

Supplementary Information

Synthesis of soft colloids with well controlled softness

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1. Synthesis of soft colloids

The synthesis of the soft colloids proceeds in two steps. In the first step, monodisperse, stable silicon oil-in-water emulsion droplets were prepared by hydrolysis and polycondensation of the 3-methacryloxypropyltrimethoxysilane (TPM) monomer, following the method described by Obey and Vincent.¹ Briefly, 1.5 ml of TPM was added to 30 ml of 0.475 M ammonium hydroxide solution (NH₄OH) under vigorous stirring for 30 min. Then, the emulsion oil droplets were allowed to grow for 10 h at 18 °C on a rolling incubator. It was found that varying the mixing ratio of TPM and NH₄OH had a noticeable effect on the final size soft colloids, whereas their monodispersity was not affected. The detailed recipe is listed in Table 1. And the effect of mixing ratio on the final size of colloid was demonstrated in Figure A1 and Figure A2. In the second step, we synthesize soft colloids with emulsion polymerization. Firstly, 9 ml of 2.2x10⁻³ g/ml sodium dodecyl sulfate solution is mixed with 6 ml of silicon oil droplets emulsion. This mixture, together with different amounts of potassium persulfate (KPS) as initiator, is added to a reaction flask at room temperature (~ 25 °C). Then the temperature of the mixture is slowly increased to 79 °C at a rate of 5 °C/min. During this process, the KPS progressively and slowly decomposes to generate radicals. More importantly, this slow process allows the radicals to diffuse. As a result, the radicals have already diffused into the oil droplets and mixed with monomer, before the majority of the polymerisation takes place at 79 °C. The reaction lasts for 6 h to complete. Longer reaction time yields the same particles. The resulting colloids were obtained after sedimentation and wash for at least three times with DI water.

We have also conducted preliminary experiments to investigate the effect of temperature on the particle syntheses, including (1) temperature ramping rate, (2) temperature that the initiator is added,

and (3) reaction temperature. We found that for either higher ramping rate (e.g. 20 °C/min) or higher initiator adding temperature (e.g. 70 °C), only particles with hard shell are produced. In those cases, the initiator decomposes so fast that many radicals are generated instantly, and they have little time to diffuse into the oil droplets. As a result, these radicals can attack the reactive groups on the droplet surface only, and hence hard shells are formed. Regarding the effect of reaction temperature, we have performed reactions at 50 °C, 60 °C and 70 °C (note: our home-made reaction apparatus, a heated tumbling stage, limits the reaction temperature below 80 °C). We obtain the same hard and soft colloids at those lower reaction temperatures, but with longer reaction time. This is reasonable since in general the lower reaction temperature, the lower polymerization rate.

2. Microscopic observations of soft colloids

Bright-field micrographs were obtained with a 63× objective at room temperature using a Zeiss inverted microscope (Zeiss Observer), equipped with a digital camera (Zeiss HS camera). The synthesized soft colloids were observed with a scanning electron microscope (SEM, Leo 982). SEM samples were prepared by drying 0.1 wt % of cleaned particles on glass cover slip and directly examined without further coating of a conductive layer. All particle sizes and size distribution were determined from the SEM images.

3. Rheological properties of suspension of soft colloids

The viscosity of the suspension of soft colloids with different softness was obtained using rotational rheometer (Mavorn Kinexus pro+). Typically 1 ml of a dilute aqueous suspensions (2% by weight) was loaded on the temperature-controlled sample plate of the rheometer. The cone-plate geometry was chosen to ensure constant shear across the colloidal sample. And a solvent trap was used to minimize any evaporation.

4. The AFM Force-deformation measurements

AFM samples were prepared by drying 0.1 wt % of cleaned particles on glass cover slip. Before starting the force measurements, the soft colloids were imaged in tapping mode, and a well-shaped particle was chosen. By repeatedly zooming in, we carefully located the top of the target sphere. A point load is applied to the particle surface through an AFM tip, and successively increased.² Thus,

we obtained a typical force versus indentation curves (see Fig. A4). This force is zero in the beginning, because the tip does not touch the particle yet. When the tip and the particle comes into contact ('point B' in Fig. A4), the particle starts to deform. At further approaching, the force starts to increase. When the force reaches the preset maximum value of 600nN, AFM stop to apply force. Then, the AFM tip starts to retract ('point A' in Fig. A4). Because the soft-spheres are viscoelastic, there are a hysteresis to AFM tip. The lines do not coincide exactly between approach and retract traces. To obtain force-deformation curve, for a fixed force F , the corresponding deformation is determined by measuring the horizontal distance between A and B in Fig. A4. We record three force curves for each same the results reported are the average of these (Fig. 3a in the main text).

