

5-7-2019

## Surfactant-Mediated Assembly of Amphiphilic Janus Spheres

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## Abstract

We investigate how amphiphilic Janus particle assembly structures, including clusters and striped two-dimensional (2D) crystals, are influenced by the addition of surfactant molecules. Janus particles are fabricated using silica particles coated with Au on one side, which is further modified with a hydrophobic self-assembled monolayer. Analysis on the cluster assembly structures suggests that in addition to hydrophobic attraction, van der Waals (VDW) attraction plays a significant role in the assembly process, which is modulated by the Au coating thickness. This is manifested by the cluster formation induced primarily by VDW forces when the hydrophobic attraction between particles is diminished by adding the surfactant. In the 2D crystal case, sodium dodecyl sulfate (SDS) and Tween 20 show opposite trends in how they affect assembly structures and particle dynamics. SDS shortens the stripes in 2D crystals and accelerates the rotation of particles, whereas Tween 20 extends the straight stripes and slows down the particle rotation. We interpret the results by considering SDS adsorption on the Au-coated hemisphere of the Janus particles and Tween 20 forming hydrogen bonds with the silica hemisphere of Janus particles. Our study offers a simple approach to change the assembly structures of Janus particles, and it provides principles and guidance for potential applications of Janus particles coupled with small amphiphilic molecules.

## Disciplines

Materials Science and Engineering

## Comments

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# Surfactant Mediated Assembly of Amphiphilic Janus Spheres

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We investigate how amphiphilic Janus particle assembly structures, including clusters and striped two-dimensional (2D) crystals, are influenced by the addition of surfactant molecules. Janus particles are fabricated using silica particles coated with Au on one side, which is further modified with a hydrophobic self-assembled monolayer. Analysis on the cluster assembly structures suggests that in addition to hydrophobic attraction, van der Waals (VDW) attraction plays a significant role in the assembly process, which is modulated by the Au coating thickness. This is manifested by the cluster formation induced primarily by VDW forces when hydrophobic attraction between particles is diminished by adding surfactant. In the 2D crystal case, sodium dodecyl sulfate (SDS) and Tween 20 show opposite trends in how they affect assembly structures and particle dynamics. SDS shortens the stripes in 2D crystals and accelerates the rotation of particles, while Tween 20 extends the straight stripes and slows down the particle rotation. We interpret the results by considering SDS adsorption on the Au-coated hemisphere of the Janus

particles and Tween 20 forming hydrogen bonds with the silica hemisphere of Janus particles. Our study offers a simple approach to change the assembly structures of Janus particles, and it provides principles and guidance for potential applications of Janus particles coupled with small amphiphilic molecules.

## Introduction

Micron-sized colloidal particles are easily visible under an optical microscope, which allows them to be used as model systems to study collective phenomena in atomic systems such as crystallization, melting, and epitaxial growth.<sup>1-4</sup> Meanwhile, colloids are widely used in industry and provide an important foundation in applications including photonics, coatings and biomedicine.<sup>5-8</sup> The interactions among conventional isotropic colloids are captured by the classical DLVO theory.<sup>9-10</sup> However, small molecules are usually asymmetric and cannot be simply represented by the conventional colloidal particles. Recently developed anisotropic colloids possess directional and anisotropic interaction, which mimic complex molecules.<sup>11-12</sup> Their interparticle interactions now depend on orientation and cannot be described by the classical DLVO theory.

Janus particles are one kind of fundamental colloidal species that are anisotropic; they are colloidal counterpart of surfactant or dipolar molecules.<sup>13-16</sup> Self-assembly of Janus particles with various morphologies and surface chemistries were initially demonstrated in computer simulations, which were inspired by the concept of “colloidal molecules”.<sup>17</sup> This idea was raised in the context of colloidal packing and photonic crystal structures created by those particles. Previous studies have shown that amphiphilic Janus particles form clusters akin to micelles.<sup>18</sup> However, there are also unique features that only exist in Janus particle systems. Since the Janus motif breaks the physicochemical symmetry on a single particle, one of the most important themes for Janus particle research is the particle orientation within a self-assembled structure, which is controlled by the anisotropic interparticle interactions. In a classical amphiphilic Janus particle system, one hemisphere of particle is coated with a thin gold layer and then rendered hydrophobic with a self-assembled monolayer of thiol molecules, while the other hemisphere is kept hydrophilic

