dominated by hydrodynamics, therefore lacking the rich tunability from chemical swimmers or ICEP swimmers	63

Table 1 A brief summary of six types of active colloids

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Table 2 Subjective scoring for features of six types of active colloids (see Appendix for details)

Type of colloids		Mechanism clarity	Synthesis simplicity	Experiment simplicity	Ease of visualizing orientation	Long term observation	Material flexibility	Degree of user control
Phoretic microswimmers	Bimetallic	★★★	★☆☆	★★★	★★☆	★☆☆	★★☆	★☆☆
	Pt Janus	★★☆	★★☆	★★★	★★★	★☆☆	★☆☆	★☆☆
	demixing	★★☆	★★☆	★☆☆	★★★	★★★	★☆☆	★★☆
	photochemical	★★☆	★☆☆	★★☆	★★☆	★★☆	★★★	★★☆
Externally powered	ICEP	★★★	★★☆	★★☆	★★★	★★★	★★★	★★★
	Quincke rollers	★★★	★★★	★★☆	☆☆☆	★★★	★★★	★★☆

2. Common active colloid systems: what and how

2.1 Chemically powered active colloids

Arguably the most studied active colloids, regardless of which community, is the type powered by surface chemical reactions. These colloids are often spheres or rods with a Janus structure (named after the two-faced Roman god of beginnings and endings, "Janus" particles generally consist of two opposite-facing segments[64]), and undergo either electrophoresis or diffusiophoresis as a result of an asymmetric chemical reaction and its resulting gradient. Two examples of chemically powered, phoretically moving active colloids are presented in this section: gold-platinum (Au-Pt) bimetallic rods/spheres (section 2.1.1), and platinum (Pt) coated Janus spheres (section 2.1.2).

Note that a large number of studies in the materials chemistry and biomedical engineering communities focus on active colloids that chemically produce bubbles and move (so called "microjets"),[65-67] but this system has rarely been studied by soft matter physicists, possibly because of its poor mono-dispersity, uniformity, and the difficulty in visualization and in achieving collective behaviours due to the presence of bubbles.

2.1.1 Au-Pt bimetallic colloids

1) Background

The "grandfather" of all synthetic active colloids, bimetallic microrods moving in hydrogen peroxide (H_2O_2) was first reported around 2004-2005, when the groups of Sen and Mallouk from Penn State [51] and the Ozin group from Univ. Toronto[68] independently discovered them. During the early days, this type of active colloid usually took the form of a bimetallic microrod (2 μm long and 200-300 nm in diameter), but bimetallic Janus microspheres were also developed later.[69] As one of the most studied phoretic active colloids, bimetallic colloids have been the subject of numerous reports on their operating mechanism,[54, 70, 71] synthesis,[72] modification and applications,[73-75] particularly among materials chemists.

2) Synthesis

Bimetallic rods are most commonly synthesized by template assisted electrodeposition (Fig. 1a).[72] Briefly, an electrically inert, porous template (anodized aluminium oxide, known as AAO membranes,[76] or polycarbonate, known as PC membranes [77]) is filled with a metal plating solution, and an electrical current is applied by an electrochemical station that reduces the aqueous metal ions into metal atoms that subsequently deposit into the template pores. By controlling what templates are being used, what metals are being plated, and the amount of charge passing through, the material composition and the rod dimensions can be tuned.

There are two ways to synthesize bimetallic spheres. The first strategy[69] starts with a typical fabrication of Janus microspheres, where a layer of metal (e.g. Au) is deposited by physical vapor deposition (PVD) on a monolayer of inert microspheres (e.g. polystyrene or PS), producing a PS Janus particle that is half coated with Au. This process is then repeated multiple times, with the coated particle reshuffling its orientation each time. This is done by removing the coated particle after each deposition and re-spreading it onto a substrate. After a few iterations of deposition, the PS particle is fully coated with Au, and one final deposition of Pt makes it a Au-Pt bimetallic sphere. The second strategy[78, 79] starts with a gold microsphere, then half-coats it with Pt by PVD, resulting in a Au-Pt Janus sphere. Au microspheres are commercially available, but can be chemically synthesized in the lab as well.[80] Note that in the case of solid gold microspheres, the particles are much denser than in the case of the PS particles, and thus are more susceptible to sedimentation.

3) Mechanism

Regardless of the form factor or synthetic method, a bimetallic colloid is believed to move in H_2O_2 by self-electrophoresis (Fig. 1b). A detailed description of this mechanism can be found in a number of excellent references.[53, 54, 81] Briefly, the oxidation and reduction of H_2O_2 preferentially occur on the Pt (anode) and Au (cathode) sides of the particle, leading to asymmetric proton fluxes out of and into the Pt and Au surfaces, respectively, and an electric field pointing from Pt to Au. Because a metallic colloid is often negatively charged in water,[53, 82] it moves in the self-generated electric field by electrophoresis, hence the name of the mechanism. There is nothing particularly special about Pt and Au; bimetallic rods made from several other metal pairs have also been shown to move in H_2O_2, and the forward-facing metal can be predicted in each case from the self-electrophoresis mechanism.[48] Although over the recent years there have been a few studies that hint at possible contributions from other mechanisms,[83, 84] most likely diffusiophoresis, the dominance of self-electrophoresis is largely unchallenged.

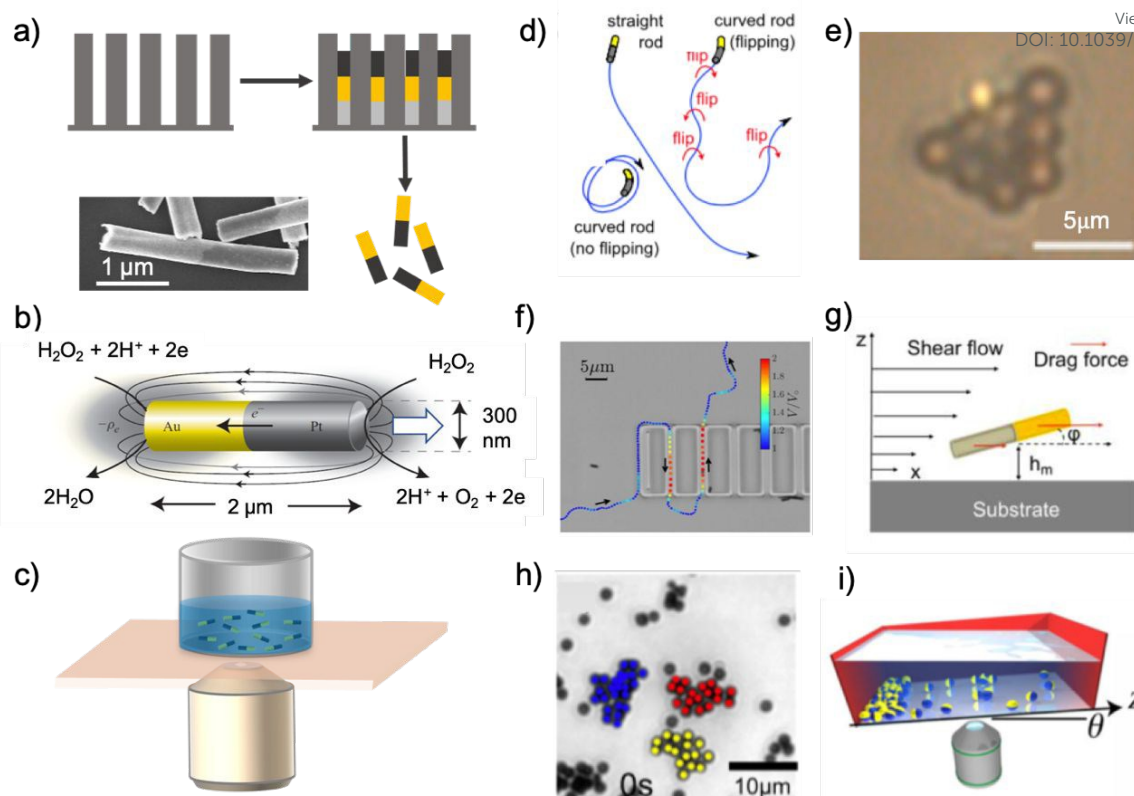4) Notable studies in soft matter physics

Figure. 1 Bimetallic microswimmers undergoing self-electrophoresis. a) Fabrication of bimetallic microrods via template assisted electrodeposition. b) Au-Pt microrod moves in H_2O_2 by generating and maintaining a proton gradient (see main text for details). Reprinted with permission from ref 71. Copyright 2011, Cambridge University Press c) Experimental setup for bimetallic microswimmers. d) Flipping dictates the curvature of trajectories for bimetallic microswimmers. Reprinted with permission from ref 89. Copyright 2013, American Physical Society. e) A moving bimetallic microswimmer assembles negatively charged tracer microspheres at its front. Reprinted with permission from ref 91. Copyright 2013, National Academy of Sciences. f) A bimetallic microswimmer speeds up in a tightly confined polymer microchannel. Reprinted with permission from ref 92. Copyright 2016, American Physical Society. g) A bimetallic microswimmer moves upstream by tilting its body. Reprinted with permission from ref 94. Copyright 2017, American Chemical Society. h) Dynamic assembly of bimetallic microspheres in H_2O_2 into clusters. Reprinted with permission from ref 78. Copyright 2012, American Physical Society. i) Sedimentation of bimetallic microspheres in H_2O_2. Reprinted from ref 98 which is licensed under CC BY 3.0, published by American Physical Society.

Although bimetallic active colloids moving in H_2O_2 have received tremendous attention in the materials chemistry community, studies from the physics community have been relatively limited.

The Shelley and Zhang labs from NYU and their collaborators carried out a few notable studies on bimetallic microrods, focusing primarily on their individual dynamics and pair-wise interactions.[85-89] In 2013 they studied the curved trajectories of these microrods and related the chirality switching of the trajectories to the flipping of rods, which are typically not perfect cylinders but rather slightly curved (Fig. 1d).[89] In a series of papers published in the coming years they focused on the dynamic assembly of trimetallic rods (as models of hydrodynamic "pushers" that push liquid outward away from their waists, or "pullers" that do the opposite),[87, 90] and their interaction with inert structures placed nearby.[86, 88] Wang et al. also reported the staggered assembly of bimetallic rods into dimers and trimers, and the formation of tracer microspheres into close packed crystals near the tip of a moving bimetallic rod (Fig. 1e).[91] In all cases they noted a strong interplay between phoretic and hydrodynamic interactions, which are echoed by numerous reports by other groups, such as a study in 2015 where bimetallic rods are found to speed up in tightly confined microchannels (Fig. 1f),[92] in contrast to a purely hydrodynamic microswimmer. More recently, Shelley and Zhang studied how a bimetallic rod moving along a substrate with a tilted angle

moves against flow, i.e. their rheotactic behaviours,[93] and discovered that such capability is dependent on the ratio of the length of the Au to the Pt segments. This is an interesting development from a previous study on the rheotaxis of similar bimetallic rods by Ren et al. (Fig. 1g).[94] There have also been a few studies on the dynamic assembly of bimetallic rods by materials chemists, but physical analysis was usually less rigorous (see ref 95 and references therein).

