

Supporting Information

Soft-Hard Janus Nanoparticles for Polymer Encapsulation of Solid Particulate

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Characterizations of macro-RAFT copolymers

Proton nuclear magnetic resonance (¹H NMR) was used to calculate the theoretical molecular weight of each block via the conversion of the monomer in the polymerization. Gel permeation chromatography (GPC) was employed to determine the molecular weight (using polyMMA standards for GPC calibration) and molecular weight distribution of the synthesized polymers. The result clearly depicts the shift of the polymer molecular weights toward higher values throughout the polymerization and low *D* was observed in all cases, which suggests that the polymerization proceeded under the control of the RAFT agent (Figure S1c). Mass spectrometry (MS) was used to confirm the polymer molecular weight and the results were consistent with that from ¹H-NMR(Figure S1a,b).

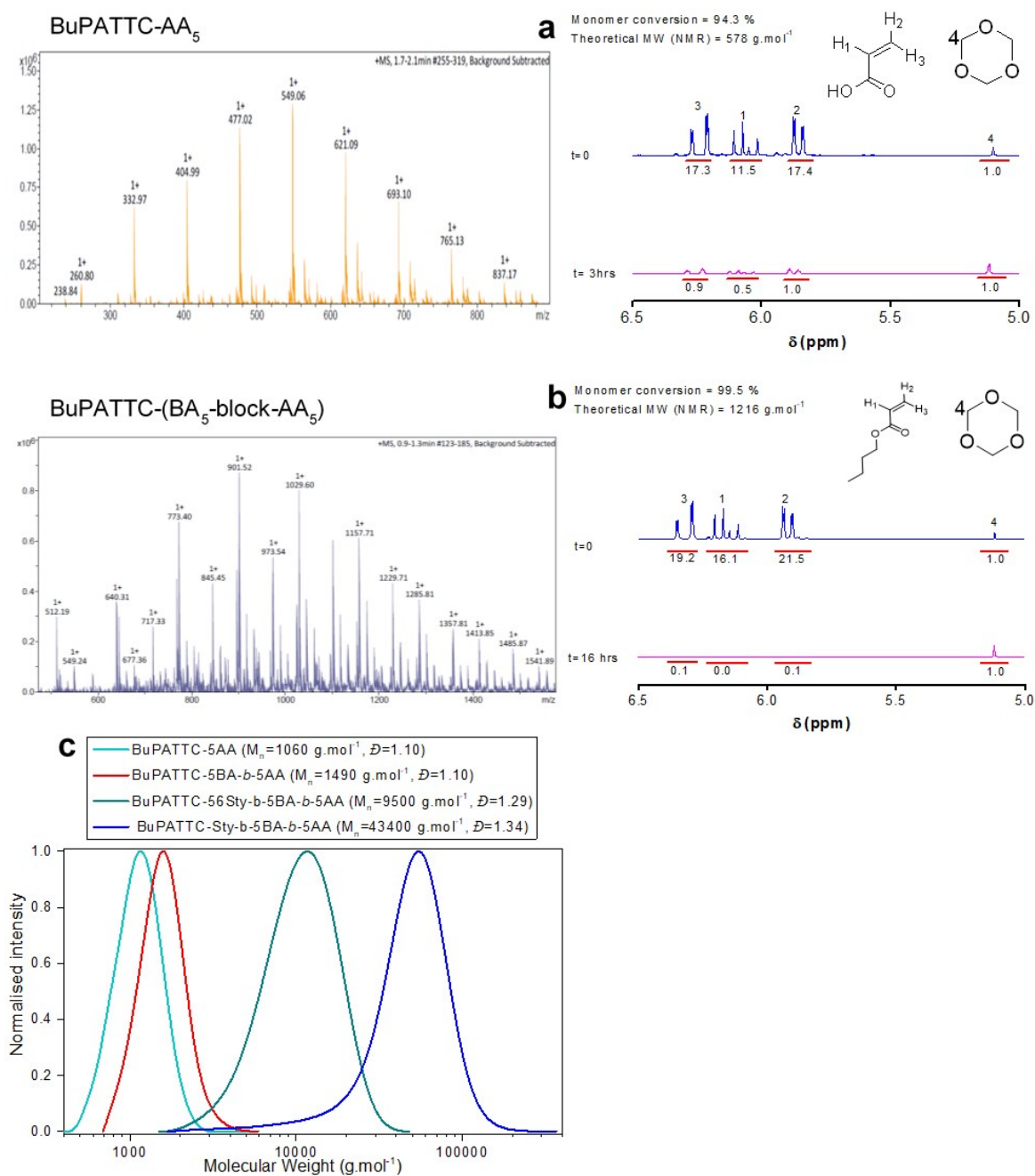


Figure S1. Characterizations of macro-RAFT copolymers. Mass spectrum and ¹H NMR spectrum of a) BuPATTC-AA₅ and b) BuPATTC-(BA₅-*block*-AA₅); c) GPC analysis of the synthesized block polymers and PS particles, as indicated in the legend. The M_n derived from GPC (1000 g/mol) and that derived from ¹H NMR (578 g/mol) are different due to the difference in hydrodynamic volume of the synthesized polymer and the polyMMA used for the GPC calibration.

