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2. **Project Title** Interfacial Phenomena of Versatile Janus Particles at Fluid Adjoining Interfaces and Their Potential Applications in the Petroleum Industry

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Introduction

Janus particles (JNPs) are colloidal objects with two regions of different interfacial characteristics, ranging in size from hundreds of nanometers to a few micrometers. Recently, various applications of JNPs utilizing the anisotropic interfacial properties have been reported in the literature. First, because of their amphiphilic nature and resultant strong adsorption preference at liquid–liquid interfaces, JNPs can be employed as robust emulsion stabilization agents. In a liquid media, Janus particles can assemble themselves into nanostructures analogous to surfactant micelles. Second, due to the difference in their translational and rotational diffusion and nonlinear optical properties, JNPs can be used as microprobes revealing structural and compositional information about domains, phases, and nanostructure of local environment. Third, owing to the distinct response of two faces to external stimuli, the incorporation of JNPs in a soft matter can lead to smart, adaptive, and reconfigurable materials. The realization of these applications requires a better understanding of particle–particle interactions and interactions between particles and the surrounding liquid and how these interactions govern the kinetics and thermodynamics of particulate assembly as well as phase behavior and stability of such assemblies. In addition, the development of scalable and generic methods to produce Janus particles is essential. This project is aimed at contributing to the area of surface and colloid science at these fronts.

Results

In the prior reporting cycles, we developed a facile method for the fabrication of spherical, silica-core, Janus nanoparticles with highly tunable hydrophilic/lipophilic balance (HLB). This method relies on controlling the relative areas of hydrophilic and lipophilic regions by changing the sinking time for a monolayer of silica nanoparticles to indent into a poly(methyl methacrylate) (PMMA) template that is kept above the glass transition temperature (T_g) of PMMA. Then, the anisotropy on the amphiphilicity is introduced by vapor phase deposition of organosilanes on the exposed (unsunked) parts of silica particles. Finally, the particle release is achieved by immersing the template in ethanol. We demonstrated that using this approach Janus nanoparticles with varying HLB ratios (i.e. 25:75, 50:50, and 75:25) can be produced and the feasibility of forming Pickering emulsions using such Janus nanoparticles. For this reporting cycle,

two different types of organosilane groups, i.e. trimethylchlorosilane (C_3H_9SiCl , *tri*) and hexyltrichlorosilane ($C_6H_{13}Cl_3Si$, *hexyl*) have been utilized to further elucidate an effect of hydrophobic chain length on interfacial properties thereof. Successful hydrophobic modifications were carried out in a custom-made chemical vapor deposition (CVD) chamber and confirmed by various characterization techniques as shown in **Fig. 1**. While the size of silica nanoparticles remains around 450 nm regardless of types of organosilane groups and HLB values, zeta

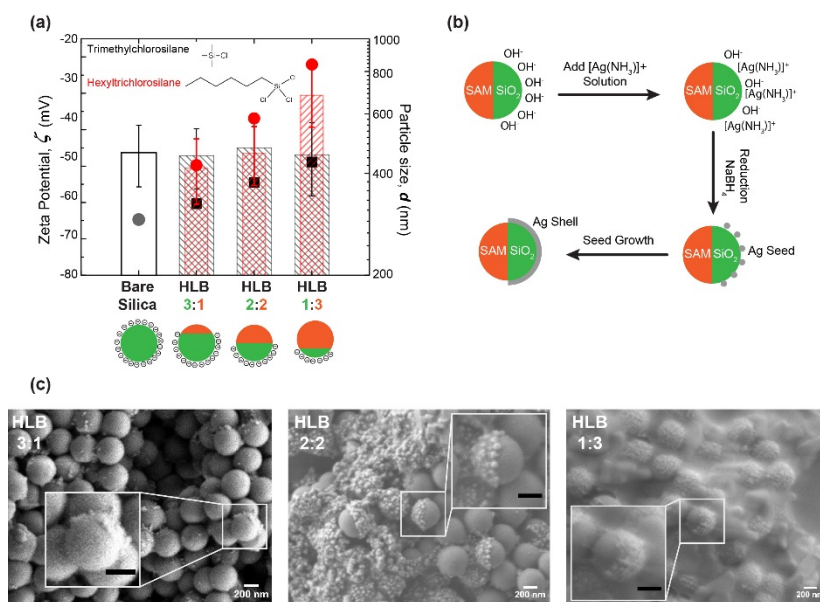


Figure 1. (a) Zeta potential, ζ (scatters) and particle size, d (columns) measured for JNPs modified with trimethylchlorosilane (black) and hexyltrichlorosilane (red) with different HLB values and corresponding schematics. (b) Mechanism of electroplating deposition of Ag on hydrophilic portion. SEM images of Ag-decorated JNP in (c).

