Supplementary Material (ESI) for Soft Matter

Colloidosomes as Micronsized Polymerization Vessels to create Supracolloidal Interpenetrating Polymer Network Reinforced Capsules

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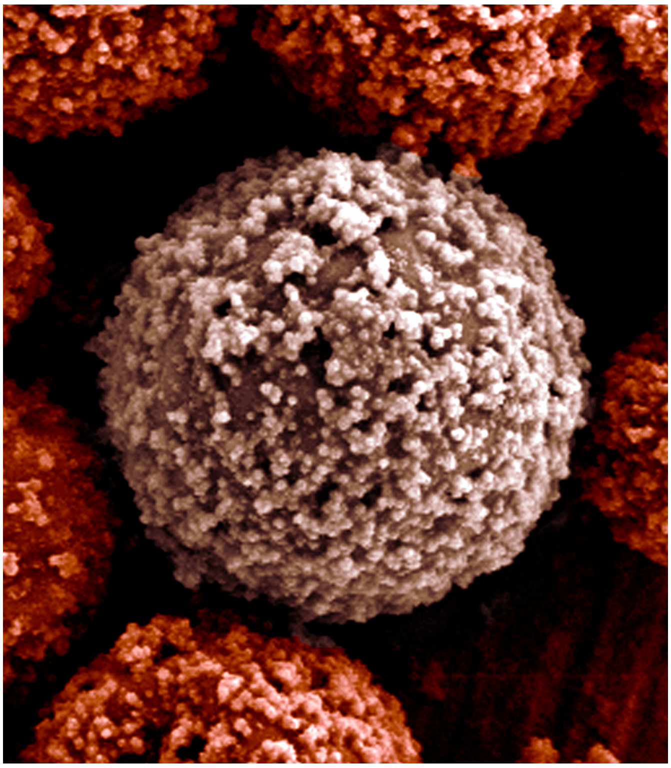
Supplementary Information



Movie BonS1.mov shows a selection of confocal *z*-slice images of a colloidosome, diameter ~180 μm, made by self-organisation of our crosslinked PMMA latex on a hexadecane droplet in water at pH 9 via handshaking. As can be clearly seen the microgel is slighty flocculated, due to its low electrostatic repulsion, but adsorbs excellent on the hexadecane-water interface.