To evaluate the mechanical properties of the soft colloids, A logarithmic plot of the AFM force-deformation curves is obtained (Fig. A5). The force–deformation curve is a line and the slope of the lines is between 1.46 and 1.76, which is close to 1.5 as predicted by the Hertzian power law (Equation A1). The results indicate that is applicable to use the Hertz model for these soft colloids:^{3,4}

$$F = E \frac{4r_{tip}^{0.5}}{3(1-\nu^2)} d^{1.5} \quad (\text{Eq. A1})$$

Where r_{tip} is the radius of the AFM tip, ν the Poisson ratio, E the Young's modulus of the soft-sphere, d stands for the deformation and F is the loading force. In fact, the Hertz model predicts a constant modulus E . we assume the $\nu= 0.5$ basing of the assumption that all particles consist of deformable but incompressible material.⁵ The r_{tip} is 10 nm at our experimentation. According to the equation A1, the Young's modulus of the S1, S2, S3 and S4 particles is 301.2 MPa, 161.9 MPa, 59.0 MPa and 35.7 MPa, respectively. These are between the modulus values of hard silica particles³ and soft microgel particles,² but closer to the microgel.

Table A1 Recipes for the preparations of silicon emulsion oil droplets

| Sample | TPM (ml) | NH₄OH (M) |
|---------------|---------------------|---------------------------------|
| M1 | 0.1 | 0.475 |
| M2 | 0.5 | 0.475 |
| M3 | 1.0 | 0.475 |
| M4 | 1.5 | 0.475 |
| M5 | 2.0 | 0.475 |
| M6 | 0.5 | 0.042 |
| M7 | 0.5 | 0.108 |
| M8 | 0.5 | 0.279 |
| M9 | 0.5 | 0.712 |

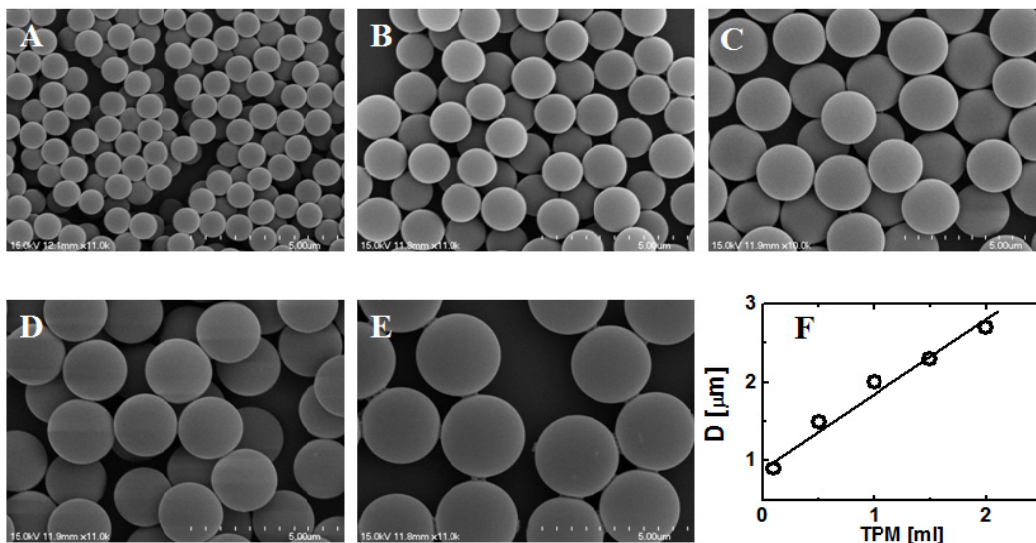


Fig. A1 SEM images of soft colloids when changing the amount of monomer, TPM. The colloids are prepared from oil-in-water emulsion under the conditions of (A) M1, (B) M2, (C) M3, (D) M4, and (E) M5, as listed in Table A1. From SEM images, we determined the particles size and size distribution. All colloids have a diameter polydispersity of 2.8 %. (F) The relation of the particle size with the amount of TPM added.

