Electronic Supplementary Information (ESI)

Syntheses and applications of concave and convex colloids with precisely controlled shapes

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S1. The formation of mutil-dimple particle

The concave seed particles are synthesized by a combination of two-stage dispersion polymerizations and a programmed feeding of cross-linker during the synthesis. Briefly, in our synthesis the DVB feeding time (six-hour in total) was divided into three stages: the feeding speed was set at 3 ml/min in the first 2 hours, then slowed to 2 ml/min in the middle 2 hours, and 1 ml/min in the last 2 hours. At the beginning of synthesis process, styrene monomer first formed to spherical particle before the adding of the DVB cross-linker. In the fast feeding DVB process, four dimples are formed as the PDVB scattered around multiple sites of particle surface. Due to steric effect, the arrangement of the four dimples resembles the vertices of a tetrahedral. In the followed slow addition of DVB, the DVB can be timely polymerized (Fig. S1(c)). So the DVB and/or PDVB could be accumulated in one location and ultimately led to the formation of a bigger single-cavity structure together with the previously formed smaller dimples at the latex surface (Fig. S1(d)).

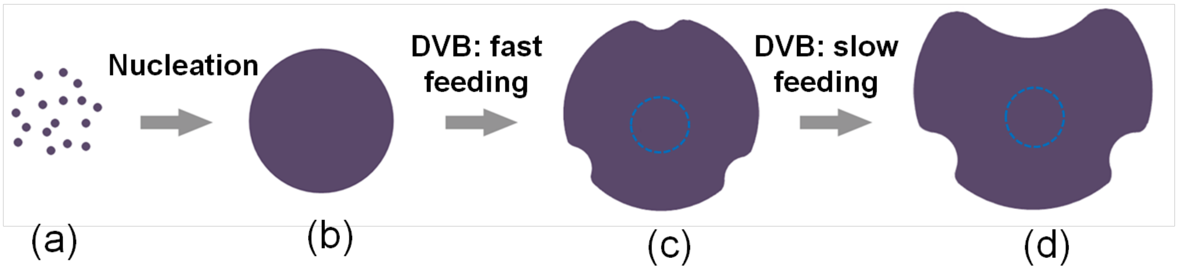


Fig. S1. Schematic of the formation process for multi-dimple particles. (a) styrene monomer; (b) polystyrenen sphere; (c) After fast feeding of DVB, four symmetrically distributed dimples are formed, the one on the backside is shown by the dashed circles; (d) One of the four dimples grows larger due to DVB/PDVB accumulation (see Fig. 2 in the main text for different views of the multi-dimple particle).

S2. The packing of hemispheres on emulsion droplets

On water-hexadecane emualsion droplets, the hemispheres are close packed with their equatorial plane parallel to the water-hexadecane interface (Fig. 6(b) - (d)). The planar orientation of the non-spherical particles at oil-water interface is considered as more energy favorable than other orientations. Fig. S2 demonstrated the difference appearances of hemisphere packings under bright-field microscope. Here we created two types of packings of the hemispheres on flat glass slides, one with spherical part of the hemisphere facing the reader, and one with equatorial plane facing the reader. These two packings were subsequently imaged using the same conditions as that of in Fig. 6. The packing discussed in the main text takes the configuration of (b), as evident from Fig. S2(b) and Fig. 6(b) in the maintext.

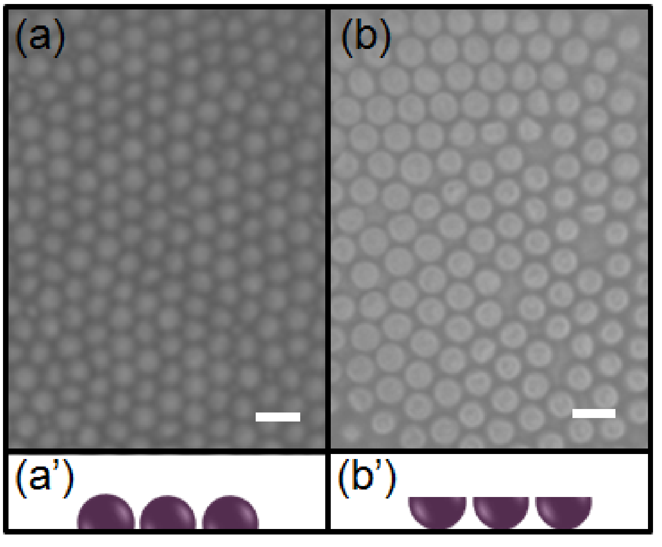


Fig. S2 Two types of hemisphere packings on a glass surface. (a), (b) bright-filed micrographs (top view), and (a'), (b') schematics (side view). Note, in (a) the equatorial plane of the hemisphere is pointing into the paper, while in (b) the equatorial plane is facing the reader. The scale bars are 4 μm.

