Pt-SiO_2 Janus Particles and the Water/Oil Interface – A Competition Between Motility and Thermodynamics

Zohreh Jalilvand,[1] Hamad Haider,[1] Jingqin Cui,[2] and Ilona Kretzschmar[1*]*

[1] Department of Chemical Engineering, The City College of New York, New York, 10031, United States

[2] Pen-Tung Sah Institute of Micro-Nano Science and Technology, Xiamen University, Xiamen, Fujian 361005, PR China

**Corresponding Authors: kretzschmar@ccny.cuny.edu, jqcui@xmu.edu.cn*

ABSTRACT

Various aspects of the behavior of Janus particles near liquid/liquid interfaces have been studied through different experimental and theoretical realizations, but the effect of motility on the behavior of Janus particles near liquid/liquid interfaces has not been investigated, yet. Here, we demonstrate the ability to engineer the behavior of highly interfacial active Janus particles near a water/oil interface by introducing motility to the system. Passive, i.e., non-motile, platinum-capped 8 μm silica (Pt-SiO_2) Janus particles exhibit a strong tendency to attach to water/oil interfaces with the Pt cap facing the oil and the SiO_2 side facing the water phase. In contrast, we show that active, i.e., motile, 8 μm Pt-SiO_2 Janus particles approach the interface, orient in a sideways fashion with the Janus boundary perpendicular to the interface, and then swim in the vicinity of the interface similar to observations reported near solid/liquid interfaces. Active Pt-SiO_2 Janus particles near the water/oil interface show motility as a result of adding H_2O_2 to the particle solution. The decomposition of H_2O_2 into O_2 and H_2O creates a non-uniform gradient of O_2 around the particle that hydrodynamically interacts with the water/decalin boundary. The interaction enables rotation of the particle within the swimming plane that is parallel to the interface but restricts rotation in and out of the swimming plane thereby preventing adsorption to the liquid/liquid interface.

KEYWORDS: Pt-SiO_2 Janus particles, motility, water/oil interface, orientation.

Introduction

The term Janus particle was first coined by Casagrande et al. in 1989 to describe the behavior of spherical amphiphilic glass particles at the oil/water interface [1]. In their work, they prepared the first Janus particles, measured their 90° contact angle at three different water/oil interfaces, and proposed a model to predict the position of asymmetrical Janus beads at the oil/water interface.[1] Ever since their initial work, continued attention has been devoted to developing the field of Janus particles both at the micro-[2] and nanoscale.[3-4] In 2001, Binks and Fletcher reported an analysis predicting that a Janus particle is three times more strongly adsorbed than its homogeneous analog[5] making Janus particles promising candidates for many applications such as breathable skin,[6] emulsion stabilization,[7-8] oil recovery,[9-11] reactive emulsions,[12] and cosmetics.[13] Further, both the dynamics of a single particle and their self-assembly at air/water and oil/water interfaces have received a lot of attention in recent years.[14-17]

Numerous experimental[18-22] and theoretical studies[5, 23-24] as well as simulations[25-27] have focused on elucidating the impact of a Janus particles' amphiphilicity, wettability, and surface morphology on its interfacial behavior at the oil/water interface. Maximizing the amphiphilicity of a Janus particle through the wettability of its two surfaces has been predicted theoretically[5, 23] and shown experimentally[18, 20-22] and in simulations[25-27] to increase the desorption energy, i.e., the depth of the energy well, of the particles compared to homogeneous particles. A deeper energy well enhances the Janus particle's interfacial activity. Therefore, Janus particles are more likely to enter liquid/liquid interfaces than leave them. Such particles, when trapped at the oil/water interface in their thermodynamic equilibrium orientation, possess a diblock structure in which each hemisphere is exposed to the fluid that it has affinity for. Thus, the Janus particle adopts an upright orientation, i.e., with the cap in the generally lighter oil phase, in which the fluid interface is pinned at the Janus boundary of the particle to maximize the contact area of each face hence minimizing the total free energy of the system. The literature further shows that tuning the amphiphilicity of Janus particle via changing the relative surface areas of the two surface regions, which leads to asymmetric amphiphilic particles with a Janus nature, is best described by the Janus balance, J, for which $J = 1$ represents the maximum in adsorption energy.[24] It has also been shown that the interaction between Janus particles at an interface is impacted through changes in surface wettability of the cap.[20] Further, Adams's et al. have shown that the particle orientation at the interface is also strongly influenced by the surface morphology, i.e., roughness, of the particles in which Janus particles with higher surface roughness were found to orient more randomly such that each face does not necessarily reside in its preferred fluid phase.[19] Another avenue that has been explored to tailor the interfacial behavior of Janus particles for the realization of specific applications is to use colloids with shapes different from the spherical shape, e.g., dumbbell and disc shapes, and the interested reader is directed towards references 28-31 for more information.

With regard to tuning the interfacial activity of Janus particles, we introduce a new parameter, motility, which enables us to engineer the behavior of Janus particles in the vicinity of a water/oil interface. Using a specially designed cell, we demonstrate that by introducing motility to the system highly surface-active Janus particles no longer adsorb in their thermodynamically preferred orientation at the water/oil interface. 8 μm platinum-coated silica (Pt-SiO_2) Janus particles are employed in the experiments, where motility is introduced to the system by adding H_2O_2 to the aqueous particle solution. Platinum serves as catalyst and decomposes H_2O_2 into oxygen and water leading to an asymmetric oxygen gradient that drives the motion of the particles. Such particles are recognized as self-propelled particles[32] with a wide range of applications[33-36] and their interaction with walls[37-40] and more recently with interfaces[41-44] has become of interest.

Our study reveals that passive Pt-SiO_2 Janus particles enter the water/decalin interface, whereas active Pt-SiO_2 Janus particles do not. Subsequently, the behavior of the self-propelled Pt-SiO_2 Janus particles with respect to the water/decalin interface is studied. We show the behavior of active Pt-SiO_2 Janus particles is comparable to that observed near a solid wall.[37-40] Overall, our work shows that the behavior of Janus particles in the water/decalin interfacial system can be engineered from a highly interfacially-active behavior that leads to irreversible particle trapping at the interface to a distinctly different preferential behavior, where motile particles reside near the water/decalin interface.

Experimental Details

8 µm Pt-SiO_2 Janus particles are fabricated using the well-established physical vapor deposition (PVD) technique. Silica beads (Fiber Optic center Inc, 8µm diameter) are cleaned via centrifugation and washing with deionized (DI) water (Millipore, resistivity 18.2 MΩ.cm at 25ºC). Cleaned silica beads are assembled into loosely-packed monolayers on pre-cleaned glass slides using a slightly modified convective assembly method.[45] Subsequently, assembled monolayers of particles are exposed to platinum vapor in a PVD machine (Ted Pella, Inc.) with a line-of-sight geometry yielding a 9±1 nm thick platinum layer on the particles that gets thinner towards the equator of the particle. After the platinum deposition, Janus particles are sonicated off the glass slides for one minute and dispersed in deionized water. Scanning electron microscopy is used to ensure uniform and smooth surface coating (see Fig. S1 in Supporting Information). In addition, the contact angle of water on a platinum-coated microscope slide prepared under the same conditions as the Pt-SiO_2 particles in air is measured as $\theta = (50 \pm 5)°$, whereas cleaned unmodified microscope glass slides exhibit contact angles below 10°.