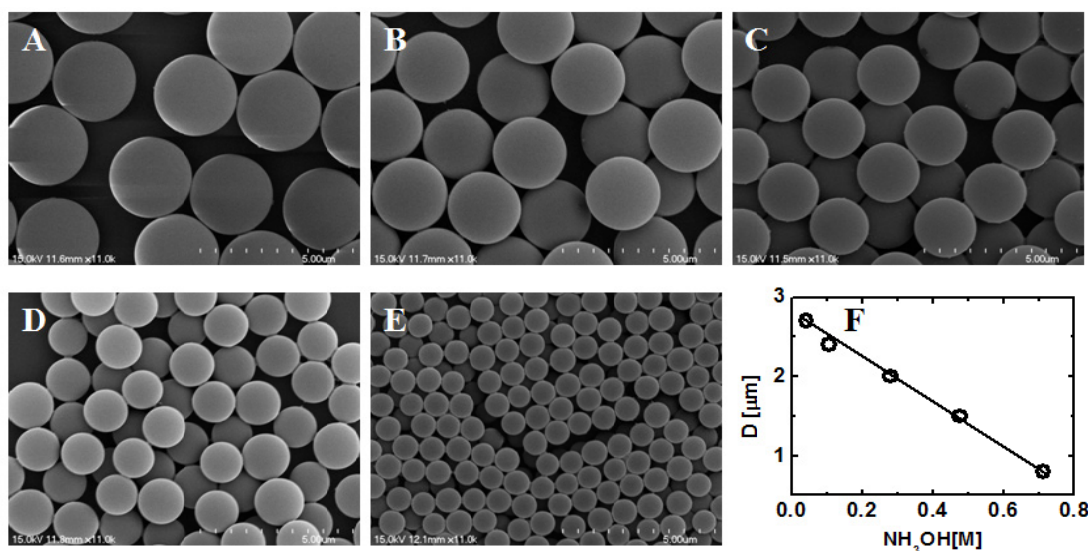


Fig. A2 SEM images of soft colloids when changing the amount of catalyst, NH₄OH. The colloids are prepared from oil-in-water emulsion under the conditions of (A) M6, (B) M7, (C) M8, (D) M2, and (E) M9, as listed in Table A1. From SEM images, we determined the particles size and size distribution. All colloids have a diameter polydispersity of ~2.7 %. (F) The relation of the particle size with the amount of NH₄OH added.

