Supporting Information for

Synthesis and assembly of colloidal particles with sticky dimples

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Experimental section

Materials

Styrene(99.9 %, Aldrich) and 2,2'-Azobis (isobutyronitrile) (AIBN, 99.9 %, Aldrich) were used as monomer and initiator, respectively, without further purification. Ethanol(Aldrich, 99.9 %), methanol(Aldrich, 99.9 %) were used as solvent. Polyvinylpyrrolidone (PVP, MW = $3x10^5$ g/mol, Junsei) was used as stabilzer for polymer particles in dispersion polymerization and decane (Aldrich) were used as oil phase.

Preparation of polystyrene particles by dispersion polymerization

Syrene monomer was passed through a neutral alumina column to remove inhibitors before use. Mixture of ethanol and deionized water was poured in round bottom flask with three necks mixture and heated up to 70 °C in oil bath while it was stirred with magnetic bars at 500 rpm. Then, PVP was dissolved in mixture. After it was purged with nitrogen gas, styrene monomer was added and then initiator (AIBN) was added in half an hour. Reaction mixture was kept stirred for 12 hours. Particles were washed by centrifugation at 3000 rpm and re-dispersion in ethanol three times. Typically, for 1 μm polystyrene particles, 30 g of ethanol and 3.6 g of water were mixed and 0.6 g of PVP was dissolved. Then, styrene monomer (2 g) was added into reaction flask. After dissolving 0.08 g of initiator in 2g of ethanol, it was added into reaction medium. For 2 μm polystyrene particles, mixture of 30.2 g of ethanol and 3.4 g of water was used as reaction medium with 0.288 g of PVP. 6 g of styrene and 0.048 g of AIBN was used as monomer and initiator, respectively. For 3 μm polystyrene particles, 33.6 g of ethanol was used as reaction medium with 0.3 g of PVP. Same amount of styrene and AIBN was used as in 2 μm polystyrene particles.

Preparation of dimple PS particles by temperature-controlled swelling process

Typically, 0.1 g of polystyrene microspheres (3 μm, 25 wt%) were dispersed in the 5 g of mixture of water and methanol (60 %) with 0.05 g of surfactant (F108) and 0.1 g of decane was added. While it was kept stirred, temperature was increased up to 60 °C and kept for 6 hours in double jacket reactor. Then, solution was cooled down to predetermined temperature.

Crater-like dimple particles and their assembly with spheres forming snowman-like clusters

Typically, 7ul of dimple particles (10 wt%) with 3ul of spherical PS particles(10 wt%) were dispersed in the 100ul of water with 4ul of surfactant (F108, 5 wt%) and 4ul of TMAH was added. Then, 100 μl of PEG (MW=600 g/mol, 10 wt%) solution and 10 μl NaCl(50 mmol) solution was added.

Characterization

Particle morphology was determined by field-emission scanning electron microscopy (FE-SEM, Hitachi S-4800, Zeiss Ultra Plus) and transmission electron microscopy (TEM, 200k, FEI). Dynamic behavior of dimples or dumbbells was observed under optical microscopy (Eclipse Ti, Nikon) with CCD camera (CoolSNAP EZ, Photometrics).

