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Surfactant-Mediated Assembly of Amphiphilic Janus Spheres

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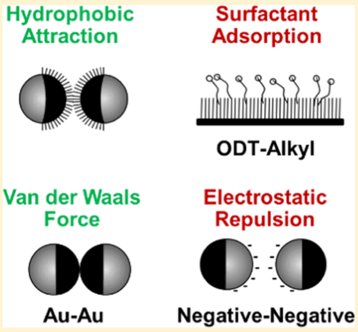
Supporting Information

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.



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.[1−4] Meanwhile, colloids are widely used in industry and provide an important foundation in applications including photonics, coatings, and biomedicine.[5−8] The interactions among conventional isotropic colloids are captured by the classical Derjaguin−Landau−Verwey−Overbeek (DLVO) theory.[9,10] 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.[11,12] 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 the colloidal counterpart of surfactant or dipolar molecules.[13−16] Self-assembly of Janus particles with various morphologies and surface chemistries was initially demonstrated in computer simulations, which were inspired by the concept of "colloidal molecules".[17] 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.[18] 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 the particle is coated with a thin gold layer and then rendered hydrophobic with a self-assembled monolayer of thiol molecules, whereas the other hemisphere is kept hydrophilic and negatively charged. Due to this built-in amphiphilicity, the hydrophobic hemispheres prefer to orient toward 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.[18] 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 two-dimensional (2D) crystals with hydrophobic stripes in which the hydrophobic hemispheres face each

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other. The long-range orientational order is characterized by slow, glassy rotational dynamics.[19]

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.[20−23] In many practical occasions, colloidal particles co-exist with small molecules that are surface active.[24] 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 Au−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.[18,19] To our knowledge, only one recent study has shown that the gold layer thickness had a strong influence on Au−silica Janus particle assembly, which suggests that VDW forces between metallic surfaces contribute to interparticle interactions.[25] It is generally difficult to probe the details of these interactions directly and disentangle their contributions separately. Here, we demonstrate that the addition of the 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. In our previous work, we studied how the addition of simple salt affects the 2D crystal structures assembled by Janus spheres, which mainly changes the ionic strength of the system.[19] Here, we examine the amphiphilic surfactants, which interact with both sides of Janus particles and induce much more complicated interactions. We also varied the Au coating thickness to examine the effect of van der Waals interactions.

Au-silica 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.[19] We chose two commonly used surfactants: anionic sodium dodecyl sulfate (SDS) and nonionic Tween 20. After analysis, changes in the assembly patterns and particle dynamics suggest that SDS weakens the overall attraction between Janus particles, whereas 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 (critical micelle concentration (CMC) = 0.06×10^{-6} mol/L at 25 °C[26]), 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.[27] A monolayer of 3 μm silica particles (Tokuyama) was deposited on a flat substrate and then coated with an 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 μm silica particles, the change in shape caused by 10−40 nm Au coating is about 0.4−1.4% of the particle diameter. The effect of the reduced sphericity on the particle assembly is negligible, as shown by previous reports.[25,28]

For Janus particle assembly, a 2D monolayer of particles was formed above a flat glass substrate using a previously published procedure.[19] Due to gravity, particles sediment onto the bottom of the chamber well. Tilting the substrate at a small angle (3−4°) allows the formation of a dilute area of particles at the upper end of a 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.[19] 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 the image analysis, we calculate the single particle autocorrelation function $C(t)$ for particles assembled in the presence of the surfactant. We found that $C(t)$ is well described by the Kohlrausch−Williams−Watts function $C(t) = \exp\left(-\left(\frac{t}{\tau}\right)^{\beta}\right)$.[19]

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 toward each other. It is generally believed that the cluster formation of amphiphilic Janus particles is governed by hydrophobic attractions between the Au-coated hydrophobic surfaces.[18] Indeed, in previous studies, hydrophobic attractions can very well explain the assembly behaviors of Au-coated Janus particles.[18,19] 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) (Figure 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 a high concentration (∼4 × CMC). Figure 1a shows the clusters of Au-40 (Au coating of 40 nm thickness) Janus particles in the presence of the nonionic surfactant Tween 20. Au-40 particles formed similar clusters at all surfactant concentrations used in this study