An experimental cell with a specialized design that allows the heavier water phase to be placed on top of the lighter oil phase is used to conduct the experiments and investigate the behavior of Pt-SiO_2 Janus particles near and at water/oil interfaces. The cell is composed of a single piece of stainless steel, which comprises two cylindrical bores of varying diameter (ratio ~1:2). Owing to the variation in diameter a ledge is created inside the cell that pins the water/oil interface because of capillary forces (capillary length for decalin/water interface, $\lambda_c \approx 7$ mm) and results in a flat interface at which the particle behavior can be monitored. The cell (schematically shown in Fig. 1A, top) made by a milling machine is then adhered to a pre-cleaned cover slip with the help of a thin layer of Norland optical adhesive 63 (Norland, Inc) providing an optical window to monitor the behavior of the particles.

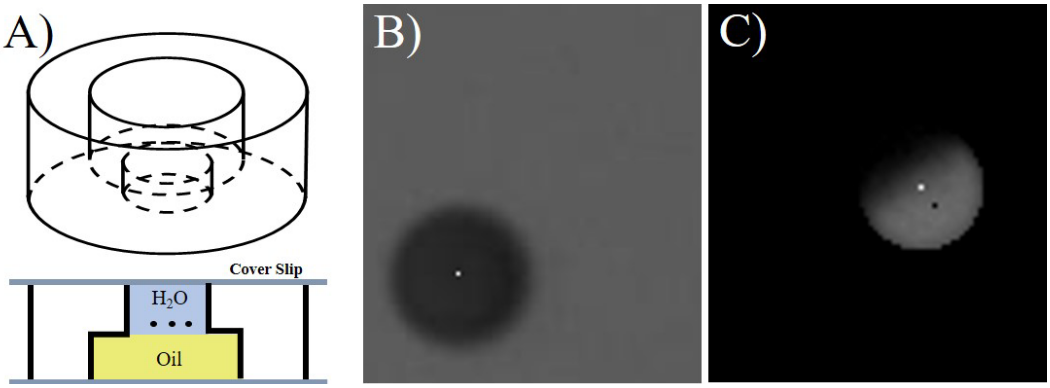

Figure 1. A) Schematic of experimental cell. Top: Two bores of varying diameter are connected and create the ledge that pins the water/oil interface. Bottom: Cross sectional view that shows the filled cell after flipping. The top bore contains the heavier water phase and the bottom bore the lighter oil phase. B) Optical image of an 8 μm Pt-SiO_2 Janus particle at the water/oil interface with the base particle centroid indicated by the white dot in a full-moon configuration when the cap is facing up or down. Note that base particle and cap centroid overlap in the configuration. C) Optical image of an 8 μm Pt-SiO_2 Janus particle in a moon-shaped configuration near the water/oil interface, black dot represents the centroid of the bright SiO_2 hemisphere and the white dot is the centroid of the Pt-SiO_2 Janus particle.

In order to study the dynamics and the behavior of both active and passive Pt-SiO_2 Janus particles near and at the water/oil interface, two different sets of experiments are carried out. For the first set of experiments that studies the behavior of passive particles, the narrower bore of the cell

(Fig.1A top) is filled first with the aqueous suspension of Pt-SiO_2 Janus particles and then the wider bore is filled with oil, i.e., decalin (decahydronaphthalene, mixture of cis and trans, 98% Fisher Scientific, ρ = 0.89 g/cm^3). Then, the cell is carefully sealed with a second microscope cover slip. Next, the cell is flipped upside down to assume the orientation shown in Figure 1A (bottom) with the heavier water phase on top of the lighter decalin phase. The passive Pt-SiO_2 Janus particles are allowed to sediment and equilibrate with the water/decalin interface for 3-5 minutes prior to any measurements.

For the second set of experiments that studies the behavior of active particles, a 6% (v/v) H_2O_2 solution is prepared from an aqueous stock solution of 30% H_2O_2 (Fisher Scientific). 20 μl of the dispersed Pt-SiO_2 Janus particle sample is gently mixed with 20 μl of aqueous 6% (v/v) H_2O_2 solution resulting in a 3% (v/v) H_2O_2 solution. The volume fraction of the Janus particles is less than 1%, i.e., dilute, such that the particle motility is not affected by neighboring particles and the formation of bubbles in the cell due to oxygen produced by the reaction is minimized. Subsequently, the narrower bore of the cell is filled first with aqueous H_2O_2/particle solution all the way to the ledge and then with decalin to fill the wide bore. Decalin is chemically stable and inert to H_2O_2 at room temperature and 3%(v/v) used in the experiments.[46] Then, the cell is carefully sealed again with the second microscope cover slip and flipped upside down (Fig. 1A. bottom). Note that the autonomous motion of particles starts immediately after the particle solution is mixed with the aqueous H_2O_2 solution and transferred into the narrower bore of the cell. For measurements, the cell is allowed to equilibrate for 3-5 minutes after being flipped to allow particles to interact with the water/decalin interface.

In order to analyze the behavior of passive and active Pt-SiO_2 Janus particles, videos of the particles are taken using an Olympus BX-51 microscope with a ×20 objective. The behavior of the

Pt-SiO_2 Janus particles is recorded for 60 seconds with a u-eye 2240c camera at a rate of 10 frames per second (fps). The videos of both passive and active Pt-SiO_2 Janus particles are then analyzed using a modified Matlab program originally written by John C. Crocker,[47] which returns frame by frame the x,y coordinates of the Pt-SiO_2 Janus particles as a function of time. The trajectories are then analyzed using the procedure described by Golestanian et al.[48] to obtain the diffusion coefficients (D) of the particles from MSD plots.

