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Supplementary Information

Self-Stratification of Amphiphilic Janus Particles at Coating Surfaces

Yifan Li,[a] *Fei Liu,*[a] *Shensheng Chen,*[c] *Ayuna Tsyrenova,*[a] *Kyle Miller,*[a] *Emily Olson,*[a] *Rebecca Mort,*[a] *Devin Palm,*[a] *Chunhui Xiang,*[d] *Xin Yong,*[c] *and Shan Jiang**[ab]

[a] Department of Materials Science and Engineering, Iowa State University of Science and Technology, Ames, IA 50011, USA

E-mail: sjiang1@iastate.edu

[b] Division of Materials Science & Engineering, Ames National Laboratory, Ames, IA 50011, USA

[c] Department of Mechanical Engineering, Binghamton University, Binghamton, NY 13902, USA

[d] Department of Apparel, Events and Hospitality Management, Iowa State University of Science and Technology, Ames, IA 50011, USA

Experimental Section

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.[1]

Styrene (4 ml), VAc (1 ml), PVP (2.0 g, a stabilizer), and AIBN (0.05 g, an initiator) were dissolved in a mixture of EtOH (25 ml, 200 proofs) and deionized water (25 ml) 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.

Synthesis of amphiphilic Janus particles: 2.5 ml PS-*co*-PVA seed particles emulsion (0.02 g/ml) were swollen with a mixture of TA (1.2 ml, a hydrophobic monomer), EGDMA (0.3 ml, a crosslinker), and Irgacure 184 (0.06 g) in the presence of PVA (2 wt %) and Pluronic F-127 (2 wt %) in an EtOH/water (2/1 by volume) solution (1.5 ml) for 8 h at room temperature. In this step, the hydrophobic monomer feeding ratio against the PS-*co*-PVA seed particles (0.05g) 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 under 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 (1/1 by volume) to remove the remaining monomers and organic additives.

Synthesis of hydrophilic binder microparticles: Phosphate microparticles were prepared by dispersion polymerization. Typically, in a 100 ml round-bottom flask, 1 g PVP was dissolved in ethanol with a total weight of 40 g under the mechanical stirring, 4 ml styrene, 0.05 g phosphoric acid 2-hydroxyethyl methacrylate ester and 0.05 g 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 under room temperature then washed and separated by centrifugation at 5000 rpm in the EtOH/water (1/1, by volume) mixture for three times. The procedure to synthesis acetic acid binder particles remains the same, with 0.05 g acetic acid in replace of phosphoric acid 2-hydroxyethyl methacrylate ester.

Synthesis of PS-co-PVAc intermediate hydrophobic nanoparticles: Intermediate hydrophobic polystyrene binder particles were synthesized by modifying the previous method.[1] Styrene (4 ml), VAc (1 ml), PVP (1.6 g, a stabilizer), and AIBN (0.05 g, an initiator) were dissolved in a mixture of EtOH (25 ml, 200 proofs) and deionized water (25 ml) 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).

Coating formulation of amphiphilic Janus nanoparticles with phosphate microparticles: Coating formulation were prepared by mixing 10 wt% amphiphilic Janus nanoparticles (0.1 g/ml) and 90 wt% phosphate microparticles (0.1 g/ml) in EtOH/water mixture (1/1, by volume). After 10 mins sonication under water bath, 300 µL mixed particle dispersion was drop coated on top of the plasma cleaned stainless steel (1cm×1cm) and dried under the room temperature overnight.

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

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 DI-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 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 from the substrate and then mounting them on a vertical sample stage. The cross-section of coating film was imaged under 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 surface roughness of each sample was quantified using the Keyence microscope analytical software. An area of the laser scan image was selected. Height data from that area was collected and analyzed to calculate the arithmetical mean height (Sa). A higher Sa value indicates higher surface roughness.

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 one 1 cycle. The water contact angles were measured after each 5 cycles of rinsing.

Force curve measurements was performed in contact mode 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 thirty-eight measurements from each of three different locations per sample.

Theoretical modeling

Theoretical analysis of Janus particle stratification: We extended a double diffusion model of drying binary colloidal mixtures proposed by Zhou et al.[2] to provide a theoretical understanding of the unique stratification behaviour of Janus particles. Our model considers a drying liquid film filled with two types of particles having different sizes. The particles are spherical and have volumes $v_i = 4\pi r_i^3/3\ \left(i = 1,2\right)$, where r_i is the particle radius for type *i*. The size ratio is thus defined as $\alpha = r_2/r_1 > 1$. Here, we denoted the smaller Janus particle to be type 1 and the bigger binder particle to type 2. The corresponding time-dependent local volume fraction and number density are $\phi_i\left(\mathbf{r},t\right)$ and $n_i = \phi_i/v_i$, respectively. The initial conditions assume both particles are distributed homogeneously with $\phi_i\left(\mathbf{r},0\right) = \phi_i^0$.