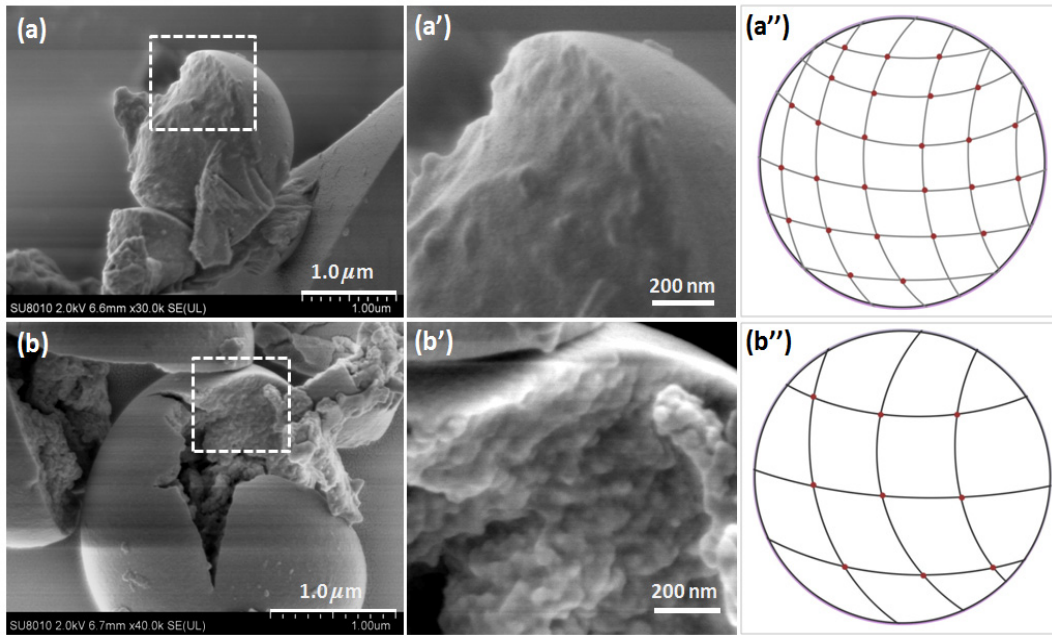


Fig. A3. SEM cross-section analysis for S1 hard colloid (a-a'') and S4 soft colloid (b-b''). For each type of the colloids, the left and middle columns show SEM images with different magnification, and the right column shows the schematic of the polymer networks. The dashed squares in (a) and (b) indicate the enlarged area shown in (a') and (b'), respectively. Note, in either case, there is no evidence of hard-shell formation, as the cross-sections appear uniform from the surface to the interior of the particles.

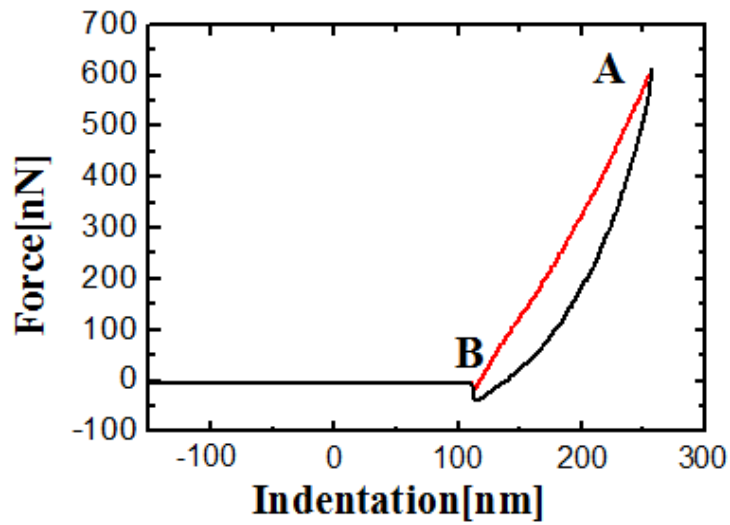


Fig. A4 Typical force-indentation curve of soft colloid. The force is fixed at 600 nN. The red line denotes the approach trace, and the black line denotes the retract trace.

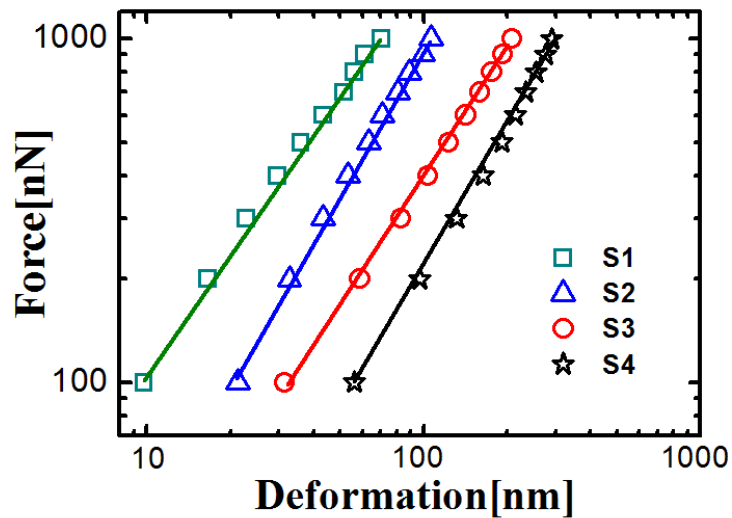


Fig. A5 AFM force-deformation curves of soft colloid. The solid lines show the fits according to equation A1.

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