Colloid Interfaces

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Synthesis of Monodisperse Bi-Compartmentalized Amphiphilic Janus Microparticles for Tailored Assembly at the Oil–Water Interface

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Abstract: *Janus particles endowed with controlled anisotropies represent promising building blocks and assembly materials because of their asymmetric functionalities. Herein, we show that using the seeded monomer swelling and polymerization technique allows us to obtain bi-compartmentalized Janus microparticles that are generated depending on the phase miscibility of the poly (alkyl acrylate) chains against the polystyrene seed, thus minimizing the interfacial free energy. When tetradecyl acrylate is used, complete compartmentalization into two distinct bulbs can be achieved, while tuning the relative dimension ratio of compartmented bulb against the whole particle. Finally, we have demonstrated that selectively patching the silica nanoparticles onto one of the bulb surfaces gives amphiphilicity to the particles that can assemble at the oil–water interface with a designated level of adhesion, thus leading to development of a highly stable Pickering emulsion system.*

Janus particles are biphasic colloids that have two parts, on opposite sides of the particles, with different compositions or properties. The advantage of using Janus particles is that their shape and chemical anisotropies are independently controllable, which allows us to give asymmetric functionality to the particles.[1] Janus particles have been explored in various applications as the building blocks for supra-nanostructures,[2] optical biosensors,[3] functional surfactants,[4] and carriers of biomacromoleclues.[5] Janus particles with chemical anisotropy are usually synthesized by employing advanced technologies, including macrophase separation during polymerization,[6] controlled drop polymerization in microfluidic channels,[7] and toposelective surface modification from particle monolayers.[8] Moreover, shape anisotropy can be achieved by means of dewetting a bulb from the seed particle,[9] controlling packing of hard spheres in confined drops,[10] and by generating elastic force in cross-linked particles.[11]

To date, the successful development of uniform Janus particles still remains a challenge mainly owing to their limitation in large-scale production, and a good example can be found in microfluidics. It is true that utilizing microfluidic techniques enables one-pot production of a variety of monodisperse Janus particles.[12] Although the versatility in providing shape and chemical anisotropies can be endowed to the Janus microparticles in the microfluidic channel by tuning fluidity, interfacial tension, and phase miscibility in drops, their intrinsically low production has hampered practical applications. We may use other synthetic methods, such as 2D sputtering and gel-trapping;[13] however, these techniques are either complicated or time-consuming. Unlike those methods, the use of the seeded polymerization technology has been considered to be the solution for this critical issue.[14] Seeded polymerization is advantageous in that a large quantity of highly monodisperse Janus particles can be produced in bulk. Uniform swelling of polymer seed particles with secondary polymerizable monomers and consecutive polymerization in a batch reactor leads to formation of Janus particles. Their colloidal anisotropies depend on the phase miscibility,[15] surface wettability,[16] and crosslinking density of seed particles.[17] The particles are highly susceptible to independently tailoring of the surface chemistry, as well as to precisely tuning the particle geometry.

Herein, we describe a straightforward method for synthesis of monodisperse Janus microparticles with controllable anisotropies, such as compartmented bulb dimensions and surface amphiphilicity. The synthesis method is based on the seeded monomer swelling and consecutive polymerization. Through this technique, we not only precisely tune the relative dimension ratio of the compartmented bulb against the whole particle, which is named "degree of Janusity" in our study, but also selectively provide the amphiphilicity to the particles. The degree of Janusity between the polystyrene (PS) seed and the polymerized poly (alkyl acrylate) (PAA) is varied by swelling the PS seed particles with a designated amount of alkyl acrylate monomers. Moreover, by treating one of the bulb surfaces with silica nanoparticles (NPs), amphiphilicity is successfully imparted to the particles. Finally, using the amphiphilic Janus microparticles, we demonstrate that they can readily assemble at the oil–water interface with a different level of adhesion, which is essential for improving the stability of the resulting Pickering emulsions.

