Janus Particles:

A New Additive for Improving Waterborne Hydrophobic Coatings Through Self-Stratification

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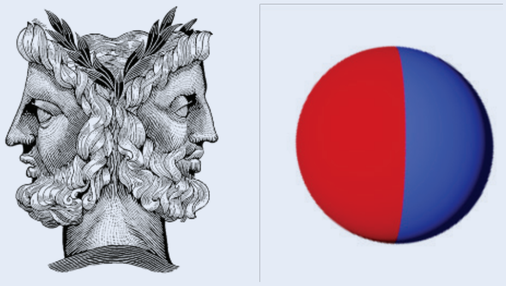
and Rebecca Mort

FIGURE 1
Roman God Janus and Janus particles.



Introduction

The coatings industry has undergone significant transformations in recent years due to the replacement of organic solvent-based coatings by waterborne emulsion latex polymer coatings. Waterborne technology has generated profound impact in industry and everyday life, producing great environmental and health benefits. The prevalence of volatile organic compounds (VOCs) in coatings has been greatly reduced, from 700 g/L in the 1940s to ~ 50 g/L in the 2010s.[1] Although waterborne coatings offer considerable benefits, challenges remain in areas such as water resistance, stability, film formation, and surface hardness, which can affect their overall performance and application.

These challenges are primarily caused by the conflicting requirements for desired properties before and after the coating dries. To maintain a stable dispersion before application, latex particles should be fully dispersible in water, i.e., hydrophilic. However, after the coating dries, water repellence, or hydrophobicity, is required. Thus, a solution that can maintain predominantly hydrophilic dispersion while rendering a hydrophobic surface after drying is necessary to make waterborne coating technology more versatile. In addition, a durable coating film demands excellent adhesion on the substrate

surface, while showing good hardness (low tackiness) at the coating-air interface. This means it is beneficial to possess different or even opposite properties on the two sides of the coating films.

One approach to combine these different properties is to apply multiple coats. It is common practice to coat primers as the first layer to provide good adhesion. After the primer is dried, a topcoat is then applied to afford more desirable surface properties. However, this approach consumes extra material, time, and effort. For applications that require both performance and fast turn-around, such as traffic coating, a simple one coat solution is strongly preferred. Another grand challenge in waterborne coating materials is to eliminate VOCs and create a "zero-VOC" paint. Such coatings will further benefit environmental and consumer health. However, removing all the VOCs will make it difficult for latex particles to form an integral coating film unless the glass transition temperature (T_g) for polymer binder is greatly reduced. This can be done by altering the polymer chemistry or adding non-evaporative coalescent molecules, however doing so will inevitably hurt coating hardness and many other properties. Therefore, technology that can guarantee film formation while providing a hard coating surface becomes the holy grail in coating research. Most ideas have been developed around two-component (2K) systems and crosslinking chemistry, which are usually much more costly and require more complicated chemistry and formulation.

In this article, we report on an innovative coating additive, Janus particles, which can significantly modify the surface properties of a waterborne coating system while leaving the bulk of its properties mostly intact. As shown in Figure 1, Janus is the name of an ancient Roman god who has two faces. Janus particles are particles that possess two different chemical make-ups, often with contrasting properties, on each side of a single particle. For example, an amphiphilic Janus particle has one hydrophilic side and one hydrophobic side, which can also be viewed as a colloidal version of a small surfactant molecule. Although Janus particles have not yet been widely used in industry, they have been studied and developed in academia for more than 30 years.

The Janus particle idea was first coined by P.G. de Gennes in his Nobel laureate lecture, where he raised the concept of soft matter.[2] He listed four different types of soft matter: polymer, surfactant, liquid crystal, and the Janus particle. In de Gennes' view, these materials are all “soft” because they are flexible and can form complex structures. The initial research progress on Janus particles was lacking due to their difficulty in synthesis. It is not straightforward to fabricate two surfaces or compositions of completely opposite properties on a single particle. Early methods involved masking part of the particles or using directional coatings to coat only half of the particles.[3] These methods can produce Janus particles with well-defined morphology, although the yield is very limited. Even with a very small quantity, the studies have shown that Janus particles form unique self-assembly structures and adsorb strongly at the interface. These particles also demonstrated intriguing behaviors in the external fields.[4-5] When one side of the Janus particles reacts with the surrounding environment and produces gas molecules, they become self-propelled active particles.[6] However, the interesting discoveries in the academic world did not simply translate to successful commercialization and broad applications in industry. After all, it was difficult to scale up the Janus particle synthesis. It is also not clear how these particles can be utilized for real-world applications.