S3. Atomic Force Microscopy (AFM) and bright-field microscopy images of the multi-dimple particles

Here we show complimentary information on the morphology of the multi-dimpled seed particle with other imaging techniques: AFM and bright-field microscopy. From Fig. S3 and S4, both AFM and bright-field microscopy images clearly shown that there is one large dimple on one side and three small dimples on the other side, which are the same morphology as observed in the SEM images of Fig. 2 (a) and (b) in the main text. In summary, the SEM, AFM and optical microscopy measurements all have conclusively demonstrated the multi-dimple nature of the seed particles.

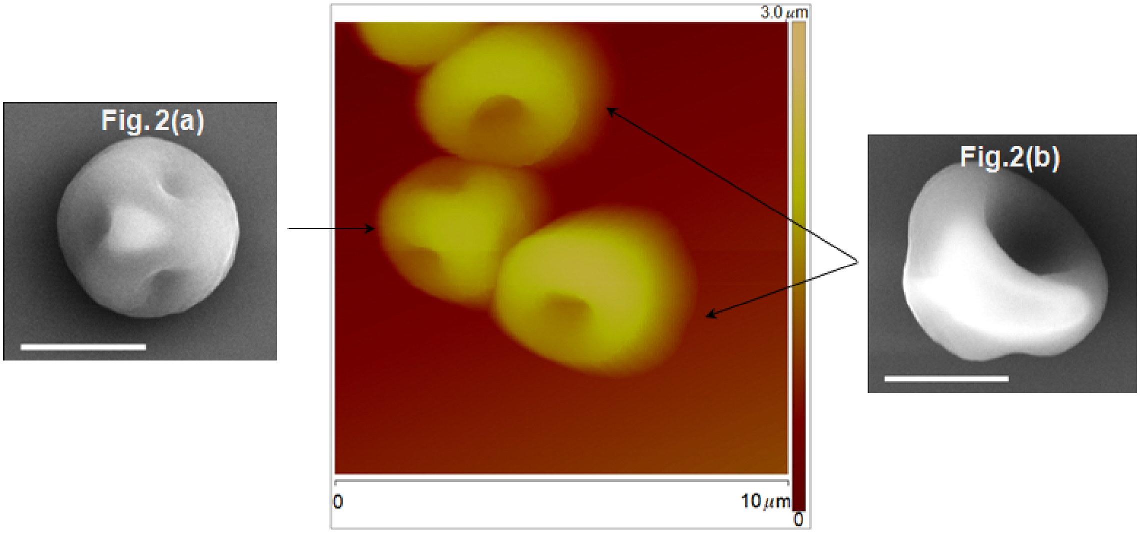


Fig. S3. AFM height images of multi-dimpled seed particles, with different views of the particle. The particle in the middle-left side shows three small dimples, with the large dimple facing the substrate, as in Fig. 2(a); and the other two particles show the large dimples, as in Fig. 2(b). The SEM images from Fig. 2(a) and (b) in the main text are shown here for comparison.