and negatively charged. Due to this built-in amphiphilicity, the hydrophobic hemispheres prefer to orient towards each other, and the clusters thus-formed adopt specific, well-defined geometries in the dilute regime. When the particle concentration increases, the clusters grow into long chains with unique three-dimensional helical structures.<sup>18</sup> Simulations further revealed that the long chain structures observed experimentally were determined by assembly kinetics instead of thermodynamic stability. When amphiphilic Janus particles are confined in a plane and their concentration is high, they self-assemble into 2D crystals with hydrophobic stripes in which the hydrophobic hemispheres face each other. The long-range orientational order is characterized by slow, glassy rotational dynamics.<sup>19</sup>

The unique structures and physics originating from the Janus sphere system inspired many research initiatives to explore the use of these particles in a broad array of fields.<sup>20-23</sup> In many practical occasions, colloidal particles coexist with small molecules that are surface active.<sup>24</sup> However, previous studies on Janus particle assembly have focused on simple model systems in the absence of amphiphilic molecules. It is easy to speculate that amphiphilic molecules will adsorb on the hydrophobic hemisphere of the Janus particles and modulate the hydrophobic attractions among particles. However, many other factors may come into play when considering specific Janus particle system and surfactant molecules, including van der Waals (VDW) force, electrostatic interactions, and hydrogen bonding, which have not been extensively considered. In the amphiphilic gold-silica Janus particle system, three forces are dominant: electrostatic repulsion between negatively charged silica hemispheres, hydrophobic interactions between thiolated gold hemispheres, and VDW forces (mainly from the gold layers). Most of the previous studies ignored the van der Waals force in Janus particle assembly.<sup>18-19</sup> To our knowledge, only one recent study has shown that the gold layer thickness had a strong influence on gold-silica Janus particle

assembly, which suggests that VDW forces between metallic surfaces contribute to interparticle interactions.<sup>25</sup> It is generally difficult to probe the details of these interactions directly and disentangle their contributions separately. Here, we demonstrate that the addition of surfactant selectively diminishes the hydrophobic attraction among particles, which can alter the balance of competing forces in Janus particle self-assembly. This provides a unique way to gauge the strength of different interactions and reveal their relative significance in the Janus particle assembly system.

Silica-Au Janus spheres with one hemisphere coated with thiol-terminated gold are used in this study to investigate the effect of different types of surfactants on the assembly structures. We discovered that the VDW forces between Au coated layers play an important role in determining the assembly structures. We further analyzed particle dynamics in the 2D crystals formed by Janus spheres under the influence of surfactant molecules using a recently developed image tracking algorithm.<sup>19</sup> We chose two commonly used surfactants: anionic sodium dodecyl sulfate (SDS) and non-ionic Tween 20. After analysis, changes in the assembly patterns and particle dynamics suggest that SDS weakens the overall attraction between Janus particles, while Tween 20 strengthens this attraction. The results can be interpreted based on the interactions of surfactants with both hydrophobic and hydrophilic hemispheres of Janus particles, which further alter the charge and hydrophobicity of the particles. This study clearly shows that adding surfactant offers a simple and effective method to change the assembly structures of amphiphilic Janus particles. More importantly, our results provide the basic principles that should be considered when using Janus particles in potential applications that involve small amphiphilic molecules.