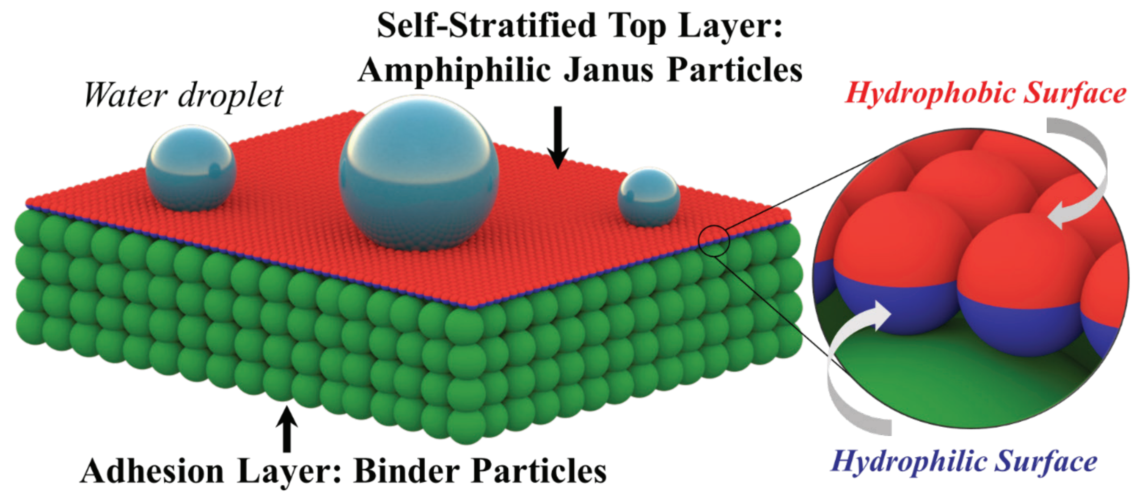
Recently, synthesis of dumbbell-like nanoparticles (both inorganic and polymeric) has emerged as an economical and scalable approach to the fabrication of Janus particles.[7-8] With a two-lobe configuration, dumbbells can be rendered with one lobe hydrophobic and the other hydrophilic.[9-11] The dumbbell shape is typically achieved via a seeded-growth method, where the seed lobe is formed first, and the second lobe is then grown on the seed particles.[12-16] However, dumbbell formation and coverage of the second lobe are sensitive to synthesis conditions.[17-18] A slight change in the reactions, such as stirring speed, monomer to seed ratio, and solvent composition, may drastically alter the final particle morphology.[19-21] With the aid of computer simulation, we gained a thorough understanding of the fundamental mechanism of Janus morphology formation. We carefully studied the reaction conditions for forming Janus particles in an emulsion polymerization and successfully obtained amphiphilic Janus particles with a wide range of sizes and well-defined geometry.

What’s more important, we discovered a unique self-stratification behavior of Janus particles.[22-23] When mixed with hydrophilic binder particles, almost all of Janus particles rapidly race to the coating’s surface. Once arrived at the interface, the hydrophobic side of the Janus particles orient towards air while the hydrophilic side orients towards the aqueous suspension. As a result, the hydrophilic half of the particles adheres to the binder as coating film dries, while the hydrophobic half faces the air interface, creating a hydrophobic surface. This process can create a water-resistant surface with different properties than the bulk of the coating.

Based on the stratification concept, we can utilize Janus particles to address many challenges in waterborne coatings. The properties dictated by the surface layer, such as tackiness, hardness, water resistance, and dirt pick-up, can be designed and optimized separately from the bulk materials.[24-28] However, conventional coating systems do not self-stratify. Previous studies demonstrated that self-stratification will only happen for polymers of specific chemistry or particle mixtures of certain size ratios when a coating suspension dries.[29-34] These constraints severely limit the application of self-stratification in common coating materials. Therefore, with the ideas demonstrated in this article, we show the proof-of-concept that the use of Janus particles as a coating additive can offer a cost-effective and scalable solution to generate stratified coatings.

