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# Surface tension anomaly observed for chemically-modified Janus particles at the air/water interface

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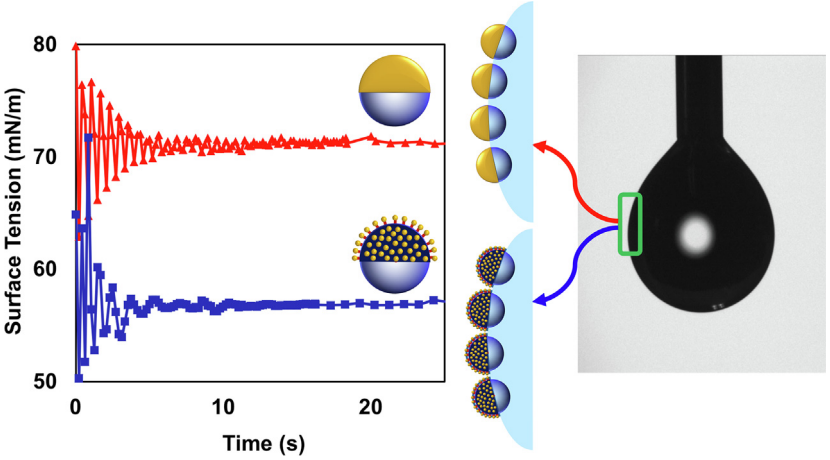
## GRAPHICAL ABSTRACT

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## ABSTRACT

The behavior of Janus particles fabricated from core silica particles decorated with gold nanoparticles on one hemisphere is studied at the air/water interface. An unexpected reduction in the effective surface tension is observed in the presence of these chemically-modified Janus particles. Experiments on the interfacial behavior of a variety of control particles, including the physically-modified Janus particles made from the same core silica particles coated with a thin gold layer, do not exhibit significant surface tension effects. We hypothesize that the chemical modification of particles in form of a Janus structure is needed to alter the surface tension and attribute the surfactant-like behavior of these particles to the presence of immersion forces.



Janus particles are a class of anisotropic colloidal particles that possess different surface properties on each hemisphere [1]. They are believed to be more effective at stabilizing fluid interfaces due to their amphiphilic nature, which could yield a 3-fold increase in their desorption energy compared to their homogeneous analogue [2]. Therefore, they are promising candidates for applications involving interfacial systems as their surface can be engineered for

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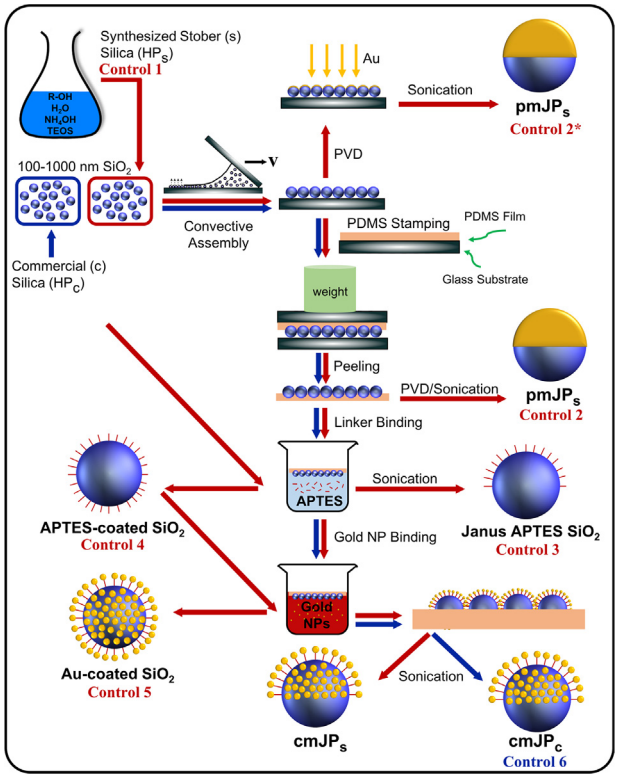
optimal interfacial properties [3–7]. Based on these predictions, studies have been conducted on the use of Janus particles in a variety of applications including emulsion and foam stabilization [8–10], polymer blends [11,12], and drug delivery [13–16]. In order to link the performance of Janus particles in such applications to their interfacial behavior, an array of fundamental studies have focused on the interfacial configuration of Janus particles [17–24], shape anisotropic Janus particles [25–30], dynamics of Janus particles at fluid interfaces [31–36], and the behavior of particle-laden interfaces to applied stresses [37–39].