The transport of particles is assumed to be one-dimensional along the height of the film (i.e., the *z* direction) and described by the standard diffusion model.[3] The conservation equation for each particle type is given by

$$\frac{\partial \phi_i}{\partial t} + \frac{\partial \phi_i U_i}{\partial z} = 0 . \tag{1}$$

$U_i\left(z\right)$ is the volume average velocity of the particles, which is determined by the balance between the thermodynamic force driven by chemical potential gradient and viscous drag force. According to the Stokes-Einstein relation, the velocity is expressed as $U_i = -\left(1/\zeta_i\right)\left(\partial\mu_i/\partial z\right) = -\left(D_i/k_\mathrm{B}T\right)\left(\partial\mu_i/\partial z\right)$ with ζ_i being the drag coefficient and $D_i = k_\mathrm{B}T / \zeta_i$ being the diffusion constant. The particle chemical potential μ_i is obtained from the free energy density of a dilute hard-sphere mixture[4]

$$\frac{1}{k_\mathrm{B}T} f\left(\phi_1,\phi_2\right) = \sum_i \frac{1}{v_i}\phi_i \ln\phi_i + \sum_{i,j} \frac{1}{v_i v_j} a_{ij}\phi_i\phi_j\,, \tag{2}$$

where $a_{ij} = \left(2\pi/3\right)\left(r_i + r_j\right)^3$ is the second virial coefficients for hard spheres.[2] The first term in Equation (2) considers particle entropy and the second term accounts for the excluded volume repulsions between particles. The chemical potential of particles can be then derived as

$$\mu_i = \frac{\partial f}{\partial n_i} = k_\mathrm{B}T\left(\ln\phi_i + 1 + 2\sum_j \frac{1}{v_j} a_{ij}\phi_j\right) \tag{3}$$

In our system, the surface-active Janus particles will strongly adsorb to the liquid-air interface, while the binder particles remain well dispersed in the film. Therefore, the chemical potential of Janus particle μ_1 is further modified with a surface adsorption term,[5]

$$\mu_1 = k_\mathrm{B}T\left[\ln\phi_1 + 1 + 2\sum_j \frac{1}{v_j} a_{1j}\phi_j - \tilde{E}_a H\left(z-h\right)\right] \tag{4}$$

where $\tilde{E}_a$ dictates the dimensionless adsorption energy per particle normalized by the thermal energy and $H\left(z-h\right)$ is the Heaviside function applicable at the interface $z = h$. The coupled diffusion equations of the concentrations of Janus and binder particles can be written as

$$\frac{\partial \phi_1}{\partial t} = D_1 \frac{\partial}{z}\left[\left(1+8\phi_1\right)\frac{\partial \phi_1}{\partial z} + \left(1+\frac{1}{\alpha}\right)^3 \phi_1 \frac{\partial \phi_2}{\partial z} - \tilde{E}_a \phi_1 \delta\left(z-h\right) \right] \tag{5}$$

$$\frac{\partial \phi_2}{\partial t} = D_2 \frac{\partial}{z}\left[\left(1+\alpha\right)^3 \phi_2 \frac{\partial \phi_1}{\partial z} + \left(1+8\phi_2\right)\frac{\partial \phi_2}{\partial z} \right]. \tag{6}$$

The derivative of $H\left(z-h\right)$ gives the Dirac delta function $\delta\left(z-h\right)$, which is regularized numerically as a Gaussian function centered at $z=h$.

The height of the film is dynamically changing during evaporation. Considering drying is at a constant rate, the interface moves with a constant speed v_0. The instantaneous interfacial position is thus given by $h(t) = h_0 - v_0 t$, where the initial film thickness is h_0. A coordinate transformation $x = z/\left(h_0 - v_0 t\right)$ is applied to address the numerical difficulties of solving Equations (5) and (6) in a domain with a moving boundary. To obtain the dimensionless diffusion equations, the time is scaled with the characteristic evaporation time $\tau = t\left(v_0/h_0\right)$. The dimensionless equations in the static spatial domain are

$$\frac{\partial \phi_1}{\partial \tau} + \frac{x}{1-\tau}\frac{\partial \phi_1}{\partial x} = \frac{1}{\mathrm{Pe}_1\left(1-\tau\right)^2}\frac{\partial}{\partial x}\left[\left(1+8\phi_1\right)\frac{\partial \phi_1}{\partial x} + \left(1+\frac{1}{\alpha}\right)^3 \phi_1 \frac{\partial \phi_2}{\partial x} - \tilde{E}_a \phi_1 \tilde{g}\left(x-1\right) \right] \tag{7}$$

$$\frac{\partial \phi_2}{\partial \tau} + \frac{x}{1-\tau}\frac{\partial \phi_2}{\partial x} = \frac{1}{\mathrm{Pe}_2\left(1-\tau\right)^2}\frac{\partial}{\partial x}\left[\left(1+\alpha\right)^3 \phi_2 \frac{\partial \phi_1}{\partial x} + \left(1+8\phi_2\right)\frac{\partial \phi_2}{\partial x} \right] \tag{8}$$

where the Peclet numbers of two types of particles are defined by $\mathrm{Pe}_1 = v_0 h_0/D_1$ and $\mathrm{Pe}_2 = v_0 h_0/D_2 = \alpha\,\mathrm{Pe}_1$. The scaled Gaussian function $\tilde{g}\left(x-1\right) = \frac{1}{\tilde{\sigma}\sqrt{2\pi}}\left(1-\tau\right)\exp\left[-\frac{1}{2}\left(1-\tau\right)^2\left(\frac{x-1}{\tilde{\sigma}}\right)^2\right]$ has a normalized standard deviation $\tilde{\sigma} = \sigma/h_0$. Here, σ determines the influential range of the adsorption behavior, which can be set based on the experimental observation. The dimensionless average velocities are

$$\tilde{v}_1 = -\frac{1}{\mathrm{Pe}_1(1-\tau)}\left[\left(\frac{1}{\phi_1}+8\right)\frac{\partial\phi_1}{\partial x}+\left(1+\frac{1}{\alpha}\right)^3\frac{\partial\phi_2}{\partial x}-\tilde{E}_a\tilde{g}(x-1)\right] \tag{9}$$

$$\tilde{v}_2 = -\frac{1}{\mathrm{Pe}_2(1-\tau)}\left[(1+\alpha)^3\frac{\partial\phi_1}{\partial x}+\left(\frac{1}{\phi_2}+8\right)\frac{\partial\phi_2}{\partial x}\right] \tag{10}$$

We consider that the concentrations of both particles converge to their bulk values away from the evaporating interface. Therefore, the corresponding local average velocities are zero. The boundary conditions become $\tilde{v}_1|_{x=0} = \tilde{v}_2|_{x=0} = 0$ and $\tilde{v}_1|_{x=1} = \tilde{v}_2|_{x=1} = -1$.