Experiment

Chemicals and reagent: Styrene (St, 99%), ethanol (EtOH, 200 Proof, 100%), polyvinylpyrrolidone (PVP, M_n = 40 000 g mol^{-1}), poly(vinyl alcohol) (PVA, Mw = 13 000-23 000 g mol^{-1}, 87-89% hydrolyzed), ethylene glycol dimethacrylate (EGDMA, 98%), 1-hydroxycyclohexyl phenylketone (Irgacure 184, 99%), Pluronic F-127 (Poloxamer 407), 2,2’-Azobis(isobutyronitrile) (AIBN, 98%), phosphoric acid 2-hydroxyethyl methacrylate ester, and vinyl acetate (VAc, 99%) were purchased from Sigma-Aldrich (USA). Tetradecyl acrylate (TA) was purchased from TCI chemicals (Japan). Peel Stop® Clear Binding Primer was purchased from Zinsser. Hardened Corrosion-Resistant 316 Stainless Steel was purchased from McMaster-Carr. Deionized triple distilled



water was used in all experiments. All chemicals were of reagent grade and used without further purification.

Synthesis of PS-co-PVA hydrophilic nanoparticles: Hydrophilic polystyrene-co-polyvinyl alcohol (PS-*co*-PVA) seed particles were synthesized by modifying the previous method.[35] Styrene, VAc, PVP, and AIBN were dissolved in a mixture of EtOH and deionized water in a 100 mL round-bottom flask. The reaction mixture was purged with argon for 15 mins to remove oxygen. Then, the polymerization was carried out at 70 °C in an oil bath while stirring at 200 rpm for 36 h. After the polymerization, the particles were washed repeatedly via centrifugation with EtOH/water mixture (1/1 by volume). Then, the obtained PS-*co*-PVAc seed particles were converted into polystyrene-co-polyvinyl alcohol (PS-*co*-PVA) using saponification, which was carried out under basic conditions (NaOH solution at pH = 10) for 8 h at room temperature. Last, the PS-*co*-PVAc particles were stored in the EtOH/water mixture (2/1 by volume) with a combination of surfactant PVA (2 wt %) and Pluronic F-127 (2 wt %). The hydrophilic particle concentration was tuned to 0.02 g/ml.

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Synthesis of amphiphilic Janus particles: An emulsion of PS-*co*-PVA seed particles was swollen with a mixture of TA, EGDMA, and Irgacure 184 in the presence of PVA (2 wt %) and Pluronic F-127 (2 wt %) in an EtOH/water solution for 8 h at room temperature. In this step, the hydrophobic monomer feeding ratio against the PS-*co*-PVA seed particles was carefully adjusted to achieve the 50:50 hydrophilic-hydrophobic volume ratio. After that, the monomers in the swollen particles were photopolymerized by UV irradiation for 5 min while tumbling at 50 rpm at room temperature. The process induced a phase separation between the PS-*co*-PVA seed phase and the secondary polymerized poly (tetradecyl acrylate) (PTA) phase. Amphiphilic PS-*co*-PVA/PTA Janus particles were then washed repeatedly with a mixture of EtOH/water to remove the remaining monomers and organic additives. The Janus particles used in this study can slowly aggregate over time by themselves; however, they are much more stable when mixed in a coating formulation. More studies are needed to evaluate the stability.

Synthesis of hydrophilic binder microparticles: Phosphate microparticles were prepared by dispersion polymerization. In a round-bottom flask, PVP was dissolved in ethanol with the mechanical stirring, styrene, phosphoric acid 2-hydroxyethyl methacrylate ester and AIBN was then added into the flask, the pH was tuned to 7 with base buffer. The solution was deoxygenated by bubbling argon for 15 min. The flask was then placed in an oil bath at 65 ± 1 °C and 60 rpm of mechanical stirring rate was applied. After polymerization for 24 h, the milky dispersion of phosphate microparticles was cooled at room temperature then washed and separated by centrifugation at 5000 rpm in the EtOH/water mixture for three times. The procedure to synthesis acetic acid binder particles remains the same, with acetic acid in place of phosphoric acid 2-hydroxyethyl methacrylate ester.