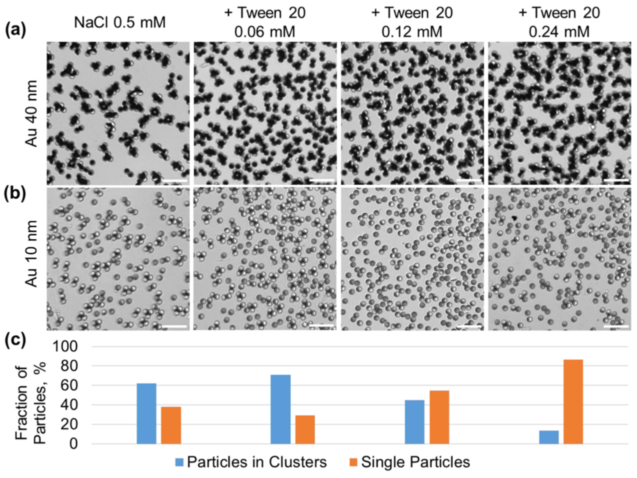

Figure 1. Clusters of Janus particle with (a) 40 nm (Au-40) and (b) 10 nm (Au-10) gold coating in the presence of nonionic surfactant Tween 20; (c) cluster distribution of Au-10 Janus particle at 0.5 mM NaCl, and with Tween 20 added at 0.06, 0.12, and 0.24 mM respectively. ∼4200 particles were counted for each experimental condition. Scale bar is 15 μm.

(0.06−0.24 mM). In contrast, Au-10 (Au coating of 10 nm thickness) Janus particles formed fewer clusters when the nonionic surfactant concentration is increased (Figure 1b). Figure 1c shows the fraction of particles assembled into clusters and the fraction of single particles, as a function of the surfactant concentration. The detailed cluster distribution analysis is shown in Figure S1 (Supporting Information). The fraction of Au-10 particles in the single particle state increases significantly as the Tween 20 concentration increases.

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.[18,19,29] However, in our system, VDW interaction has to be considered to explain the cluster formation in the presence of the surfactant. Since Au has a large Hamaker constant,[30] 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.[25] 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 and 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 the 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 nonionic surfactant, Au-40 Janus particles assemble into clusters of similar sizes regardless of the amount of added surfactant (Figure 2a). At the same ionic concentration, assembly of Au-10 Janus particles can be disrupted by adding an anionic surfactant (Figure 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, the addition of SDS can overcome the VDW forces between Au-10 Janus particles but not Au-40 Janus particles. It has been previously discovered that adding NaCl will promote more cluster formation among Janus spheres. However, when the Au coating is thin and particle concentration is relatively low, no significant change was observed for the fraction of single particles when NaCl concentration is changed from 0.5 to 1 mM.

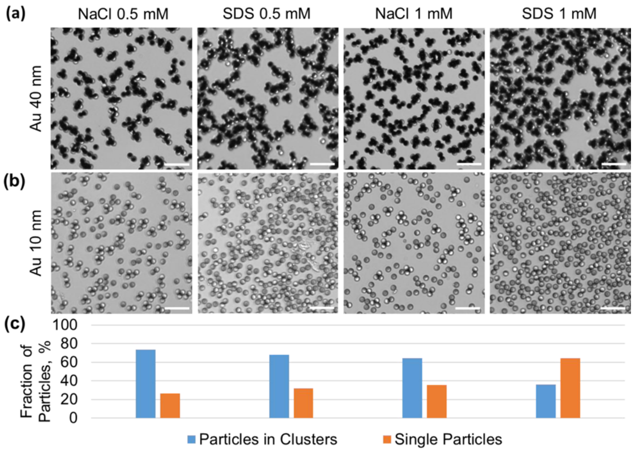

Figure 2. Clusters of Janus particle with (a) Au-40 and (b) Au-10 under the presence of anionic surfactant SDS; (c) cluster distribution of Au-10 Janus particles at 0.5 mM NaCl, 0.5 mM SDS, 1 mM NaCl, and 1 mM SDS. ∼4200 particles were counted for each experimental condition. Scale bar is 15 μm.