The coupled equations were solved by the MATLAB Partial Differential Equation Toolbox. To match the experimental conditions, the size ratio of the two particles was set to 3.25. The Peclet numbers were $\mathrm{Pe}_1 = 12$ and $\mathrm{Pe}_2 = 39$. Initial volume fractions were set to $\phi_2^0 = 0.01$ and $\phi_1^0 = \phi_2^0/30$ to satisfy the dilute regime limitation of the theory.[2] Note that the absolute concentrations used in the model were lower than experimental values but the concentration ratio was consistent. We set the adsorption strength to be $\tilde{E}_a = 20$ to represent irreversible adsorption of typical Janus particles.[6] Further increase in $\tilde{E}_a$ accelerates the stratification rate and the Janus particle density at the interface, but does not change the behavior of density evolution qualitatively. To better compare with the time-resolved confocal microscopy results in experiment, the model was solved with an initial domain thickness $h_0 = 200$ µm and an adsorption range of $\sigma = 3$ µm.

Supporting Materials

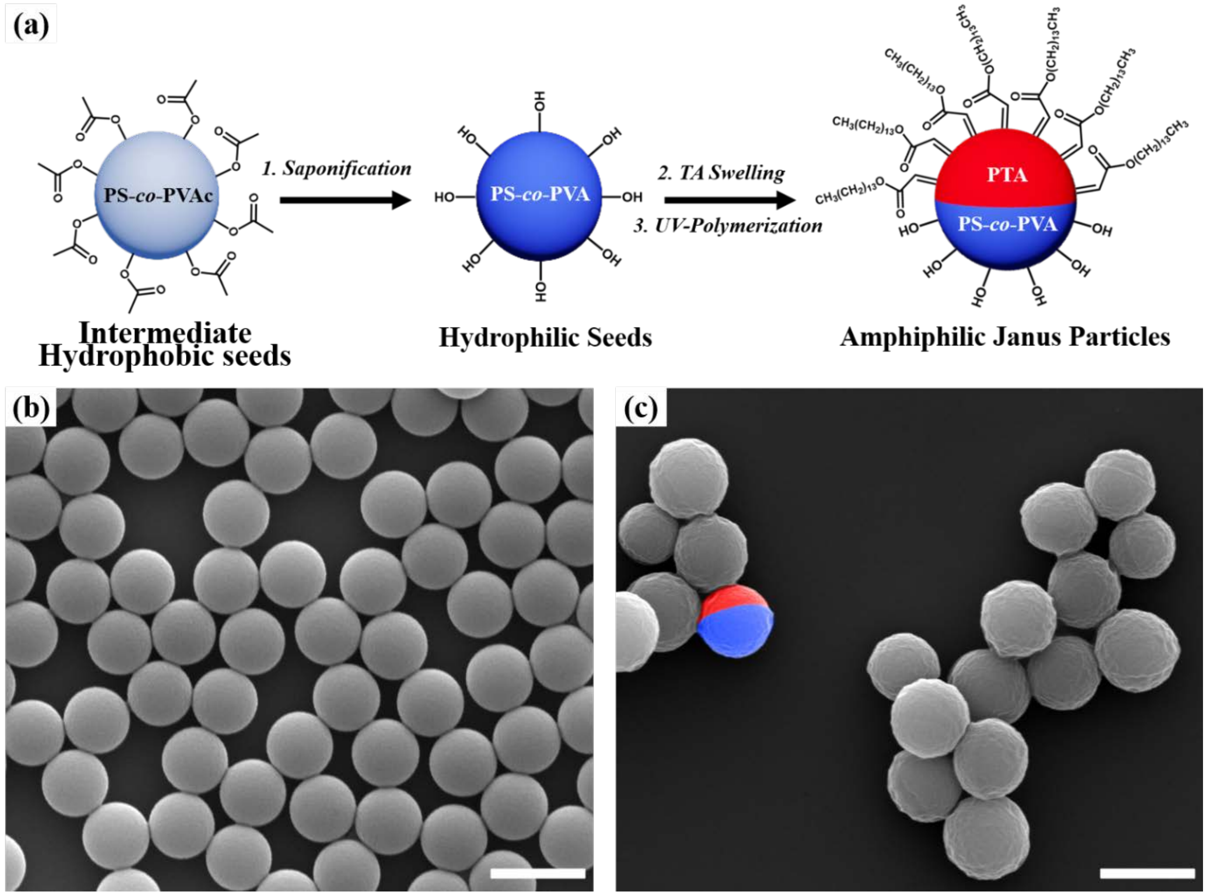

Figure S1. (a) Schematic illustration for the synthesis of amphiphilic Janus particles consisting of PS-co-PVA and PTA side. (b) SEM images of PS-co-PVA hydrophilic seed nanoparticles. (c) SEM images of amphiphilic Janus particles. Scale bars are all 500 nm.