Coating formulation of amphiphilic Janus nanoparticles with phosphate microparticles: Coating formulation was prepared by mixing 5-10 wt % amphiphilic Janus nanoparticles (0.1 g/ml) and 90-95 wt % microparticle binders (0.1 g/ml) in aqueous suspension. After 10 mins sonication in a water bath, 300 µL mixed particle dispersion was drop coated on top of the plasma cleaned stainless steel (1 cm × 1 cm) and dried at room temperature overnight.

Coating formulation of amphiphilic Janus nanoparticles with commercial primer: The stainless steel (1 cm x 1 cm) was pre-coated with 300 µL commercial primer, after fully being dried at the room temperature, the coating formulation was prepared by mixing 15 wt % amphiphilic Janus nanoparticles and 85 wt % commercial primer (diluted with deionized water at 15 wt %). After 10 mins sonication in a water bath, 300 µL mixed coating was drop coated on top of pre-coated stainless steel (1 cm × 1 cm).

Characterization of Materials: Fluorescent labeling of phosphate binder particles and amphiphilic Janus particles was conducted by immersing phosphate particles into FITC ethanol solution and amphiphilic Janus particles into Nile red ethanol solution. Excess FITC/Nile red molecules were removed by repeated washing with deionized water by centrifugation for more than five times. Stratification evolution and stacks of plane images at varying depths within the coating formulation was monitored using Zeiss 780 confocal microscope with excitation wavelength of 488 nm for FITC and 561 nm for Nile red. A second-order polynomial equation was fit to the detected intensity as a function of depth from the surface, which was then used to define a baseline, to correct for the depth dependence of the detected intensity. The shape and morphology of the particles were observed by a scanning electron microscope (FEI Quanta 250) at an accelerating voltage of 10 kV, an optical fluorescent microscope (Leica DMi8) was used to capture the bright-field image. Samples were prepared by scratching small pieces of coating film off the substrate and then mounting them on a vertical sample stage. The cross-section of coating film was imaged with the scanning electron microscope (FEI Quanta 250) at an accelerating voltage of 10 kV. The surface topology was imaged by a confocal-laser 3D scanning microscope (Keyence).

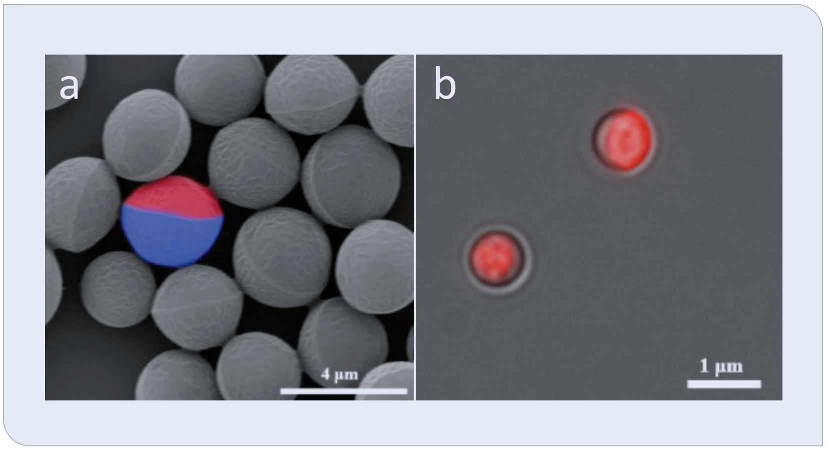
The static contact angle of one water droplet (~5 µl) on the coating surface was measured on an optical tensiometer contact angle measuring system (Dyne Technology) at room temperature (25 °C). The contact angle was repeated three times at different sites on the same surface side. The 1 cm × 1 cm formulated coating surface was rinsed with organic solvent EtOH and THF (90/10 by volume) for 1 min as 1 cycle. The water contact angles were measured after each 5 cycles of rinsing.

Force curve measurements were performed in contact mode atomic force measurement (AFM) using cantilever deflection. Bruker Dimension Icon AFM was used in Air Contact mode with Bruker SNL-10 AFM tips. The cantilever's spring constant, k = 0.47 N/m, was determined by thermal tune calibration method built into the Nanoscope software. Average rupture force values were obtained based on 38 measurements from each of three different locations per sample.

