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Supplementary Materials

Compressible Colloidal Clusters from Pickering Emulsions and Their DNA Functionalization

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Materials and Methods

Materials

Styrene (previously filtered with inhibitor remover, 99%, Sigma-Aldrich), potassium persulfate (KPS, 95%, Samchun), sodium chloride (NaCl, 99%, Junsei), tetrahydrofuran (THF, 99%, Sigma-Aldrich), hexafluorobenzene (HFB, 99.5%, Sigma-Aldrich), dichloromethane (DCM), triethylamine (TEA), methanesulfonyl chloride (MsCl), dimethylformamide (DMF), sodium azide (NaN_3), methanol (MeOH), diethyl ether, hydrochloride acid (HCl), polystyrene-*b*-poly (ethylene oxide) diblock copolymer (PS-*b*-PEO, Mw=6,900 g/mol, PS=1,300 g/mol, and PEO= 5,600 g/mol), deionized water (DI water). Customized oligonucleotides are dibenzocyclooctyne-amine (DBCO)-Cy3-*TTT TTT TTT TTT TTT TTT CCTCC* and DBCO-Cy5-*TTT TTT TTT TTT TTT TTT GGAGG* (Integrated DNA Technologies, Inc.).

Methods

Preparation of Polystyrene particles

Polystyrene particles were synthesized using surfactant-free emulsion polymerization under a nitrogen atmosphere. 0.03 g of NaCl, 2 ml of styrene, and 18 ml of DI water were added into a 3-necked round bottom flask equipped with a condenser. The reactor was gradually heated to 70°C with a stirring using a magnetic stirrer at a speed of 500 rpm. To start polymerization, 0.02 g of KPS dissolved in 2 ml of DI water was added into the reactor. The reaction was carried out for 20 hours. After the reaction, the PS particles were washed several times with DI water using centrifugation and re-suspended in DI water.

Incorporation of PS-b-PEO-N_3 into Polystyrene particles

PS-*b*-PEO-N_3 was prepared using a previously reported method.[1] Briefly, we activated the hydroxyl groups of PS-*b*-PEO and reacted with NaN_3 to make azide functional end groups. Then, we incorporated the PS-*b*-PEO-N_3 into PS particles using the swelling/deswelling method. First, 100 µL of 1 mM PS-*b*-PEO-N_3 solution, 50 µL of PS particles (10% w/v), and 250 µL of DI water were mixed in a microcentrifuge tube. Then, 200 µL of THF was added to the suspension and the mixture was shaken vigorously for 40 minutes (swelling step). During the swelling step, the hydrophobic PS block of PS-*b*-PEO-N_3 penetrates into the surface of PS particles while the hydrophilic PEO-N_3 brushes remains in water phase. Then, 1 mL of DI water was added to mixture to decrease the fraction of THF below 10% (deswelling step). As a result, the PS block is physically trapped inside the particles. The block copolymer coated PS particles were washed at least three times with DI water using centrifugation.

Clustering of azide(N_3*)-functionalized PS Particles*

We added 100 μL suspension of azide-functionalized PS particles (1% w/v) into 3 mL of DI water first followed by 300 μL of HFB. The mixture was emulsified using a probe-type ultrasonic with 30% ultrasonic amplitude for 10 seconds (VCS-750 Vibra Cell Ultrasonic, Sonics & Materials Inc.) After the emulsification, HFB oil droplets were gradually removed using rotary evaporator under a vacuum (50 mBar) for 15 minutes at room temperature (Rotavapor R-210, Buchi). Azide-functionalized PS particles on the surface of HFB droplets form various size of clusters after the HFB droplets disappear completely.

Fractionation of clusters using density gradient centrifugation

To fractionate different sized clusters, we used density gradient centrifugation technique. The gradient medium (5-60% of glycerol solution) was prepared in 15 ml glass tube using a gradient mixer. Suspension of clusters (400 μl) was loaded carefully on the top of gradient solution. The sample was centrifuged for 30 minutes at 1300 RCF. We confirmed discrete bands and collected them separately. The collected clusters were washed carefully with DI water several times.

DNA coupling with azide group on PS particles using click chemistry

We redispersed the clusters in 40 μl of TE buffer (pH 8, salt concentration was adjusted to 150 mM with NaCl). 10 μl of 100 μM DBCO-modified DNA strands was added into the cluster suspension. The sample was shaken at a speed of 1000 rpm for 24 hours. After the DNA coupling reaction, DNA-coated clusters were washed with DI water several times.