Several studies have used bimetallic microspheres to probe the dynamic assembly of active colloids, and in these studies the Janus particles were made by coating a gold sphere with Pt. In an early study from 2012,[78] Theurkauff et al. reported a cluster phase at an intermediate density of Au-Pt microspheres moving randomly in H_2O_2, and proposed that the phase separation is due to a chemotactic mechanism similar to bacterial aggregation (Fig. 1h). The same group later conducted a more systematic and complete experimental study of similar assembly process.[79] Using much more robust statistical data, they were able to understand the cluster size distribution and fluctuations, and proposed a model where colloidal orientations were random. The same group also studied the non-equilibrium sedimentation of the same Au-Pt bimetallic spheres (Fig. 1i), and rationalized their observation with an effective temperature[96, 97] that is dependent on the colloid activity.[98] Such an effort to describe a non-equilibrium process using equilibrium concepts represents an important branch of

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thinking where active colloids (of different varieties, see below) are useful as a model system.

5) Pros and cons

Bimetallic rods or spheres could appeal to soft matter physicists for two reasons. First, their propulsion mechanism has for the most part been elucidated. The distributions of ions, electric field and flow field around a moving bimetallic rod or sphere are relatively well-understood[71, 91, 99] (but experimental measurements are scarce), facilitating efforts in modelling and understanding experimental observations. Second, the choice of colloidal shapes, whether rod or sphere, might be a useful feature because many motile bacteria have slender bodies, whereas spheres are easier to model and generate clusters that are more regular in shapes. Particles of more complex shapes sometimes offer new opportunities for richer phenomena.

Bimetallic microswimmers have several important limitations. First, the use of H_2O_2 has been notorious, not necessarily because of its toxicity (an important issue for biomedical engineers), but more because the generation of bubbles and the experimental difficulties that entails. Efforts in replacing H_2O_2 in this particular propulsion mechanism are largely fruitless,[100] although clever engineering designs can mitigate this problem (see ref 101 and discussion in the following section for an excellent example). Note that active colloids with a Pt coating, regardless of mechanisms or shapes, often suffer from the issue of bubbles in H_2O_2 because of the supreme catalytic performance of Pt in decomposing H_2O_2 into O_2.[102, 103] It is also a major source of energy inefficiency.[99]

The second limiting factor lies in material synthesis. Either electrochemical deposition or the solution-based synthesis of gold microspheres is not exactly within the comfort zone of many experimental physicists. The electrochemical synthesis of rods is more straightforward in its physical principle, but requires multiple steps, a three-electrode deposition cell, and (in some cases) hazardous chemicals. The chemical synthesis of gold spheres, on the other hand, requires some chemical skill, but can be done with typical chemistry lab equipment. A collaboration with materials chemists is probably more efficient and effective. Neither method, however, produces samples of narrow size distributions or perfect morphology. In particular, rods appear curvy and tend to rotate when moving,[89] while spheres are rough on the surface and the metallic coatings are often asymmetric. These imperfections are often frowned upon by physicists, as they undermine the experiment reproducibility and cause complications.

Finally, under typical conditions the speeds of bimetallic microswimmers are known to be roughly inversely proportional to the ionic strength in the solution, and often drop to the level of Brownian motion at salt concentrations at ~ mM levels.[53, 104] The salt-reduced speed reduction is primarily attributable to the reduced strength of the self-generated electric field, ultimately leading to a decreased propulsive force. To understand why the field is weaker at high salt, consider Ohm's Law, which states that the current density (which depends primarily on H_2O_2 concentration) is equal to the product of solution conductivity and electric field, and consider the aqueous solution to be an Ohmic resistor. When salt is added, the conductivity increases,

while the current (which depends mainly on H_2O_2 concentration) remains constant; thus, the electric field decreases. This salt limitation poses challenges to biomedical or environmental applications of bimetallic swimmers in which the liquid typically contains salt at mM concentrations or more. On the other hand, even to soft matter physicists who are not focused on practical applications, the requirement of a low-salt solution presents a challenge to laboratory skills and equipment. However, there is reason to be optimistic that this limitation may at least be mitigated, if not conquered: a recent study showed that using a silicon nanowire-based self-electrophoretic microswimmer (which moves by a combination of light and 1,4-benzoquinone as energy sources),[105] by tuning the wires' aspect ratio and coating the surface with a polyelectrolyte coating, the self-electrophoretic speed is increased in high-ionic-strength media (i.e., the speed reduction is partially mitigated),[106] although it still decreases overall.

Note that the salt effect applies to all microswimmers undergoing self-electrophoresis and ionic diffusiophoresis, i.e. almost all chemically powered active colloids discussed in this review.

Before continuing, we briefly comment on the ability to steer an active colloid, a feature equally useful for practical applications and fundamental physical studies. This subject has been reviewed extensively in recent review articles.[107-109] Taking bimetallic colloids as an example, they can be readily steered with an externally applied magnetic field (a handheld magnet often suffices), provided the colloidal particle has been made magnetic. This can be done by coating the particle with a nickel or iron layer with physical vapor deposition techniques, by inserting a Ni segment in a metal microrod during electrodeposition,[110, 111] or by incorporating magnetic nanoparticles (such as iron oxide).[112] These techniques are quite generalizable, and can be easily applied to the other types of active colloids that we discuss below (with the possible exception of Quincke rotation – we are unaware of studies that have coupled magnetic guidance with this mechanism.).

2.1.2 Pt-Janus colloids

1) Background

Although the development of Au-Pt microrods ignited the explosion of active colloids research over the last two decades, it was arguably the introduction of Pt coated Janus microspheres moving in H_2O_2 in 2007 that truly kindled interest among physicists.[57] Since then, this type of active colloid has quickly emerged as a popular choice for model systems, thanks to its ease of fabrication and a minimum requirement of chemical knowledge or equipment. Even though its dominance has been challenged recently by externally powered colloids discussed in section 2.2 and 2.3, Pt coated Janus microspheres remains an important model system of active colloids.

2) Synthesis

The ease of the synthesis of Pt-coated Janus microspheres is perhaps one of its best qualities (Fig. 2b). It starts with depositing a monolayer of inert microspheres, typically made of polymer (such as polystyrene, or PS) or silicon dioxide (SiO_2), on a flat substrate (typically a glass slide or a piece of Si wafer). This can be done in a variety of ways (via Langmuir-Blodgett
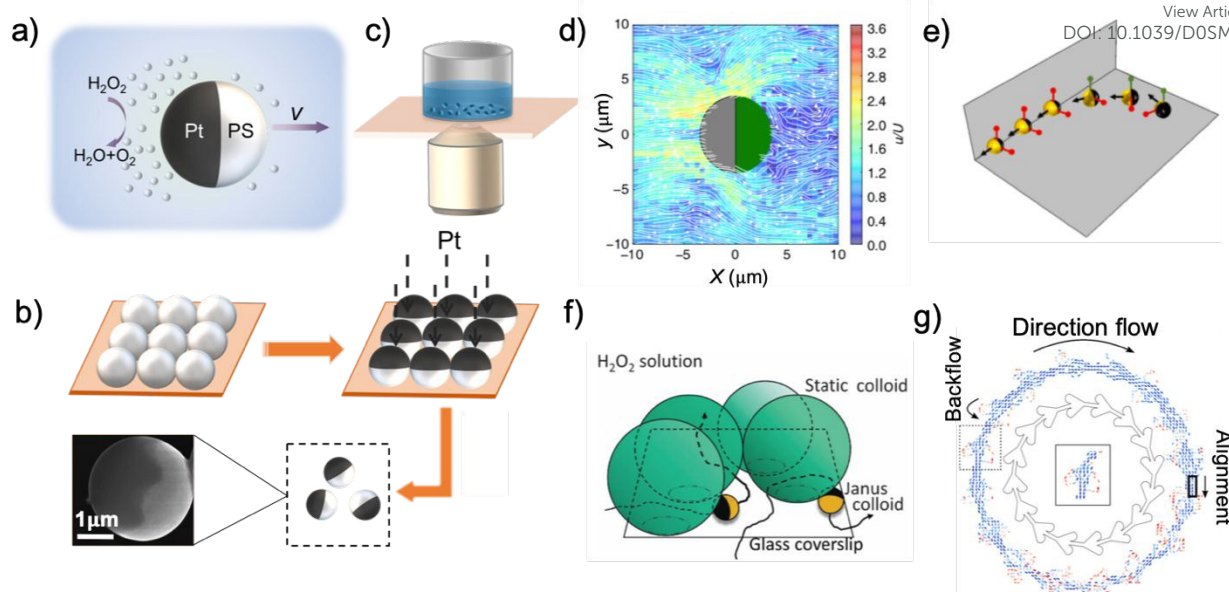
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Figure. 2 Pt-coated spherical microswimmers. a) This microswimmer moves by asymmetrically catalysing the decomposition of H_2O_2 into water and oxygen. b) Fabrication of Pt-coated Janus microswimmers via physical vapor deposition. Scanning electron micrograph at bottom left shows the uneven edges of the Pt layer produced by evaporation. c) Experimental setup for observing its motion. d) Experimentally measured flow field around a Pt-coated swimmer in H_2O_2. Reprinted from ref 124 which is licensed under CC BY 4.0, published by Springer Nature. e) A Pt-coated swimmer preferentially moves close and along a wall. Reprinted from ref 126 which is licensed under CC BY 4.0, published by Springer Nature. f) Pt-coated swimmers move within closely packed, large tracer microspheres. Reprinted from ref 129 which is licensed under CC BY 3.0, published by Royal Society of Chemistry. g) A series of heart-shaped microfluidic ratchets rectify the flow of Pt-coated microswimmers. Reprinted with permission from ref 130. Copyright 2018, American Chemical Society.

trough,[113] controlled evaporation,[114] or water-oil interface,[115] for example), but straightforward methods as simple as drop-casting a colloidal suspension often works well enough, unless a colloidal crystal of high quality is required. Then, a thin layer of Pt metal (typically ~ 10 nm or less) is physically deposited on the microspheres by either an (thermal or e-beam) evaporator or a sputtering machine. Because of the shadowing effect of the microspheres, this deposition typically leads to a Janus structure where only the top hemisphere is coated with metal. Once the deposition is finished, the Janus particles can be released from the substrate by mild sonication in water or ethanol, or by gentle scaping with a razor blade. When added in H_2O_2 aqueous solutions of ~ 1-5 wt%, these particles typically move with their uncoated hemisphere pointing forward at speeds on the order of 1-10 μm/s.