## **Experimental Section**

1-octadecanethiol (ODT), Tween® 20 ( $\text{CMC} = 0.06 \times 10^{-6} \text{ mol/L}$  at  $25 \text{ }^\circ\text{C}$ ), hexadecyltrimethylammonium bromide (CTAB) were purchased from Sigma-Aldrich. Didodecyldimethylammonium bromide (DDAB) was purchased from TCI America. Sodium dodecyl sulfate (SDS) was purchased from ThermoFisher Scientific. Amphiphilic Janus particles were fabricated following a previously developed procedure<sup>26</sup>. A monolayer of  $3 \text{ }\mu\text{m}$  silica particles (Tokuyama) was deposited on a flat substrate and then coated with a Au layer of 10, 20 or 40 nm thickness on top of a thin 2 nm chromium adhesion layer via directional electron-beam evaporation. Upon completion of coating, the Au surface was cleaned with oxygen plasma and rendered hydrophobic with ODT. Subsequently, particles were released from the underlying substrate via brief sonication. Because the Au coating blocks the light, the coated hemisphere appears black under an optical microscope. Depending on the Au coating thickness, Janus particles have different contrast. For  $3 \text{ }\mu\text{m}$  silica particles, change in shape caused by 10-40 nm Au coating is 0.4-1.4 % of diameter and is negligible..<sup>25,27</sup>

For Janus particle assembly, a 2D monolayer of particles was formed above a flat glass substrate using a previously published procedure.<sup>19</sup> Due to gravity, particles sediment onto the bottom of the chamber well. Tilting the substrate at a small angle ( $3\text{-}4^\circ$ ) allows the formation of a dilute area of particles at the upper end of substrate and continuous monolayer of particles at the lower end.

For rotational dynamics analysis, we followed the above procedure to generate 2D crystals and used particle tracking code we developed earlier.<sup>19</sup> The ability to quantitatively analyze the position and orientation of Janus particles enables us to track particle motions precisely and calculate the diffusion dynamics (both translational and rotational) by taking time-lapsed images. Based on the data obtained from image analysis, we calculate the single particle autocorrelation

function  $C(t)$  for particles assembled in the presence of surfactant. We found that  $C(t)$  is well described by the Kohlrausch-Williams-Watts function  $C(t) = \exp\left(-\left(\frac{t}{\tau}\right)^\beta\right)$ .<sup>19</sup>

## Results and Discussion

In the dilute regime, colloidal particles self-assemble into clusters, which we define as two or more particles aggregated with their Au coated hemisphere oriented towards each other. It is generally believed that cluster formation of amphiphilic Janus particles is governed by hydrophobic attractions between the Au coated hydrophobic surfaces.<sup>18</sup> Indeed, in previous studies, hydrophobic attractions can very well explain the assembly behaviors of Au-coated Janus particles.<sup>18-19</sup> When surfactant molecules are added to the system, they will adsorb onto the hydrophobic hemisphere of the Janus particles and effectively shield the hydrophobic attraction between particles. In other words, if hydrophobic interaction is the only attraction that is responsible for the cluster formation, then adding surfactant molecules should disrupt the clusters. Indeed, we found this to be the case when Au coating layer thickness is small (10 nm) (Fig. 1). However, when the Au coating thickness increases to 40 nm, adding surfactant does not change the cluster formation of amphiphilic Janus particles, even at high concentration ( $\sim 4x$  CMC). Figure 1a shows the clusters of Au-40 (Au coating of 40 nm thickness) Janus particles in the presence of non-ionic surfactant Tween 20. Au-40 particles formed similar clusters at all surfactant concentrations used in this study (0.06 – 0.24 mM). In contrast, Au-10 (Au coating of 10 nm thickness) Janus particles formed fewer clusters when the non-ionic surfactant concentration is increased (Fig. 1b). Fig. 1c shows the fraction of particles assembled into clusters and the fraction of single particles respectively, as a function of the surfactant concentration. The detailed cluster

distribution analysis is shown in fig. S2. The fraction of Au-10 particles in the single particle state increases significantly as the Tween 20 concentration increases.