Results and Discussion

The detailed morphologies of Janus particles obtained through an emulsion polymerization is shown in **Figure 2**. It is worth noting that under the SEM, the boundary on Janus particles was shown very clearly **(Figure 2a)**, although it is not possible to tell which side is hydrophobic or hydrophilic. However, when particles are labeled with hydrophobic red fluorescent dye, only one side of Janus particles lights up, clearly indicating the hydrophobic side **(Figure 2b)**.

FIGURE 2
(a) A scanning electron microscope (SEM) image of Janus particles, artificial color added to indicate two lobes on the Janus particle. (b) Fluorescent imaging of corresponding Janus particles, with the hydrophobic lobe labeled with red dye.

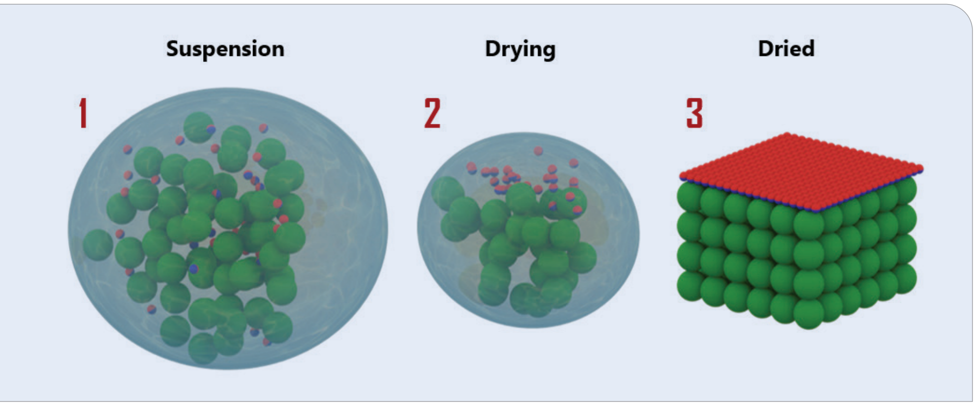


A schematic plot of the application procedure is shown in **Figure 3**. The confocal microscopy scan shows Janus particles reach the coating surface within 5 mins of the application. In our approach, Janus particles are formulated as a straightforward drop-in additive that can be directly applied to the waterborne latex coating system. This means our method is fully compatible with current commercial products, and only a relatively small quantity of Janus particles is needed to cover the surface and change the surface-related coating properties. The bulk materials of the coating film remain intact, which helps maintain the coating performance that is unrelated to surfaces. The advantages are obvious—there is no need to completely redesign the current coating system and manufacturers can quickly adapt the new method by simply adding Janus particles in their product lines.

After the mixed coating is fully dried in an ambient environment, we can see from **Figure 4a,b** that Janus particles exclusively cover the surface and render the coating surface hydrophobic, with contact angle changed from 31° without Janus particles to 128° with Janus particles (**Figure 4c**). The bulk materials of the coating film remain intact, highlighting the potential advantages of our technology. There is no need to use a typical two-coat system to get the coatings with hydrophilic, strong adhesion properties at the substrate interface, and hydrophobic properties at the air interface.[3] In addition, the behavior of Janus particles with different Janus balance (JB), defined in this study as the percentage of the hydrophobic side's surface area, was also investigated. Janus particles with a low Janus balance (JB = 20%) did not demonstrate any stratification (**Figure 4e**). On the other hand, Janus particles with larger hydrophobic patches (JB = 40%) showed stratification (**Figure 4f**), but there was a small fraction of the coating surface that was not covered by Janus particles, resulting in less complete stratification than that of Janus particles with JB = 50% (**Figure 4b**). The contact angle measurement shown in the insets correlates well with the observations at the single particle level. These findings suggest that adsorption energy, which is determined by the JB, plays a crucial role in active self-stratification. When the adsorption energy is low (JB = 20%), no stratification occurs. On the other hand, larger adsorption energy (JB = 50%) results in the most complete stratification.

To determine the mechanical properties of the surface, AFM was used to measure surface forces (**Figure 5**). The force-distance curve obtained during the retraction of the AFM tip from the surface of the primer coating without the addition of Janus particles showed strong adhesion of the top layer, which is expected as the primer's function is to provide adhesion as a base coat. This adhesion causes the primer coating surface to feel tacky to the touch, which can result in poor hardness, stain resistance, and dirt pick-up performance if used without a topcoat. However, when Janus particles were added to the primer formulation, the self-stratified coating showed lower adhesion of the top layer, resulting in a less sticky surface. The average value of the rupture force of a tip from the primer surface decreased to approximately one-third (from 42 nN to 16 nN), and the range was reduced to approximately one-seventh (from 210 nm to 30 nm). This demonstrates that Janus particles not only render the hydrophilic coating film into a hydrophobic surface but also effectively improve the surface properties, such as hardness and tackiness of a commercial product.