The orientation of both passive and active Pt-SiO_2 Janus particles is tracked through the platinum cap (Pt cap), which acts as a mask so that a Janus particle appears in different configurations with distinguishable bright and dark regions different from the background, i.e., moon-shaped configurations. In the analysis based on a previously published technique,[49] the image sequences from the Pt-SiO_2 Janus particle videos are first converted to gray-scale frames. Two weighted centers of a Janus particle in each frame, namely both the centroid of its circular diffraction ring and the centroid of its bright SiO_2 hemisphere, are identified with a different Matlab particle tracking script. Figure 1B represents a Pt-SiO_2 Janus particle at the water/decalin interface with its two centroids overlapping when its configuration is at full moon, i.e., a dark disk, as the particle faces cap up or down with respect to the camera. Figure 1C represents the centroid of the bright SiO_2 hemisphere of a Pt-SiO_2 Janus particle with a black dot and the center of the Pt-SiO_2 Janus particle itself is represented with a white dot (background is subtracted for more accurate measurements) near the water/decalin interface. The diffraction ring centroid is the actual particle body center, and its x,y coordinates are analyzed to acquire the particle's orientation and trajectories. The line connecting the two centroids, together with one side of the image frame, defines the specific orientation (azimuthal angle φ) of the Pt-SiO_2 Janus particle within the image plane. To determine the particle orientation out-of-the-image plane (zenith angle θ), a cosinusoidal relationship of the zenith angle with the brightness intensity of a moon-phase shape is employed assuming the Pt-SiO_2 Janus particles are coated with hemispherical Pt-caps.[50] Then, based on the two angles the overall angular deviation of the Pt-SiO_2 Janus particle in the three-dimensional space at each time step is estimated.

Ideally, the integrated optical intensity of each image of the same particle in a sequence stays constant, however, variations are expected (and observed) partially due to the particle drifting in and out of the focus plane, and partially due to the limitation of the image analysis. To track the system error, we use a similar procedure to process sequences of plain 8 μm SiO_2 spheres near a solid wall or at the decalin/water interface. The optical intensities of particle images are compared to estimate the variation of θ angles caused by arbitrary optical fluctuation employing the same cosinusoidal relationship used for the Janus particles. The raw and processed images, as well as the results are summarized in Figures S2 and S3 (Supporting Information). Based on the results, the combined uncertainty in θ originating from both instrumentation and data analysis is ~20°.

Results and Discussion

The behavior of both passive and active 8 μm Pt-SiO_2 Janus particles at and near the water/decalin interface is studied in two separate sets of experiments. First, the behavior of passive Pt-SiO_2 Janus particles at the water/decalin interface is analyzed using an established mean square displacement (MSD) method to measure the diffusivity of the particles along with the rotational behavior of the particles. Then, the dynamics of the active Pt-SiO_2 Janus particles is studied by characterizing the rotational behavior of the active particles near the water/oil interface. Finally, the two systems are compared and discussed with respect to their differences and similarities.

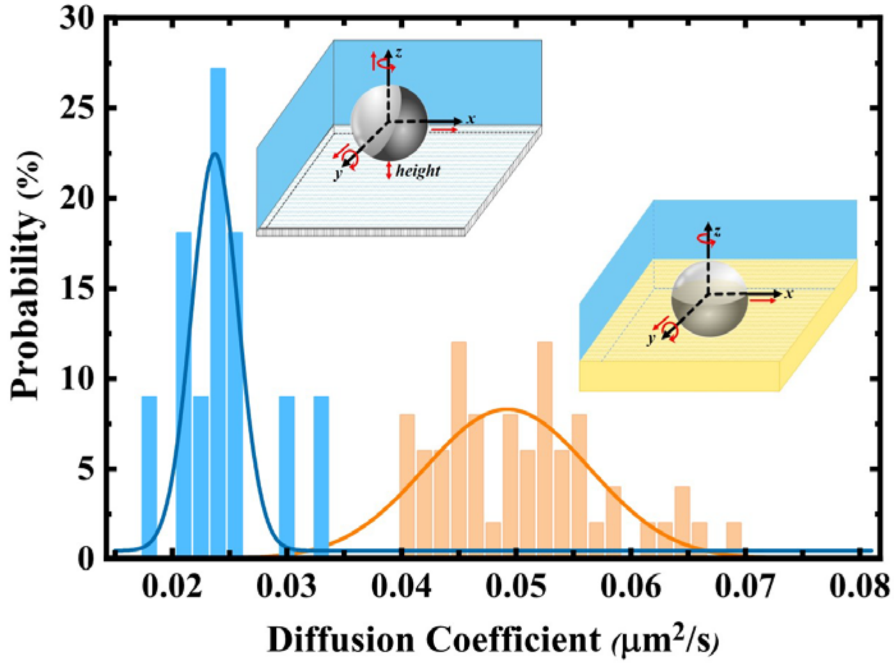

Figure 2. Diffusion coefficient of 8 μm Pt-SiO_2 Janus particles at the water/decalin interface (orange histogram) and diffusion coefficient of the same particles near a SiO_2 wall (blue histogram). Both systems are measured in the absence of H_2O_2 and thus are passive systems (see text). Insets show particle position relative to the water/decalin and water/SiO_2 wall interface.

Behavior of passive Pt-SiO_2 Janus particles at water/oil interface. Although the behavior of passive Pt-SiO_2 Janus particles is known at an oil/water interface in which the particles tend to be attracted to the interface with the metal cap facing the oil phase;[20] we are interested in understanding how their behavior differs from that of passive Pt-SiO_2 Janus particles near a liquid/solid interface, i.e., a SiO_2 wall. One avenue to elucidate the interaction of passive Pt-SiO_2 Janus particles with liquid/liquid and liquid/solid interfaces, without optically observing the particles adsorb onto the interface, is to measure the diffusivity of the particles. Figure 2 depicts the experimentally measured diffusion coefficients of 8 μm Pt-SiO_2 Janus particles at the water/decalin interface (orange histogram) as well as the diffusion coefficients of 8 μm Pt-SiO_2 Janus particles near a wall (blue histogram). The diffusion coefficient data is obtained from linearly fitting of the experimental measurements of the MSD with $\Delta r^2(\Delta t)>=4\Delta t$ (see supporting information Fig. S4), which indicates that passive Pt-SiO_2 Janus particles only exhibit Brownian motion. Figure 2 illustrates the spread of diffusivities observed for passive Pt-SiO_2 particles near a solid SiO_2 wall and at the water/decalin interface. Analysis of Figure 2 reveals that there are two clearly identifiable distributions, one with a maximum near 0.023 $\mu m^2/s$ and the second with a maximum near 0.050 $\mu m^2/s$ (Table S1, Supporting Information). The binary distribution of the values indicates that the passive Pt-SiO_2 particles exhibit a greater diffusion coefficient at the water/decalin interface (orange bars, 0.050 ± 0.007 $\mu m^2/s$) compared to the same particles near the SiO_2 wall (blue bars, 0.023 ± 0.004 $\mu m^2/s$). The enhanced diffusivity observed for passive Pt-SiO_2 Janus particles when compared to their analogs near the water/solid interface indicates that they are trapped at the water/decalin interface and experience diffusion in only two dimensions, while their counterparts at the wall show 3D diffusion (see Figure 2 insets). They behave as freely-suspended particles at a liquid/liquid interface of two immiscible fluids (decalin and water) with similar viscosities (decalin < 3 *mPa.s* and water = 1 *mPa.s*). Assuming that the particles sit at the interface with a contact angle of 90°, one can calculate an average viscosity experienced by the particles at the water/decalin interface.[51] The equivalent of this assumption is to average the two-dimensional (2D) diffusion coefficients for water ($D_{2D,water}= 0.081\mu m^2/s$) and decalin ($D_{2D,decalin}= 0.027\mu m^2/s$) yielding $D_{2D,avg}= 0.054\mu m^2/s$, which is close to the observed $D_{trapped} = 0.050 \pm 0.007$ $\mu m^2/s$.