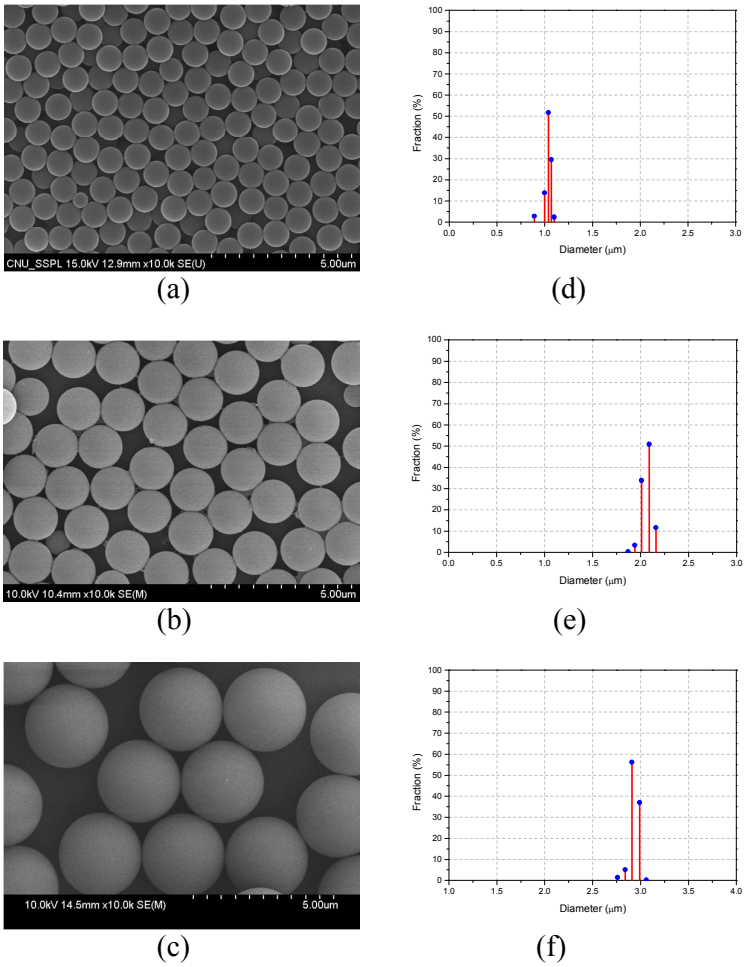
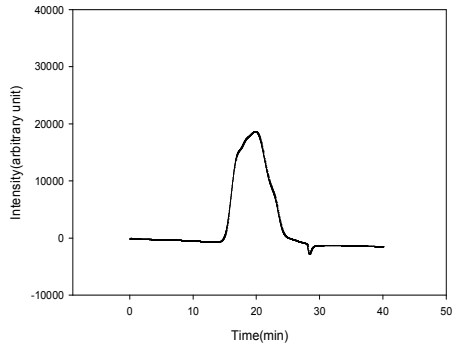
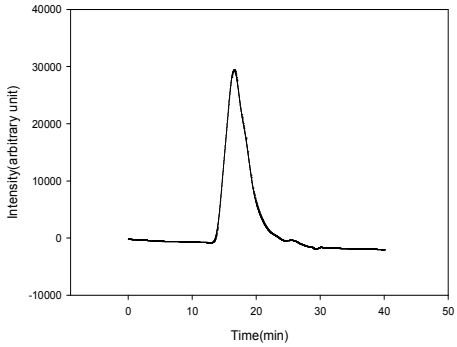


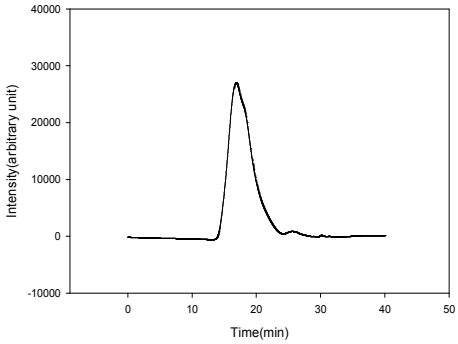
Figure S1. SEM images of polystyrene microspheres with (a) 1 μm, (a) 2 μm, and (c) 3 μm in diameter by dispersion polymerization with PVP (MW=300 kg/mol). Size distributions of polystyrene microspheres with (d)1 μm, (e) 2 μm, and (f) 3 μm in diameter by measuring (a) 573, (b) 906, (c) 594 particles on SEM images, respectively.



(a)



(b)

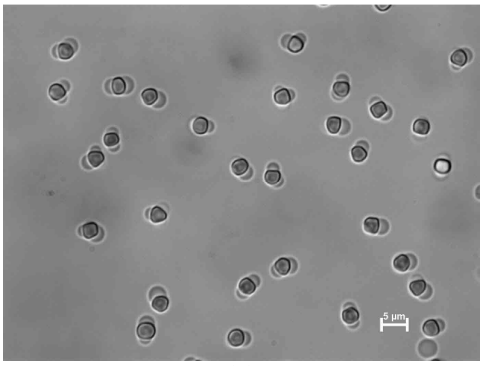


(c)

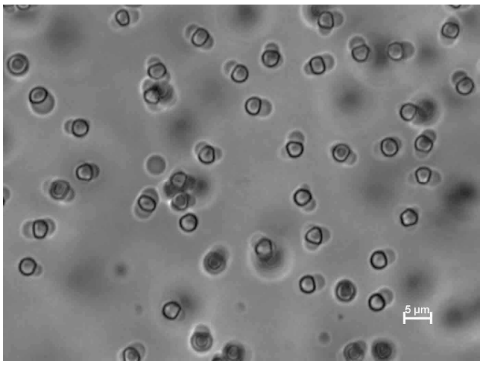
Figure S2. Molecular weight distributions of polystyrene microspheres with (a) 1 μm, (b) 2 μm, and (c) 3 μm in diameter by gel permeation chromatography(GPC).