Physical vapor deposition (PVD), in the form of evaporation or sputtering, is a very common method preferred by physicists in producing active colloids of Janus structures. Although this method is not free of caveats (see the pros and cons section below), it is fairly straightforward, and produces particles of almost identical properties in large quantities. Besides, the Janus feature makes it possible to distinguish the two hemispheres under an optical microscope, critical for tracking the particle's orientation. Most active colloid studies by soft matter physicists therefore use particles made by the PVD method.

The main challenges associated with the PVD fabrication approach are that it is difficult to scale and requires access to expensive equipment (e.g., a sputter coater or electron beam evaporator). To mitigate these issues, Ebbens's group developed an alternative procedure to PVD to affordably produce large batches of Pt/silica Janus particles.[116] Briefly, a Pickering emulsion is synthesized that traps the colloids at the

oil/water interface; the mixture is then cooled, solidifying the nonpolar phase into a wax. The mixture is then dried, leaving spheres partially submerged in wax, on whose surfaces platinum is chemically grown. This method requires significantly less platinum to produce the same batch of active colloids that exhibit similar speed distributions to more conventional methods. It also does not require the use of expensive PVD equipment. One potential challenge with this method is in precisely controlling the fraction of the particle surface that is coated with metal. Variation in the coating fraction is likely to correlate with polydispersity in swimming speed.

3) Mechanism

The straightforwardness of the synthesis methods for Pt-Janus colloids belies a controversial and likely complicated mechanism for their self-propulsion in H_2O_2. This is counter-intuitive, given how simple the reaction appears to be, i.e. the catalytic decomposition of H_2O_2 into water and oxygen on the surface of Pt (Fig. 2a). Earlier in its development, the mechanism was believed to be neutral (non-ionic) self-diffusiophoresis,[57] arising from an asymmetric distribution of the reactant (H_2O_2) and the product (O_2) and their different interactions with the particle surface.[117, 118] However, theoretical and experimental progress over the last few years have increasingly emphasized the contribution of an electrophoretic mechanism (see next section). Unfortunately, these important developments have not permeated the entire community, and the neutral diffusiophoresis mechanism is still being invoked by many to describe Pt-Janus colloids. The exact physical details underlying this mechanism remain incompletely understood.

4) Notable studies in soft matter physics

Studies of the physics underlying the motion of Pt-Janus colloids can be organized into two main topics. The first topic is the

relentless effort over the years in first describing, then understanding, the single particle dynamics. The series of studies by Howse,[57] Ke et al.[119] Ebbens et al.[55] and Dunderdale et al.[120] have collectively given a good description of how (but not why) a Pt-Janus colloid moves. In addition, these studies have established a well-adopted analytical protocol (based on mean squared displacement, or MSD) to extract a number of important quantities from the particle tracking data, including the particle's apparent velocity and its apparent diffusion coefficients (both translational and rotation), that are critical for understanding their collective behaviours, for example.

In terms of understanding the propulsion mechanism, as was briefly mentioned in the last section, recent studies have overturned the neutral diffusiophoresis mechanism traditionally held true for Pt-Janus colloids moving H_2O_2. The first clue of this inconsistency was a decrease in its speed in the presence of a small amount of salt, a typical sign for self-electrophoretic active colloids, but not for those moving by neutral phoresis.[121, 122] To reconcile it, Golestanian and co-workers proposed a mechanism that involved charged intermediates of the reaction and variations in reactivity that are hypothesized to result from variations of coating thickness (a common side-effect of the PVD synthesis route),[121, 123] two factors largely ignored in previous studies. A very recent experimental study, the authors argue, supports this mechanism by mapping the flow field around a Pt-Janus colloid moving in H_2O_2 (Fig. 2d).[124] On the other hand, the Poon lab proposed that H_2O_2 dissociates into ionic species,[125] and believe that the propulsion mechanism is self-electrophoresis.[122] The dust has yet to settle on the exact mechanism of this active colloid.

The second popular topic for Pt-Janus colloids is their dynamics in complex environments with obstacles. Specifically, Das et al.[126] and Simmchen et al.[127] independently reported how Pt coated PS or SiO_2 microsphere move in H_2O_2 preferably along topological structures such as walls or trenches (Fig. 2e). Similar Janus swimmers were found to be trapped into a circular trajectory in a dense colloidal crystal (Fig. 2f),[128, 129] and can even by rectified by ratchet-shaped obstacles (Fig. 2g).[130] The nature of this strong attraction to a solid boundary is believed to be a combination of phoretic and hydrodynamic interactions.[131-134] Other less explored topics for Pt-Janus colloids include their non-equilibrium sedimentation,[101] cross-stream migration[135] and chemotaxis.[136]

5) Pros and cons

The PVD-based method used to produce Janus particles is both a blessing and a curse for Pt-Janus colloids. The commercial availability of monodisperse polymer or SiO_2 microspheres, and the relatively easy access to a PVD equipment, made this method popular among physicists. However, as noted in a few experimental studies, the metal coating is not as uniform as one naively expects, producing uneven thickness and incomplete coverage, which in turn could lead to circular or even helical trajectories.[37, 137] Furthermore, because Pt is much heavier than the microsphere being coated or water, the Janus particle naturally orients with the Pt hemisphere pointing downward, and tend to move against gravity in H_2O_2 (i.e. negative

gravitaxis).[138] In fact, the bottom-heaviness of many other Janus active colloids might cause similar gravitaxis. These issues put practical constraints on using these colloids as model systems for active Brownian particles moving in 2D.

In addition, a highly catalytic metal such as Pt is necessary for propulsion, yet O_2 bubbles are inevitably generated, not at the Pt surface but at random spots in the fluid, such as defects on glass substrates. These bubbles form when the local O_2 concentration exceeds the solubility limit and obstruct experiments as they do in the case of AuPt bimetallic colloids. This issue worsens for rough Pt coatings or large particles.[139, 140] Experiments with high number density of Pt-containing particles are therefore difficult and rare. One notable exception is the study by Palacci et al. in 2010 where the sedimentation of PS-Pt Janus colloids at a packing density of 0.05 v/v % was examined.[101] To mitigate the bubble issue within such a dense suspension, and to maintain a constant concentration of all chemicals involved over a long period of observation time (hours), the authors developed a microfluidic device that allowed the mass exchange of both the reactant and the product molecules with an external reservoir. This clever design is indeed effective, yet its complicated construction perhaps limits its widespread adoption.

2.2 Light-powered active colloids

Light as an energy source is tantalizing for many reasons. For active colloids, the use of light confers unique benefits such as easy external power and control, and excellent tunability in intensity, wavelength, polarization, and temporal modulation.[141-146] Although the momentum of photons can be directly harvested to propel microparticles (so called "photon nudging"), examples are rare,[147, 148] whereas secondary effects such as the photothermal effect (see 2.2.1) or photochemical reactions (see 2.2.2) are more popularly exploited in the design of active colloids powered by light.

2.2.1 Janus colloids demixing water-lutidine

1) Background

In 2011 and 2012,[58, 149] two papers published from the Bechinger lab ushered in a new active colloid system: Janus colloids that move under light in a binary mixture of water and lutidine. Since then, this system has been used by the same group in a series of interesting studies,[150-158] boasting good tunability and controllability.

2) Synthesis

These Janus particles are typically inert microspheres (e.g. SiO_2) half coated with a thin layer (~20 nm) of gold, fabricated by the same PVD techniques described above. It is sometimes mentioned that the gold layer is functionalized with COOH-terminated polar or non-polar thiols to render it hydrophilic or hydrophobic, respectively, important for the propulsion mechanism discussed below. More recently, a thin layer (~20 nm or more) of carbon (in the form of graphite) is used in place of gold, because both materials show photothermal properties (see below), but carbon induces a smaller van der Waals attraction among particles (thus less unwanted aggregation). In addition, particles of other geometries can be coated in the same way. For example, an "L" shaped particle with one arm
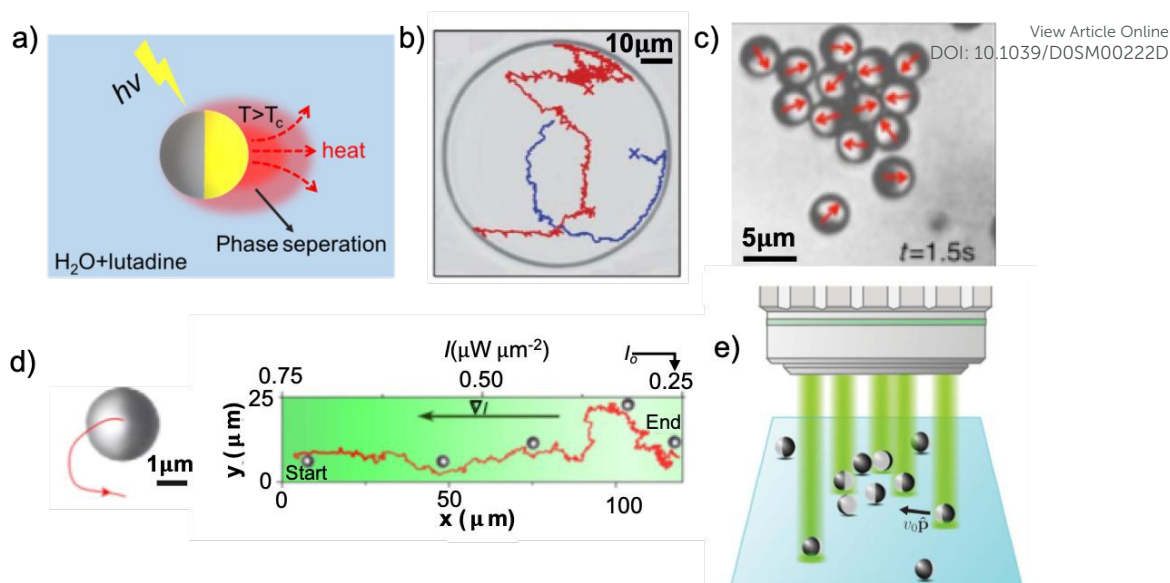
Figure. 3 Janus microswimmers demixing water-lutidine. a) These microswimmers heat up asymmetrically under light, and locally de-mix a critical binary mixture of water and lutidine. b) Microswimmers preferentially move along walls of a circular confinement. Reprinted with permission from ref 149. Copyright 2011, Royal Society of Chemistry. c) Microswimmers spontaneously form clusters. Reprinted with permission from ref 157. Copyright 2013, American Physical Society. d) In a light gradient, microswimmers respond to a phoretic torque and undergo phototaxis. Reprinted from ref 154 which is licensed under CC BY 4.0, published by Springer Nature. e) Via a feedback loop-controlled illumination scheme, individual microswimmers adjust their speeds according to how many neighbours they "see", eventually forming groups. Reprinted with permission from ref 152. Copyright 2019, The American Association for the Advancement of Science.