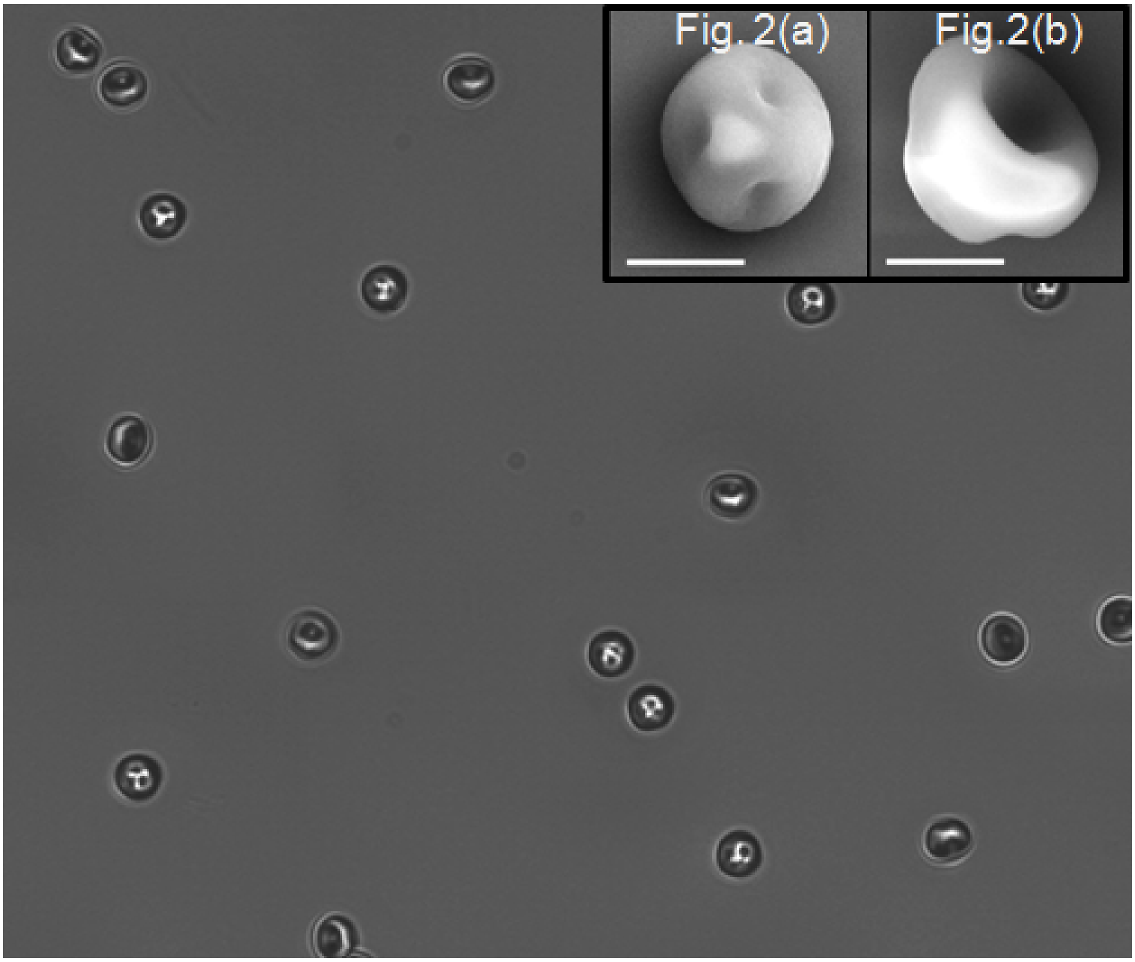


Fig. S4. Bright-field microscopy image of multi-dimpled seed particles, with different views of the particles. Inset, SEM images from Fig. 2 in the main text, for comparison.

S4. The yields of the syntheses, the shape and size distributions of the as-synthesized concave and convex particles

Regarding the yield , we use the following method to estimate the yield of for each type of particle: before and after each reaction, with microscopy, we counted and calculated the number density (number of particle per volume) of seed particle and the resulting non-spherical particle in the reaction suspension. Then from the ratio of the number density before and after polymerization, we worked out how many seed particles have been converted into resulting concave and convex particle, i.e. the yield. The distribution of particle size and shape can be evaluated by image analysis of the SEM micrographs. Due to the non-spherical shape of the concave and convex particles, we choose the maximum length of the particle as a measurement of size, and the ratio of maximum length and minimum length of the particle as an indication of the shape. The yield, shape and size distributions are given in Table S1. The seeded emulsion polymerization methods used in our syntheses gives high yield, and produces particles with narrow size and shape distributions.

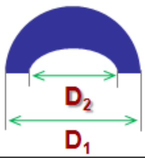
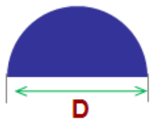
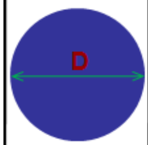
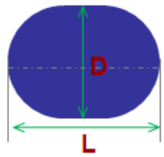
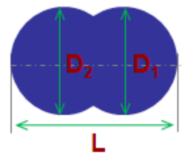
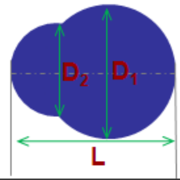
Particle type	Bowl	Hemi-sphere	Sphere	Ellipsoid	Peanut	Snowman
						
Yeild	91%	90%	93%	90%	93%	94%
Size (μm)	D_1= 2.90± 0.053 D_2= 1.68± 0.045	D= 2.93± 0.059	D= 2.94± 0.055	L=3.74± 0.073 D=3.01± 0.062	L=3.99± 0.065 D_1=3.05± 0.056 D_2=2.94± 0.054	L=4.47± 0.063 D_1=3.80± 0.061 D_2=3.06± 0.059
Shape	D_2/D_1= 0.58 ± 0.021	D= 2.93± 0.059	D= 2.94± 0.055	L/D= 1.24 ± 0.044	L/D_1=1.32± 0.035 D_1/D_2=1.03± 0.041	L/D_1=1.17 ± 0.030 D_2/D_1=0.81± 0.025

Table S1. The yield of the syntheses, the shape and size distributions of the as-synthesized concave and convex particles. The errors in size and shape description are the standard deviation from measurements of 50 particles in the SEM images. Each error is directly evaluated from measured value and no error propagation is used in the calculations. The various lengths used in the calculations are indicated in the graphs in the first row.