In order to characterize the orientation and rotational behavior of the passive Pt-SiO_2 particles, a previously published imaging analysis technique[49] is applied (Fig. 3). A representative optical image is shown in Figure 3A. The platinum coating on the SiO_2 particle acts as a mask where the dark area corresponds to the Pt cap and the brighter area represents the SiO_2 portion allowing the asymmetrical character of the particle to potentially be observed. Passive Pt-SiO_2 particles are found to align their Janus boundary with the interface indicating a cap-up or -down orientation and as a result appear as black circles in the image.

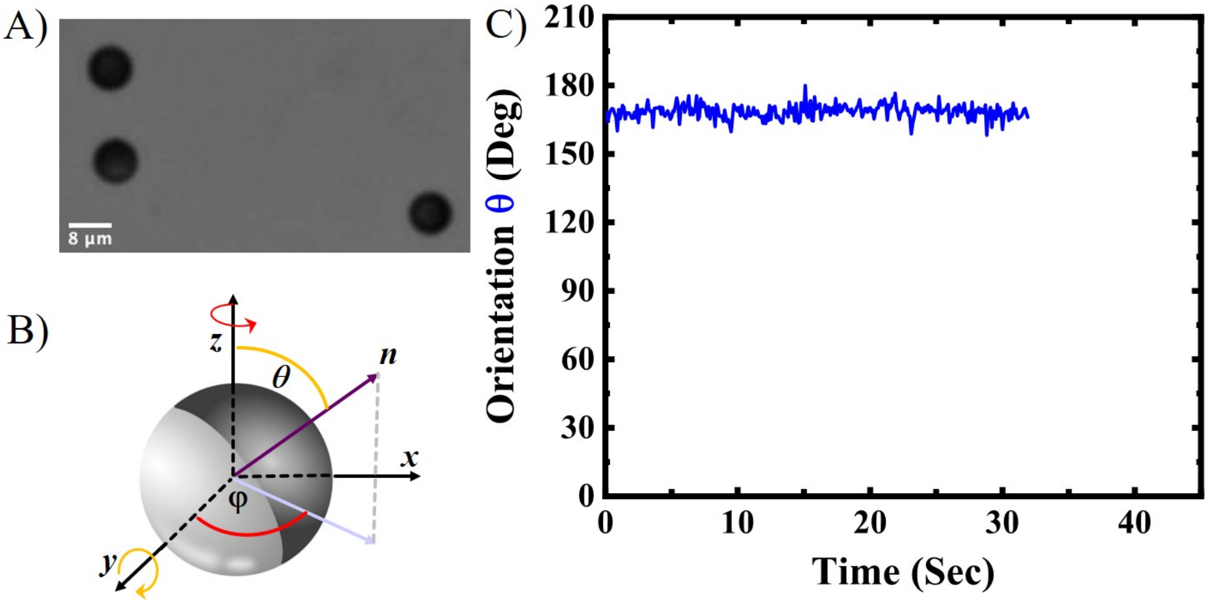

Figure 3. A) 8 μm Pt-SiO_2 Janus particles attached to the water/decalin interface (passive system) tend to align their Pt-cap downward since the Pt-cap prefers the oil phase over the water phase. In addition, the bottom heaviness of the particles due to the Pt cap contributes to the orientation of the particles (see text). Imaging is done from the top in transmission mode. B) 3D schematic of a Pt-SiO_2 Janus particle, representation of the orientation of the particle, particle's rotation with respect the *x*-*y* plane and *z*-axis is denoted by θ and φ, respectively. C) Orientation of the Pt-SiO_2 Janus particle's surface normal vector (***n***) with respect to the *x*-*y* plane (θ), representing the particle rotation in-and-out of the *x*-*y* plane. The water/decalin interface is parallel to the *x*-*y* plane.

The orientation of the Pt-SiO_2 Janus particle with respect to the *x*-*y* plane (θ) is defined as the angle between the normal to the interface (*z*-axis) and normal to the Janus's cap (***n***) as shown in Figure 3B. The particle's position is defined with respect to the interface, in which the particle's *x*-*y* plane is parallel to the interface. Figure 3C shows that the orientation (θ) of passive Pt-SiO_2 Janus particle does not change drastically over time but is rather uniform around 165±15°. The uniformity of θ confirms that the Pt-SiO_2 Janus particles stay in the same orientation at the water/decalin interface once they are trapped in good agreement with previous theoretical models and experimental reports[1, 5, 20] and the microscopy images reported in Figure 3A. The deviation of θ from 180° is likely a result of thermal motion that gives the Pt-SiO_2 Janus particles rotational flexibility (~ ±20°) at the interface (for additional data see supporting information Fig. S5). Detection of the orientation of the particle with respect to the z-axis (φ) and therefore the particle's rotation around the normal of the imaging plane is not feasible, so one may assign an arbitrary value, i.e., 0 or 180, for φ without actually detecting any changes in the circular object.

In order to test the irreversible adsorption of the passive 8μm Pt-SiO_2 Janus particles to the water/decalin interface, the cell is flipped, left sitting for ~5 minutes and then turned back to the initial state. Passive Pt-SiO_2 Janus particles are found trapped at the water/oil interface after the procedure. This finding is in good agreement with expectation, because of the Janus character of the particles. It is most likely that the particles have assumed a cap-down orientation at the water/decalin interface. The Pt cap prefers the oil phase compared to the water phase due to its more hydrophobic nature, whereas the charged SiO_2 surface prefers the aqueous phase due to its polar nature. Furthermore, the Pt cap with a higher density than silica (ρ_{Pt} = 21.45 g/cm^3 vs ρ_{SiO2} = 2.65 g/cm^3)[52] renders the particles bottom heavy supporting a cap-down orientation.[53] Additionally, the geometry of the cap contributes to the cap-down orientation of the particles because the center of mass of the particle shifts toward the Pt-coated portion, especially in the case of larger particles.[54]

Behavior of active Pt-SiO_2 Janus particles at water/decalin interface. In the second set of experiments, H_2O_2 is introduced to the solution of Pt-SiO_2 Janus particles in order to study the impact of added motility on the system. In Figure 4A, the representative microscope image indicates that active Pt-SiO_2 Janus particles do not exhibit the same orientation and rotational behavior as passive Pt-SiO_2 Janus particles (Fig. 3A). Inspection of Figure 4A reveals that the active particles align their Janus boundary with the interface in a sideways manner in which the particles appear as half dark and half bright in good agreement with previous reports of active Janus particles near a solid wall.[38] In the active system, the Pt cap decomposes H_2O_2 into water and oxygen thereby triggering the particle's autonomous motion owing to the concentration gradient of oxygen, i.e., chemical field, formed across the particle from the Pt-cap side of the particle to its SiO_2 backside (Fig. 4B). The solute molecules, i.e., O_2, within the boundary layer interact differently with the particle due to the concentration gradient around the particle, which drives the motion of the particle.[34, 55-63] The presence of the interface modifies the chemical and hydrodynamic fields around the particle, which couples back to the particle and causes the sideways orientation (Fig. 4B).[37, 44, 53]