Measuring the change in the surface tension of fluid interfaces in the presence of particles has been used in the literature to assess the surface activity of particles [40,41]. Nanoparticles have shown to reduce the interfacial tension [42,43]; however, adding a Janus character to the particle enhances the surface activity and causes a more pronounced reduction of the surface tension [44,45]. The behavior of gold nanoparticles (~3.5 nm) capped half with hexanethiol and half with 2-(2-mercapto-ethoxy) ethanol has been examined at both air/water and decane/water interfaces resulting in a more effective reduction of the surface tension compared to uniformly thiolated gold nanoparticles [46]. Thiolated gold/iron oxide Janus nanoparticles (~14 nm) have been shown to reduce the hexane/water interfacial tension to 22.5 mN/m, a value much lower in comparison to that obtained with the homogeneous counterparts [47]. The interfacial activity of silver-based Janus nanoparticles (~200 nm) is measured to be significantly higher at both air/water and decane/water interfaces compared to silica and poly (methyl methacrylate) homogeneous particles at equivalent particle concentrations [48]. These polymer-coated silver Janus particles reduce the surface tension and exhibit a surface activity similar to amphiphilic molecules but with much larger area per particle [49].

Reduction of air/water and oil/water surface tension has also been reported with larger particles. Iron oxyhydroxide particles (average length of ~0.6 μm) have been found to reduce the mineral oil/water interfacial tension (~62 mN/m) to 15.5 mN/m after 19 h [50]. Suspensions of charge-stabilized titania particles (~0.04–1.4 μm) are shown to reduce the air/water surface tension significantly when increasing the mass loading of particles to 5% [51]. Addition of spherical glass beads (~40–70 μm) decreases the air/water surface tension with a more pronounced effect upon the addition of tetradecyltrimethylammonium bromide cationic surfactant [52].

Here, we focus on micron-sized Janus particles to examine the key factors determining their surface activity at the air/water interface. Since the system at hand is a heterogenous system composed of air/water/solid particles, surface tension values reported here represent the effective surface tension for the air/water interface. Therefore, the word surface tension throughout this work refers to the effective air/water surface tension in the presence of particles. We report on the interfacial behavior of a unique class of surface-tension reducing Janus particles that are obtained through a chemical modification route in which a surface-active ligand is immobilized on one half of the particle surface. We examine their impact on the air/water surface tension and discuss the important role that the type and geometry of surface modification play in the interfacial behavior.

The fabrication of Janus particles studied here is a multi-step process as shown in Scheme 1. Silica core particles ($HP_s$, standard deviation ⩽8%) with diameters of 300, 500, and 1000 nm are synthesized using a modified Stöber & Fink method [53] and cleaned in piranha solution prior to use. Next, a monolayer of silica particles is assembled on a glass substrate using the convective assembly technique [54]. A polydimethylsiloxane (PDMS) stamping technique is used to partially embed the particles. After stamping, functionalization of the exposed side of silica particles is carried




**Scheme 1.** Synthesis protocol used for the fabrication of chemically-modified Janus particles and various control particles.