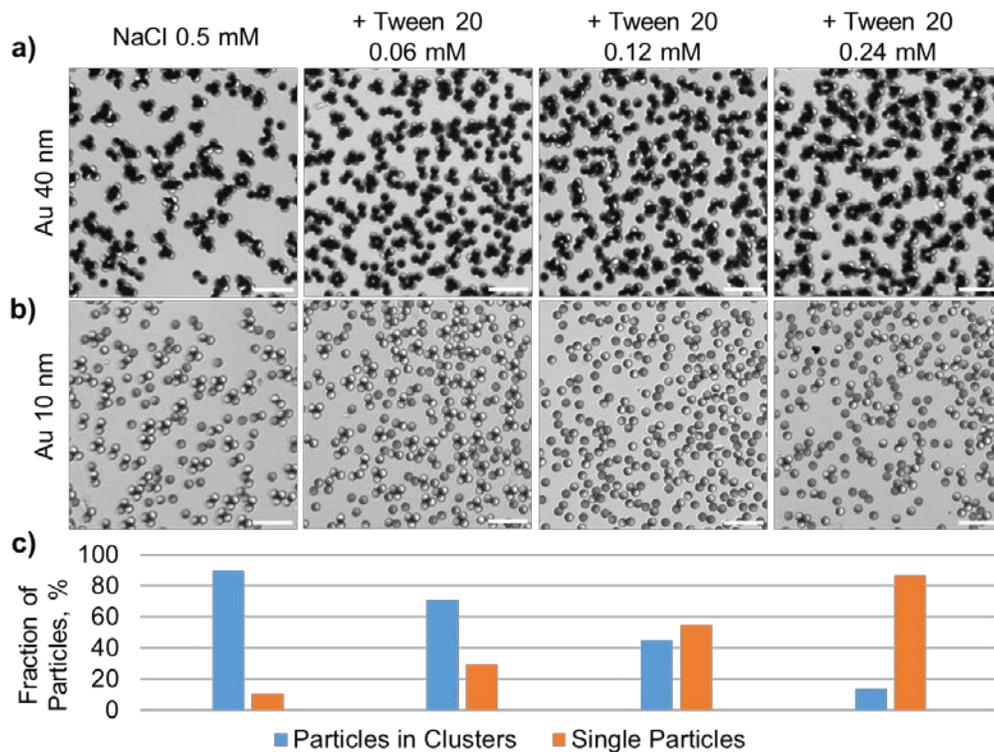


Fig. 1 a) Clusters of Janus particle with a) 40 nm (Au-40) and b) 10 nm (Au-10) gold coating in the presence of non-ionic surfactant Tween 20; c) Cluster distribution of Au-10 Janus particle at 0.5 mM NaCl, and with Tween 20 added at 0.06 mM, 0.12 mM, and 0.24 mM respectively.

~3000 particles were counted for each experimental condition. Scale bar is 15  $\mu$ m.

In most of the previous studies, VDW forces are not considered in Au coated Janus colloid systems, since they are believed to be much weaker than the hydrophobic forces.<sup>18-19, 28</sup> However, in our system VDW interaction has to be considered to explain the cluster formation in the presence of surfactant. Since Au has a large Hamaker constant,<sup>29</sup> the Au coating layer may generate significant VDW attractions when particles are in close proximity even though the layer is ~1% of

the total diameter. One study pointed out that the VDW force in Au-coated Janus particles is at least partially responsible for the cluster formation of these particles.<sup>25</sup> In our case, the first consideration is the surfactant adsorption on the hydrophobic hemisphere of Janus particles. In principle, the surfactant adsorption should eliminate the hydrophobic attractions among particles because surfactant molecules shield the hydrophobic surface. The second consideration is the VDW force due to the Au coating layer on the particles. Intuitively, VDW attraction between Au-Au is much stronger for the Au-40 Janus particles than the Au-10 Janus particles, although the absolute value of the force is not easy to probe. Our results suggest that Tween 20 can only break the clusters assembled by Au-10 Janus particles, but not those assembled by Au-40 Janus particles. This indicates that the adsorption of surfactant molecules can overcome the VDW forces among Au-10 particles and separate the clusters. On the other hand, the adsorption of surfactant cannot separate the clusters formed by Au-40 particles. The VDW attraction among Au-40 particles is strong enough to hold the clusters together even in the presence of surfactants.