	M_n (g/mol) ¹ H NMR	M_n (g/mol) GPC	Distribution	Conversion	Table S1
BuPATTC-AA ₅	578	1,060	1.1	94.3%	Molec
BuPATTC-(BA ₅ - <i>b</i> -AA ₅)	1,216	1,490	1.1	99.5%	ular
Uncross-linked PS seeds		9,500	1.29	96.7%	weight
PS particles		43,400	1.34	97.1%	and

ution of macro-RAFT copolymers and PS particles

Characterizations of polystyrene seed latex

The seed particles were characterized by transmission electron microscopy (TEM, Figure S2a), while the polymer was characterized by GPC using N,N'-dimethylacetamide (DMAc) as the eluent against poly(Sty) standards. GPC characterization showed that the polymerization was completely under RAFT control, producing polymer with molecular weight of 9500 g/mol with low D of 1.3, shown in Figure S1c. Throughout this process, micelles and particles were stabilized by the imparted negative charge due to the deprotonated AA units, with Zeta potential measured to be -60 mV.

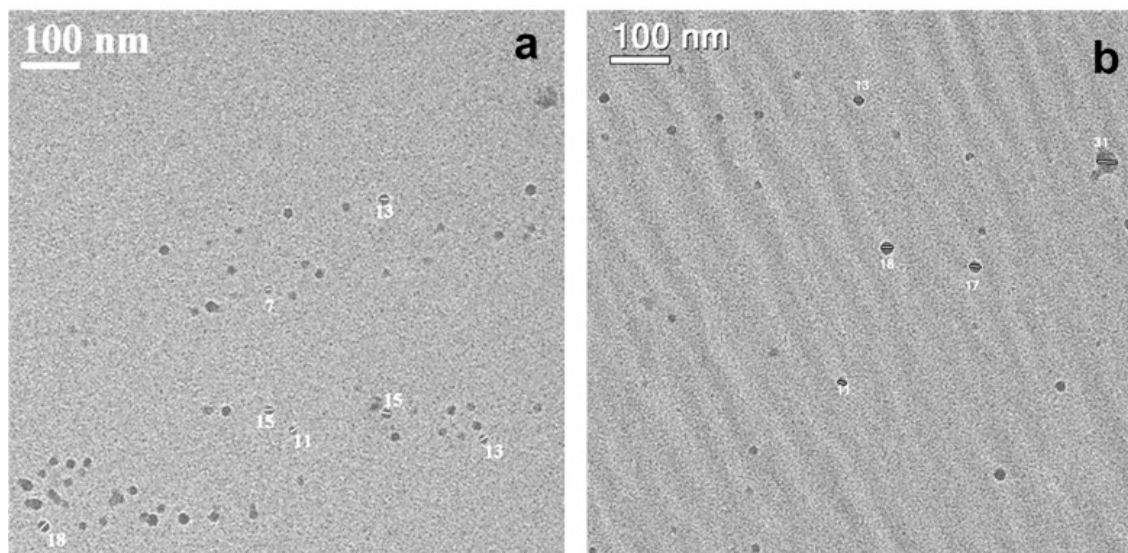


Figure S2. TEM micrographs of a) uncrosslinked and b) crosslinked PS seed latex.

Synthesis of snowman shaped PS Janus nanoparticles (all-PS Janus) using PS seed latex using 16 % (by weight) DVB cross-linker relative to the seed particles

All-PS Janus particles were typically synthesized using the following procedure. In a 500 mL round bottom flask, the previously prepared PS seed latex (100 g) was diluted with water (150 g). To this latex, V-501 (0.15 g) and DVB (1.2 g) were added and mixed for 5 minutes. The flask was then sealed and purged with nitrogen for 10 min. It was then immersed in an oil bath heated to 70 °C with stirring. After 1 h, deoxygenated styrene (40 mL, 37.5 g) was injected into the flask at a rate of 10 mL·h⁻¹. The temperature was then maintained at 70 °C with continued stirring overnight once all the styrene was added to yield a slightly coagulated but stable latex. After glass wool filtration, the final latex had a solids content of 14.4 %. This latex was used later for encapsulation of Coral Red C pigment.

Snowman shaped all-PS Janus prepared using DVB cross-linker at different concentrations relative to the seed particles

Scaled down reactions were carried out to examine the effect of DVB cross-linker concentrations on particle morphologies. For an example, to synthesize 9.5 % DVB crosslinked seed latex, in a 100 mL round bottom flask, the previously prepared PS seed latex (20 g) was diluted with water (30 g). To this latex, V-501 (0.03 g) and DVB (0.13 g) was added and mixed for 5 minutes. The flask was then sealed and purged with nitrogen for 10 min. It was then immersed in an oil bath heated to 70 °C with stirring. After 1 h, deoxygenated styrene (8 mL, 7.3 g) was injected into the flask at a rate of 2 mL·h⁻¹. The temperature was then maintained at 70 °C with continued stirring overnight once all the styrene was added to yield a slightly coagulated but stable latex.