Table S1. Molecular weight distributions of polystyrene microspheres by gel permeation chromatography(GPC).

Styrene	Ethanol	Water	AIBN	PVP	Size	M_n	M_w	Polydispersity(=M_w/M_n)
2.0g	32.0g	3.6g	0.080g	0.600g	1μm	13291	49309	3.7099
6.0g	30.2g	3.4g	0.048g	0.288g	2μm	50422	174193	3.4547
6.0g	33.6g	0.0g	0.048g	0.300g	3μm	36935	117364	3.1776



(a)



(b)

Figure S3. SEM images of polystyrene particles (3 µm) after swelling and deswelling process in (a) water – methanol mixture (b) water – ethanol mixture

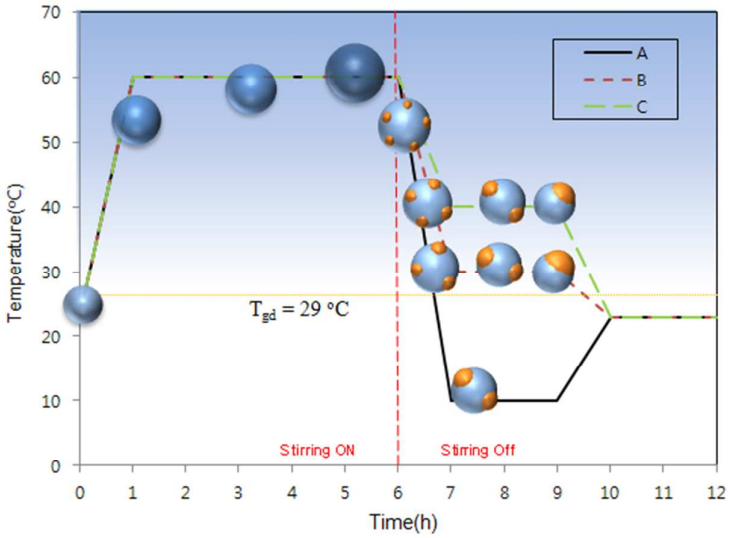
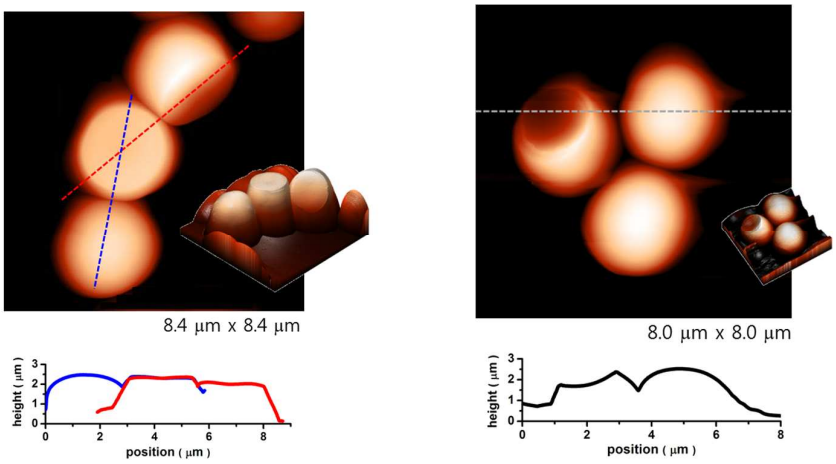
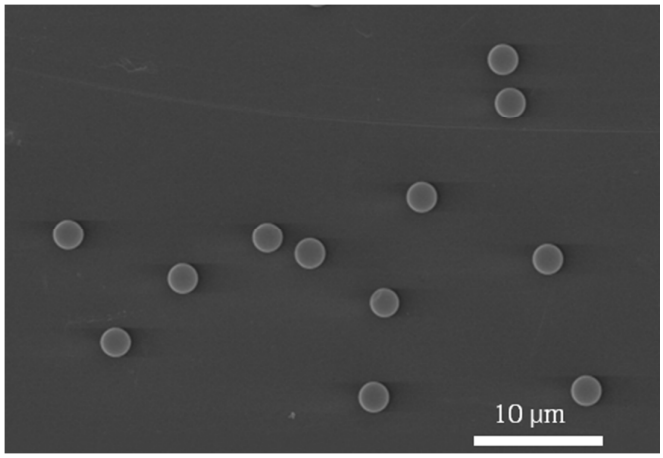