out using a 2 mM solution of (3-aminopropyl) triethoxysilane (APTES) in methanol for 30 min [55,56]. The siloxane group of APTES readily adheres to the $SiO_2$ surface, whereas the amino group on the other end of the APTES molecule is available for binding of gold nanoparticles. A colloidal gold suspension (~18 ± 3 nm) is synthesized using the Turkevich method [57]. Next, the stamped and APTES-functionalized silica monolayer is placed upside down onto the suspension of synthesized gold nanoparticles for 5 min to allow for the binding of gold nanoparticles to the APTES-functionalized silica surface. After the chemical modification, only the Janus particles ($cmJP_s$) that are ~50% embedded in the PDMS film are released by heating the film at 80 °C for 10 min and are then suspended in water by sonication. A more detailed

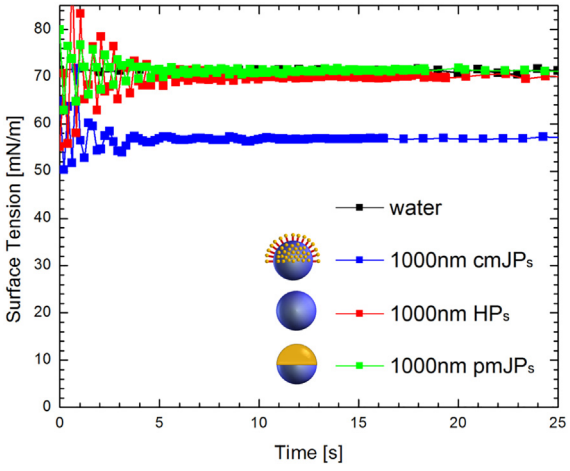



**Fig. 1.** Time-dependent surface tension for $HP_s$, $pmJP_s$, and $cmJP_s$.

description of the synthesis protocol and the limitations of the synthesis are provided in the Supporting Information.

A set of 5 control particles (Scheme 1) is fabricated to isolate the effect of anisotropic chemical surface modification on the resulting interfacial behavior of the cmJP$_s$. In addition, the supernatant of the cmJP solution is tested to ensure that no unbound APTES or other surface-active species are present that could impact the surface tension. Measurements of the surface tension evolution in time are carried out at ambient pressure and temperature using the attention theta tensiometer. First a water pendant droplet is created and then the particles of interest are deposited at the air/water interface from a suspension. Initial oscillations in the measured surface tension values result from the deposition step and capture the process from the moment the particles are added up to the point where oscillations are damped out (see Supporting Information & Supporting Video).

The first set of experiments examines the interfacial behavior of HP$_s$ (Control 1), physically-modified Janus particles (pmJP$_s$, Control 2), and cmJP$_s$ and their impact on the air/water surface tension. The 1000 nm HP$_s$ are used as core particles in these experiments. A 5 nm-thick titanium layer followed by a 20 nm gold coating is used in making pmJP$_s$. The time evolution of the air/water surface tension upon the addition of each particle type to the interface is depicted in Fig. 1. The air/water surface tension measurement is also provided as the baseline. Whereas a pronounced reduction of surface tension is recorded for cmJP$_s$ ($57.1 \pm 2.4$ mN/m), HP$_s$ and pmJP$_s$ do not alter the surface tension, highlighting that a Janus character is required but not sufficient to obtain the surfactancy characteristics in a particle.

In Control 3 and Control 4 experiments (Fig. 2, Scheme 1), we used silica particles that are only modified with the surface-active APTES linker molecules. In one case, the modification is carried out only on one hemisphere (Control 3, Janus character) and in the other case, modification is done uniformly over the entire surface of the particle (Control 4). As shown in Fig. 2, neither of these particles impact the air/water surface tension. Therefore, the observed drop of surface tension for cmJP$_s$ shown in Fig. 1 is not solely due to the presence of the APTES linker molecules on the particle. Next, we use chemically-modified particles that are functionalized with the APTES linker molecules and gold nanoparticles (Control 5); however, the difference between these particles and the cmJP$_s$ is that Control 5 particles are uniformly modified over their surface and lack the Janus character. As can be seen in Fig. 2, no change in the air/water surface tension is observed after depositing these particles at the interface indicating that the chemical modification by itself does not yield a change in the surface tension and the Janus character is an essential element. We also investigated the supernatant of cmJP$_s$ to check for any residual synthesis agents that might be causing the surface tension drop but did not observe any impact on the surface tension (Fig. 2). Additionally, we used the commercially available silica particles (HP$_c$) in fabrication of cmJP$_c$ labeled as Control 6 in Scheme 1. Analogous to the cmJP$_s$ particles, the cmJP$_c$ repeatedly give rise to a drop in surface tension (see Supporting Information). These findings confirm that the origin of core silica particles does not play a role but the chemical modification does.