The same experiment using SDS shows a similar trend. Since the addition of a charged surfactant to a solution also changes the ionic strength, in the control experiment we match the ionic strength by adding the same molar amount of NaCl. Similar to cluster formation in the presence of non-ionic surfactant, Au-40 Janus particles assemble into clusters of similar sizes regardless of the amount of added surfactant (Fig. 2a). At the same ionic concentration, assembly of Au-10 Janus particles can be disrupted by adding anionic surfactant (Fig. 2b-c). Since surfactant adsorption introduces negative charges on the hydrophobic hemisphere and induces stronger repulsion between the particles, the addition of SDS tends to push particles further apart. This directly competes with the VDW attraction, which strongly depends on the interparticle distance.

Like Tween 20, addition of SDS can overcome the VDW forces between Au-10 Janus particles, but not Au-40 Janus particles.

The adsorption of surfactants on the hydrophobic surface has been extensively studied.<sup>30-32</sup> It is estimated that the adsorption energy is  $\sim 10-15 k_B T$  (where  $k_B$  is the Boltzmann constant) for both Tween 20 and SDS on thiolated gold substrate. Based on literature<sup>25, 33</sup>, we estimate that the VDW attraction is  $\sim 10 k_B T$  for Au-10 Janus particles and  $\sim 18 k_B T$  for Au-40 particles at 25 nm separation distance.<sup>33</sup> These values roughly agree with our observation.

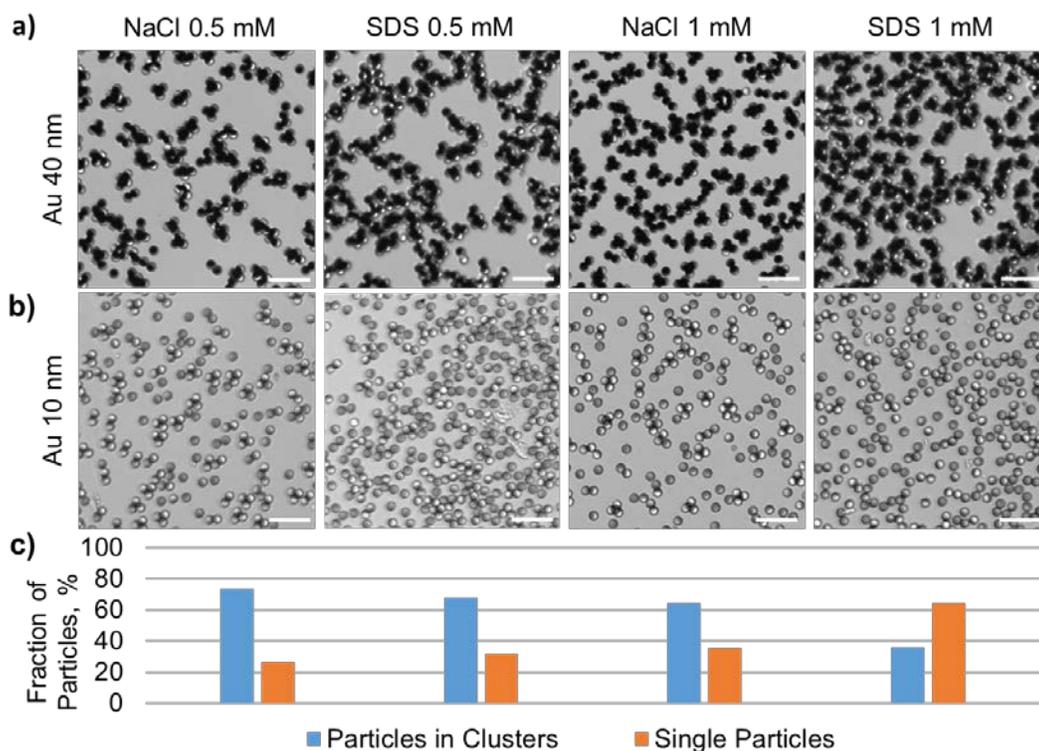


Fig. 2 Clusters of Janus particle with a) Au-40 and b) Au-10 under the presence of anionic surfactant SDS; c) Cluster distribution of Au-10 Janus particles at 0.5 mM NaCl, 0.5 mM SDS, 1 mM NaCl, and 1 mM SDS respectively.  $\sim 3000$  particles were counted for each experimental condition. Scale bar is  $15 \mu\text{m}$ .