potentials tend to increase with more modification, which is more pronounced for the longer alkyl chained silane molecules (**Fig. 1 (a)**) as anticipated. This trend is in good agreement with contact angle (θ) measurements data, which effectively increased as modifying silica nanoparticles more hydrophobically (from $\theta \approx 96^\circ$ to 131° for *tri* and from $\theta \approx 134^\circ$ to 144° for *hexyl* as changing HLB from 3:1 to 1:3). The surface modification has been successfully visualized by an electroless plating method by silver as shown in **Figs. 1 (b) and (c)**. The selective adsorption of $[\text{Ag}(\text{NH}_3)_2]^+$ ions can occur only on negatively charged silica particles through electrostatic attractions, giving rise to asymmetric decorations of silver shell layers as an indication of hydrophilic (unmodified) portions of silica particles.

The lateral interactions between JNPs with different HLB values and their interfacial stability are key parameters to understand for producing long-lived Pickering emulsions. To address this important aspect of the project, we utilized the Langmuir trough, in which we can generate the areal compression-decompression cycles according to areas occupied by JNPs (**Fig. 2**). Several observations are worth to note; at a given surface pressure, the area occupied by a particle increased with increasing hydrophilic ratio. Namely, the interparticle spacing between particles was the smallest between bare silica particles and the largest between Janus particles with 75% lipophilic region. This was attributed to the presence of polar and dissociating silanol and silicic acid groups on silica particles, which interacts favorably with water. The organosilane groups on Janus particles experience hydrophobic interactions and hence, tend to keep particles away from each other. We also observed a larger hysteresis between compression and decompression behavior for Janus compared to bare particles. One possible reason behind this difference is the forced insertion of amphiphilic Janus particles into the sub-phase and the resultant irreversible formation of micellar aggregation. The surface pressure has a more exponential-like dependence on the particle spacing for bare silica particles while the surface pressure depended on the particle spacing linearly/polynomially for Janus particles. The presence of exponential dependence suggests that the electrostatic interactions are still major factors controlling the lateral dynamics of silica particles at air-liquid interface.

Future work

This year (the final project year), we will construct colloidal models to describe the lateral interactions of Janus nanoparticles and compared the developed models with the observed pressure-area isotherms. We will also evaluate the ability of Janus nanoparticles to clean-up oil spills at air-water interface and obtain insights into the timescales of these processes. Furthermore, we plan to extend the concept of electroless plating from silver to copper, which is less expensive and more feasible in large-scale oil recovery applications.

Impact of The Research on the PI's Career and Participating Students

Through this research, my group has gained expertise on the synthesis of very high-quality and monodisperse silica nanoparticles in the range of 20 nm and 400 nm. We have utilized this expertise on the preparation of several proposals (recently submitted) for federal funding agencies for longer-term funding. The transport studies that we have conducted with Janus nanoparticles have established the basis of our recently funded project with DOE on the colloidal-facilitated transport of energy-related contaminants in the geosystems and environment. Overall, this ACS PRF grant has helped me to develop new skill and expertise in the area of colloidal particle synthesis, Janus nanoparticles, and the transport and interactions of anisotropic nanoparticles. Students working on this project have gained hands-on experience on the synthesis and characterization of Janus nanoparticles. In addition, these students have attended ACS colloids conference, which helped to improve communication and scientific discussion skills. Furthermore, students are preparing several manuscripts summarizing our research findings to the scientific community at large. This experience would help students to develop better technical writing skills.

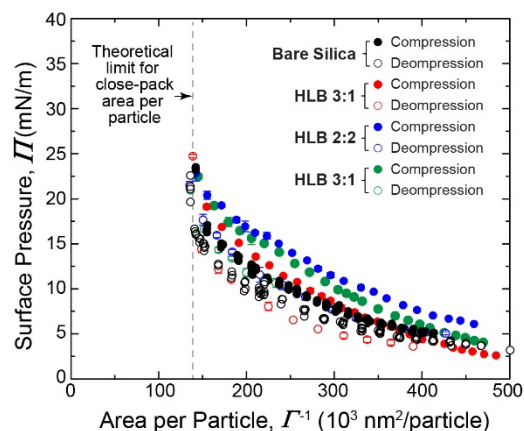


Figure 2. Pressure, Π , versus interfacial area normalized by initial amount of particle dispersed, Γ^{-1} , for bare particles, JNPs of HLB = 3:1, JNPs of HLB = 1:1, and JNPs of HLB = 1:3. Data points obtained during compression are plotted in solid symbols while those obtained during decompression are plotted in empty symbols. JNPs used in this experiment were all modified with *hexyl*.