To further explore the interfacial behavior of cmJP$_s$ particles and investigate the effect of particle size on the ensuing surface tension, we have studied cmJP$_s$ that are made with 300 and 500 nm core silica particles (Fig. 3). All samples exhibit a reduction in the air/water surface tension and there is a more pronounced effect at smaller particle sizes with the 300 nm cmJP$_s$ yielding a surface tension of ~49 mN/m, a value comparable to those of commercial surfactants [58,59].

Since a reduction of surface tension for homogeneous particles of nanometer size range has been reported in the literature [60,61], we tested HP$_s$ of various sizes and do not observe any impact on the surface tension (see Supporting Information).

The lack of change in the surface tension with HP$_s$ confirms that the unexpected reduction of the surface tension with the cmJP is not due to the core particle in itself but stems from its unique Janus cap geometry. In light of these observations, we hypothesize that the route taken for the Janus modification of particles (physical vs. chemical) is consequential. The Janus structure has two aspects to it; on one hand, it brings together two surfaces of distinct wettability difference, which defines the particle's amphiphilicity. On the other hand, the cap geometry adds roughness features to the particle surface that can invoke additional forces.

Based on the data available on the wettability of core silica particles (<10°–59°) [8,39,62–64] and the Janus cap in cmJP (73°–84°) [62,64], pmJP (67°) [39,62], and the APTES-coated Janus particles (54°–72°) [65], we expect similar amphiphilicty values for these particles although cmJP is slightly more amphiphilic. Considering that neither the pmJP nor the APTES-modified Janus particles impact the surface tension despite their Janus nature, we believe that amphiphilicity is not the dominating factor in reducing the surface tension in case of cmJP. Although experiments with more amphiphilic pmJP need to be carried out to support this claim.

From a cap geometry point of view, in cmJP, the presence of linker molecules yields a gap (~0.7–0.8 nm) between the core silica

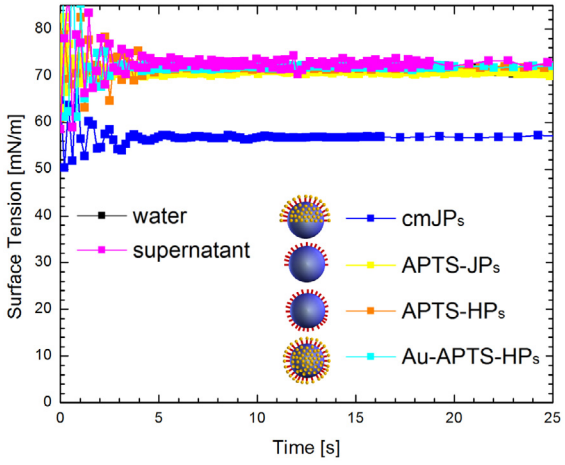



**Fig. 2.** Time-dependent surface tension for control particles 3, 4, 5, and the supernatant of the cmJP$_s$ suspension.