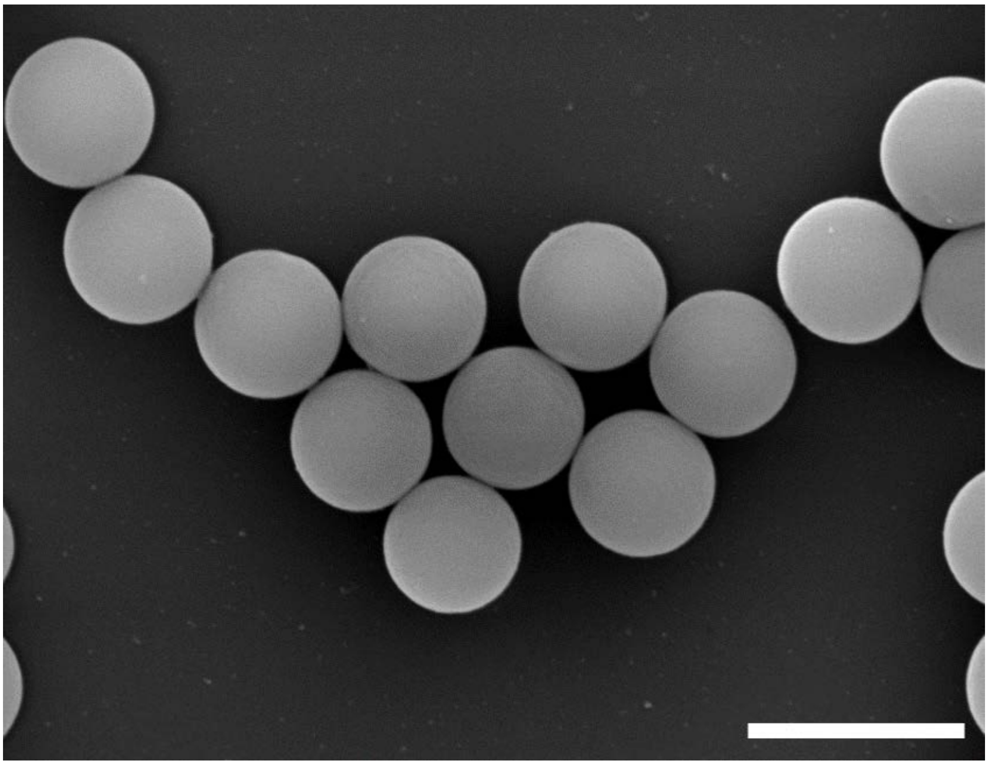

Figure S2. SEM images of phosphate binder particles. Scale bar is 2 µm.

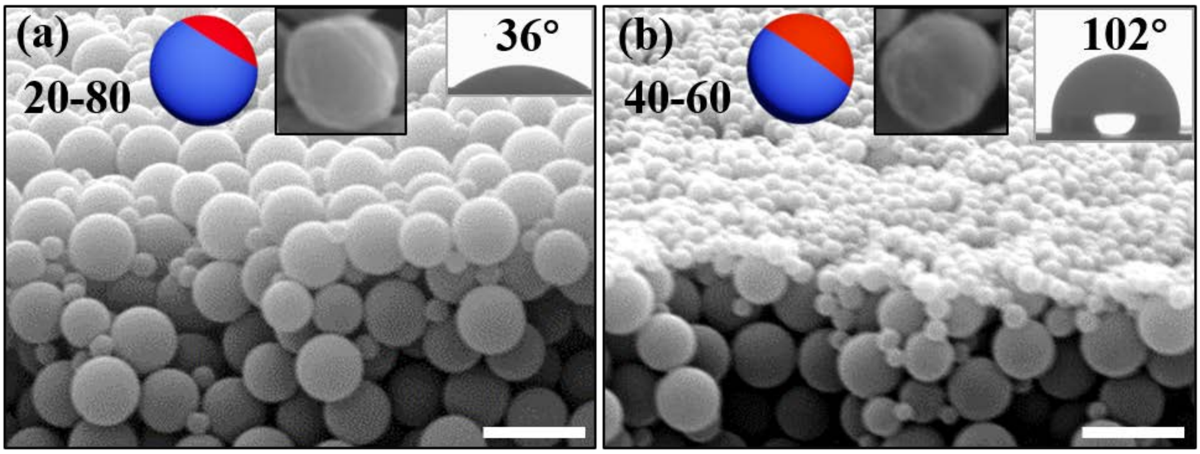

Figure S3. Structures of coating films added with the amphiphilic Janus particles with different hydrophobic/hydrophilic surface area ratio (Janus balance): a) 20-80; b) 40-60. Insets are SEM images of Janus particles and photos of contact angle. Scale bar is 2 µm.