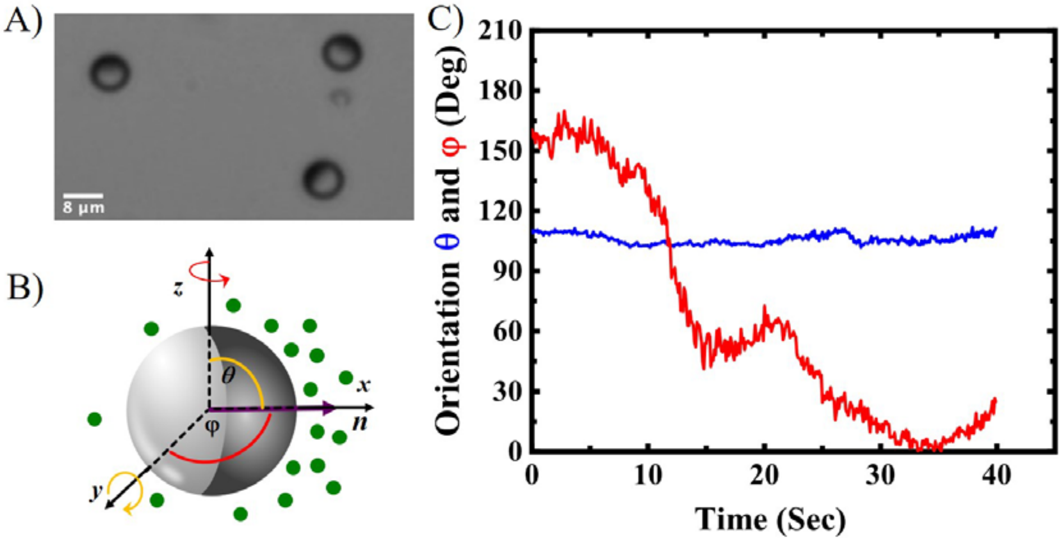

Figure 4. A) 8 µm Pt-SiO_2 Janus particles reorient in a sideways manner with respect to the water/decalin interface due to presence of H_2O_2 (active system), where the dark area corresponds to the Pt-cap and the SiO_2 side appears lighter in color. Imaging is done from the top in transmission mode. B) 3D schematic of active Pt-SiO_2 Janus particle, representation of the orientation of the particle, particle's rotation with respect the x-y plane and z-axis is denoted by θ and φ, respectively. The green dotes represent the oxygen molecules generated due to the surface reaction. C) Representation of the changes in the orientation of the Pt-SiO_2 Janus particle's surface normal vector with respect to the x-y plane (θ) and z-axis (φ), θ angle represents the rotation of the particle in-and-out of the x-y plane (blue line) and the φ angle represents rotation of the particle around the z-axis (red line).

The autonomous motion of the particle is a combination of both propulsion and Brownian motion owing to its active and passive parts and thus the orientation of the particle is also subject to both random Brownian motion and propulsion. Figure 4C clearly illustrates that the active particles' rotation in-and-out of the swimming plane (x-y plane parallel to the interface) is constrained (blue line) to a value of $\theta \sim 110°$, which agrees with the half dark-half bright configuration observed under the optical microscope for the active Pt-SiO_2 Janus particles (Fig. 4A). Such confinement effects caused by the presence of the solid interface have been listed as limiting the rotation of active Janus particles near solid interfaces owing to the formation of image dipoles and the presence of an asymmetric chemical field around the particle as the driving force for particle propulsion.[64] Note, the $\theta \sim 110°$ rather than 90° is a result of the heaviness of the Pt cap that tends to tilt the Pt-cap slightly towards the interface. Analysis of the orientation of the particle with respect to the z-axis (φ) shown in Figure 4C (red line) samples a range of angles between ~0-180° within the swimming (x-y) plane over the 40s interval of observation. Additional data for other particles (see Supporting Information Fig. S6 and S7) shows that the Pt-SiO_2 Janus particles explore the whole 360° angle range. Analysis of the mean square angular displacement (MSAD) results in a rotational diffusion coefficient of $D_r = 0.25$ Deg^2s^{-1} and angular velocity of $\omega = 0.65$ Deg s^{-1}. The rotational diffusion coefficient of the active Pt-SiO_2 Janus particles is less than the theoretical bulk rotational diffusion coefficient $\frac{k_B T}{8\pi\mu R^3} = 0.35$ Deg^2/s owing to confinement effects caused by the nearby water/decalin interface in good agreement with Wang et al.'s observation.[42]

In analogy to the irreversibly adsorbed passive 8 μm Pt-SiO_2 Janus particles, the adsorption of the active 8 μm Pt-SiO_2 Janus particles to the water/oil interface is tested by flipping the cell for ~5 minutes and then turning it back to the initial state. After flipping the cell back to its original configuration, active Pt-SiO_2 Janus particles are no longer found trapped at the water/oil interface in good agreement with the observed, energetically-unfavorable sideways orientation and autonomous motion.