coated with gold was propelled under light in a water-lutidine mixture, to showcase that gravitaxis can arise from shape anisotropy alone.[158]

3) Mechanism

According to its discoverers, this system is propelled by a unique mechanism that contains three parts (Fig. 3a). First, the metal (or carbon) cap of a Janus particle absorbs light (532 nm, at a power level of $\sim\mu W/\mu m^2$) and releases heat, which increases the local temperature around the cap. Janus particles are suspended in a critical binary mixture of water and 2,6-lutidine of a critical temperature of 307 K, above which the liquid demixes into water and lutidine phases. Note that the composition of the mixture is key in determining the success of this experiment (a mass fraction of lutidine of 0.286 is commonly used). In the third and final step, the demixed water and lutidine accumulates preferentially at the hydrophilic and hydrophobic surfaces, respectively. This concentration gradient of water and lutidine, and the difference in their interactions with the surface, then moves the particle via self-diffusiophoresis. The Janus particle moves away from the hydrophilic cap, which is typically the coated cap. The exact nature of this phoresis has sparked some theoretical investigations that followed.[159-161]

4) Notable studies in soft matter physics

Light-powered Janus colloids demixing water-lutidine have been used by the Bechinger group as a model system to study a variety of topics related to complex and crowded environments.[7, 8, 162] In one of the earliest reports published in 2011, these Janus colloids were placed among microstructures where their interactions with obstacles were examined (Fig. 3b).[149] They showed preferential attachment to walls similar to previous reports of other phoretic microswimmers (see the above two sections). A few years later, the motion of these Janus colloids in viscoelastic liquid (a mixture of water and

propylene glycol propyl ether added with 0.05% polyacrylamide) was studied.[155] Because of the non-Newtonian nature of the surrounding medium, a surprising coupling between the particle's directional motion and its rotational diffusion was discovered. On a related note, a very recent study shows that the rotational diffusion of the same Janus particles immersed in a dense population of Brownian colloids dramatically changes as the system undergoes glass transition,[150] suggesting the possibility of using these active colloids as probes to characterize complex materials.

A second topic is related to phototaxis. Phototaxis refers to the directional migration of a synthetic or natural microswimmer towards (positive phototaxis) or away from (negative phototaxis) the light source, and is commonly found for light-powered active colloids.[143-145] The Bechinger lab reported in 2016 that Janus colloids demixing water-lutidine experience a strong diffusiophoretic torque in a light intensity gradient and thus move down the gradient, i.e. negative phototaxis (Fig. 3d).[154] By manipulating the particle properties, however, similar Janus particles could be made to undergo positive phototaxis, and this effect was later used to demonstrate a directional migration against traveling waves of light similar to chemotactic microorganism *Dictyostelium*.[151]

The third topic that has gained a lot of attention over the recent years is cluster formation and collective behaviours of active colloids, and water-lutidine demixers are again quite useful in this regard. In 2013 it was first reported that Janus colloids demixing water-lutidine phase separated into large clusters and a dilute gas phase at large number densities (Fig. 3c).[157] A minimum model of self-locking mechanism was proposed, neglecting possible contributions from phoretic, alignment or hydrodynamic interactions. In a follow-up work,[156] the authors mixed a small amount (1%) of these active colloids with passive particles, and observed dynamic clusters and local

melting, and eventually large defect-free domains of colloidal crystals similar to a few other reports.[163-165] Finally, in two recent studies[152, 153] the authors demonstrated an excellent capability, via an external feedback loop, to tune the individual mobility of Janus colloids depending on their neighbours. In one study, particles adjusted to the number density of their groups and self-organized into clusters of various sizes and densities similar to the quorum sensing of a bacterial colony.[153] In a follow-up study, a different sensing criterion, i.e. how many peers a Janus colloid could "see" in its field of view, controls the formation of groups (Fig. 3e).[152]

5) Pros and cons

Janus colloids demixing water-lutidine exhibit many ideal attributes for a model system: ease of fabrication, reaction-free, ease of external manipulation, good tunability, uniformity, etc. The papers from the Bechinger lab are a good testimony to these benefits. Other advantages include very low light intensity required to activate the colloids (thus minimizing optical radiation forces), and the possibility to conduct experiments with a concentrated suspension over a long period of time, due to the minimum change of the environment.

However, the fact that most (if not all) of the *experimental* reports on this system come from one research lab hints at potential pitfalls. One possible source for this lack of widespread adoption might be the experimental difficulty associated with precisely controlling the temperature (the use of a flow thermostat was mentioned[58]) and the chemical compositions (a slight deviation from the required concentration could fail an experiment). Given how effective this model system appears to be, and the various of topics one could investigate with it, we encourage the soft matter physics community to investigate this system in further detail to gain insight into its underlying principles and improve its reproducibility.

2.2.2 Photochemically powered active colloids

1) Background

Light is a versatile energy source. It can power active colloids by a photothermal effect discussed in the last section, and also excite electrons and fuel chemical reactions, which in turn propel particles via phoretic mechanisms described in section 2.1. The earliest examples of photochemically propelled active colloids date back to 2009 and 2010, when the Sen lab showed that microparticles made of AgCl and TiO_2 moved in water under illumination.[166, 167] Over the years, materials chemists have designed active colloids made of various photocatalytic materials, such as TiO_2,[168, 169] ZnO,[170] Fe_2O_3,[171] g-C_3N_4,[172] and $BiVO_4$,[173] to name a few, and demonstrated their usefulness in biomedical and environmental applications. Among these materials, TiO_2 (titania) and Fe_2O_3 (hematite) are the most popular among physicists (for good reasons) and are thus discussed in more detail in this section. Both materials are well-known photo-semiconductors with decades of intense research, good news for using them as model systems.

2) Synthesis

Both TiO_2 and Fe_2O_3 microparticles are typically synthesized by chemical methods. In the case of TiO_2, microspheres with a diameter of ~ 1-2 μm can be readily synthesized by a variety of methods (Fig. 4a).[59, 61, 174] Larger spheres can also be made, following ref 175 and references therein, but are rare in the literature of active colloids. The synthesized TiO_2 microspheres are then calcinated in a furnace usually at ~ 400-500 ℃ to convert TiO_2 to the anatase crystalline phase, which significantly improves their photocatalytic performance.

To further enhance it, and to break symmetry at the same time, the TiO_2 microsphere is typically half-coated with a thin layer of gold or platinum by PVD (See the mechanism section for details).[176] The resulting TiO_2-Au or TiO_2-Pt Janus colloids can move in water when irradiated with UV light, but moves much faster if H_2O_2 or ethanol/methanol are added in the solution because the new reaction is more thermodynamically favorable.[166] Our own experience shows that TiO_2-Pt swimmers move faster than those coated with Au, possibly because of the superior catalytic performance of Pt over Au, or a difference in their work function. Cu can also be used as the coating metal in place of Pt or Au,[177] and interesting changes in particle dynamics were observed as the chemicals and lighting conditions were varied. Note that a thin layer of TiO_2 can also be deposited by physical methods on inert (e.g. SiO_2) microspheres, which after calcination also show autonomous and directional motion in H_2O_2 under light.[60, 178] These SiO_2-TiO_2 swimmers are typically slower than those mentioned above.

Active colloids based on hematite often come in two forms: dimers and peanut-shapes. The synthesis of hematite dimers consists of two steps.[59, 179] First, hematite particles of a roughly cubic shape and ~600 nm in size are synthesized by mixing NaOH with $FeCl_3$ and incubating for days. These nano-cubes can then be partially encapsulated in a polymer microsphere (TPM) via a sophisticated de-wetting process,[180] resulting in a dimer with a unique shape: a large polymer microsphere with a small hematite cube protruding from its back (see Figure 4c). We note that the same dimers can also move by self-thermophoresis in a defocused laser beam,[181] or roll in a rotating magnetic field,[182] but these propulsion mechanisms are not discussed here in detail. Peanut-shaped hematite colloids[183-185] are synthesized with a slight twist of the synthetic protocol.[186] Because hematite is a photo-semiconductor with a bandgap of 2.2 eV, green or blue light is used to propel hematite-based active colloids. [185]

3) Mechanism

Although they differ in synthesis, swimmers made of TiO_2 and Fe_2O_3 share similar propulsion mechanisms (Fig. 4b) that begin with photo-excitation of electrons to the conduction bands, and the migration of electrons and holes to the surface of the material. There, electrons and holes reduce and oxidize chemicals present in the solution, respectively, leading to a gradient of (neutral and charged) chemical species that ultimately propel the particle via phoresis. The details of this phoretic propulsion are, however, different for these two systems.