PS particle synthesis using different concentrations of DVB cross-linker, DVB, 2.5 and 4.5 % by weight of PS seed latex, were carried out. Experimental conditions were listed in Table S2. For comparison, latex with no crosslinker was also synthesized under the same conditions. However, in this case styrene monomer injection commenced immediately after the immersion of the round bottom flask in the oil bath.

Table S2. Preparation of all-PS Janus using various DVB concentrations. DVB was initially polymerized for 1 h at 70 °C, followed by the addition of styrene, which was fed at a rate of 2 mL·h⁻¹.

Sample	DVB (g)	DVB (%)	PS seed latex (g)	V-501 (g)	Water (g)	Styrene (g)	Solids (%)
1	0.000	0.0	20	0.039	30.1	7.25	13.7
2	0.030	2.5	20	0.027	30.0	7.25	14.5
3	0.056	4.5	20	0.029	30.0	7.25	13.6
4	0.128	9.5	20	0.026	30.2	7.25	12.4

5	1.2	16.0	100	0.15	10	36.24	14.4
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Synthesis of fluorescent film-forming Janus nanoparticles using PS seed latex

Fluorescent film-forming Janus particles (Fluor-FF Janus) were synthesized in the same way as for FF Janus, only additional fluorescent monomer, 1-pyrene methyl methacrylate (PyMMA, 0.1 g), was included during the seed crosslinking stage. Drying the Fluor-FF Janus latex at room temperature (25° C) produced a clear film which was crack free and fluorescent under the UV lamp (Spectroline, 365 nm). For higher solids content fluorescent film-forming Janus particles, PS seed latex was used without dilution with water. The amount of materials used in the whole process was double compared to the standard one mentioned above. While SDS (0.1 g) was added during the reaction to provide additional stability to the latex. The final product had 32% solids. After drying, the latex produced a clear film which was also fluorescent under the UV lamp. This latex was denoted Fluor-high-solids-FF Janus.

Large scale synthesis of Janus nanoparticles

This same procedure was also employed to successfully synthesize approximately 1.5 kg FF Janus latex (non-fluorescent latex) at 39% solids from 1 kg of similar PS seed with all the other materials scaled up accordingly (Figure S3).

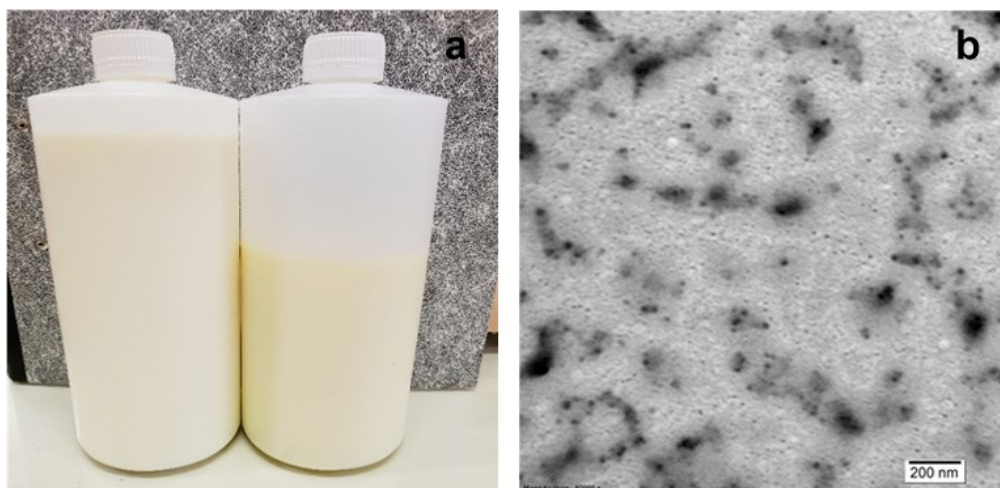


Figure S3. a) Photograph of the product of the large scale synthesis of Janus particles: 1.5 kg FF Janus latex sample. b) TEM micrograph of the FF Janus nanoparticles synthesized on this large scale.

Polymer encapsulation using Janus particles

Encapsulation of Titanium dioxide pigments using Fluor-FF Janus

Titanium dioxide was encapsulated as follows. The pigment powder (R706-Dupont, 1 g) was mixed with a latex containing Fluor-FF Janus (5 g) and water (10 g) in a glass scintillation vial to produce a white dispersion. This dispersion was further dispersed using an ultrasonic probe for 2 minutes. The white dispersion was characterized by TEM (Figure 6a), SEM (Figure 6b) and TGA (Figure 4Sa).