Note that in order to compare the behavior of the Pt-SiO_2 Janus particles in the passive and active systems, the particles have been investigated under the same conditions with the same particle solution and cap thickness as well as the same oil. We demonstrate that passive Pt-SiO_2 Janus particles are inclined to adsorb to the interface and show increased diffusivity. As the Pt-SiO_2 Janus particles approach the water/oil interface from the water (top phase), they assume a thermodynamically favorable orientation aided by gravity due to their bottom heaviness, i.e., the Pt cap is in a downward orientation. The Pt-cap hemisphere prefers the oil phase owing to its neutral and more hydrophobic character, while the SiO_2 hemisphere prefers the water phase since it has a negative zeta potential in water and is hydrophilic. Further, the Pt cap is polarizable as it is metallic in nature, yielding additional attractive interactions with the negatively charged water/decalin interface and supporting the adsorption of Pt-SiO_2 Janus particles to the interface with the Pt cap facing the oil phase, while minimizing the electrostatic repulsion between the negatively charged SiO_2 surface and the interface. The Debye length in the system studied here is 0.3 μm based on the ionic strength of the DI-water used (10^{-6} mM). These findings are in good agreement with previous theoretical and experimental observations of passive Pt-SiO_2 Janus particles as highly interfacially-active components that tend to adsorb to the interface. On the other hand, for the first time, we show that exposing Pt-SiO_2 Janus particles to H_2O_2 solution causes them to exhibit a very different behavior with respect to the water/oil interface. The micron-size particles get close to the interface but they do not attach to the interface overcoming the high interfacial activity of passive Pt-SiO_2 Janus particles in the absence of H_2O_2. Besides the electrostatic double layer interaction between the negatively charged side of the Pt-SiO_2 Janus particles and the negatively charged water/decalin interface that repels the particles away from the interface, the driving force that arises due to the addition of H_2O_2, i.e., propulsion, contributes to keeping particles above the interface. The hydrodynamic interaction between the active Pt-SiO_2 Janus particles and the interface as well as the chemical field around the active Pt-SiO_2 particles, align them in a sideways manner in which the Janus particle's normal is parallel to the swimming plane, i.e., parallel to the interface and perpendicular to gravity. The side-ways orientation represents the thermodynamically least favorable configuration for entering the interface and prevents active Pt-SiO_2 Janus particles from attaching to the interface. Therefore, active Pt-SiO_2 Janus particles tend to stay in the vicinity of the interface in their side-ways configuration within a confined range of θ orientations and varying φ orientations, which resembles the behavior found for active Janus particles near a wall.[37-39, 53, 65-66] The varying φ orientations are attributed to the thermal fluctuations that contribute to the motion of the particles along with the directional propulsion of the particles; hence, the orientation of the particles within the plane is subject to the random forces and changes with time. Additionally, unlike in the case of the passive Pt-SiO_2 particles, turning the cell of active Pt-SiO_2 Janus particles around and turning it back to its initial state does not show any particles near the interface. They are able to escape owing to the fact that they are suspended near the interface and their self-propulsion, i.e., chemical activity, is not sufficiently large to overcome the gravitational force to keep the active Pt-SiO_2 particles in sliding states along the interface.[67] As a result, active Pt-SiO_2 Janus particles near a water/decalin interface tend to stay in the vicinity of the interface and do not enter the interface, whereas the passive Pt-SiO_2 Janus particles have a very strong tendency to jump onto the water/decalin interface to lower the free energy of the system.

To generalize these findings, the potential impact of surface wettability and Debye length on the observed behavior is discussed. Modification of the Pt cap and/or addition of salt to the aqueous H_2O_2 solution would likely lead to a suppression of particle motility. Brown et al.[68] showed that addition of even 10^{-2} mM salt (NaCl or KBr) resulted in a ~30% decrease of the catalytic activity of the Pt surface and a complete cessation of motion at 1 mM concentration for 2 μm Pt-coated polystyrene particles. In addition, salt will also lead to a reduction of the Debye length through screening of the electrostatic double layer repulsion between the SiO_2 surface of the particle and the liquid/liquid interface needed to stabilize the particle near the interface. Thus, one would expect upon addition of salt to see active Pt-SiO_2 particles slow down and eventually enter the interface. Hydrophobic modification of the SiO_2 surface is expected to reduce the stability of active Pt-SiO_2 particles near the interface as it will also lead to a screening of the electrostatic double layer repulsion. An interesting future experiment would involve using optically-activated swimmers, e.g., Au-TiO_2[69-70] and Cu-TiO_2,[71] or electric field responsive swimmers, e.g., Pt-SiO_2,[72] which would allow determination of the exact swimming velocity needed to keep the particle out of the interface.

Conclusions

In summary, we are able to engineer the behavior of Pt-SiO_2 Janus particles at and near the water/decalin interface by switching between passive and active systems, respectively, by means of introducing motility to the system. We demonstrate that besides surface characteristics that govern the behavior of the Pt-SiO_2 Janus particles at or near the water/decalin interface, a novel approach is employed to engineer the interfacial behavior of the Pt-SiO_2 Janus particles, which influences the interaction between particles and the surrounding solution. Hence, addition of H_2O_2 to the solution and then consequently motility to active Janus particles near a water/decalin interface quenches the interfacial activity of Pt-SiO$_2$ Janus particles and prevents them from adsorbing to the interface. In turn, the active Pt-SiO$_2$ Janus particles stay close to the interface with the Janus normal parallel to the swimming plane in which the particle rotates freely within the plane but the out-of-plane rotation of the particle is constrained due to the confinement effects of the interface and the modified chemical and flow field around the particle alluding to the same behavior found for active particles near a wall.

Acknowledgements

This work was supported by the National Science Foundation under awards CBET-1264550 and 1705565. J.C. acknowledges National Natural Science Foundation of China (No. 21303143).

Supporting Information

The supporting information provides SEM images of Pt-SiO$_2$ particles, θ uncertainty calculation details, MSD analysis, additional rotational analysis, and MSAD analysis for passive and active Pt-SiO$_2$ particles.

References

1. Casagrande, C.; Fabre, P.; Raphael, E.; Veyssié, M., “Janus beads”: realization and behaviour at water/oil interfaces. *Europhys. Lett.* **1989,** *9* (3), 251-255.
2. Zhang, J.; Grzybowski, B. A.; Granick, S., Janus Particle Synthesis, Assembly, and Application. *Langmuir* **2017,** *33* (28), 6964-6977.
3. Walther, A.; Muller, A. H., Janus particles: synthesis, self-assembly, physical properties, and applications. *Chem. Rev.* **2013,** *113* (7), 5194-5261.
4. Agrawal, G.; Agrawal, R., Janus nanoparticles: recent advances in their interfacial and biomedical applications. *ACS Appl. Nano Mater.* **2019,** *2* (4), 1738-1757.
5. Binks, B. P.; Fletcher, P. D. I., Particles adsorbed at the oil−water interface: A theoretical comparison between spheres of uniform wettability and “Janus” particles. *Langmuir* **2001,** *17* (16), 4708-4710.
6. De Gennes, P.-G., Soft matter. *Rev. Mod. Phys.* **1992,** *64* (3), 645.
7. Walther, A.; Hoffmann, M.; Müller, A. H., Emulsion polymerization using Janus particles as stabilizers. *Angew. Chem. Int. Ed.* **2008,** *47* (4), 711-714.
8. Fujii, S.; Yokoyama, Y.; Miyanari, Y.; Shiono, T.; Ito, M.; Yusa, S.-i.; Nakamura, Y., Micrometer-sized gold–silica Janus particles as particulate emulsifiers. *Langmuir* **2013,** *29* (18), 5457-5465.