On a TiO_2-Au Janus microsphere, electrons migrate to the surface of Au (because the work function of Au is lower than the Fermi level of TiO_2) and reduce water into H_2 (and possibly other intermediates that are not discussed in detail here), while holes

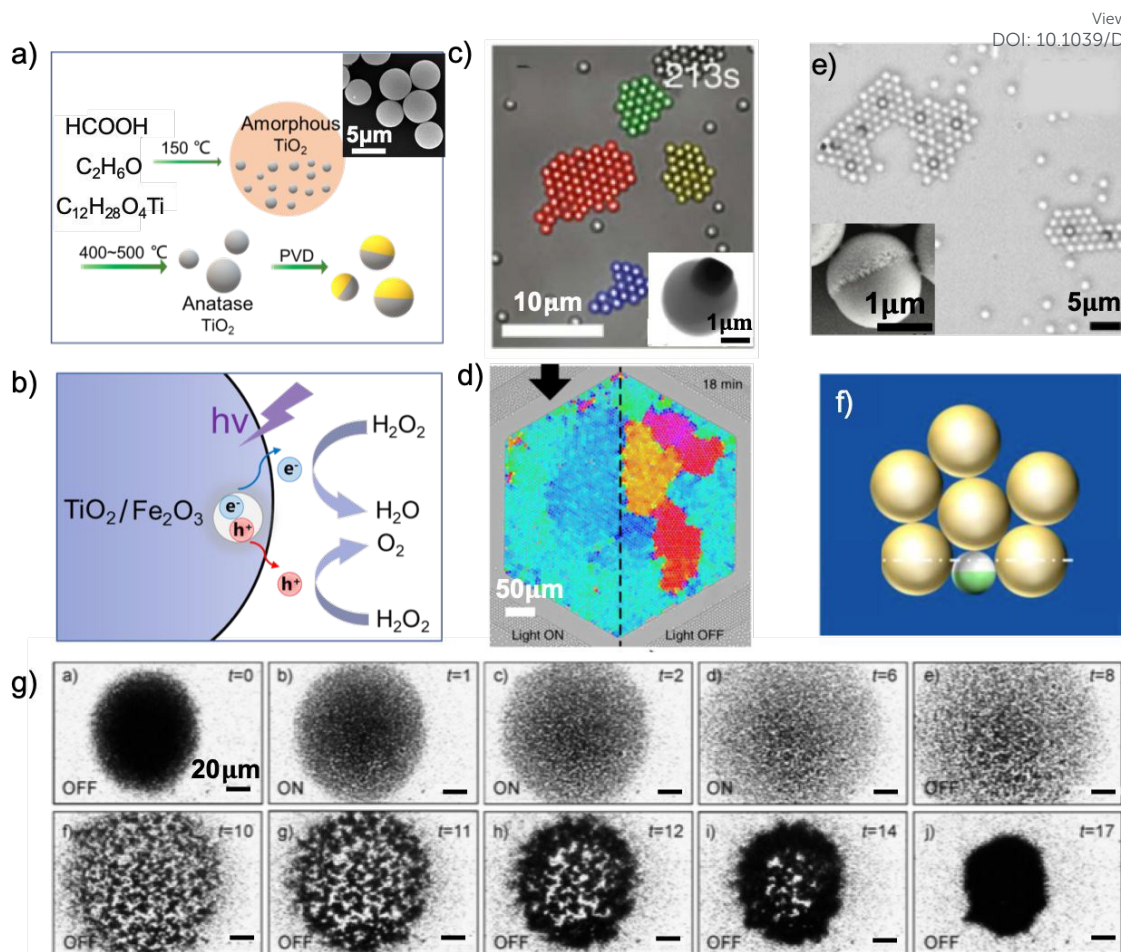Soft Matter Accepted Manuscript

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Figure. 4 Photochemically powered active colloids. a) Typical hydrothermal synthesis of TiO_2-metal Janus microspheres (inset: scanning electron micrograph of obtained TiO_2 microspheres). b) Photocatalysis on the surface of a TiO_2 or Fe_2O_3 microparticle, where photo-generated electrons and holes reduce and oxide H_2O_2, respectively. c) Light induced dynamic clustering of TPM-Fe_2O_3 colloids as living crystals. Reprinted with permission from ref 190. Copyright 2013, The American Association for the Advancement of Science. d) Light induced annealing of inert microspheres into close-packed crystals by photochemically powered Fe_2O_3 colloids. Reprinted from ref 164 which is licensed under CC BY 4.0, published by Springer Nature. e) and f) SiO_2-TiO_2 (e) or TiO_2-metal. Reprinted with permission from ref 60. Copyright 2017, John Wiley and Sons. (f) Janus microspheres attract inert microspheres into crystalline clusters. Reprinted with permission from ref 191. Copyright 2017, American Chemical Society. g) Light induced expansion (ON) and spontaneous contraction (Light OFF) of an ensemble of TiO_2 microparticles. Reprinted with permission from ref 167. Copyright 2009, John Wiley and Sons.

accumulate at the surface of the uncoated TiO_2 and oxidize water into O_2. This process is called water splitting and has been intensely studied for the last few decades primarily because of its potential in energy harvesting and environmental remediation.[187] The key reason why this process moves a TiO_2-Au particle, as illustrated nicely in ref 61, is that the protons generated at the anode (TiO_2) flow through the solution immediately adjacent to the particle surface to reach the cathode (Au) under the influence of a self-generated electric field. On the Au cathode surface, the protons are consumed, and the electric field associated with the proton gradient propels the negatively charged particle in exactly the same way as how a bimetallic rod or sphere moves in H_2O_2, i.e. self-electrophoresis. A TiO_2-metal Janus swimmer typically moves towards the uncoated TiO_2 cap. In addition, the optional presence of hole or electron scavengers, such as H_2O_2, alcohols and hydroquinone, provide new avenues to consume the electron-hole pairs, increasing the particle speed. As with other realizations of self-electrophoresis, in the case of TiO2/metal particles, the addition of an inert electrolyte leads to an overall decrease of the self-propelled speed.

Janus particles containing Fe_2O_3 are also believed to be driven by self-diffusiophoresis.[188] On the Fe_2O_3, H_2O_2 is photocatalytically decomposed into water and O_2, producing concentration gradients of neutral chemical species such as H_2O_2 and O_2, and possibly other charged intermediates. Such a Janus particle moves towards the Fe_2O_3 end.[59] The speed of photochemically propelled hematite colloids was found to be sensitive to the ionic strength of the liquid medium,[59] suggesting an electrokinetic mechanism, rather than neutral diffusiophoresis.[189] In addition, thermal contributions cannot be eliminated given the decomposition of H_2O_2 is exothermic. SiO_2 microspheres half coated with TiO_2 are likely propelled by a similar mechanism, and move with the TiO_2 cap leading.[60] The exact mechanism remains unknown at this point, but the self-generated electric field, if present, should show a very different profile than the dipole-like field around a TiO_2-Au swimmer.

4) Notable studies in soft matter physics

The physics studies of photochemically powered active colloids have primarily focused on the topic of dynamic assembly and self-organization, arising from a strong phoretic interaction between an active particle and its neighbours. For example, Palacci et al. described in a seminal study published in 2013 how

hematite-TPM dimers spontaneously formed dynamic colloidal crystals under light ("living crystals"), apparently via a combination of osmotic and phoretic attractions (Fig. 4c).[190] More recently, two studies from the Palacci lab extended the dynamic assembly of these dimers to a larger scale. In one beautiful study from 2018, they demonstrated the assembly of active hematite-TPM dimers into rotating gears under spatiotemporal illumination. These micro-gears then further assemble and synchronize into a rotating cluster via chemical coupling. A more recent study published in 2019 (Fig. 4d),[164] on the other hand, demonstrates the strong interaction between an active hematite-TPM dimer and its passive neighbours, and the usefulness of such interaction in greatly accelerating the formation of close-packed colloidal crystals (i.e. "annealing"). Similar interactions with tracer particles were also discovered for SiO_2-TiO_2 colloids as well (Fig. 4e).[60] TiO_2-Pt or TiO_2-Au colloids, on the other hand, move with a self-generated, dipole-like electric field, and therefore readily collect charged tracer particles in a close-packed fashion, preferentially on the TiO_2 (photoanode) cap (Fig. 4f).[191] This pattern of assembly is not unlike a previous study of bimetallic rods collecting tracer microspheres (see Fig. 1e).[91] A beautiful demonstration of the interactions among active, pure TiO_2 microparticles can be found in Fig. 4g, where a cluster TiO_2 was toggled by light between expansion (light on) and contraction (off), resembling a firework.[167] Interested readers are directed to a more recent work for details.[192]

5) Pros and cons

There are legitimate reasons why a physicist might feel cautious experimenting with photochemically powered active colloids. They often require a slightly more sophisticated optical setup than a regular microscope, and release neutral or charged chemicals of unknown identities and concentrations as they move. Phoretic and hydrodynamic interactions are intertwined and rather complex, often too much so to build faithful models. Last but not least, the chemical synthesis is often significantly more involved than what a typical physical lab is comfortable with. In fact, even for many chemistry labs, it takes many trials and errors to produce TiO_2 or hematite particles of well-controlled shapes and uniformity, let alone various modifications that might be required for special purposes. All these challenges—large variations, unexpected deviations, unknown chemicals and complicated interactions—could combine into a situation that a physicist might consider "messy".

Despite these thorny issues, photochemical active colloids also bring rosy prospects. A unique advantage of most of the chemically-powered active colloids discussed so far, and something electrically powered colloids discussed below lack, is a long-ranged chemical interaction that mimics how insects or microorganisms communicate. It is often this interaction, sometimes complicated by the accompanying osmotic flows, that leads to emergent, collective behaviours such as swarming, predator-prey effects, synchronization and even waves.[141, 167, 175, 193] Photochemically powered colloids, among all types of chemical swimmers, can be better controlled in terms of intensity and time, and can be made fuel-free (i.e. moving in pure water). Compared to water-lutidine demixing colloids,

which also boast these features, photochemical swimmers are arguably easier to implement, and have received a wider adoption among research labs worldwide.

Even their tricky synthesis can be advantageous, providing endless possibilities for tuning material shapes,[35, 194] compositions and surface functionalization that endow the resulting particles with unique properties. Specifically, a few labs around the globe, ours included, are making an effort in synthesizing monodisperse, highly efficient, visible-light driven active colloids based on TiO_2 microspheres, preferably in a large quantity that produce no bubbles, to meet the demand of physical studies of high population density. Progress in this front might usher in a new era of model active colloids.

2.3 Electrically powered active colloids

2.3.1 Janus colloids in alternating-current electric fields (ICEP)

1) Background

During the 1960s-1980 Russian scientists first studied the response of metallic colloids to applied electric fields,[195-199] which was later introduced to the broader scientific community (especially in the West) by Bazant and Squires, who coined the name induced-charge electrokinetic phenomena (ICEK) to describe them.[200-202] In the following years, they[203] and Yariv[204] predicted the existence of an interesting variation of ICEK, induced-charge electrophoresis (ICEP), for an asymmetric colloid exposed to an electric field. This concept of ICEP was then demonstrated experimentally by Bazant, Velev, and coworkers in 2008, where a metallodielectric Janus microsphere moved autonomously under an AC electric field.[62] Since then, numerous studies have focused on propulsion mechanisms,[205-207] motion dynamics,[208-213] dynamic self-assembly,[214-217] and collective behaviours such as active turbulence,[218, 219] phase separation,[220] swarming and clustering[221] (see below for an expanded discussion of related studies). Janus colloids powered by AC electric fields have become a popular choice for active matter research.