The adsorption of surfactants on the hydrophobic surface has been extensively studied.[31−33] It is estimated that the adsorption energy is ∼10−15 k_BT (where k_B is the Boltzmann constant) for both Tween 20 and SDS on the thiolated gold substrate. Based on the literature,[25,34] we estimate that the VDW attraction is ∼10 k_BT for Au-10 Janus particles and ∼18 k_BT for Au-40 particles at 25 nm separation distance.[34] These values roughly agree with our observation.

Au-10 particles can still form 2D structures with good crystallinity before adding the surfactant. However, as the surfactant concentration increases, the structures become amorphous, and the particle orientation starts to become random. (Figure S2). The observation again indicates that adding surfactant may induce more repulsion among particles when the Au coating thickness is small (<10 nm), which is consistent with the results from the cluster formation study.

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 (Figure S3).

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When cationic surfactant was added, we observed that all particles were frozen in space without the Brownian motion. The system is likely not equilibrated, and the assembly is kinetically trapped. Since cationic surfactant neutralizes the charges on both the glass substrate and silica hemisphere of the Janus particles, particles irreversibly attached the substrate. Therefore, the analysis procedure used for on the nonionic anionic system is not applicable here.

We further studied interparticle interactions in the presence of nonionic 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 (Figure 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 particle for 2D crystal experiments. At this thickness, the assembly structures will not be disrupted by the adsorption of the 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. The range for SDS is 0.5−2 mM, which is below CMC concentration of SDS (~8.2 mM at 25 °C). We selected these concentrations deliberately to keep the ionic strength consistent with the NaCl control samples. The concentration range for Tween 20 used in this study is 0.06−0.24 mM, which is equivalent to 1−4 CMC. Considering the average particle−particle surface distance in the 2D crystal is ~200 nm, it is unlikely that micelle would bridge the colloids. A short video of the particle dynamics can be viewed in the Supporting Information. A particle tracking algorithm developed previously was applied to analyze the position and rotation of each individual particles (Figure S4).[19]

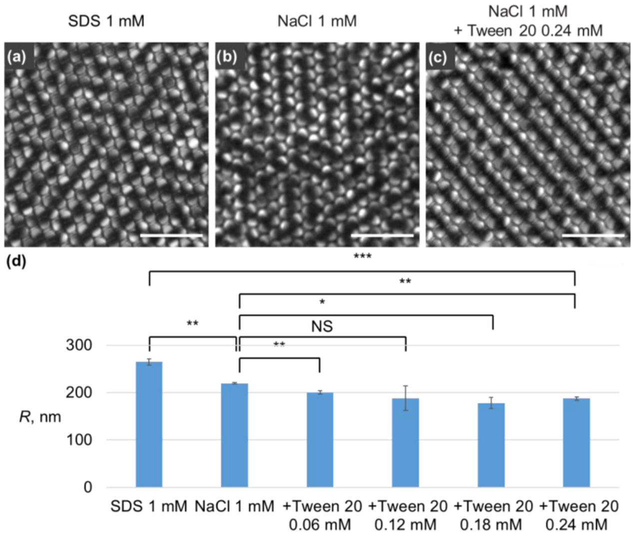

Figure 3. Janus 2D crystal (a) at 1 mM SDS (b) 1 mM NaCl, and (c) with nonionic surfactant added at 0.24 mM Tween 20 and 1 mM NaCl. Scale bar is 15 μm. (d) Average interparticle distance, R, of 2D Janus crystal as a function of the surfactant's concentration. Unpaired t-tests with Welch's correction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

Interestingly, Figure 3 shows that anionic and nonionic 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 (Figure 3a), whereas Tween 20 promotes exceptionally longer stripes in the crystal structures (Figure 3c).