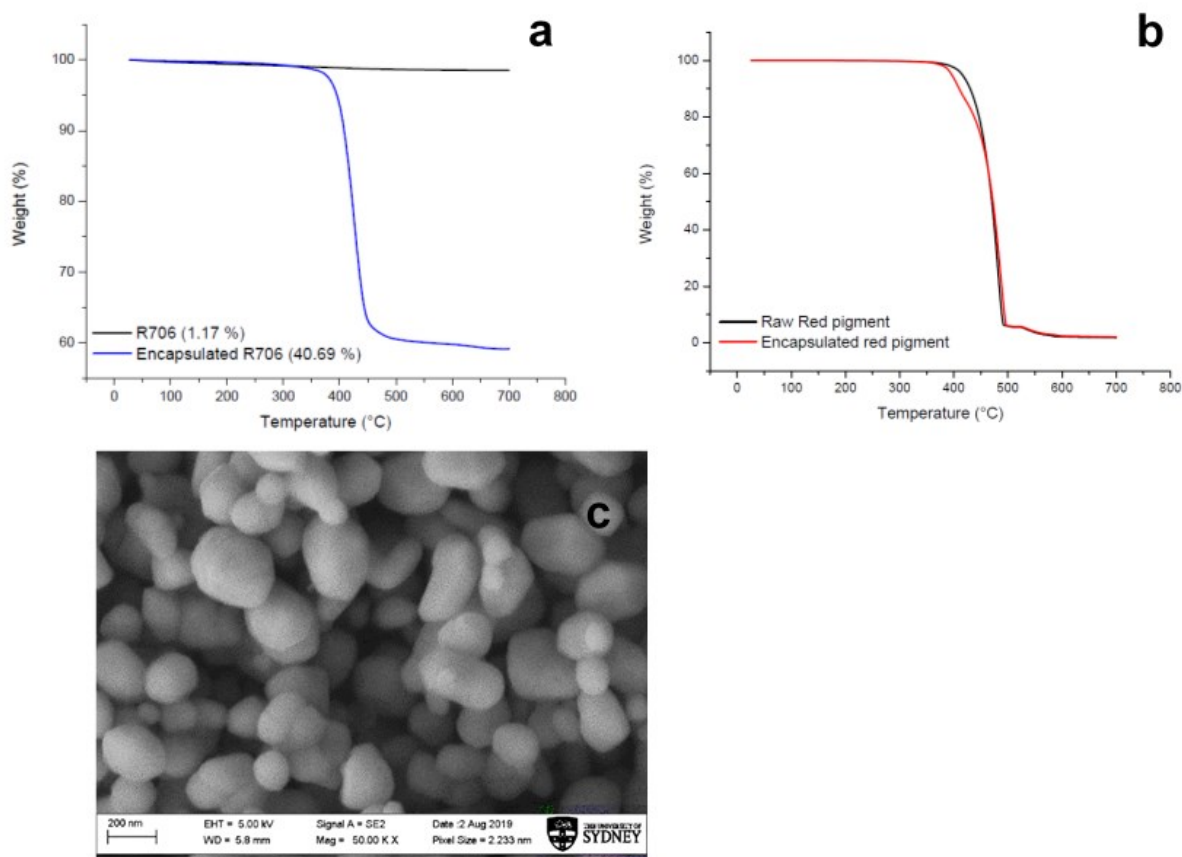


Figure S4. TGA analysis of a) titanium dioxide pigment and b) Coral Red C pigment coated by Fluor-FF Janus. c) SEM micrograph of plain titanium dioxide pigment, showing a smooth featureless surface.

Coating of MWCNTs using Fluor-FF Janus

Multi-wall carbon nanotubes (MWCNTs, Nanolab, 0.05 g) were mixed with a latex containing Fluor-FF Janus (5 g), ethanol (0.5 g) and water (5 g) in a glass scintillation vial to produce a black dispersion. This dispersion was further dispersed using an ultrasonic probe for 1 minute. SDS (0.01 g) was added to the dispersion which was then followed by another 1 minute ultrasonication. The product was centrifuged and washed 3 times with water to remove un-adsorbed Fluor-FF Janus.

Coating of DPP Coral Red C pigment using Fluor-FF Janus

The red pigment (0.1 g) was mixed with Fluor-FF Janus (5 g) in a scintillation vial. The vial was subjected to sonication in a sonic bath (Branson) for 1 minute to produce a red dispersion. TGA confirmed the polymer decomposition starting at 400 °C (Figure S4b).

Coating of DPP Coral Red C pigment using all-PS Janus

The red pigment (0.5 g) was mixed with all-PS Janus (5 g), water (25 g) and toluene (5 g) in a small beaker. The mixture was mixed using an overhead stirrer at 2,000 rpm for 5 minutes. The dispersion was then sonicated for 1 minute using an ultrasonic probe. SDS (0.06 g) was subsequently added to the dispersion which was further sonicated for another minute to produce a red dispersion. 1 g of this pigment dispersion was put into a glass scintillation vial and heated at 70 °C for 10 minutes. The encapsulated pigment was then characterized by TEM (Figure S5).