Figure S4. Morphological evolution of polystyrene particles (3 μm) with dimples in temperature-controlled swelling and deswelling process in the water-methanol mixture. The heating-cooling path can be programmed (D-E) to obtain different particle morphologies

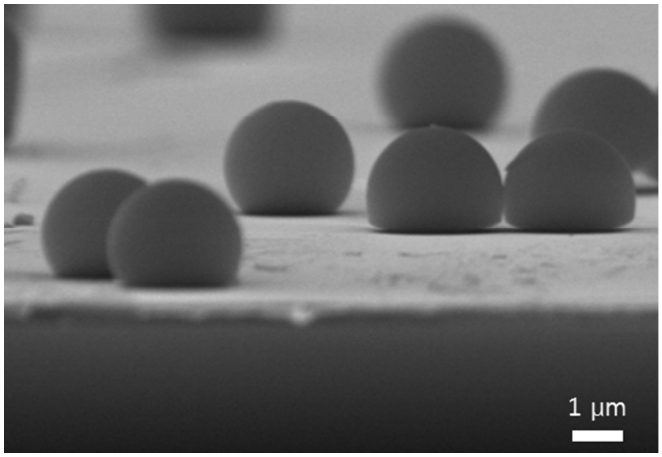


(a) (b)

Figure S5. Topographic images and height profiles of dimple particles with (a) flat and (b) crater-like cavities.

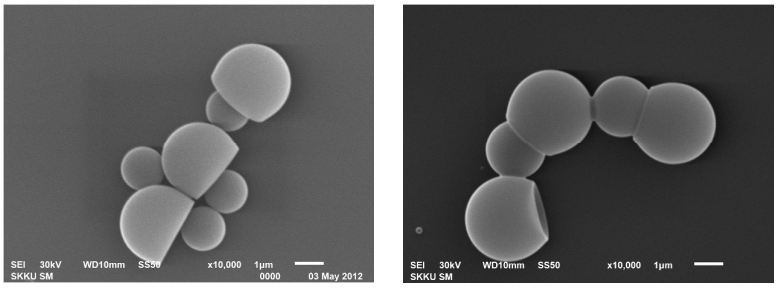


(a)



(b)

Figure S6. (a) Top-view and (b) side-view SEM images of dimple particles on polystyrene films, which was prepared by dipping polystyrene-coated silicon wafer substrate into diluted dimple particle suspension in water (0.5 wt%) for 3 h and washing residue with water.



(a) (b)

Figure S7. Crater-like dimpled particles (3 μm) were assembled with (a) 1-μm, (b) 2-μm PS microspheres.

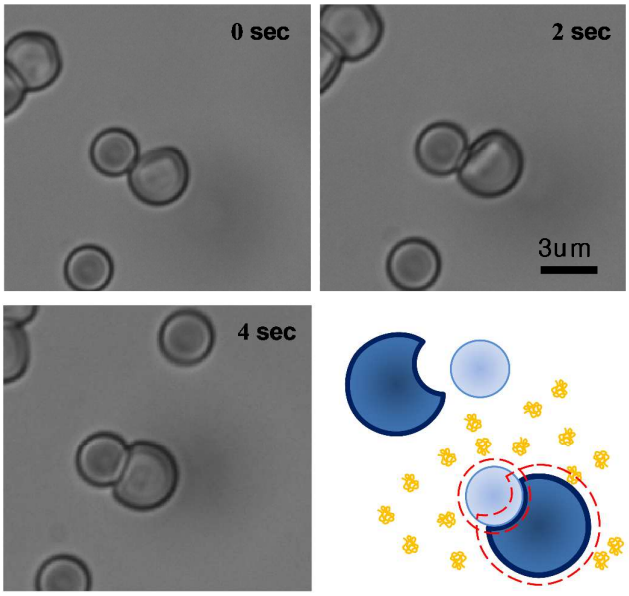


Figure S8. Crater-like dimple particles and their assembly with spheres forming snowman-like clusters.