Particle tracking results in Figure 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, whereas Tween 20 induces higher overall attraction among particles (Figure 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.[19]

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 nonionic 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 β) and slower dynamics (larger relaxation time τ) compared to NaCl and SDS (Figure 4b). On the other hand, SDS leads to faster rotation dynamics compared to NaCl and nonionic samples (Figure 4a). Samples with SDS also possess a higher stretching parameter for the crystal structure (Figure 4b). All these

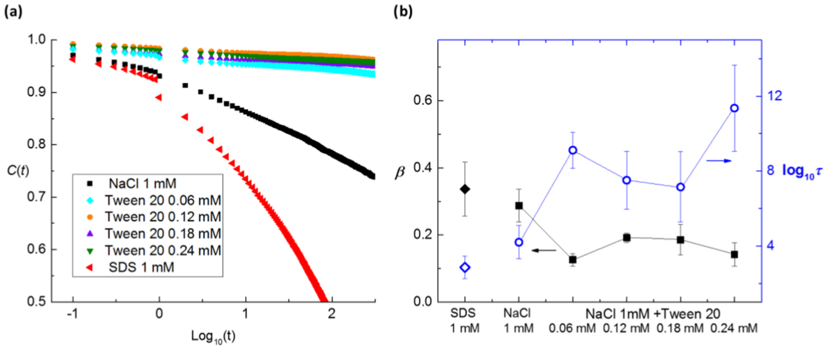

Figure 4. Effect of surfactants on particle dynamics in the 2D Janus crystals. (a) Single-particle angular autocorrelation function $C(t)$ and (b) stretching parameter β and relaxation time τ in the presence of salt, nonionic (Tween 20) and anionic (SDS) surfactants.

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 nonionic. However, on the hydrophilic silica hemisphere, the ethylene oxide groups will form hydrogen bonds with the silanol groups.[35−37] The consumption of the charged silanol groups reduces the overall negative charges and decreases the repulsion among the particles.[35,38] 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 in the relaxation time and stretching parameter for samples at different Tween 20 concentrations. Since Tween 20 surfactant modulates both repulsion and attraction forces on both hemispheres of the Janus particles, an increase of Tween 20 concentration may have a nonlinear effect on the relaxation time and the stretching parameter.

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 the 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 the 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 are 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.

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.langmuir.9b00500.

> Image of particle counting with ImageJ; optical images of Au-10 Janus particle assembly in the close-packed area under the presence of Tween 20; optical images of Au-20 Janus particle assembly under the presence of cationic surfactants, CTAB and DDAB; table of 2D Janus crystal parameters; image of location and orientation of the particle features in Janus 2D crystal at NaCl 1 mM + Tween 20 at 0.12 mM; plot of relaxation time and stretching parameter (PDF)
>
> Particle dynamics (AVI) (AVI) (AVI)

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Lu, P. J.; Weitz, D. A. Colloidal particles: crystals, glasses, and gels. *Annu. Rev. Condens. Matter Phys.* **2013**, *4*, 217−233.

(2) Wang, Y.; Wang, Y.; Zheng, X.; Ducrot, É.; Yodh, J. S.; Weck, M.; Pine, D. J. Crystallization of DNA-coated colloids. *Nat. Commun.* **2015**, *6*, No. 7253.

(3) Ganapathy, R.; Buckley, M. R.; Gerbode, S. J.; Cohen, I. Direct measurements of island growth and step-edge barriers in colloidal epitaxy. *Science* **2010**, *327*, 445−448.

(4) Gasser, U.; Weeks, E. R.; Schofield, A.; Pusey, P.; Weitz, D. Real-space imaging of nucleation and growth in colloidal crystallization. *Science* **2001**, *292*, 258−262.

(5) Lohse, S. E.; Murphy, C. J. Applications of colloidal inorganic nanoparticles: from medicine to energy. *J. Am. Chem. Soc.* **2012**, *134*, 15607−15620.