Surface Evolver Simulations

We used Surface Evolver package, developed by Kenneth Brakke [2,3], to simulate the cluster formation of colloidal particles anchored at emulsion interface. The simulation code we used in this study was originally developed by Lauga et al.[4] Interfacial tension of emulsion drops was set to 1, whereas that of particles exposed to a continuous phase was set to 30. The high interfacial tension of particles prevents the deformation during the calculation. To satisfy Young's relation at the triple line for a contact angle of 30°, the interfacial tension of particles exposed to water was set to 30.707. Four particles were lined up along the emulsion interface as observed under optical microscopy. The particle volume was set to 0.015625 (= 0.253), whereas the initial volume of emulsion drops was set to 1. To impose a hard-sphere interparticle potential, interparticle interaction energy was set as follows:

$$U_r = e^{10\left(1-\frac{r_{cc}}{d}\right)},$$

where r_{cc} is the center-to-center distance between two particles and d is the diameter of particles. Surface Evolver minimizes total energy of the system through iteration by a gradient descent method, where the total energy includes interfacial energy and interparticle potential. To simulate the assembly of particles at the interface of shrinking drop, the volume of emulsion drops was reduced in a factor of 0.1 at each step and a new configuration with minimum total energy was obtained.

References

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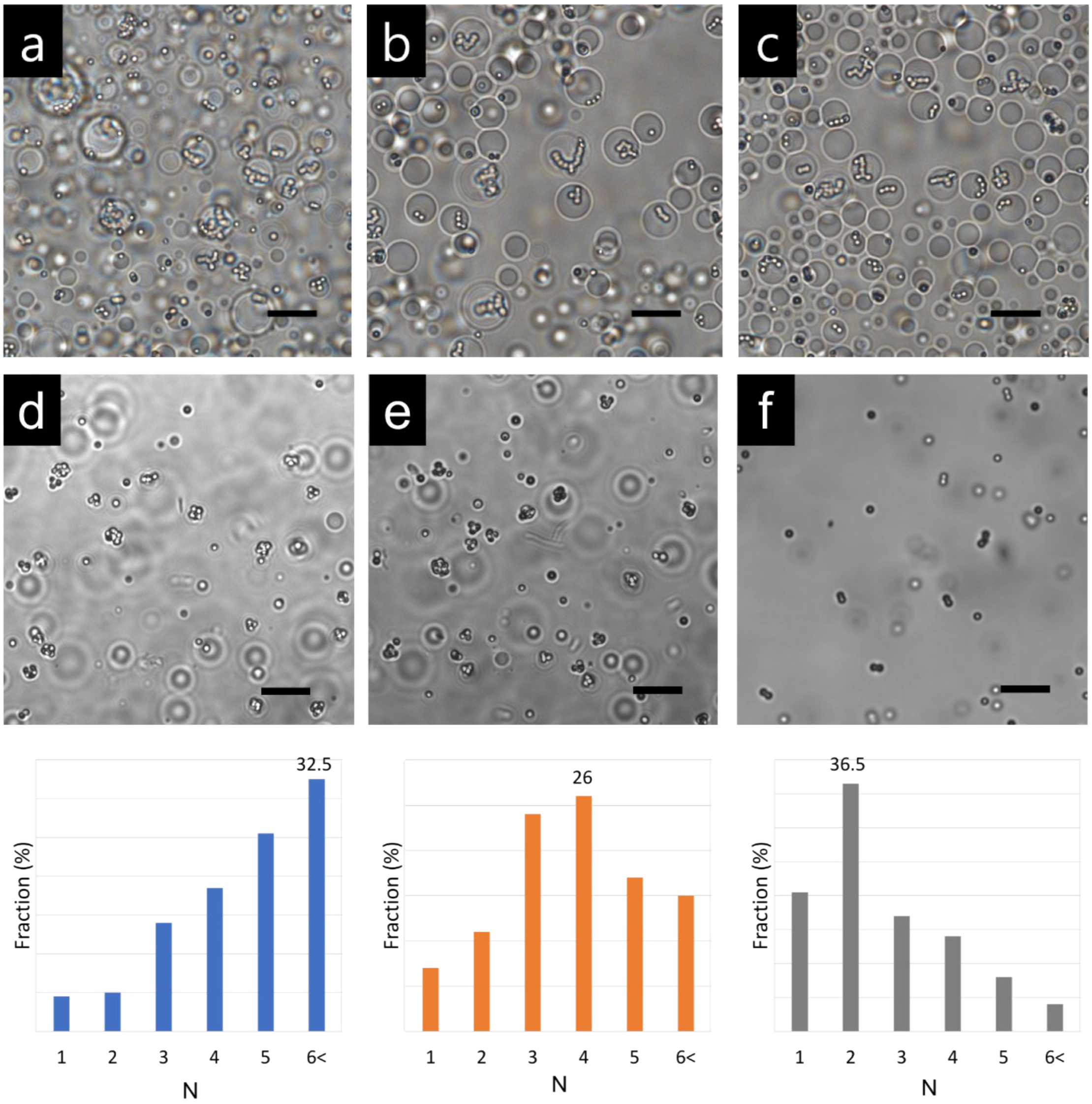

Figure S1. (a-c) Optical micrographs of HFB-in-water emulsions with PS particles, which were prepared by ultra-sonication for (a) 3, (b) 10 and (c) 30 seconds and (d-f) colloidal clusters from emulsions in (a), (b), and (c) after the evaporation of HFB. Bottom panel of (d-f) shows corresponding statistical distribution of the number of constituent particles in colloidal clusters. Scale bars are 10 μm.