2) Synthesis

Typically, a metal-dielectric Janus microsphere, such as Au-PS or Au-SiO_2, is fabricated by PVD as detailed previously. Occasionally, an additional nickel (Ni) layer can be deposited, or in place of gold, to enable magnetic manipulation or steering. In principle, particles of geometries other than spheres can be propelled by the same mechanism, such as microspinners with three arms demonstrated by Yossifon and Velev,[213] but most studies have focused on the simplest Janus microspheres.

It is important to note that small deviations from a perfect, uniform metal cap, a common defect from PVD, can lead to uneven driving forces and therefore circular trajectories of colloids.[69, 222] This defect, however, can be exploited to produce swimmers that move in unique patterns, such as 3D helices.[212] Similar effect has also been reported for chemically powered active colloids.[37]

3) Mechanism

This type of active colloids is propelled by a mechanism termed induced-charge electrophoresis, or ICEP (Fig. 5a), which has been elucidated extensively.[204] Briefly, electrons redistribute in an electrically conducting microparticle in the presence of an
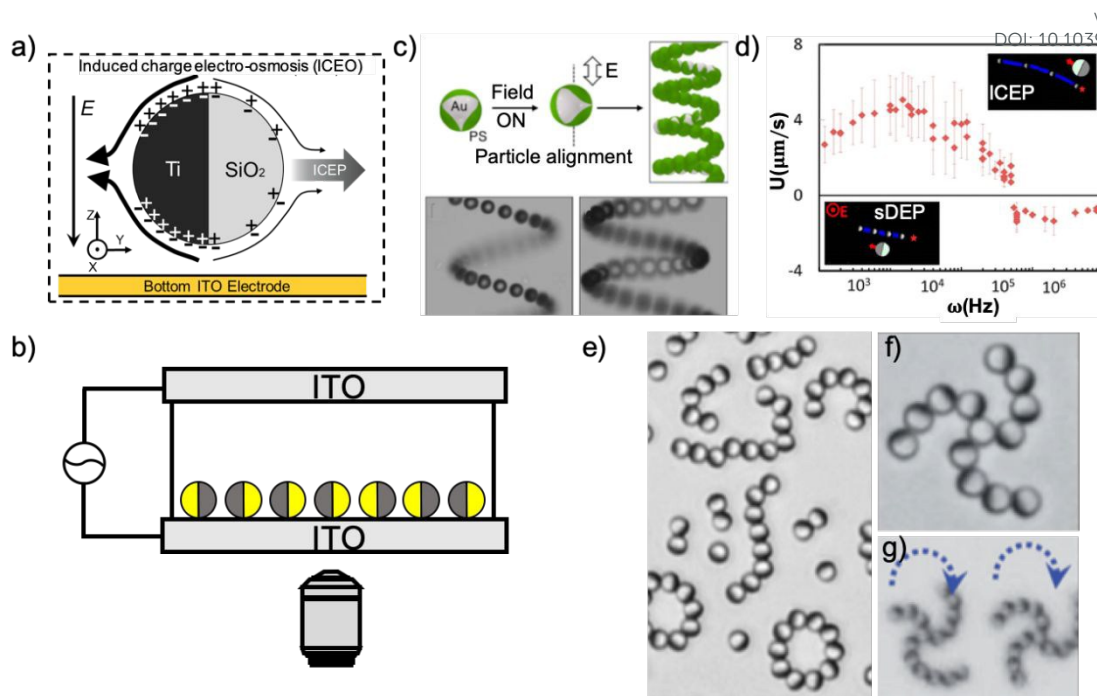
Figure. 5 Janus microswimmers moving under AC electric fields via ICEP. a) Operating mechanism of ICEP, arising from asymmetric polarization of the two hemispheres of a metal-dielectric Janus microsphere under an electric field (see main text for details). b) Experimental setup for a stacked configuration comprising two conductive ITO surfaces. c) A microsphere with gold patches experience torques due to ICEO under an AC electric field, and moves in controlled, helical trajectories. Reprinted from ref 212 which is licensed under CC BY 4.0, published by Springer Nature. d) At driving frequencies typically above tens of kHz, a Janus microsphere is known to move to the direction opposite to typical ICEP, an effect proposed by some researchers to arise from self-dielectrophoresis, or sDEP. Reprinted with permission from ref 207. Copyright 2016, American Chemical Society. e)-g) Dynamic assembly of ICEP microswimmers into interacting chains. (e) Reprinted from ref 214 which is licensed under CC BY 3.0, published by Institute of Physics. (f)(g) Reprinted with permission from ref 216. Copyright 2016, Royal Society of Chemistry.

external electric field, a process called "polarization", producing an electric dipole. This dipole then leads to a non-uniform surface charge, which attracts from the solution charged ions having the opposite polarity to the local surface charge ("induced charges"), which couple to the external electric field and produce an electroosmotic flow on the particle surface. Because these charges are induced by the electrical polarization, for a stationary conductive surface this flow is called induced-charge electro-osmosis, or ICEO. In the case of a freely suspended metal-dielectric Janus microsphere (e.g. SiO_2-Ti or PS-Au), however, this ICEO flow is much stronger at the metal side, because the metal cap polarizes much more intensely than the dielectric cap. The Janus particle therefore moves by the imbalanced ICEO flow, with the dielectric end leading. A typical range of AC frequencies for ICEP to occur is on the order of 1-10 kHz, below which strong surface electrohydrodynamic effects (EHD) occur, leading to large scale convection and particle assembly.[223-225] Electric field switching at higher frequencies, on the other hand, are too fast for ions to catch up, so ICEP disappears.

This mechanism can be implemented in two configurations. First, two planar electrodes can be deposited on the same substrate in parallel to each other, with a gap of predefined distance in between, L, and connected to a function generator that outputs alternating current signals of amplitude ΔV across two electrodes. Under this electric field, whose magnitude is $\Delta V/L$, Janus particles re-align so their equators lie perpendicular to the long axis of electrodes. They then move along a straight line parallel to the electrodes. In the second and more commonly employed configuration (Fig. 5b), two conductive electrodes (typically glass slides or cover slips coated with indium tin oxide, or ITO) are stacked on top of each other with a spacer in between that defines the gap. In this configuration, Janus particles are free to roam near the bottom electrode in 2D in random trajectories, transverse to the applied electric field. This configuration is therefore more popular among experimentalists. Interdigitated microelectrodes can also be used to study ICEP active colloids, and interesting collective behaviours have been reported (see below).[219]

Although the above mechanism is more intuitive for DC electric fields, it works equally well (arguably better) in AC fields, because then the signs of the induced charges and the direction of the electric field always change concurrently. AC electric field, rather than DC, is often used in these experiments for a number of practical reasons. First, the use of AC electric field minimizes 1) hydrolysis at high voltages required to drive this mechanism (typically a few V), and 2) bulk electrophoresis of charged particles. Moreover, AC frequency offers a wide range of tunability, both in particle speeds and directionality, and in their pair-wise interactions and collective behaviours. More specifically, the polarizability of a particle (and its electrical double layer) is dependent on the driving frequency.[226]

4) Notable studies in soft matter physics

A number of studies have focused on the individual dynamics of an ICEP swimmer, starting from the pioneering study by Velev et al. on a SiO_2-Ti Janus particle between two planar electrodes with AC electric fields.[62] Similar propulsion can also be realized with dimers of metal and dielectric microspheres[211] and patchy particles with lobes of different polarizability.[38] Later, both Suzuki et al.[208] and Boymelgreen et al.[209] studied spinning

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doublets made of Janus particles undergoing ICEP. Moreover, the metal coating is often not perfect for a Janus particle and leads to spontaneous and chiral rotation. Taking advantage of this feature, Mano et al. devised a feedback-based particle guiding strategy to steer an ICEP swimmer in arbitrary trajectories by switching its dynamics between a straight "run" and a rotating "tumble" phase.[210] This imperfection also inspired Lee et al. to intentionally fabricate Janus particles with metal patches of particular shapes and asymmetry, thus moving in helical trajectories in 3D under AC electric fields (Fig. 5c).[212] Moving one step further, Brooks et al. show via simulation that the symmetry of ICEO flow can be broken on an asymmetrically shaped particle of a single material, thus producing directional motion.[227] Similar effects have been experimentally observed by Ma et al. for a PS-dimer of lobes of different sizes.[228]

One of the most intriguing, and potentially useful, features of an ICEP swimmer is its directional reversal at high driving frequencies (Fig. 5d), typically larger than tens of kHz, observed in a variety of ICEP systems regardless of shapes and materials.[207, 208, 213, 228] This is surprising, given that classical ICEP breaks down at such high frequencies, because ions diffuse too slowly to catch up with the alternating electric field. A mechanism was proposed by Boymelgreen et al,[207] who argued that the localized non-uniform electric field gradient between the sedimented particle and the substrate nearby moves the particle by a self-dielectrophoresis (sDEP) mechanism. Alternatively, a very recent theoretical analysis by Hashemi Amrei et al. [229] invoked a recent theory of asymmetric rectified electric field (AREF, proposed by[230, 231]) to explain this reversal of flow, relying mostly on a mismatch of ion mobilities in an alternating electric field.

The other notable feature of ICEP swimmers is their pairwise interactions, composed mainly of dipolar and hydrodynamic (ICEO) contributions. The dipolar interactions arise from the electrical polarization of the colloidal particles and are repulsive in-plane for those polarized in the same directions, and attractive otherwise. Importantly, because this polarization is dependent on materials and AC frequency, the dipolar interaction between two colloids can be switched between attraction and repulsion by varying driving frequencies. Quite a few studies have exploited this tunability. For example, their assembly into dynamic multimers have been reported.[216, 217] The phase space of particle interactions was extended by Jing et al. via the same parameter-tuning, and collective states such as swarms, chains, clusters and isotropic gases were observed for SiO_2-Ti Janus particles.[221] Flagella-like chains of Janus particles were also reported by Nishiguchi et al. (Fig. 5e) and Jie et al. (Fig. 5f, g).[214] The collision of these particles, under the additional influence of a magnetic field, was argued later to play the role of active temperature.[220] Finally, at high number density, a strong pairwise repulsion between ICEP swimmers give rise to active turbulence, mesoscopic turbulence exhibited by active particles, especially in strongly confined geometries.[218] This topic has over the recent years attracted much attention in the active matter community,[232-238] and ICEP swimmers might provide a fertile test ground.