FIGURE 3
Schematic representation of formulating self-stratified hydrophobic coating.



Because the majority of Janus particles are stratified to the top surface, there is very little left in the bulk coatings. Therefore, adding Janus particles will not negatively impact the bulk coating properties. To investigate the durability of the self-stratified coating surface with Janus particles, organic solvents (EtOH/THF, 90/10 by volume) were used to rinse the surface of the coating films. Coating films formed by mixing homogeneous hydrophobic particles (of the same hydrophobic surface as the Janus particles), and phosphate binder particles were chosen as a control. Images of the cross-sections of the coating films after rinsing in **Figure 6** clearly demonstrate that the self-stratified coating surface maintain their structure integrity, and surface hydrophobicity is unchanged. The resistance highlights the completeness of the densely packed monolayer of amphiphilic Janus particles formed during the self-stratification process and the strong adhesion offered by the phosphate binder particles. In comparison, the control sample that does not possess the stratified structures **(Figure 6b)** was destroyed in rinsing with solvent **(Figure 6d)**. Because the hydrophobic homogeneous particles randomly dispersed within the binder

FIGURE 4
(a) Schematic diagram for the coating structures formed by active self-stratification of amphiphilic Janus particles mixed with binder particles. (b) SEM image of the cross-section view of dried coating structures. Scale bar: 2 µm. Inset shows the asymmetric morphology of a typical Janus particle with Janus balance (percentage of hydrophobic surface area) ~ 50%. Scale bar: 100 nm. (c) Contact angles of the coating surface before and after adding the Janus particles. (d-f) SEM images of the cross-section view of coating structures added with homogeneous particles and Janus particles of different Janus balances: (d) Homogeneous hydrophilic particles. (e) Amphiphilic Janus particles with Janus balance ~ 20%. (f) Amphiphilic Janus particles with Janus balance ~ 40%. Insets show the corresponding contact angles of the coating surfaces. Scale bars: 2 µm.[22]

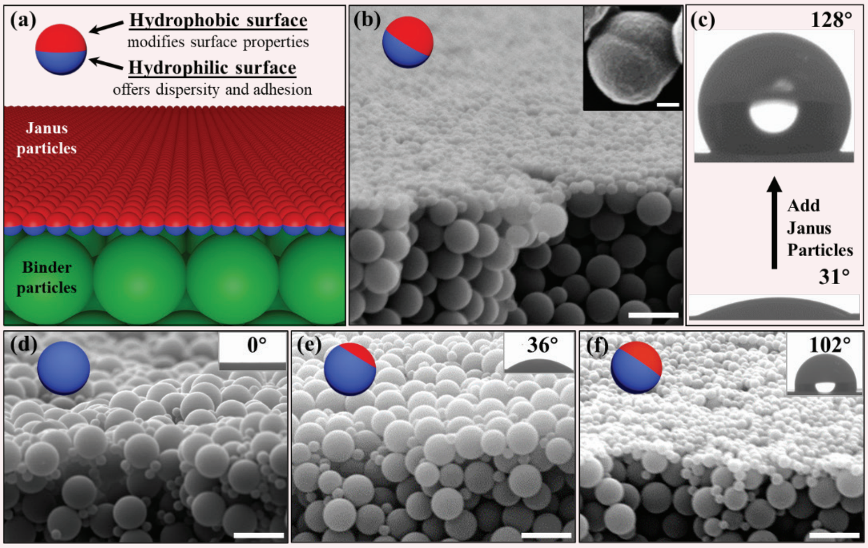


FIGURE 7
SEM images of coating films formed by commercial primer binder added with Janus particles.[22]