Janus particle assembly in the presence of common cationic surfactants (CTAB and DDAB) did not show equilibrated assembly structures, as particles adsorbed strongly at the glass substrate in the presence of cationic surfactant (Fig. S1). Probably, cationic surfactant induces a positive charge on both sides of the particle through hydrophobic interactions and bilayer formation. Positively charged particles can be kinetically trapped on a negatively charged substrate via electrostatic interactions. Experimentally, assembly structures are not relaxed and seem to be random over a wide range of surfactant concentrations. Therefore, no analysis is carried out in this study with cationic surfactant.

We further studied interparticle interactions in the presence of non-ionic and anionic surfactants in the 2D crystals formed by amphiphilic Janus particles. Amphiphilic Janus particles form unique crystal structures with intriguing patterns of black and white stripes, where the hydrophobic and hydrophilic hemispheres segregate (Fig. 3a-c). These stripes are dynamic and have kinks that allow the stripes to change directions. The Janus boundary of each sphere orients perpendicular to the substrate so that two distinct halves can be clearly observed. We deliberately choose Au-20 Janus particles for 2D crystal experiments. At this thickness, the assembly structures will not be disrupted by the adsorption of surfactant. In addition, this thickness provides the level of contrast needed for the image analysis. Au-40 particles were not chosen as the Au coating becomes too heavy and interferes with the orientation of particles. A particle tracking algorithm developed previously was applied to analyze the position and rotation of each individual particle (Fig. S3).<sup>19</sup>

Interestingly, Fig. 3 shows that anionic and non-ionic surfactants influence the pattern in the crystal structure very differently, in contrast to their similar influence on clusters formed in the

dilute regime. 2D crystals with added SDS are less ordered and have many kinks in hydrophobic stripes (Fig. 3a), while Tween 20 promotes exceptionally longer stripes in the crystal structures (Fig. 3c).