5) Pros and cons

A few features of this propulsion mechanism make it attractive as a model system for active colloids. First, the system is powered by an electric field, thus fuel-free, and the magnitude of the driving force and particle interactions can be readily modulated externally. Second, no chemical reaction is involved, so the system is rather clean and well described and understood. Third, it is stable over a long period of time (on the order of hours), and for a large population density, thus ideal for studies of collective behaviours. Last but certainly not the least, the unique property of tuneable polarizability, and thus pairwise interactions, opens up tremendous opportunities for soft matter research.

The widespread adoption of ICEP swimmers in soft matter research is perhaps limited by a few practical issues. First, although each component of this system, such as particle fabrication, electrode assembly, electric field generation, microscopy setup, is not particularly difficult, building a functional experimental setup does take some training and investment (speaking from our own experience). Second, the operation of ICEP swimmers is very sensitive to the solution conductivity, and thus can suffer from poor reproducibility between parallel experiments. Naturally, this also means that parameters reported by literatures should be taken with a healthy dose of doubt. Finally, in most, if not all, of reported experiments of ICEP swimmers, the electric field is applied uniformly so that each particle experiences more or less the same driving force. This certainly makes experiments easy, but lacks the versatility and complexity in energy landscape that is offered by light actuation (see section 2.2.1 for examples).

2.3.2 Dielectric colloids in direct-current electric fields (Quincke rollers)

1) Background

It has long been known that a dielectric sphere immersed in a conducting fluid would spontaneously rotate under an external DC electric field, an effect first discovered in the late 1800s,[239] and subsequently referred to as Quincke rotation.[240] It has been largely overlooked in the recent decades, especially in the soft matter community, until being exploited by Bricard et al in 2013 as a propulsion strategy for micro-rollers.[63] Since then, a number of experimental studies have emerged, with a variety of foci that span individual propulsion, complex environments, and collective behaviours. A detailed description of these studies is given in part 4 of this section.

2) Experimental details

Unlike other active colloid systems, Quincke rollers are bare dielectric microspheres, such as poly(methymethacrylate) (PMMA) or PS, that do not have any additional functionalization or coating. We here describe how the experiments are conducted, based on existing literature. Typically, an experimental chamber is constructed by stacking two ITO glass slides together with a spacer (tape, parafilm or silicone) in between. The gap is often on the order of ~ 100 μm and filled with polymer microspheres suspended in an organic solvent (typically hexadecane). The packing density of microspheres determine their collective dynamics, as will be seen in part 4 of this section. A small amount (~ 10^{-2} to 10^{-1} mol/L) of surfactant such as AOT (dioctyl sulfosuccinate sodium salt) is added to the
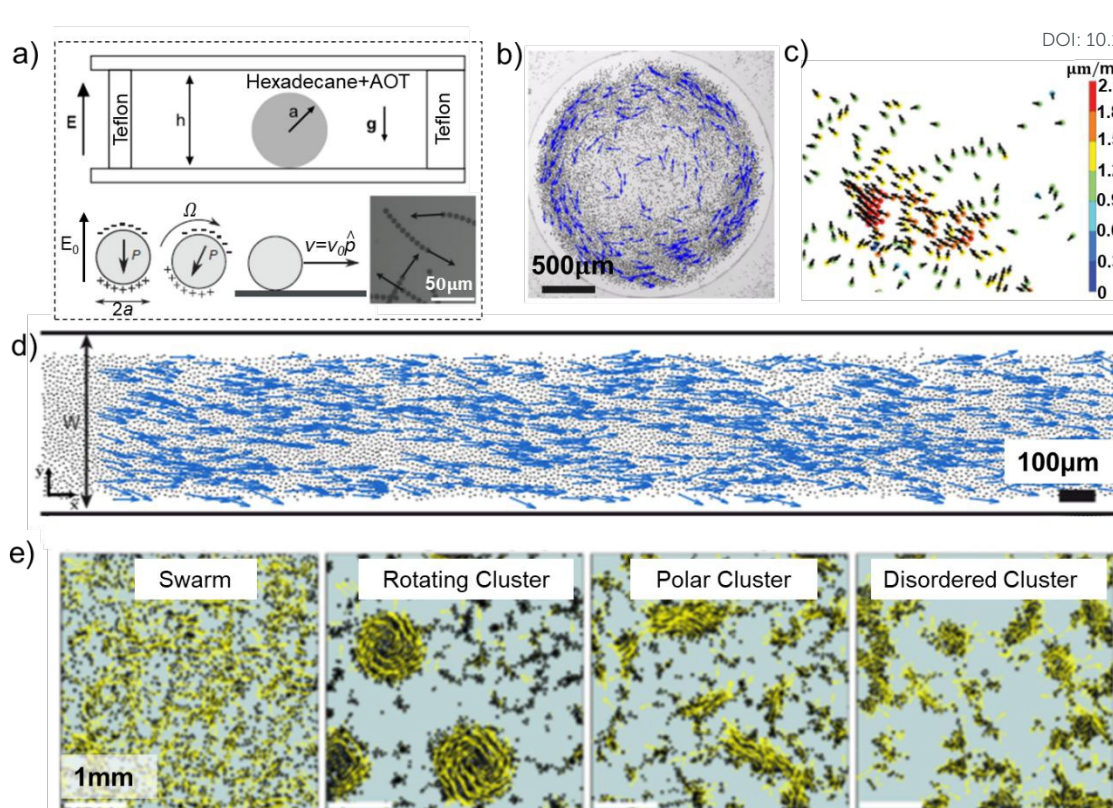
Figure. 6 Quincke rollers- uniform microspheres spontaneously rolling under a DC electric field. a) Experimental setup and operating mechanism of Quincke rollers (see main text for details). Reprinted with permission from ref 241. Copyright 2019, Royal Society of Chemistry. b) Confined in a circular structure, many Quincke rollers spontaneously form a vortex. Reprinted from ref 243 which is licensed under CC BY 4.0, published by Springer Nature. c) Pair-wise interactions lead to acceleration of Quincke rollers at low driving magnitude. Reprinted with permission from ref 251. Copyright 2018, Royal Society of Chemistry. d) A moving "slug" of densely packed Quincke rollers that spontaneously align their velocities when confined in a racetrack. Reprinted from ref 244 which is licensed under CC BY 4.0, published by American Physical Society. e) Quincke rollers of run-and-tumble or Lévy walk dynamics self-assemble into various dynamic structures. Reprinted with permission from ref 250. Copyright 2019, American Physical Society.

liquid to provide ions necessary for the mechanism. Importantly, Pradillo et al. discovered that whether AOT is dry or contains a small amount of water determines whether microspheres roll on the substrate or hover.[241] A DC electric field on the order of 1V/µm, generated by a voltage amplifier, is applied across the liquid, and needs to be larger than a critical strength for microspheres to roll.

3) Mechanism

The operating mechanism of Quincke rotation (Fig. 6a) has been explained in detail in recent literature (see ref 241 for an expanded yet accessible discussion). Briefly, the dielectric particle polarizes in the opposite direction to the external electric field, creating an instability that readily breaks symmetry above a threshold electric field. Once it begins rotating, the angular velocity of a microsphere scales linearly with the applied electric field. Importantly, the symmetry breaking does not dictate which direction the particle rotates in. They are therefore free to explore the entire 2D plane transverse to the applied field (just like ICEP swimmers between two ITO electrodes), a feature critical for active colloids. Finally, these micro-rollers are inevitably coupled to each other by dipolar and hydrodynamic interactions,[63] which prove critical for the collective behaviours of a dense population described below.

4) Notable studies in soft matter physics

A quick survey of recent literature yields roughly a dozen experimental studies of Quincke micro-rollers, pioneered by a study published in *Nature* in 2013,[63] where Bricard et al. first demonstrated that dielectric PMMA microspheres rolling under DC electric field can assemble into a swarming band. Specifically, they observed a transition of millions of these micro-rollers, confined in a microchannel of a racetrack shape, from a gas state to a polar liquid state as the particle packing density was increased to ~10^{-2} (i.e. 1%), a surprisingly small density for collective behaviours to occur. The band then moves with a constant speed along the racetrack. Topics such as sound propagation have also been explored within this colloidal active liquid.[242] The same rollers were later found to spontaneously organize into a rotating vortex when confined not by a racetrack, but by a circular boundary (Fig. 6b).[243] By further increasing the particle density to ~0.55, a second transition from polar liquid to a dynamic solid slug was observed (Fig. 6d).[244] This first order transition was argued to be the first experimental demonstration of the popular concept of motility-induced phase separation (MIPS).[245]

Other notable studies of Quincke rollers from these authors and a few other groups can be roughly put into three storylines. The first line focuses on individual propulsion of Quincke rollers, including an excellent article by Pradillo et al. on the strong and surprising influence of roller dynamics by a small amount of additives such as water.[241] In addition, Das and Lauga proposed a theoretical model that predicts that DC electric field can also move asymmetrically shaped particles to move in the bulk via the same Quincke rotation mechanism.[246] Quincke rollers of

other shapes, such as ellipsoid,[247] drops[248] and a bead-flagella dimer,[249] have also been studied. A very recent study by Karani et al.[250] has given this story a new twist, by applying pulses of DC electric fields with a down time over which a Quincke roller depolarizes (Fig. 6e). By varying experimental parameters, including the durations of on and off signals, and the ratio between the down time over a characteristic charging time for the colloid, a Quincke roller can exhibit trajectories reminiscent of run-and-tumble or Lévy walk for bacteria, and assemble into dynamic clusters.

The second line of research studied the influence of driving forces on roller dynamics. For example, at low particle densities, Lu et al. noticed that hydrodynamic and dipolar pairing between two Quincke rollers enhanced their speeds by as much as 50% (Fig. 6c),[251] yet this effect disappeared at a higher driving electric field as dipolar repulsion between two rollers began to dominate. In a different study, Mauleon-Amieva et al. observed,[252] by gradually increasing the E field while keeping the packing fraction at ~ 0.03, a transition of rollers from a fluid state to amoeba-like active crystals, then to an active gas state, and finally to a polar liquid state with a moving band phase that was also reported by Bricard et al. [63] A key ingredient that distinguishes their observations from others is a previously reported electrohydrodynamic flow[224, 253-255] near the substrate that works as a pump to collects microspheres into a crystalline structure.