9. Luo, D.; Wang, F.; Zhu, J.; Cao, F.; Liu, Y.; Li, X.; Willson, R. C.; Yang, Z.; Chu, C.-W.; Ren, Z., Nanofluid of graphene-based amphiphilic Janus nanosheets for tertiary or enhanced oil recovery: High performance at low concentration. *Proc. Natl. Acad. Sci.* **2016,** *113* (28), 7711-7716.
10. Peng, B.; Zhang, L.; Luo, J.; Wang, P.; Ding, B.; Zeng, M.; Cheng, Z., A review of nanomaterials for nanofluid enhanced oil recovery. *RSC Adv.* **2017,** *7* (51), 32246-32254.
11. Yang, L.; Wang, T.; Yang, X.; Jiang, G.; Luckham, P. F.; Xu, J.; Li, X.; Ni, X., Highly stabilized foam by adding amphiphilic Janus particles for drilling high temperature and high calcium geothermal wells. *Ind. Eng. Chem. Res.* **2019,** *58*, 9795-9805.
12. Faria, J.; Ruiz, M. P.; Resasco, D. E., Phase ‐ selective catalysis in emulsions stabilized by Janus silica ‐ nanoparticles. *Adv. Synth. Catal.* **2010,** *352* (14 ‐ 15), 2359-2364.
13. Fujii, S.; Yokoyama, Y.; Nakayama, S.; Ito, M.; Yusa, S.-i.; Nakamura, Y., Gas bubbles stabilized by Janus particles with varying hydrophilic–hydrophobic surface characteristics. *Langmuir* **2017,** *34* (3), 933-942.
14. Bradley, L. C.; Chen, W.-H.; Stebe, K. J.; Lee, D., Janus and patchy colloids at fluid interfaces. *Curr. Opin. Colloid Interface Sci.* **2017,** *30*, 25-33.
15. Fernandez-Rodriguez, M. A.; Rodriguez-Valverde, M. A.; Cabrerizo-Vilchez, M. A.; Hidalgo-Alvarez, R., Surface activity of Janus particles adsorbed at fluid–fluid interfaces: theoretical and experimental aspects. *Adv. Colloid Interface Sci.* **2016,** *233*, 240-254.
16. Kumar, A.; Park, B. J.; Tu, F.; Lee, D., Amphiphilic Janus particles at fluid interfaces. *Soft Matt.* **2013,** *9* (29), 6604-6617.
17. Binks, B. P., Particles as surfactants—similarities and differences. *Curr. Opin. Colloid Interface Sci.* **2002,** *7* (1-2), 21-41.
18. Ondarçuhu, T.; Fabre, P.; Raphaël, E.; Veyssié, M., Specific properties of amphiphilic particles at fluid interfaces. *J. Phys.* **1990,** *51* (14), 1527-1536.
19. Adams, D. J.; Adams, S.; Melrose, J.; Weaver, A. C., Influence of particle surface roughness on the behaviour of Janus particles at interfaces. *Colloids Surf. A* **2008,** *317* (1-3), 360-365.
20. Park, B. J.; Brugarolas, T.; Lee, D., Janus particles at an oil–water interface. *Soft Matt.* **2011,** *7* (14), 6413-6417.
21. Knapp, E. M.; Dagastine, R. R.; Tu, R. S.; Kretzschmar, I., Effect of Orientation and Wetting Properties on the Behavior of Janus Particles at the Air–Water Interface. *ACS Appl. Mater. Interfaces* **2019**.
22. Razavi, S.; Lin, B.; Lee, K. Y. C.; Tu, R. S.; Kretzschmar, I., Impact of Surface Amphiphilicity on the Interfacial Behavior of Janus Particle Layers under Compression. *Langmuir* **2019,** *35* (48), 15813-15824.
23. Aveyard, R., Can Janus particles give thermodynamically stable Pickering emulsions? *Soft Matt.* **2012,** *8* (19), 5233-5240.
24. Jiang, S.; Granick, S., Janus balance of amphiphilic colloidal particles. *J. Chem. Phys.* **2007,** *127*, 161102.
25. Gao, H.-M.; Lu, Z.-Y.; Liu, H.; Sun, Z.-Y.; An, L.-J., Orientation and surface activity of Janus particles at fluid-fluid interfaces. *J. Chem. Phys.* **2014,** *141* (13), 134907.
26. Razavi, S.; Koplik, J.; Kretzschmar, I., The effect of capillary bridging on the Janus particle stability at the interface of two immiscible liquids. *Soft Matt.* **2013,** *9* (18), 4585-4589.
27. Fan, H.; Resasco, D. E.; Striolo, A., Amphiphilic Silica Nanoparticles at the Decane− Water Interface: Insights from Atomistic Simulations. *Langmuir* **2011,** *27* (9), 5264-5274.
28. Ruhland, T. M.; Gröschel, A. H.; Ballard, N.; Skelhon, T. S.; Walther, A.; Müller, A. H.; Bon, S. A., Influence of Janus particle shape on their interfacial behavior at liquid–liquid interfaces. *Langmuir* **2013,** *29* (5), 1388-1394.
29. Park, B. J.; Lee, D., Equilibrium orientation of nonspherical Janus particles at fluid–fluid interfaces. *ACS Nano* **2012,** *6* (1), 782-790.