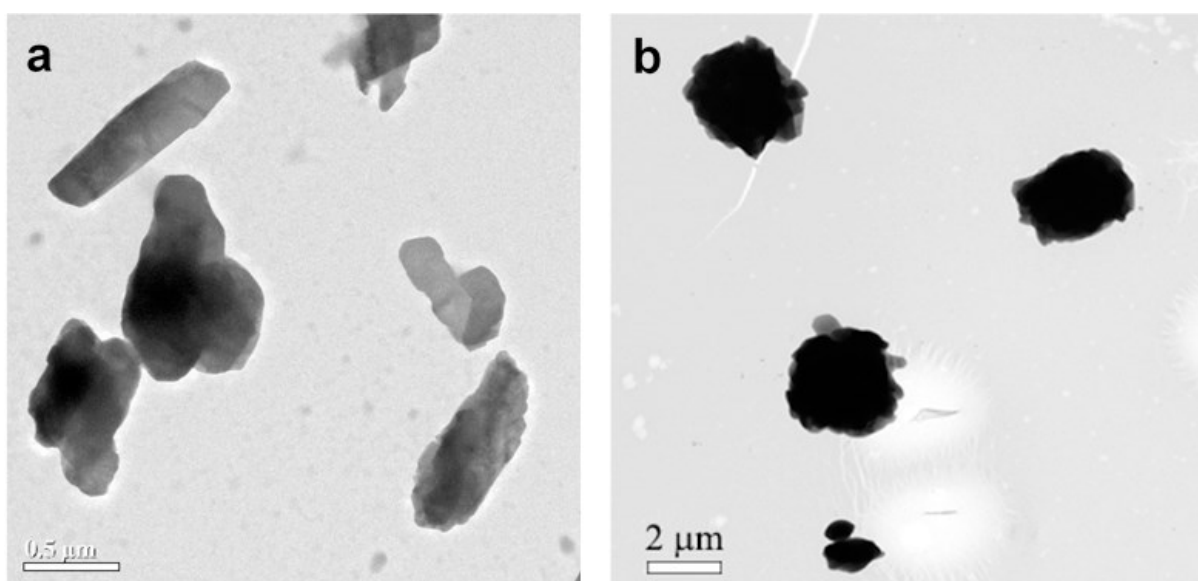


Figure S5. TEM micrographs of a) Coral Red C pigment uncoated; and b) coated using all-PS Janus. (The all-PS Janus used here was prepared using 16% (by weight) DVB cross-linker relative to the seed particles.)

Encapsulation of calcite particles using Fluor-FF Janus

Calcite particles (Omyacarb 10) were encapsulated as follows. Omyacarb white powder (0.25 g) was mixed with a latex containing Fluor-FF Janus (5 g) and water (5 g) in a glass scintillation vial to produce a white dispersion. This dispersion was further dispersed in a sonic bath (Branson) for another 2 minutes. The final dispersion was centrifuged and washed with water before characterization.

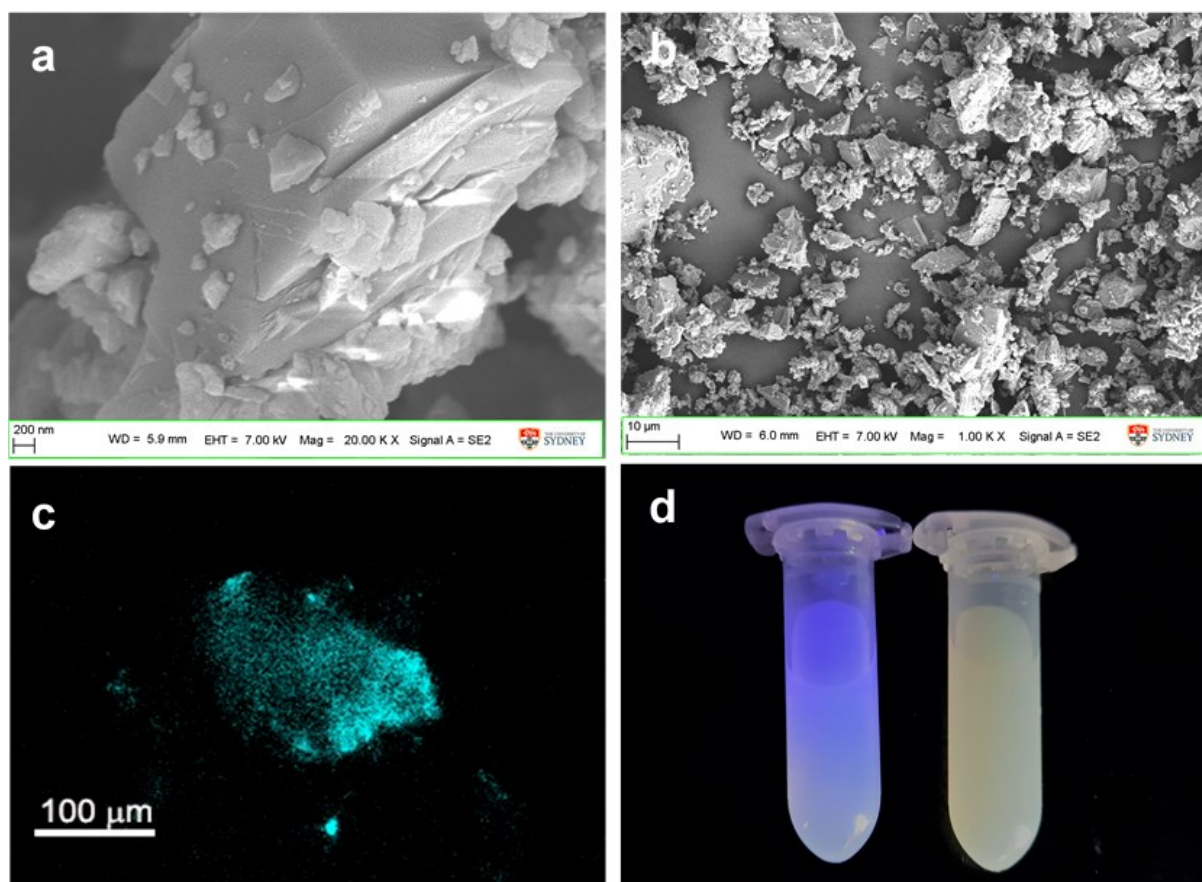


Figure S6. SEM micrographs of a & b) plain Omyacarb 10 calcite particles; c) fluorescence confocal micrograph of a calcite particle coated in Fluor-FF Janus under 405 nm laser light; e) Suspension of Fluor-FF Janus nanoparticles (left) and PS seed nanoparticles under 365 nm UV light.