The third line of research puts micro-rollers in a complex environment and examines their collective behaviours, such as among randomly positioned posts,[256, 257] or against an external flow.[258] The experiments with post obstacles reveal that, at low particle densities, rollers undergo a smooth transition from diffusion, to sub-diffusion, to localized swimming, upon increasing post concentrations.[256] At high roller densities, on the other hand, their collective motion in the form of polar liquid can survive in the face of a small amount of post obstacles. However, as obstacles become dense, the roller current is redistributed into a river network.[257] The analogy of a flowing swarm of rollers to a "river" becomes even more fitting when these micro-rollers are exposed to an external flow. How do these two flows, one by active particles and the other by water molecules, interact with each other? The answer, revealed by Morin and Bartolo,[258] was that rollers behave similarly to magnetic spins under an external magnetic field, in that isolated rollers align their direction readily with the external flow, while a swarming band of rollers confined in a racetrack showed hysteresis, i.e. the band maintained its direction and shape until abruptly reversing at a higher flow rate. Interestingly, an effective bending elasticity of the flowing band causes a wave-like distortion within the band before it reverses.

5) Pros and cons
There are many advantages of using Quincke rollers as active colloids. The particle synthesis cannot be any simpler (there is nothing to synthesize, unless one wishes to make the particles on their own), which is excellent news to researchers who are either not familiar with chemical or physical fabrication techniques, or do not have access to these facilities. Certain

chemicals are still involved, such as hexadecane or AOT, but there is no apparent chemical reaction and these chemicals are easily accessible. The experiment also appears straightforward, but not without caveats. Foreseeable challenges include the use of a DC voltage as high as hundreds of volts (requiring a voltage amplifier, and raising safety concerns), and how to prevent nonuniformity in the electric field distribution that might cause unwanted side effects, such as dielectrophoresis or even a change in collective behaviours (interesting behaviours nevertheless).

The biggest advantage of this system, as a *Nature* comment from Michael Shelley puts it, is perhaps "the apparent completeness of the explanatory theory".[259] Because no chemical reaction is involved, the propulsion of, and the interactions among, Quincke rollers are solely governed by well-defined and understood physics. This, in principle, enables a complete theoretical description of their isolated and collective behaviours, and simulations that recover all observations, a luxury rarely enjoyed by other active colloid systems. The flip side, however, is the lack of rich behaviours exhibited by chemical swimmers such as predator-prey effect[167] or oscillations,[193, 260, 261] that stem from chemical communications and even nonlinearity. In addition, the likely presence of other electrohydrodynamic effects, such as that reported and exploited by ref 252, needs to be taken into consideration when designing Quincke roller systems and when interpreting data.

3. Concluding remarks

This review article has given a general introduction to some of the most popular systems of synthetic active colloids, emphasizing their synthesis, operating mechanisms, and notable studies from the soft matter community. Even though an emphasis has been placed on soft matter physics, let us not make the mistake of thinking that active colloids only matter within this community. In fact, a significant portion of publications on this topic reside in other disciplines such as materials chemistry, biomedicine, and microrobotics, each with their own interests and perspectives. Materials chemists, for example, are more concerned with synthesizing particles of novel materials with intriguing properties, which then enable the fabrication of active colloids (or "micromotors" as they are commonly known in this community) that swim faster, bind stronger, or interact with each other. Synthesis aside, the interests of materials chemists and soft matter physicists are very much aligned, in the sense that both groups desire samples of controlled, interesting properties. A cross-talk between these two groups is therefore encouraged (an intended purpose of this article).

We have also observed a recent research trend of active colloids, both within the soft matter community and in other disciplines, geared towards understanding their dynamics in a complex environment.[7, 8, 131, 262, 263] Such environments can manifest in the form of obstacles and boundaries, or densely packed neighbours that induce collective behaviours. Studies on this topic are attractive for various reasons. To materials chemists and engineers, practical applications of micromotors

or microbots often occur in scenarios that involve complex environments (e.g. human blood vessels). To soft matter physicists, on the other hand, research is often motivated by an interest to model and understand living active matter, including bacterial cells, birds, fish and even the society, that often reside in a complex environment. In addition, dynamic, spatiotemporal patterns of various shapes and sizes, found with active colloids in complex environments, are also an endless source of fascination and wonder.

Before we conclude, we briefly address reproducibility, an important practical issue that an experimentalist must be aware of. In general, active colloid experiments are quite sensitive to ambient temperature, humidity, sample preparation, presence of trace impurities, the voltages or light applied, and other laboratory conditions. It is therefore unsurprising to see reports of different speed, directionality, or collective behaviours for the same type of active colloids from different labs, or even within the same lab, conducted under seemingly identical conditions. Much of this uncertainty originates from a poor understanding of the operating mechanisms of active colloids, lack of standardized experimental protocols, and the fact that everyone does things differently. It is therefore difficult to comment on the exact reproducibility of any type of active colloid, not to mention formulate a quantitative ranking. However, readers should note that all six types of active colloids discussed in this review, when properly executed, should give qualitatively the same results across different trials, such as the order of magnitude of their propulsion speeds, their directionalities, the nature of interparticle interactions, and whether emergent behaviours are expected. Most importantly, once the learning curve is overcome, results become quite repeatable within the same lab.

With these comments, we hope this article is useful in informing soft matter physicists about the various features, advantages and limitations associated with a few important active colloids, so they can choose the best model system for their studies (see Table 1 and 2 for a summary). It is also our sincere hope that such information can inspire new discoveries or even new types of active colloids that address some of the issues identified here, or exhibit novel properties. Let us remain creative and open-minded in wielding the powerful tools of active colloids, while remembering that it is the creativity that made Da Vinci, not the pencils in his hands.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

Notes and references

Appendix: An explanation for the scores in table 2

i. Mechanism clarity

The missing star for bimetallic colloids represents the latest research progress that suggest a coexistence of self-electrophoresis, which has been popularly considered the only mechanism, with self-diffusiophoresis, which arises from the concentration gradient of neutral molecules such as O_2 and H_2O_2. The exact ratio of these two contributions on the overall propulsion of a bimetallic active colloid remains unknown, but it is generally believed that self-electrophoresis still dominates.

Photochemical active colloids are known to be powered by photochemical reactions, but the exact nature of these reactions, along with what is being produced, is often unknown (see main text for details). Mechanisms are therefore somewhat speculative.

Although self-diffusiophoresis has been proposed for water-lutidine demixers, the exact mechanism of how this occurs has not been settled entirely.

ii. Ease of visualizing orientation

It is slightly difficult to distinguish the two hemispheres of a bimetallic particle under an optical microscope. However, the two ends of a bimetallic rod, such as Ag-Au or Au-Pt, that reflect light of very different colors can be distinguished under dark field of a microscope, if the rod is sufficiently large (e.g. ~ 2-3 µm long and 200-300 nm in diameter). Ref. 54 gives an excellent example.

Quincke rollers do not have a Janus structure because they are made entirely of homogeneous dielectric microspheres. The possibility of a Janus Quincke roller is therefore interesting.

iii. Long term observation

Due to the gradual depletion of chemical fuels (e.g. H_2O_2), and the production of oxygen bubbles (elaborated in section 2.1.2), it is experimentally challenging to monitor the dynamics of bimetallic colloids, Pt-coated colloids, or sometimes photochemical colloids, for an extended period of time. The time window is often limited to within an hour, or even minutes if the particle population is dense.

iv. Degree of user control

It is typically difficult to modulate *in situ* the speeds of chemically powered active colloids, other than by adding more fuels directly into an open chamber, or increasing the temperature of the solution either by directly heating it up, or applying laser that heats it up.[264, 265] These techniques are less effective or precise than external modulation offered by active colloids powered by electromagnetic waves. In addition, their interparticle interactions are hardly tuneable *in situ*.

Because ICEP swimmers exhibit both dipolar and hydrodynamic interactions at low frequencies, and that their polarizability is sensitive to the driving frequency of AC electric fields, this system offers the richest possibilities for external modulation of interparticle interactions, both in terms of the speed and directionality of swimmers, and also how they interact and the collective behaviours that emerge.

v. Material flexibility is a quantitative answer to the question "how feasible is it to swap one material for another with this active colloid system?" For the bimetallic self-electrophoretic colloids, their 2-star rating reflects the wide variety of noble metals that yield similar locomotive behaviour, as shown in detail by Wang et al..[54] For the Pt-Janus spheres, only Pt appears to have the requisite turnover rate to be an acceptable catalyst for the decomposition of H_2O_2 that yields consistent locomotion, thus it earns 1 star. For water-lutidine demixing, only carbon and gold have proven effective from the literature, earning a rating of 1 star. In general, a wide variety of materials can be used for photochemical swimmers, earning 3 stars. Similarly, Quincke rotation and ICEP can and have been realized with a variety of dielectric materials and metal coatings (in the case of ICEP), thus motivating a 3-star rating for each.

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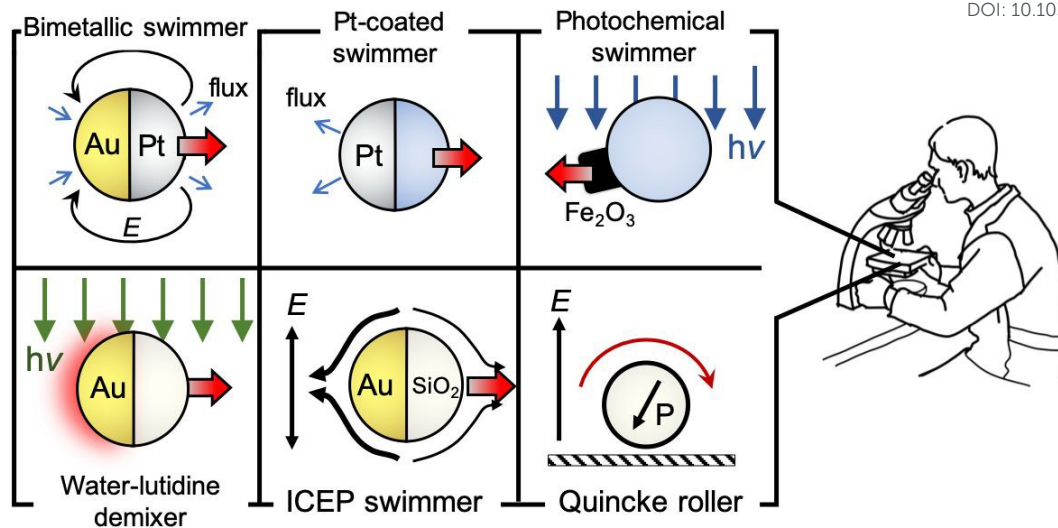
This review article provides practical, experimentally relevant details on six common types of active colloids useful for soft matter research.

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