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The utilization of the seeded swelling and consecutive polymerization method allowed us to produce uniform Janus microparticles in large-scale productions (Figure 1 A). The seed particles used in this approach were linear PS particles synthesized using the dispersion polymerization method (Figure 1 B). The PS seed particles were monodisperse in their size, because they were generated by following the nucleation and growth mechanism during polymerization in a polar medium.[18] In a typical synthetic procedure, the 3 μm-sized PS seed particles, which were finely dispersed in 2 wt % of PVA in the mixture of EtOH/water, were uniformly swollen with the mixture of tetradecyl acrylate (TA), ethylene glycol dimethacrylate (EGDMA), and Irgacure 184 in EtOH/water (3:2 v/v). The complete diffusion of monomers could be confirmed in 5 h at room temperature without any particle aggregation or coalescence (Figure 1 C). Under these swelling conditions, the volume of the PS seed particles could be increased by factors of five, while maintaining the initial size uniformity. The monomers in the swollen particles were photo-polymerized at room temperature, which induced phase separation between the PS seed and the newly polymerized PAA phase. Upon UV irradiation, typically, the TA-swollen PS particles turned into PS/PTA Janus particles (Figure 1 D). The biphasic compartmentalization of the Janus particles was confirmed by selectively labeling one of the bulbs with a fluorescence probe (Figure 1 E). The Janus microparticles synthesized in our study were spherical, meaning there was no geometrical deformation of particles during the phase separation (Figure 1 F). Moreover, the particle size increased in micrometer scales after seed polymerization, which typically depended on the monomer swelling ratio (Figure 1 G).

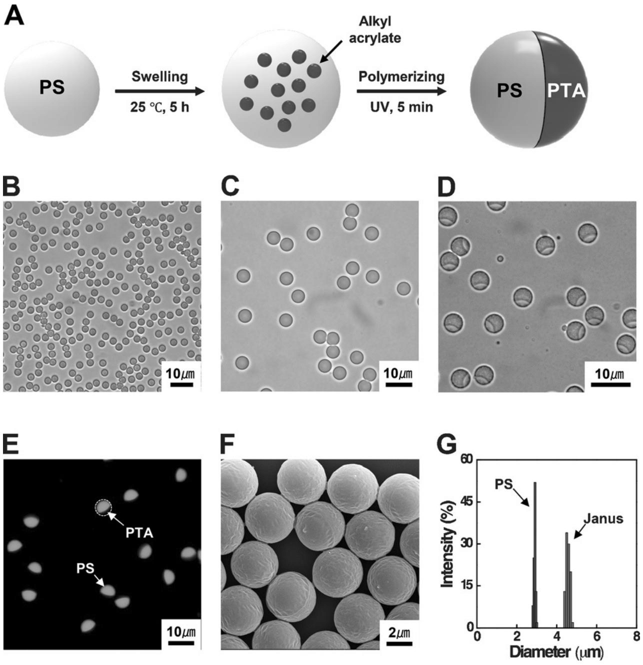

Figure 1. A) Synthesis of the Janus microparticles. Bright-field microscope images of B) PS seed particles, C) monomer-swollen PS particles, and D) PS/PTA Janus particles after photo-polymerization. E) Fluorescence microscope image of PS/PTA Janus particles. PS was co-polymerized with 9-vinylanthracene to label the PS seed phase. F) SEM image of PS/PTA Janus particles. G) Particle size distributions of the PS seed particles and Janus particles.

As the polymer particles composed of two different polymer pairs exhibit various types of morphologies associated with the thermodynamic and kinetic preferences,[19] we sought to determine how the Janus particle morphology was obtained in response to the phase miscibility and medium solvency. Our approach for fine tuning the phase miscibility between the PS seed and PAA was to use alkyl acrylate monomers having different alkyl chain lengths. When the monomers with a short alkyl chain length ($C<14$) were polymerized in the swollen PS particles, either total escape of the monomers or their partial phase separation was observed (Figure 2 A,B). These results come from the high monomer solubility in the continuous phase and the relatively good affinity of PAA for PS, respectively. When the TA monomer ($C=14$) was incorporated, a distinctively bi-compartmentalized Janus morphology could be successfully obtained (Figure 2 C). Generation of this morphology is generally associated with minimization of the total free energy.[20] Interestingly, using the monomer with a long alkyl chain length ($C>14$) produced a sandwich-shaped particle morphology (Figure 2 D). We attribute this result to the fact that PAA with long alkyl chains increased the hydrophobicity and chain flexibility against the PS, which favorably enlarges the contact area, and thus eventually leads to formation of the sandwich morphology.[21] We also found that the medium solvency was critical for determining the particle morphology (Figure 2 E–H), because the final equilibrium state is determined solely by the changes in the interfacial tensions of three phases (PS, PAA, and water).