30. Tu, F.; Park, B. J.; Lee, D., Thermodynamically Stable Emulsions Using Janus Dumbbells as Colloid Surfactants. *Langmuir* **2013,** *29* (41), 12679-12687.
31. Liang, F.; Liu, B.; Cao, Z.; Yang, Z., Janus colloids toward interfacial engineering. *Langmuir* **2017,** *34* (14), 4123-4131.
32. Ebbens, S. J.; Howse, J. R., In pursuit of propulsion at the nanoscale. *Soft Matt.* **2010,** *6* (4), 726-738.
33. Patra, D.; Sengupta, S.; Duan, W.; Zhang, H.; Pavlick, R.; Sen, A., Intelligent, self-powered, drug delivery systems. *Nanoscale* **2013,** *5* (4), 1273-1283.
34. Wang, W.; Duan, W. T.; Ahmed, S.; Mallouk, T. E.; Sen, A., Small power: Autonomous nano- and micromotors propelled by self-generated gradients. *Nano Today* **2013,** *8* (5), 531-554.
35. Parmar, J.; Vilela, D.; Villa, K.; Wang, J.; Sánchez, S., Micro-and Nanomotors as Active Environmental Microcleaners and Sensors. *J. Am. Chem. Soc.* **2018,** *140* (30), 9317-9331.
36. Wang, X.; In, M.; Blanc, C.; Malgaretti, P.; Nobili, M.; Stocco, A., Wetting and orientation of catalytic Janus colloids at the surface of water. *Faraday Discuss.* **2016,** *191*, 305-324.
37. Uspal, W. E.; Popescu, M. N.; Dietrich, S.; Tasinkevych, M., Self-propulsion of a catalytically active particle near a planar wall: from reflection to sliding and hovering. *Soft Matt.* **2015,** *11* (3), 434-438.
38. Ebbens, S. J.; Howse, J. R., Direct observation of the direction of motion for spherical catalytic swimmers. *Langmuir* **2011,** *27* (20), 12293-12296.
39. Jalilvand, Z.; Pawar, A. B.; Kretzschmar, I., Experimental study of the motion of patchy particle swimmers near a wall. *Langmuir* **2018,** *34* (50), 15593-15599.
40. Das, S.; Garg, A.; Campbell, A. I.; Howse, J.; Sen, A.; Velegol, D.; Golestanian, R.; Ebbens, S. J., Boundaries can steer active Janus spheres. *Nat. Commun.* **2015,** *6*, 8999.
41. Wong, F.; Dey, K. K.; Sen, A., Synthetic micro/nanomotors and pumps: Fabrication and applications. *Annu. Rev. Mater. Res.* **2016,** *46*, 407-432.
42. Wang, X.; In, M.; Blanc, C.; Würger, A.; Nobili, M.; Stocco, A., Janus colloids actively rotating on the surface of water. *Langmuir* **2017,** *33* (48), 13766-13773.
43. Fei, W.; Gu, Y.; Bishop, K. J. M., Active colloidal particles at fluid-fluid interfaces. *Curr. Opin. Colloid Interface Sci.* **2017,** *32*, 57-68.
44. Popescu, M. N.; Uspal, W. E.; Domínguez, A.; Dietrich, S., Effective Interactions between Chemically Active Colloids and Interfaces. *Acc. Chem. Res.* **2018,** *51* (12), 2991-2997.
45. Prevo, B. G.; Velev, O. D., Controlled, Rapid Deposition of Structured Coatings from Micro- and Nanoparticle Suspensions. *Langmuir* **2004,** *20*, 2099-2107.
46. Decaline was exposed to 6% (v/v) aqueous H_2O_2 solution for 3 hours and no decompoisiton products were detected. .
47. Crocker, J. C.; Hoffman, B. D., Multiple-Particle Tracking and Two-Point Microrheology in Cells. *Method Cell Biol.* **2007,** *83*, 141-178.
48. Howse, J. R.; Jones, R. A. L.; Ryan, A. J.; Gough, T.; Vafabakhsh, R.; Golestanian, R., Self-motile colloidal particles: From directed propulsion to random walk. *Phys. Rev. Lett.* **2007,** *99* (4).
49. Cui, J.; Long, D.; Shapturenka, P.; Kretzschmar, I.; Chen, X.; Wang, T., Janus particle-based microprobes: Determination of object orientation. *Colloids Surf. A* **2017,** *513*, 452-462.
50. Anthony, S. M.; Hong, L.; Kim, M.; Granick, S., Single-Particle Colloid Tracking in Four Dimensions. *Langmuir* **2006,** *22* (24), 9812-9815.
51. Pozrikidis, C., Particle motion near and inside an interface. *J. Fluid Mech.* **2007,** *575*, 333–357.
52. Los Alamos National Lab, N. U., *T-4 Handbook of Material Properties Data Bases, Vol Ic, Equation of State*. 1984.
53. Simmchen, J.; Katuri, J.; Uspal, W. E.; Popescu, M. N.; Tasinkevych, M.; Sánchez, S., Topographical pathways guide chemical microswimmers. *Nat. Commun.* **2016,** *7*, 10598.
54. Rashidi, A.; Issa, M. W.; Martin, I. T.; Avishai, A.; Razavi, S.; Wirth, C. L., Local Measurement of Janus Particle Cap Thickness. *ACS Appl. Mater. Interfaces* **2018,** *10* (37), 30925-30929.
55. Staffeld, P. O.; Quinn, J. A., Diffusion-induced banding of colloid particles via diffusiophoresis: 2. Non-electrolytes. *J. Colloid Interface Sci.* **1989,** *130* (1), 88-100.

56. Anderson, J. L.; Prieve, D. C., Diffusiophoresis caused by gradients of strongly adsorbing solutes. *Langmuir* **1991,** *7* (2), 403-406.
57. Anderson, J. L.; Prieve, D. C., Diffusiophoresis: migration of colloidal particles in gradients of solute concentration. *Sep. Purif. Methods* **1984,** *13* (1), 67-103.
58. de Graaf, J.; Rempfer, G.; Holm, C., Diffusiophoretic Self-Propulsion for Partially Catalytic Spherical Colloids. *IEEE T Nanobiosci.* **2015,** *14* (3), 272-288.
59. Sabass, B.; Seifert, U., Dynamics and efficiency of a self-propelled, diffusiophoretic swimmer. *J. Chem. Phys.* **2012,** *136* (6), 064508.
60. Golestanian, R.; Liverpool, T. B.; Ajdari, A., Propulsion of a molecular machine by asymmetric distribution of reaction products. *Phys. Rev. Lett.* **2005,** *94* (22), 220801.
61. Popescu, M. N.; Uspal, W. E.; Dietrich, S., Self-diffusiophoresis of chemically active colloid. *Eur. Phys. J.* **2016,** *225*, 2189–2206.
62. Ajdari, A.; Bocquet, L., Giant amplification of interfacially driven transport by hydrodynamic slip: Diffusio-osmosis and beyond. *Phys. Rev. Lett.* **2006,** *96* (18), 186102.
63. Popescu, M. N.; Dietrich, S.; Tasinkevych, M.; Ralston, J., Phoretic motion of spheroidal particles due to self-generated solute gradients. *Eur Phys J E* **2010,** *31* (4), 351-367.
64. Berke, A. P.; Turner, L.; Berg, H. C.; Lauga, E., Hydrodynamic attraction of swimming microorganisms by surfaces. *Phys. Rev. Lett.* **2008,** *101* (3), 038102.
65. Crowdy, D. In *Particle self-diffusiophoresis near solid walls and interfaces*, 4th Micro and Nanoflows Conference, UCL, London, UK, 7-10 September 2014; UCL, London, UK, 2014.
66. Crowdy, D. G., Wall effects on self-diffusiophoretic Janus particles: a theoretical study. *J. Fluid Mech.* **2013,** *735*, 473-498.
67. Das, S.; Jalilvand, Z.; Popescu, M. N.; Uspal, W. E.; Dietrich, S.; Kretzschmar, I., Floor- or ceiling-sliding for chemically active, gyrotactic, sedimenting Janus particles. *Langmuir* **2020**, in same issue.
68. Brown, A.; Poon, W., Ionic effects in self-propelled Pt-coated Janus swimmers. *Soft Matt.* **2014,** *10* (22), 4016-4027.
69. Sridhar, V.; Park, B.-W.; Sitti, M., Light-Driven Janus Hollow Mesoporous TiO2–Au Microswimmers. *Adv. Funct. Mater.* **2018,** *28* (25), 1704902.
70. Dong, R.; Zhang, Q.; Gao, W.; Pei, A.; Ren, B., Highly Efficient Light-Driven TiO2–Au Janus Micromotors. *ACS Nano* **2016,** *10* (1), 839-844.
71. Wang, L.; Popescu, M. N.; Stavale, F.; Ali, A.; Gemming, T.; Simmchen, J., Cu@TiO2 Janus microswimmers with a versatile motion mechanism. *Soft Matt.* **2018,** *14* (34), 6969-6973.
72. Demirörs, A. F.; Akan, M. T.; Poloni, E.; Studart, A. R., Active cargo transport with Janus colloidal shuttles using electric and magnetic fields. *Soft Matt.* **2018,** *14* (23), 4741-4749.

Table of Content Figure (TOC):