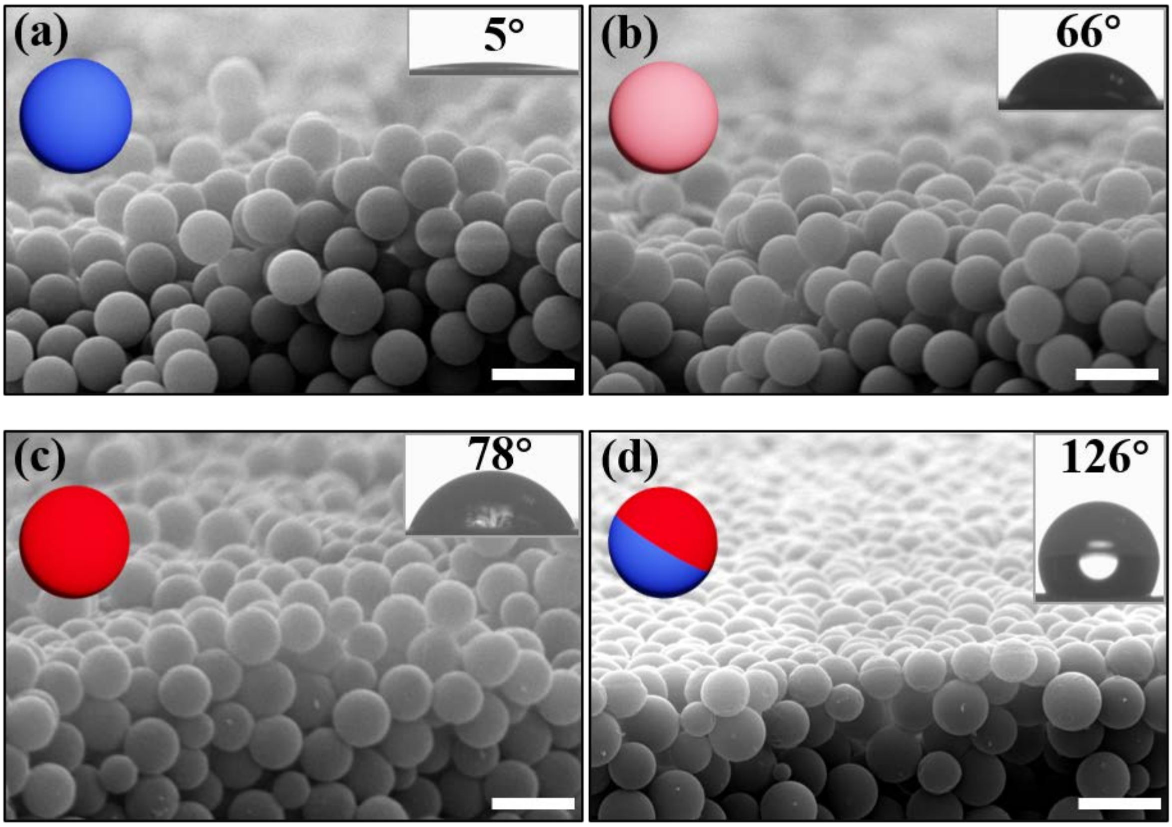

Figure S4. SEM images of the cross-section view of coating structures added with 1 µm homogeneous particles of different hydrophobicity and Janus particles with JB ~ 50%: a) Homogeneous hydrophilic particles, b) Homogeneous intermediate hydrophobic particles, c) Homogeneous hydrophobic particles, d) Amphiphilic Janus particles with JB ~ 50%. Insets show the corresponding contact angles of the coating surfaces (scale bars are all 2 µm).

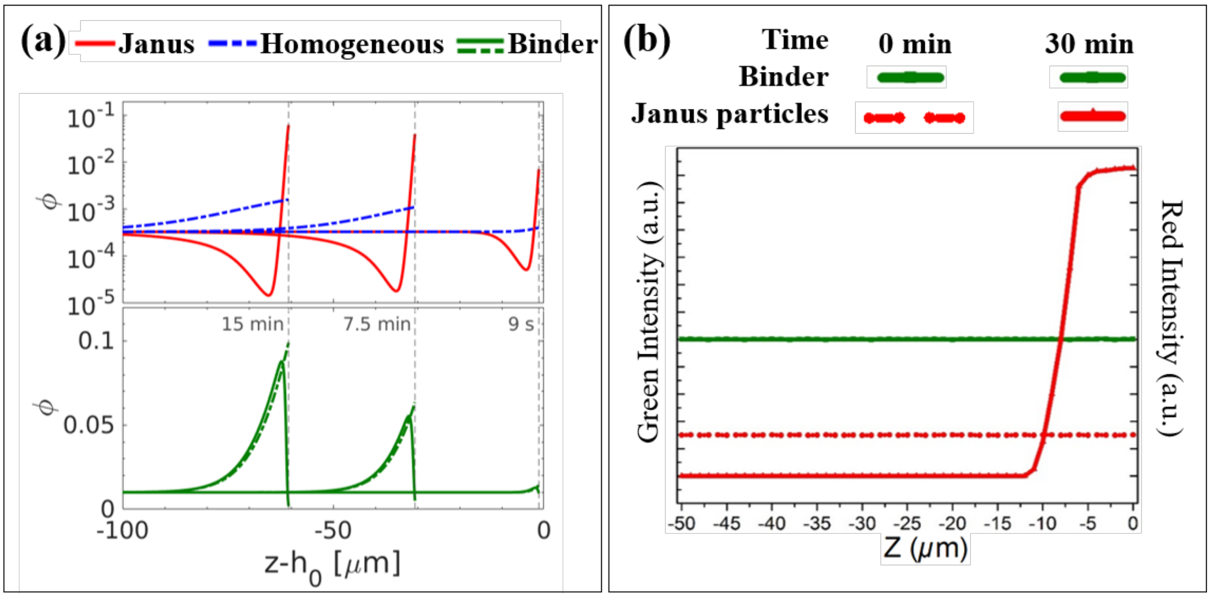

Figure S5. a) Theoretical comparison of time evolution of particle concentration profiles for the binary mixtures: Janus particles with binder particles (solid lines) and homogeneous particles with binder particles (dashed lines); (b) Integrated intensities of red (Janus particles) and green (binder) channels close to the top surface, as a function of the vertical distance, z. The surface is represented at z = 0. A correction was made for the depth dependence of the detected fluorescence intensity.