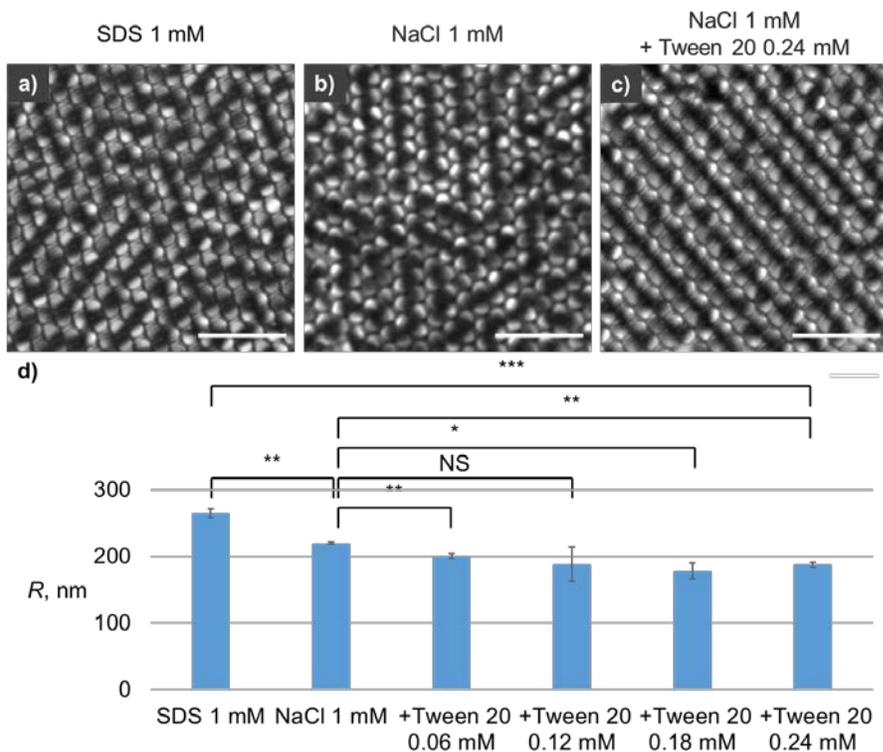


Fig. 3 Janus 2D crystal a) at 1 mM SDS b) 1 mM NaCl and c) with non-ionic surfactant added at 0.24 mM Tween 20 and 1 mM NaCl. Scale bar is 15  $\mu\text{m}$ . d) Average interparticle distance,  $R$ , of 2D Janus crystal as a function of surfactant's concentration. Unpaired t-tests with Welch's correction were performed for statistical analyses. NS denotes not significant; \* denotes  $P < 0.05$ ; \*\* denotes  $P < 0.01$ , \*\*\* denotes  $P < 0.001$ , where  $P$  is probability value. Error bars correspond to standard deviation with  $n = 3$ .

Particle tracking results in Fig. 3 show that the average interparticle distance in samples with SDS is higher than those with the same molar amount of NaCl but no SDS. In contrast, adding Tween 20 shortens the average interparticle distance. These results suggest that SDS increases the

overall repulsion among particles, while Tween 20 induces higher overall attraction among particles (Fig. 3d). Interestingly, simulation studies in a previous work showed that increasing the effective hydrophobic attraction promotes the formation of long ordered stripes in 2D Janus crystals.<sup>19</sup>

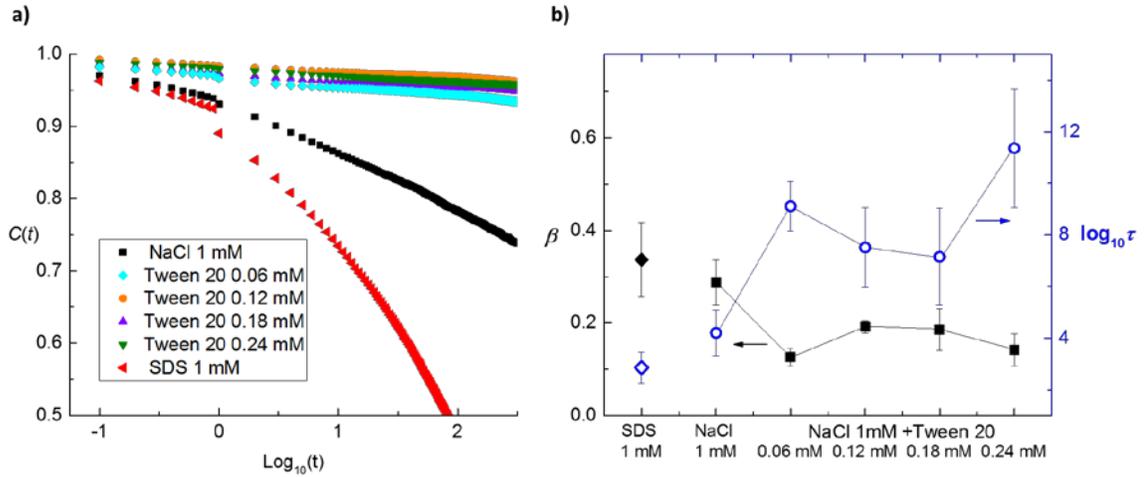


Fig. 4 Effect of surfactants on particle dynamics in the 2D Janus crystals. a) Single-particle angular autocorrelation function  $C(t)$  and b) stretching parameter  $\beta$  and relaxation time  $\tau$  in the presence of salt, non-ionic (Tween 20) and anionic (SDS) surfactants.