(6) Boles, M. A.; Engel, M.; Talapin, D. V. Self-Assembly of Colloidal Nanocrystals: From Intricate Structures to Functional Materials. *Chem. Rev.* **2016**, *116*, 11220−11289.

(7) Shi, E.; Li, H.; Yang, L.; Zhang, L.; Li, Z.; Li, P.; Shang, Y.; Wu, S.; Li, X.; Wei, J.; Wang, K.; Zhu, H.; Wu, D.; Fang, Y.; Cao, A. Colloidal Antireflection Coating Improves Graphene−Silicon Solar Cells. *Nano Lett.* **2013**, *13*, 1776−1781.

(8) Kirillova, A.; Marschelke, C.; Friedrichs, J.; Werner, C.; Synytska, A. Hybrid Hairy Janus Particles as Building Blocks for Antibiofouling Surfaces. *ACS Appl. Mater. Interfaces* **2016**, *8*, 32591−32603.

(9) Levine, S. Problems of stability in hydrophobic colloidal solutions, I. On the interaction of two colloidal metallic particles. General discussion and applications. *Proc. R. Soc. London, Ser. A* **1939**, *170*, 145−164.

(10) Verwey, E. J. W.; Overbeek, J. T. G.; Overbeek, J. T. G. *Theory of the Stability of Lyophobic Colloids*; Courier Corporation, 1999.

(11) Zhao, K.; Mason, T. G. Assembly of colloidal particles in solution. *Rep. Prog. Phys.* **2018**, *81*, No. 126601.

(12) Morphew, D.; Chakrabarti, D. Clusters of anisotropic colloidal particles: from colloidal molecules to supracolloidal structures. *Curr. Opin. Colloid Interface Sci.* **2017**, *30*, 70−80.

(13) Jiang, S.; Chen, Q.; Tripathy, M.; Luijten, E.; Schweizer, K. S.; Granick, S. Janus Particle Synthesis and Assembly. *Adv. Mater.* **2010**, *22*, 1060−1071.

(14) Tu, F.; Lee, D. Shape-Changing and Amphiphilicity-Reversing Janus Particles with pH-Responsive Surfactant Properties. *J. Am. Chem. Soc.* **2014**, *136*, 9999−10006.

(15) Yan, J.; Han, M.; Zhang, J.; Xu, C.; Luijten, E.; Granick, S. Reconfiguring active particles by electrostatic imbalance. *Nat. Mater.* **2016**, *15*, 1095.

(16) Yan, J.; Bloom, M.; Bae, S. C.; Luijten, E.; Granick, S. Linking synchronization to self-assembly using magnetic Janus colloids. *Nature* **2012**, *491*, 578.

(17) Glotzer, S. C.; Solomon, M. J. Anisotropy of building blocks and their assembly into complex structures. *Nat. Mater.* **2007**, *6*, 557.

(18) Chen, Q.; Whitmer, J. K.; Jiang, S.; Bae, S. C.; Luijten, E.; Granick, S. Supracolloidal reaction kinetics of Janus spheres. *Science* **2011**, *331*, 199−202.

(19) Jiang, S.; Yan, J.; Whitmer, J. K.; Anthony, S. M.; Luijten, E.; Granick, S. Orientationally Glassy Crystals of Janus Spheres. *Phys. Rev. Lett.* **2014**, *112*, No. 218301.

(20) Wang, K.; Liu, X.-K.; Chen, X.-H.; Yu, D.-G.; Yang, Y.-Y.; Liu, P. Electrospun Hydrophilic Janus Nanocomposites for the Rapid Onset of Therapeutic Action of Helicid. *ACS Appl. Mater. Interfaces* **2018**, *10*, 2859−2867.

(21) Zhang, L.; Chen, Y.; Li, Z.; Li, L.; Saint-Cricq, P.; Li, C.; Lin, J.; Wang, C.; Su, Z.; Zink, J. I. Tailored Synthesis of Octopus-type Janus Nanoparticles for Synergistic Actively-Targeted and Chemo-Photothermal Therapy. *Angew. Chem., Int. Ed.* **2016**, *55*, 2118−2121.