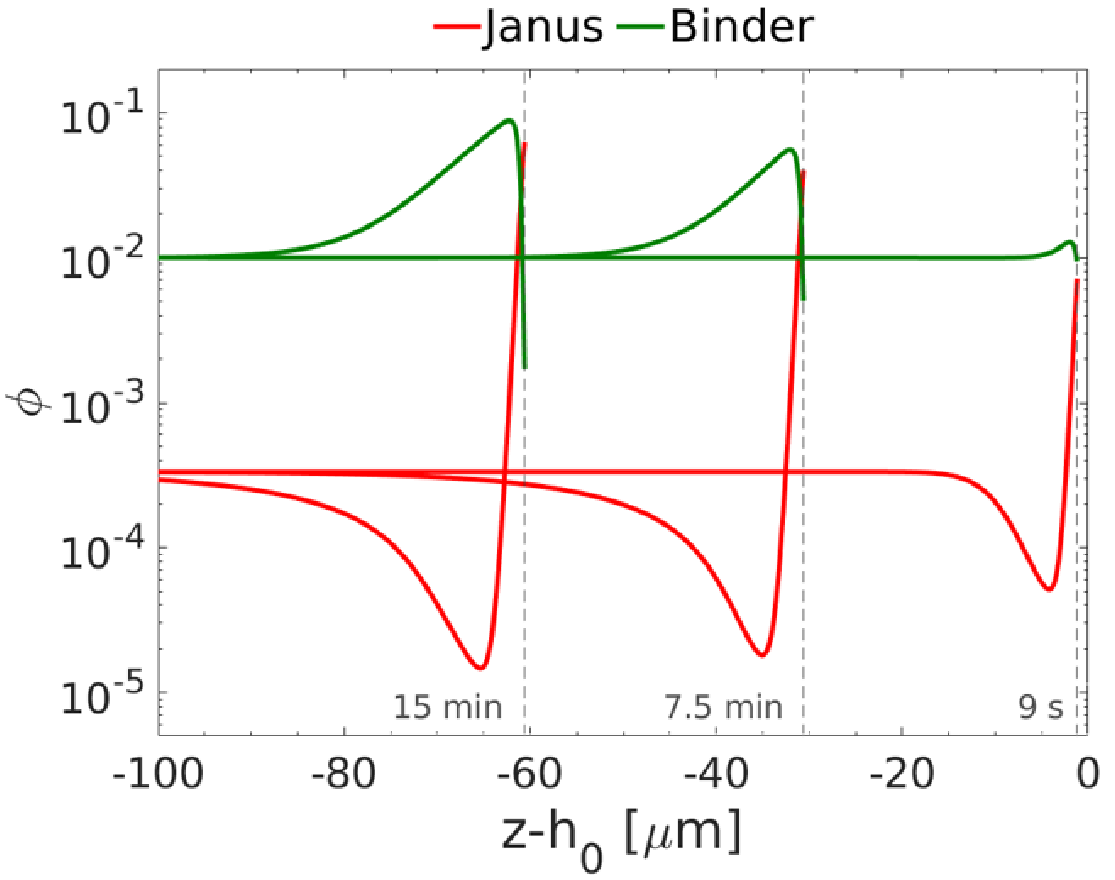

Figure S6. Comparison between theory-predicted concentrations of Janus particles and binder particles in the binary mixture during evaporation.