For a better understanding of the formation of the bi-compartmentalized Janus particle morphology, we tried to predict the particle shape. In principle, the shape of the particles was estimated by calculating the total free energy for the three interfaces: PS (1)-water (2), water (2)-PAA (3), and PS (1)-PAA (3). The total interfacial free energy given by the sum of the three interfacial energies is $G=\gamma_{12}S_{12}+\gamma_{23}S_{23}+\gamma_{13}S_{13}$, where γ_{ij} and S_{ij} are the interfacial tension and the interfacial area between two phases i and j.[22] For facile prediction, we assume that the volume ratio of the two bulbs is controllable near unity and the surface tension between the two bulbs is small, $\gamma_{12},\ \gamma_{23}\gg\gamma_{13}\approx 1\ \mathrm{mN\,m^{-1}}$.[23] When γ_{12} and γ_{23} are sufficiently high, the spreading coefficients ($S_i=\gamma_{jk}-\gamma_{ij}-\gamma_{ik}$) are $S_1>0$, $S_2<0$, and $S_3<0$, thus leading to a core–shell structure in which phase 3 forms the core owing to its higher surface tension ($\gamma_{23}>\gamma_{12}$).[24] When γ_{12} and γ_{23} are too low to be determined, but still have the tension, a spherical Janus particle morphology composed of PS and PAA bulbs can be obtained. We also realized that to obtain untruncated bi-compartmentalization while maintaining the spherical particle shape, it is essential that the surface tension values of each bulb to the medium should be similar to each other (for example, $\gamma_{12}\approx\gamma_{23}\geq 4\ \mathrm{mN\,m^{-1}}$; see the Supporting Information).