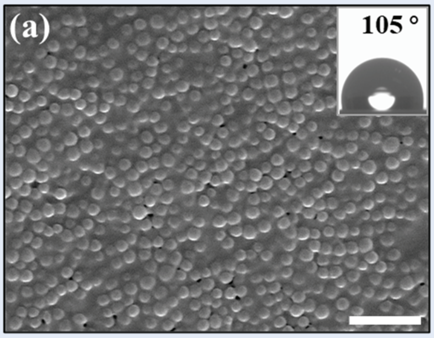


FIGURE 5
Representative force-distance curves recorded during retraction of AFM tip from the coating film surfaces.[22]

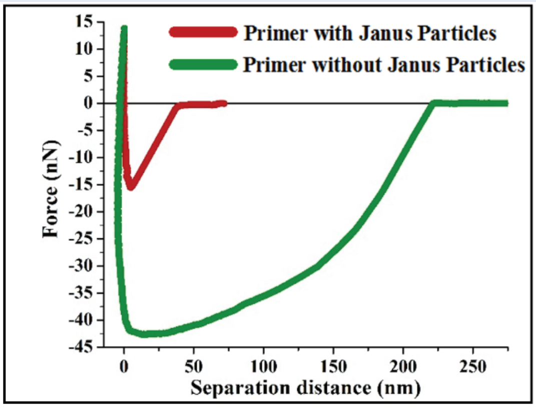
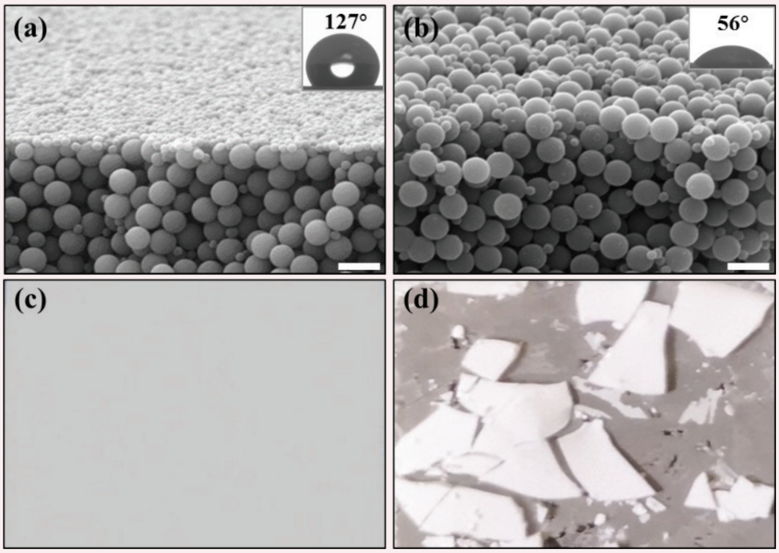


FIGURE 6
SEM images and photos of the dried coating films after rinsing: (a) Films formed with Janus particles. (b) Films with hydrophobic particles. (c) Photo of the coating film added with Janus particles after rinse. (d) Photo of the coating film added with homogeneous particles after rinse.[22]



matrix, they acted as the defects and significantly weakened the coating integrity and adhesion. The contact angle of dried coating films with added Janus particles after rinsing remained high at 127°. These results suggest that Janus particles help create a more durable hydrophobic surface.

To further assess the compatibility of Janus particles with commercial coating products, we incorporated them into a widely used commercial primer. Again, successful stratification was observed, which demonstrates the straightforward integration of our approach into existing products. Specifically, we added Janus particles directly to the commercial primer. **Figure** 7 illustrates the self-stratification of Janus particles at the surface of the commercial primer coating. The binder particles of the primer have a glass transition temperature much lower than room temperature, enabling them to form a continuous film after the coating film is dried. Most of the coating surface was covered with self-stratified Janus particles, leading to an increase in contact angle from 0° to 105°.

Conclusion

In this study, we present a novel approach to achieve self-stratification using amphiphilic Janus particles. These particles can be easily produced on a large scale through cost-effective emulsion polymerization. More importantly, they can be added directly to current waterborne coating systems as a drop-in additive. By adding a small amount of Janus particles, they can rapidly self-stratify at the surface, resulting in durable hydrophobic coatings with strong adhesion. The approach we propose here is not only economically viable but also scalable for commercial production. Successful incorporation of Janus particles into existing coating products validates the versatility and efficacy of our approach, opening new avenues for the development of functionalized coatings. Furthermore, the active self-stratification offers a novel strategy to fabricate hierarchical structures, which may find broader applications in other research areas involving colloidal systems. ❊

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