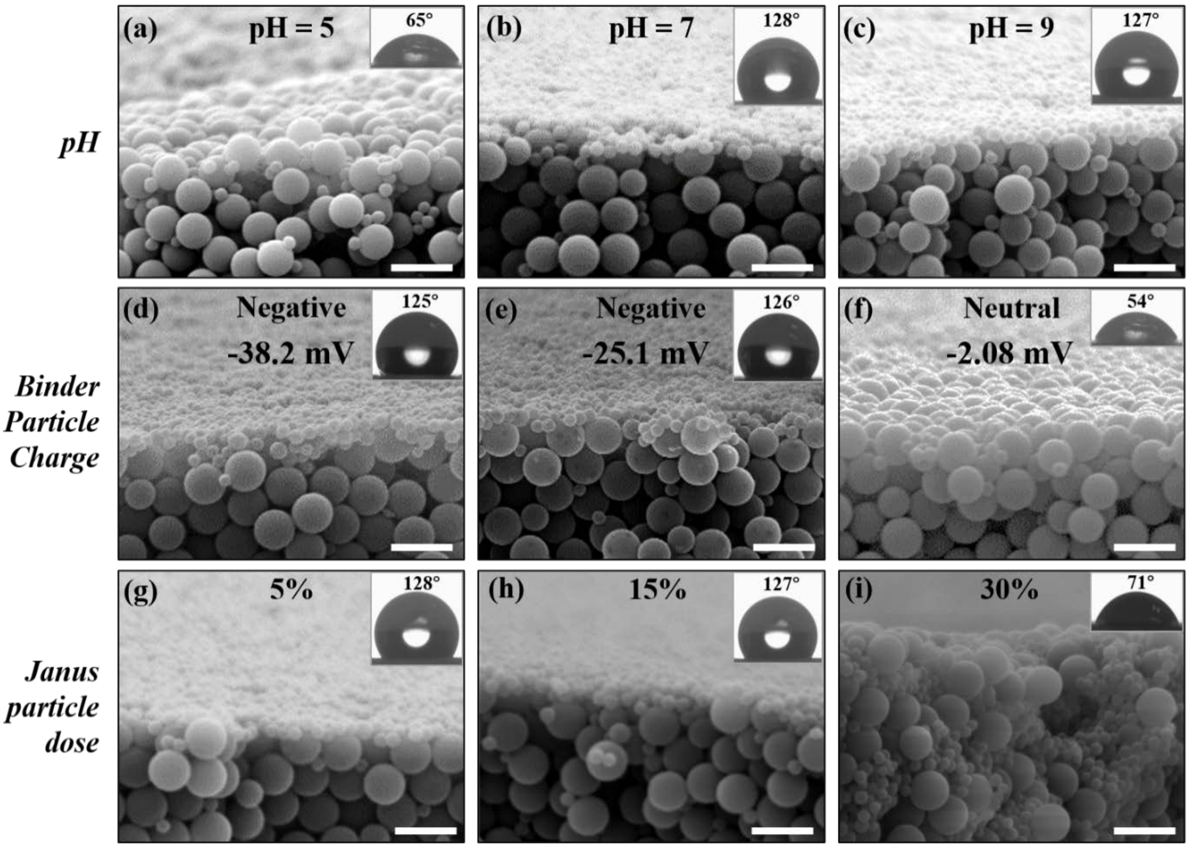

Figure S7. Comparison of coating film structures: a-c) Films formed under different pH values; d-f) Films formed with binder particle of different surface charges; g-i) Films formed with different concentrations of Janus particles. Scale bars are all 2 µm.

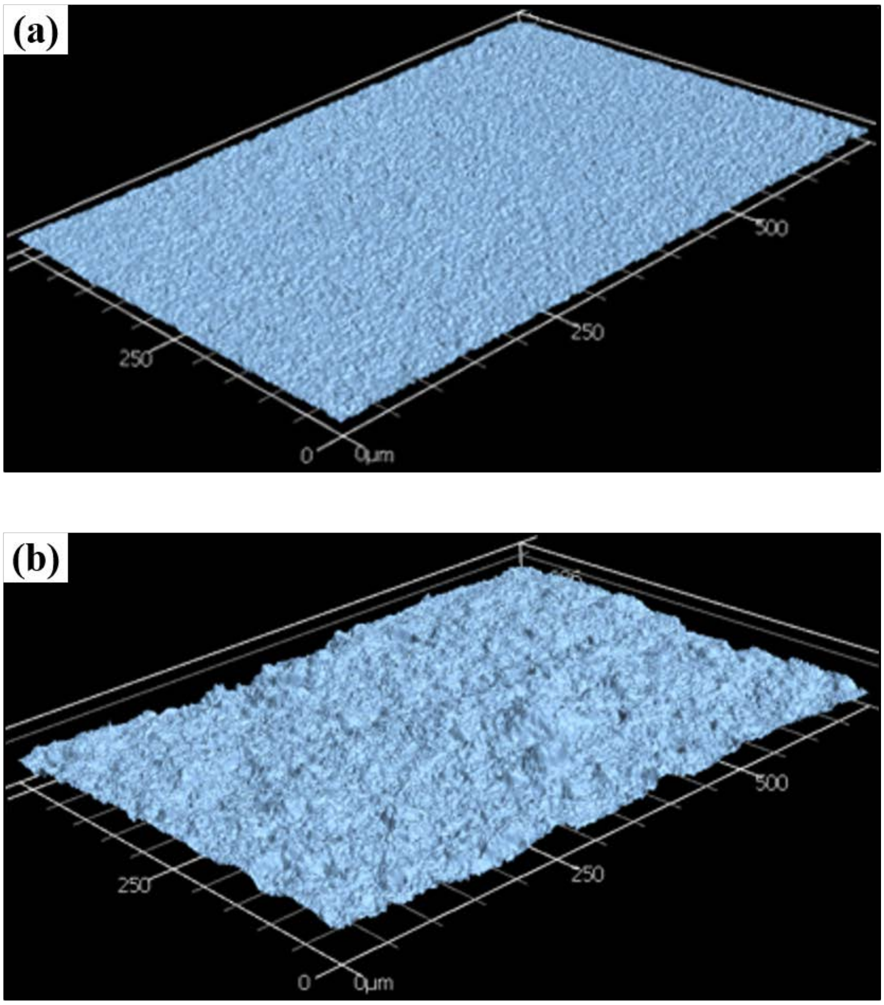

Figure S8. Surface topology: (a) Stratified coating composed of amphiphilic Janus particles and phosphate binder particles; (b) Non-stratified coating composed of hydrophobic homogeneous particles and phosphate binder particles.