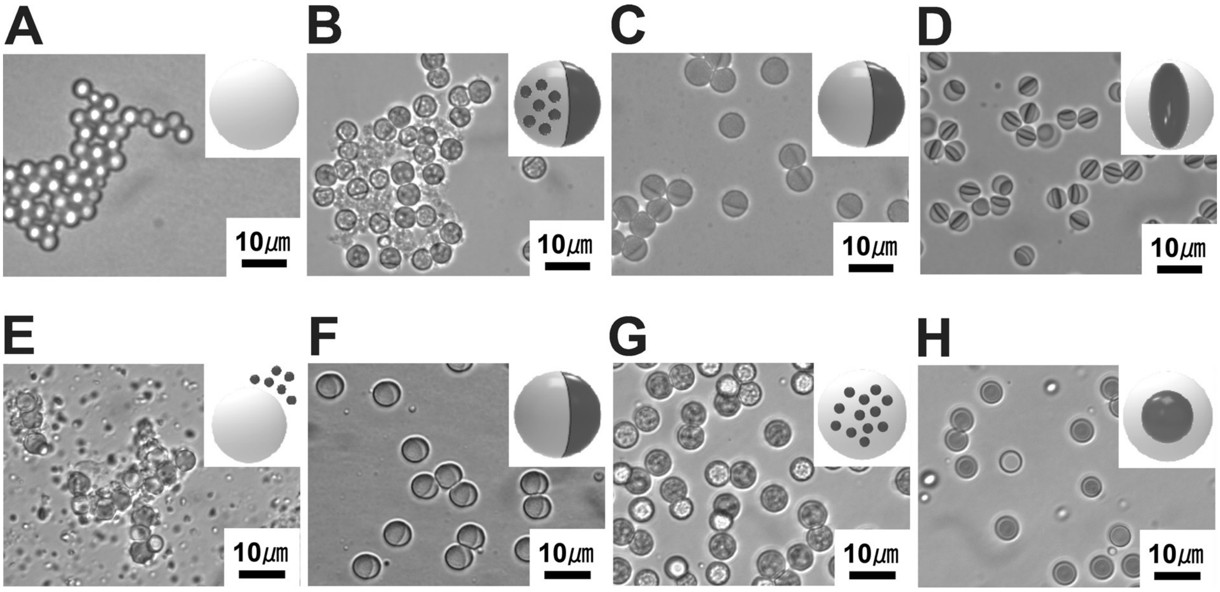

Figure 2. Bright-field microscope images of the particles produced by varying the alkyl chain length of monomers: A) hexyl acrylate, B) dodecyl acrylate, C) tetradecyl acrylate, and D) hexadecyl acrylate, and by controlling the medium solvency: E) EtOH/water = 4:1 (v/v), F) EtOH/water = 3:2 (v/v), G) EtOH/water = 2:3 (v/v), and H) EtOH/water = 1:4 (v/v).

The advantage of using our particulation approach is that we could precisely manipulate the degree of Janusity. The degree of Janusity is defined as D/D_0, where D is the shorter diameter of the PTA bulb and D_0 is the whole diameter of a Janus particle. Under our synthetic conditions, the degree of Janusity could be tuned in the range of 0.25–0.5 by solely varying the monomer swelling ratio, while maintaining the particle size monodispersity and the bi-compartmentalized Janus morphology (Figure 3). Below $D/D_0 \approx 0.25$, some irregular phase separation was observed because of the thermodynamically favorable dissolution of PTA in the PS phase at such low volume fractions. In contrast, above $D/D_0 \approx 0.5$, the monomer swelling did not proceed uniformly owing to the limited monomer diffusivity into the PS seed. Having established the synthetic procedure, our interest shifted imparting specific surface functionality to the particles. More specifically, we patched silica NPs on one of the bulb surfaces of the Janus microparticles, thus enabling fabrication of amphiphilic Janus microparticles (Figure 4A). It is well known that the PS particles produced by dispersion polymerization are sterically stabilized by PVP that has been covalently grafted onto the primary particles.[25] In our study, the presence of PVP on the PS particles could be confirmed by XPS analysis (Figure 4B). Therefore, the silica NPs could patch on the PS compartment through hydrogen bonding with PVP, allowing us to produce amphiphilic Janus particles (Figure 4C,D).

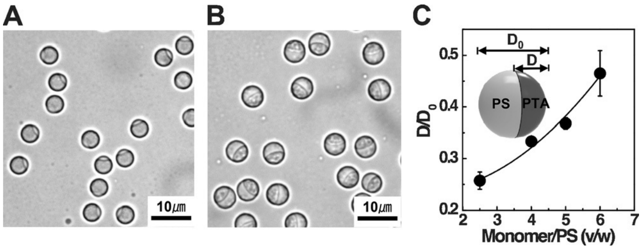

Figure 3. Bright-field microscope images of the Janus microparticles produced by varying the monomer/PS swelling ratio: A) $D/D_0 = 0.25$ and B) $D/D_0 = 0.5$. C) The degree of Janusity of the Janus particles produced by increasing the monomer/PS swelling ratio.

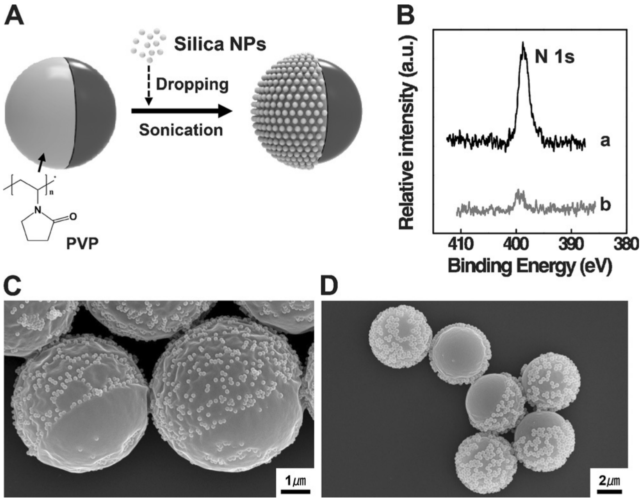

Figure 4. A) Patching nanoparticles on one of the bulbs of the Janus microparticles. B) N 1S XPS spectra: a) PS seed particles and b) PS/PTA Janus particles. SEM images of patched Janus particles: C) 100 nm silica NPs, D) 300 nm silica NPs.