To further quantify the effect of the added surfactant, we analyzed the orientational dynamics of the 2D crystals. Figure 4 reveals different effects of the non-ionic surfactant (Tween 20) and anionic surfactant (SDS) on the local dynamics of 2D Janus crystals. The angular autocorrelation function  $C(t)$ , which quantifies the rotational diffusion of individual particles, shows that adding Tween 20 leads to more heterogeneous relaxation (smaller stretching parameter  $\beta$ ) and slower dynamics (larger relaxation time  $\tau$ ) compared to NaCl and SDS (Fig. 4b). On the other hand, SDS leads to faster rotation dynamics compared to NaCl and non-ionic samples (Fig. 4a). Samples with SDS also possess a higher stretching parameter for the crystal structure (Fig.

4b). All these observations can be explained by considering the interactions of surfactants with both the hydrophobic thiolated Au hemisphere and hydrophilic silica hemisphere. For SDS, the interactions are only involved with the hydrophobic hemisphere of the Janus particles. The adsorption of the hydrophobic anion will increase the overall negative charge of the particles, which creates stronger repulsion among particles and pushes them farther apart. This in turn decreases the hydrophobic attractions. For Tween 20, the interactions involve both hydrophobic and hydrophilic hemispheres of the Janus particles. The adsorption on the hydrophobic hemisphere will not change the overall charge since the surfactant is non-ionic. However, on the hydrophilic silica hemisphere, the ethylene oxide groups will form hydrogen bonds with the silanol groups<sup>34-36</sup>. The consumption of the charged silanol groups reduces the overall negative charges and decreases the repulsion among the particles.<sup>34, 37</sup> The net result is an increase of the overall attraction among Janus particles that brings the particles closer to each other. This in turn increases the VDW attraction among particles. We did not observe a clear trend within an error bar for samples at different Tween 20 concentrations. As adding surfactant modulates both repulsion and attraction forces between the particles, increase of surfactant's concentration can have a non-linear effect on the relaxation time and stretching parameter.

## **Summary and Conclusions**

By carefully examining the effect of different surfactants on the assembly structures of amphiphilic Janus particle system, we gain several insights in this study. First, the VDW force plays an important role in determining the Janus particle assembly structures. Changing the thickness of the Au coating can effectively adjust the magnitude of the VDW forces among the particles. The adsorption of surfactant on the hydrophobic hemisphere of Janus particles can

disassemble Janus particle clusters when Au coating thickness is small (10 nm) and VDW attraction is weak. When Au coating thickness is high (40 nm), VDW attraction overpowers the effect of surfactant adsorption, and maintains the clusters formed by Janus particles. In the 2D crystals, adding SDS weakens the attraction among particles due to the adsorption of the dodecyl sulfate anion on the hydrophobic hemisphere of Janus particles. This leads to larger interparticle distances, shorter hydrophobic stripes and faster rotational dynamics. On the other hand, adding Tween 20 strengthens the overall attraction among particles due to the hydrogen bonding of the ethylene oxide with the silanol groups on the hydrophilic hemisphere of Janus particles. The adsorption lowers the overall charge on Janus particles and shortens the interparticle distance. This in turn increases the attraction among the particles, which leads to longer stripe features, slower rotation dynamics and longer relaxation time.

The knowledge gained in this study provides the foundation and principles of engaging amphiphilic Janus particles together with amphiphilic small molecules in potential applications. Specifically, it is important to consider surfactant adsorption on both hemispheres of Janus particles. The surfactant can weaken the hydrophobic attraction among Janus particles. However, interactions beyond hydrophobic attractions may dominate the system, such as VDW forces, depending on the chemistry of the Janus particles. Moreover, interactions of surfactants with the hydrophilic hemisphere is also important. Ultimately, the assembly structures are determined by the delicate balance of the attractive and repulsive forces among the Janus particles. Surfactant molecules may modulate both forces in the system.

## **Acknowledgements**

SJ would like to thank Iowa State University for the Start-up Fund, Presidential Interdisciplinary

Research Seed (PIRS) Grant and 3M for the Non-tenured Faculty Award. The authors would like to thank Dr. Stephen Antony at the Sandia National Laboratories for developing the tracking code used in this study.

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TOC Figure