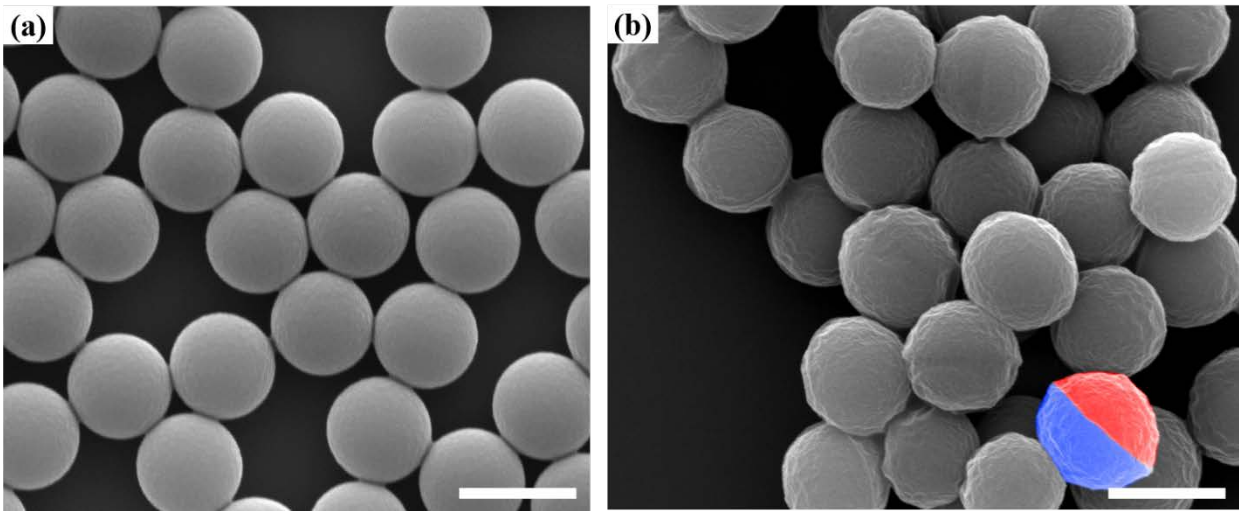

Figure S9. SEM images of polymer particles synthesized by emulsion polymerization: (a) 880 nm PS-co-PVA hydrophilic seed particles; (b) 1 μm amphiphilic Janus particles further synthesized using the seed in (a). Scale bars are all 1 μm.

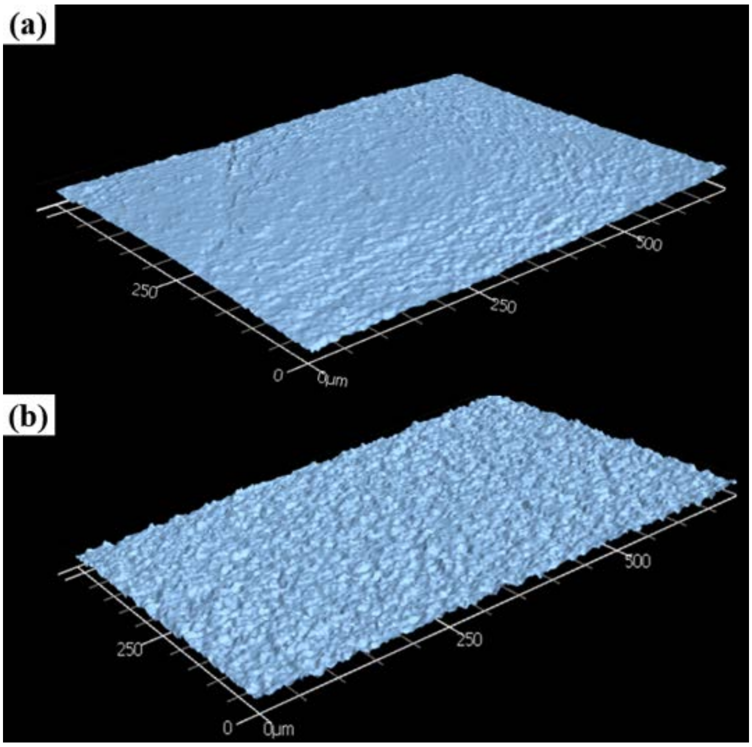

Figure S10. Confocal scanning 3D image for surface topology of: (a) Coating formulated with commercial primer added with 400 nm Janus particles; (b) Coating formulated with commercial primer added with both 400 nm and 1.0 µm Janus particles.

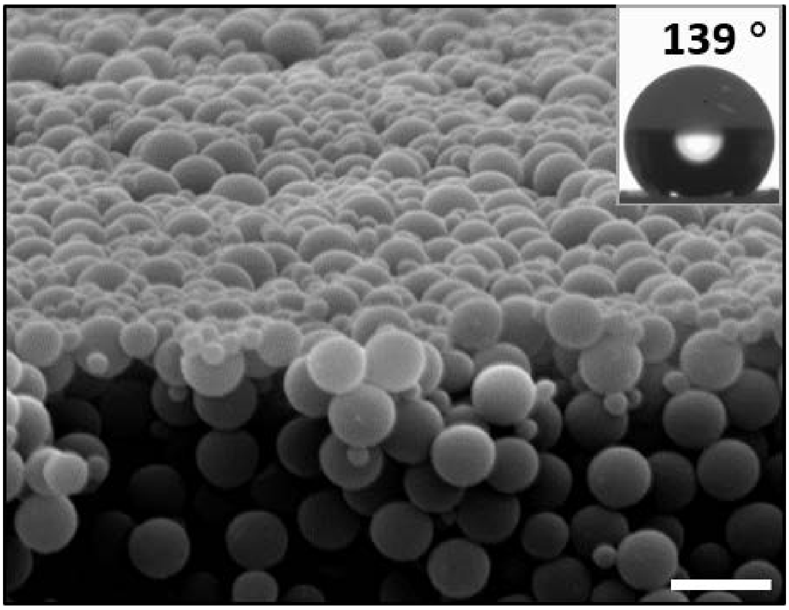

Figure S11. SEM image of coating structures of binder particles (1.3 µm) added with two Janus particles of different sizes (1 µm and 400 nm). Inset is contact angle of the coating surface. Scale bars is 2 µm.

References:

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