As shown in SEM micrographs in Figure S6a and b, calcite particles used in this work were crystalline in structure and polydisperse in size. The mean particle size stated by the supplier

is 10 microns, but we observed particles ranging from 100 nm to 50 microns. The coating of the calcite particles by FF Janus particles was visualized by the incorporation of fluorescent monomer PyMMA during the seed crosslinking step. As shown in Figure S6d, Fluor-FF Janus latex strongly emitted purple color under 365 nm UV light while PS seed particles did not. By confocal microscopy, it was found that calcite particles emitted a blue-green color under laser excitation at 405 nm wavelength (Figure S6c) after dispersion in Fluor-FF Janus. The image confirmed the presence of Fluor-FF Janus on calcite in its dispersed state.

Once dried, the surface morphology of the coated calcite was observed by SEM (Figure S7a, b): as in the case of titanium dioxide, MWCNTs and the Coral Red C pigment, the coated surface is bumpy, due to the protrusion of the hard PS lobe. By TEM (Figure S7c), the encapsulating polymer shell thickness on the examined particle was found to vary between 5 nm to 30 nm. SEM and TEM micrographs showed that FF Janus were very effective to completely seal the calcite particles including sharp edges and holes on the surface. Some of the protruding polymer bumps are larger than the size of a single crosslinked seed. These bumps probably result from the adsorption of aggregates or multilayer packing in some areas. FF Janus aggregation was expected in the presence of calcite, due to Ca^{2+} cations in the water phase.