(22) Liu, S.-S.; Wang, C.-F.; Wang, X.-Q.; Zhang, J.; Tian, Y.; Yin, S.-N.; Chen, S. Tunable Janus colloidal photonic crystal supraballs with dual photonic band gaps. *J. Mater. Chem. C* **2014**, *2*, 9431−9438.

(23) Pang, X.; Wan, C.; Wang, M.; Lin, Z. Strictly biphasic soft and hard Janus structures: synthesis, properties, and applications. *Angew. Chem., Int. Ed.* **2014**, *53*, 5524−5538.

(24) Jiang, S.; Van Dyk, A.; Maurice, A.; Bohling, J.; Fasano, D.; Brownell, S. Design colloidal particle morphology and self-assembly for coating applications. *Chem. Soc. Rev.* **2017**, *46*, 3792−3807.

(25) Shemi, O.; Solomon, M. J. Effect of surface chemistry and metallic layer thickness on the clustering of metallodielectric Janus spheres. *Langmuir* **2014**, *30*, 15408−15415.

(26) Wan, L. S.; Lee, P. F. CMC of polysorbates. *J. Pharm. Sci.* **1974**, *63*, 136−137.

(27) Miller, K.; Tsyrenova, A.; Anthony, S. M.; Qin, S.; Yong, X.; Jiang, S. Drying mediated orientation and assembly structure of amphiphilic Janus particles. *Soft Matter* **2018**, *14*, 6793−6798.

(28) Yan, J.; Bloom, M.; Bae, S. C.; Luijten, E.; Granick, S. Linking synchronization to self-assembly using magnetic Janus colloids. *Nature* **2012**, *491*, 578.

(29) Fernández, M. S.; Misko, V.; Peeters, F. Self-assembly of Janus particles into helices with tunable pitch. *Phys. Rev. E* **2015**, *92*, No. 042309.

(30) Israelachvili, J. N. *Intermolecular and Surface Forces*; Academic Press, 2011.

(31) Kronberg, B. Thermodynamics of adsorption of nonionic surfactants on latexes. *J. Colloid Interface Sci.* **1983**, *96*, 55−68.

(32) Sigal, G. B.; Mrksich, M.; Whitesides, G. M. Using Surface Plasmon Resonance Spectroscopy To Measure the Association of Detergents with Self-Assembled Monolayers of Hexadecanethiolate on Gold. *Langmuir* **1997**, *13*, 2749−2755.

(33) Szymczyk, K.; Zdziennicka, A.; Jańczuk, B. Effect of Polysorbates on Solids Wettability and Their Adsorption Properties. *Colloids Interfaces* **2018**, *2*, 26.

(34) Ederth, T. Computation of Lifshitz−van der Waals forces between alkylthiol monolayers on gold films. *Langmuir* **2001**, *17*, 3329−3340.

(35) Nooney, R. I.; White, A.; O'Mahony, C.; O'Connell, C.; Kelleher, S. M.; Daniels, S.; McDonagh, C. Investigating the colloidal stability of fluorescent silica nanoparticles under isotonic conditions for biomedical applications. *J. Colloid Interface Sci.* **2015**, *456*, 50−58.

(36) Parida, S. K.; Dash, S.; Patel, S.; Mishra, B. Adsorption of organic molecules on silica surface. *Adv. Colloid Interface Sci.* **2006**, *121*, 77−110.

(37) Lijour, Y.; Calves, J.-Y.; Saumagne, P. Infrared study of the adsorption of non-ionic surfactants on silica. *J. Chem. Soc., Faraday Trans. 1* **1987**, *83*, 3283−3293.

(38) Zhu, Y.; Fu, T.; Liu, K.; Lin, Q.; Pei, X.; Jiang, J.; Cui, Z.; Binks, B. P. Thermoresponsive Pickering emulsions stabilized by silica nanoparticles in combination with alkyl polyoxyethylene ether nonionic surfactant. *Langmuir* **2017**, *33*, 5724−5733.

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