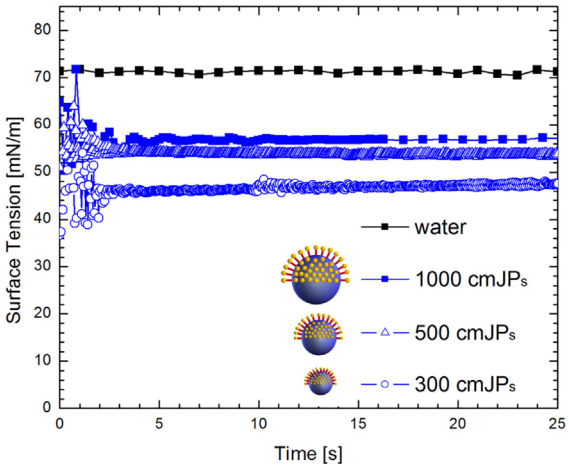
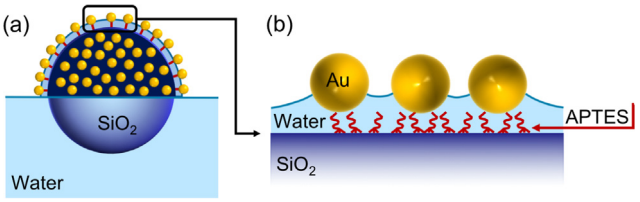



**Fig. 3.** Time-dependent surface tension for 300, 500, and 1000 nm cmJP$_s$.




**Scheme 2.** Hypothesis for the observed surface tension activity of cmJP. The gap created by the APTES linker molecule results in the close proximity of gold nanoparticles to the core silica particle surface, which gives rise to immersion forces.

particle and the gold nanoparticle functionalization on each individual cmJP (Scheme 2a). The resulting geometry is analogous to the presence of particles trapped in a thin liquid film in the vicinity of a solid boundary (Scheme 2b). We conjecture that the close vicinity of gold nanoparticles to the core silica particle leads to immersion forces in the Janus cap. The capillary forces acting between particles trapped at interfaces can be classified as the flotation forces (forces acting between floating particles attached to an air/water interface) and the immersion forces (forces acting between particles partially immersed in a liquid layer on a solid substrate) [66,67]. It has been established that the immersion capillary forces are orders of magnitude larger than the flotation capillary forces and are larger than the thermal energy, even for submicron particles. For instance, the flotation capillary forces for particles with $R\sim10$ μm are on the order of $kT$, whereas the immersion capillary forces are ~100 $kT$ for particles of 10 nm diameter. In our system with cmJPs residing at the air/water interface, the cmJPs are experiencing flotation forces with respect to each other. However, each individual cmJP experiences additional immersion forces in their Janus cap because of the nearness of the gold nanoparticles to the silica surface (~0.7-0.8 nm). Once the gold nanoparticles breach the air/water interface, menisci form around their protruding portions that stabilize the thin liquid film in the Janus cap as shown in Scheme 2a. The immersion forces caused by the menisci prevent further thinning of the liquid film. Owing to these immersion forces, both the gold nanoparticles and the aminosilane linkers in the gap are in contact with the liquid film in the Janus cap as depicted in Scheme 2b. As a reference, APTES itself is highly surface-active and reduces the air/water surface tension to 20 mN/m (measured using a 3.7 μL drop of a 2 mM APTES solution). The surface activity of APTES molecules in conjunction with the reported effect of nanoparticles in reducing the surface tension of fluid interfaces [42,43,68] support our hypothesis that the immersion forces stabilizing a thin liquid film within the Janus cap of the cmJP are likely responsible for the observed anomalous surface activity.

We would like to highlight that these observations have not been reported previously. The discovered phenomenon may be harnessed to reduce the surface tension using lower quantities of surface-active agents by employing cmJP as the carrier. Our findings have opened up a new set of questions regarding the behavior of Janus particles at interfaces. Further studies are required to examine our hypothesis regarding the impact of the linker molecule and gold nanoparticles on the surface of the cmJP. For example, molecular dynamic simulations can be employed to probe the interfacial behavior of cmJP, especially the presence of immersion forces, and shed light on the origin of the anomalous surface tension drop.

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## Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.jcis.2019.09.084.

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