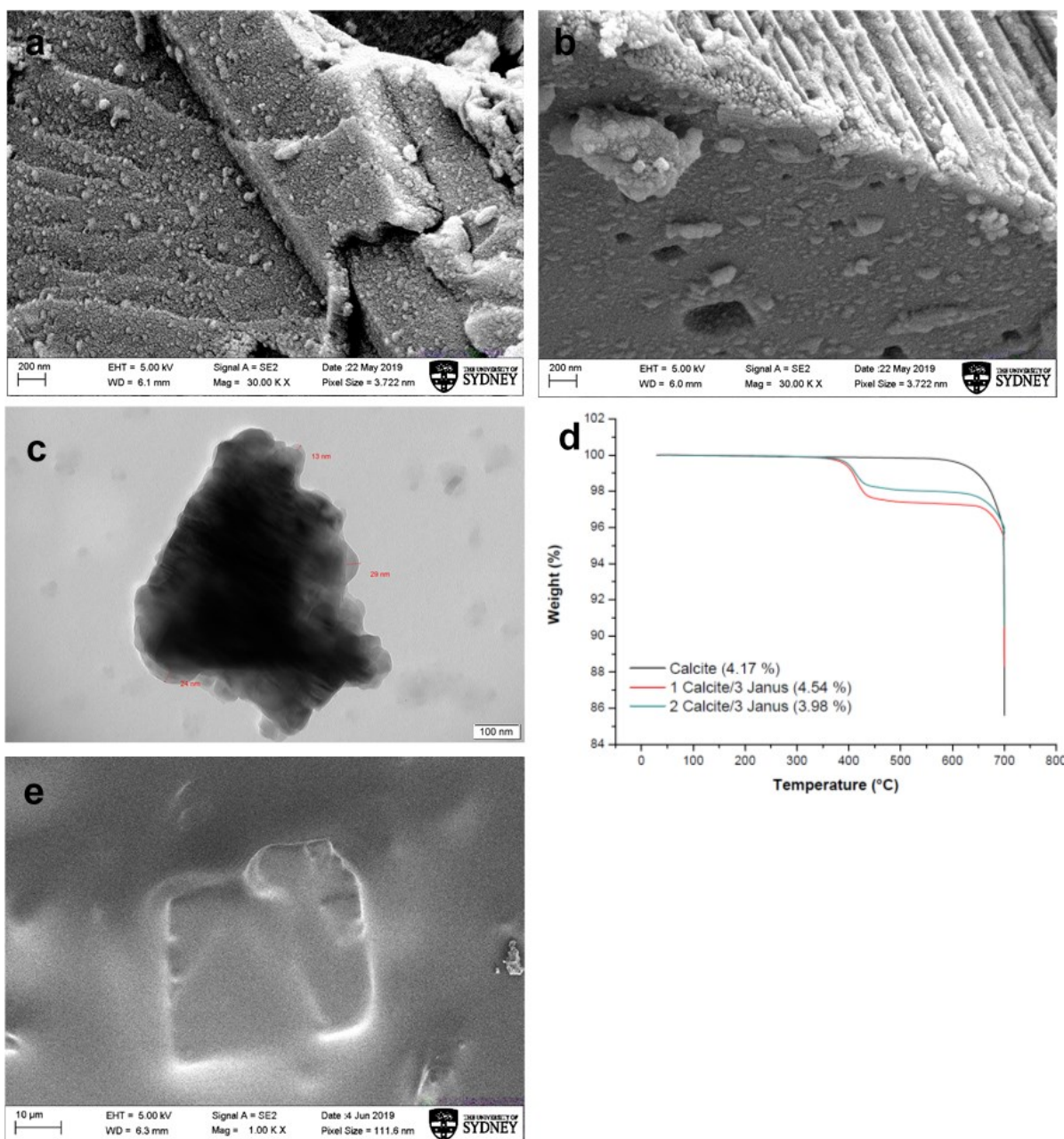


Figure S7. SEM micrographs (a, b), TEM micrograph (c) and TGA analysis (d) of polymer coated calcite particles using Fluor-FF Janus. (e) SEM micrograph of Fluor-high-solids-FF Janus coated calcite.

Encapsulation of calcite particles for blue food dye stain resistant film using Fluor-high-solids-FF Janus

The Fluor-high-solids-FF Janus was used in the preparation of stain resistant film. Calcite powder (Omyacarb 10, 20 g) was first dispersed in the Fluor-high-solids-FF Janus latex (30 g latex, 9.6 g polymer) at 1,000 rpm for 5 minutes using an IKA (Labortechnik) overhead mixer with a two-blade impeller to produce a viscous white paste. A commercial binder (50 g latex, 23 g polymer, AcronalEco 7603, Dow Chemical) was blended with the paste at 2,000 rpm for another 5 minutes. After mixing, roughly 10 mL of the white blended material was transferred onto the surface of a Leneta card (Leneta Com. Inc). A white wet film was produced after drawing down the blend using a 50-micron drawdown bar coater (Sheen). The Leneta card was left drying at 50 °C in an oven over 24 hours prior to the blue food dye (Queen) stain testing. The polymer film was hazy white. Calcite content in the dry film was calculated to be 38 wt.%. A dry polymer film was prepared in the same manner but on a glass slide for SEM characterization

The stain resistance test was carried out as follows. A paper towel ribbon (1 × 3 cm) was placed on polymer coated Leneta card. Blue dye was applied on the ribbon and left at room temperature (approximately 25 °C). After 1 hour, the ribbon was removed, and the stained area was wiped with paper towel. Excess dye was further removed by applying Ajax Spray and Wipe three times followed by wiping with paper towel. Stain appearance was recorded by camera and compared with standard film (Figure 6e).

The sealing effect was further confirmed by SEM in Figure S7e in which a very large calcite crystal with dimension of approximately 50 × 50 micron can be seen fully covered by the polymer film. The polymer coating significantly reduces access to the hydrophilic diffusion pathways made by the calcite, leading to great improvement in stain resistance.

Table S3.

Pigment	Particle size*	Surface property	Thickness of FF Janus coating (nm)	Information on the pigments used for encapsulation
R706 TiO ₂	302 ± 1 nm	Negative (at pH = 8)	10 - 30	
DPP Coral Red C	0.3 - 2 μm	Hydrophobic	10 - 40	
Calcite	0.1 - 50 μm	Positive (at pH = 10)	5 - 30	
MWC nanotubes	10 - 60 nm	Hydrophobic	6 - 100	

*The hydrodynamic size of TiO₂ was obtained from DLS. The size of the other particles was obtained from TEM micrographs.

AFM micrographs of Janus nanoparticles

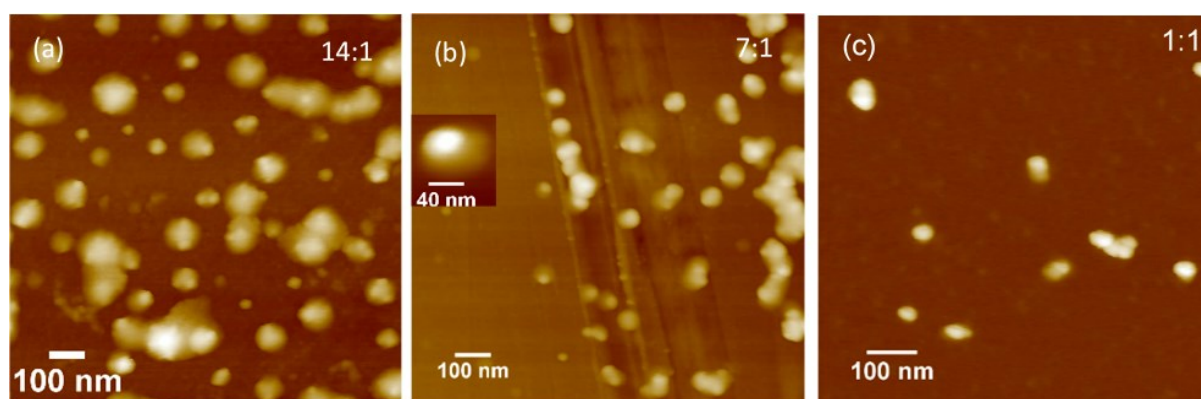


Figure S8. AFM micrographs of film-forming Janus nanoparticles with soft P(MMA-*co*-BA) lobes and hard crosslinked PS seeds synthesized at different ratios of P(MMA-*co*-BA) and PS. The P(MMA-*co*-BA)/PS ratio is 14/1 for (a), 7/1 for (b), and 1/1 for (c). The sample in (b)

has higher solids content (32%) FF Janus compared to the one in Figure 4. Particle suspensions