To further demonstrate the practical applicability of our silica NPs–patched amphiphilic Janus microparticles, we assembled them at the oil–water interface as colloid surfactants, which enables production of stable Pickering emulsions. Surprisingly, we observed that each bulb of the amphiphilic particles was wetted by the compatible liquid phase: the hydrophilic silica NP–patched bulb was wetted by water, and the hydrophobic PTA bulb was wetted by hexadecane (Figure 5 A, B). More interestingly, the degree of Janusity determined the contact angle of amphiphilic particles at the assembled interface (Figure 5 C). Because of this unique wetting behavior, the Pickering emulsions made with our amphiphilic Janus particles showed different structural stability depending on the degree of Janusity (Figure 5 D). The particles having D/D_0 near 0.5 showed remarkably improved drop viability, which was comparable to the case using low D/D_0. In the Pickering emulsion system, the adhesion energy (E) of a particle is directly proportional to the area taken by the particle, as expressed by $E = \pi a^2 \gamma (1 \pm \cos\theta)^2$, where a is the radius of a particle, γ is the interfacial tension, and θ is the contact angle.[26] Regarding our results, it is therefore reasonable to conclude that the adhesion energy of the particles could be maximized as D/D_0 gets closer to 0.5, which is essential for enhancing the structural stability of Pickering emulsion drops.[27]

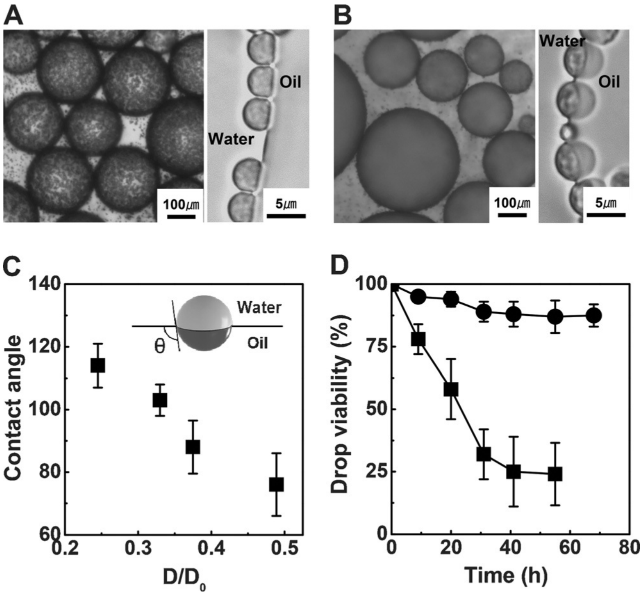

Figure 5. Bright-field microscope images of the Pickering emulsions stabilized by silica-NP-patched Janus particles with the different degrees of Janusity: A) $D/D_0 = 0.25$ and B) $D/D_0 = 0.5$. The inset images show adhesion of amphiphilic Janus particles at the hexadecane–water interface. C) Contact angles of silica NP-patched Janus particles at the hexadecane–water interface. D) Viability of Pickering emulsion drops at 50 °C: $D/D_0 = 0.25$ (■) and $D/D_0 = 0.5$ (●).

In conclusion, this study has introduced an effective approach for synthesizing monodisperse PS/PTA Janus microparticles with a controllable degree of Janusity and surface amphiphilicity. The controlled phase separation of PS and PTA was successfully confirmed through bright-field and fluorescence microscope analyses. We have also found that the relative dimension ratio of the compartmented bulb against the whole particle, which corresponds to the degree of Janusity, could be tunable in the range of 0.25–0.5, by simply varying the monomer swelling ratio. Moreover, we showed that silica NPs could be patched selectively on the PVP-coated PS bulb surface, thereby imparting amphiphilicity to the Janus particles. The Pickering emulsions stabilized by the amphiphilic Janus particles showed excellent emulsion stability because of the maximized adhesion energy. Taking advantage of the insight gained from this work, our next studies will focus on the synthesis of functional NP-patched Janus particles. We expect that they would have potential either for development of a catalytically activated Pickering emulsion-based microreactor, or for fabrication of two-dimensional particle-arrayed flexible biosensors and actuators.

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