Synthesized FF Janus nanoparticles	Particle height* by AFM (nm)	Average size by DLS (nm)	PDI from DLS	were deposited on hydrophilic silicon surfaces and imaged in air.
P(MMA-co-BA) : PS= 1:1	17 ± 4	38	0.7	
P(MMA-co-BA) : PS =7:1	20 ± 3	33	0.4	
P(MMA-co-BA) : PS = 14:1	24 ± 3	45	0.27	

Table S4. Size of the synthesized FF Janus as a function of different ratios of P(MMA-co-BA) and PS as obtained by AFM and DLS.

*Particle height: the particle height refers to the hard PS lobe.

Surface tension measurements

The surface activity of all particle dispersions and pure SDS solution were determined by pendant drop method using a KSV CAM 200 goniometer. To get the surface tension of an SDS solution as a function of SDS concentration, the same stock SDS solution (77.1 mM) was diluted by cross-linked spherical polystyrene seed particles, PS Janus particles, FF seed

particles, and FF Janus particles, as well as Milli-Q water. All particle dispersions contained 1 wt.% solids.

Table S5. Surface tension of the seed and Janus particle suspensions in milli-Q water

Particle suspension	Surface tension (mN/m)
PS seed	66.3 ± 0.3
PS-Janus	67.6 ± 0.4
FF-Janus	66.6 ± 0.6

Calculation of adsorbed SDS

The calculation of SDS absorbed on the surface of the particles is described below. For simplicity, all particles are considered spherical, and particle size was derived from DLS results.

SDS absorption (mol/m²)

= (CMC of SDS in the presence of particles - CMC of SDS) × volume of suspension (SDS plus particles) / surface areas of all particles in the suspension

The surface area of all particles in the suspension was calculated using the equation below:

$$S_p = N_p \times 4\pi r^2 = 3w/(r\rho)$$

where N_p is the number of particles in the sample, w is the latex weight, r is the particle radius and ρ is the mass density of the polymer in the particles. The diameter of the particles was measured by DLS, as shown in Table 1. The density of polystyrene particle was assumed to be 1.05 g/cm³. The density of film forming particle was assumed to 1.10 g/cm³.

Gel permeation chromatography method

Gel permeation chromatography (GPC) was performed using UFLC Shimadzu Prominence system comprising a DGU-20A degasser, a LC-20AD pump, a SIL-20A HT automatic injector, a CTO-20A column oven, a RID-10A refractive index detector, a RF-20A fluorescence detector and a SPD-M20A Diode array detector Shimadzu UV/vis detector. A 50 x 7.8 mm guard column and two 300 x 7.8 mm linear columns (10^4 and 10^5 Å pore size, 5 µm particle size) were used for the analyses. *N,N'*-dimethylacetamide (DMAc) (HPLC grade, 0.05% w/v of 2,6-dibutyl-4-methylphenol (BHT), 0.03% w/v of LiBr) with a flow rate of $1 \text{ mL} \cdot \text{min}^{-1}$ and a constant temperature of 50 °C was used as the mobile phase, with an injection volume of 50 µL. The unit was calibrated using commercially available linear poly(methyl methacrylate) standards (0.5 - 1000 kDa, Polymer Laboratories). The samples $4 \text{ mg} \cdot \text{mL}^{-1}$ were dissolved in 2 mL of DMAc and filtered through 0.45 µm PTFE filters.

Sample preparation for GPC

Carboxylic acid groups of the copolymers were modified into methacrylate units using trimethylsilyldiazomethane as a methylating reagent. A total of 4 mg of each sample was dissolved in 2 mL of THF at room temperature. The yellow solution of trimethylsilyldiazomethane in hexane was added dropwise at room temperature into the polymer solution. Upon addition, bubbles (nitrogen) appeared and the solution became instantaneously colorless. Addition of the methylation reagent was continued until the solution became yellow and no more gas formation was observed. Then, an excess of methylating reagent was added, and the solution was stirred overnight at room temperature. The solvent was then removed under reduced pressure and the methylated polymer was used for GPC. It is noted that the polymer latex was neutralized using HCl 0.2 M prior to drying, methylating and subsequent dissolution in the DMAc for GPC.

NMR Spectroscopy

¹H-NMR spectra were recorded using a Bruker ACF300 (300 MHz) spectrometer, with (CD₃)₂SO used as a solvent. All chemical shifts are stated in ppm (δ) relative to tetramethylsilane, referenced to the chemical shifts of residual solvent resonances (1 H). The number of scans was 16 as the default for all polymer samples. Monomer conversion of macro-RAFT copolymers were determined using ¹H-NMR.