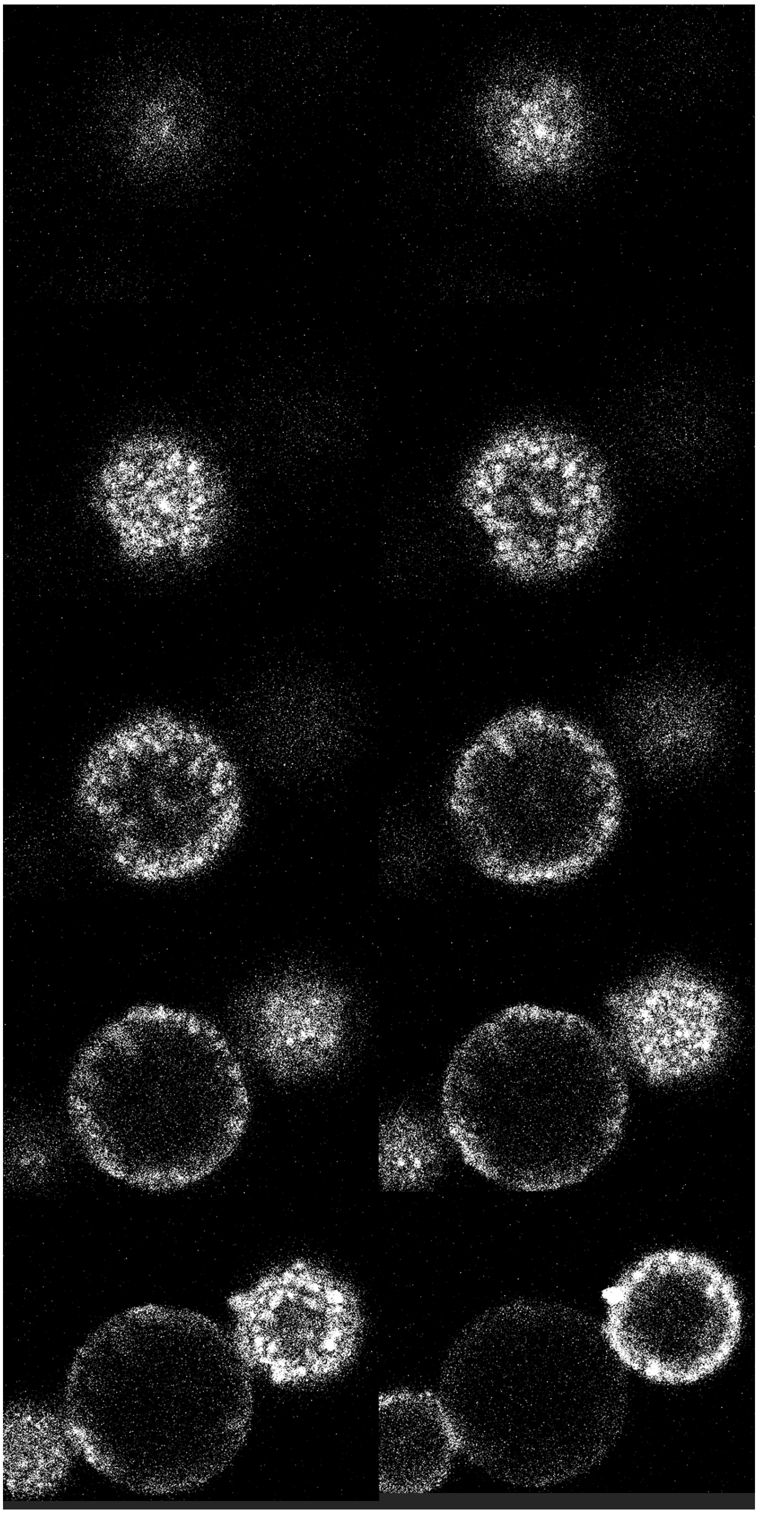


Figure S2. Series of confocal *z*-slices (from top left to bottom right) of polymerized supracolloidal capsules suspended in water in presence of sodium salt bis(2-ethylhexyl) sulfosuccinate (AOT). The diameter of the bright capsule in the bottom right image is approximately 15 μm.

As a crude estimate the colloidosome diameter can be predicted from the following expression:

$$d_{oil} \quad = \quad \pi \cdot Cov \cdot \left(\frac{1}{w_{part}}\right) \cdot \left(\frac{\rho_{part}}{\rho_{oil}}\right) d_{part} =$$

$$\pi \cdot 1.0 \cdot \left(\frac{1}{0.04}\right) \cdot \left(\frac{1.1}{0.80}\right) 0.153 \quad = \quad 16.5$$

In which *Cov* represent the coverage expressed as the ratio of the effective area covered by the building blocks and the total area of the oil droplet, w_{part} is the weight ratio of building blocks used with respect to the amount of oil phase, ρ_{oil} and ρ_{part} being the densities of the oil phase and the building blocks in g cm^{-3}, d_{oil} and d_{part} being the diameters of the colloidosome and the building blocks in µm.

Hereby we have made the following assumptions:

(i) the liquid-liquid interface is fully covered,
(ii) no excess particles in both the water and/or oil phase,
(iii) a 2-D square lateral packing,
(iv) uniform spherical building block and droplet sizes,
(v) building block dimensions negligible with respect to size of colloidosomes.

We start with uniform spherical building blocks and droplet sizes. When we neglect the building block dimensions we can approximate the total surface of the oil droplet with a flat surface, the building blocks half submerged into it.

$$a_{oil} \quad = \quad \pi\, d_{oil}^{2}$$

The area of the building blocks obviously is similar. However the effective area they cover is larger when we assume a 2-D square packing. This area for one building block is:

$$a_{part} \quad = \quad d_{part}^{2}$$

We now need to calculate to total number of oil droplets and the total number of particles, from:

$$N_{oil} \quad = \quad \left(\frac{m_{oil}}{\rho_{oil}}\right) \Big/ \frac{\pi}{6} d_{oil}^{3} \qquad\qquad N_{part} \quad = \quad \left(\frac{m_{part}}{\rho_{part}}\right) \Big/ \frac{\pi}{6} d_{part}^{3}$$

The total coverage can be expressed as:

$$Cov \quad = \quad \frac{A_{part}}{A_{oil}} \quad = \quad \frac{a_{part}\; N_{part}}{a_{oil}\; N_{oil}} \quad = \quad \frac{1}{\pi} \left(\frac{m_{part}}{\rho_{part}}\right)\left(\frac{\rho_{oil}}{m_{oil}}\right)\left(\frac{d_{oil}}{d_{part}}\right) \quad = \quad \frac{1}{\pi} \; w_{part} \left(\frac{\rho_{oil}}{\rho_{part}}\right)\left(\frac{d_{oil}}{d_{part}}\right)$$

When we assume total coverage, *Cov = 1*, and no excess particles we can estimate the diameter of the colloidosomes:

The thickness of the shell, *h*, can be related to monomer conversion, *x*, via the following expression:

$$x = \frac{\dfrac{m_{hex}}{m_{mon}\,\rho_{hex}} + \dfrac{1}{\rho_{mon}}}{\dfrac{1}{\rho_{mon}} + \dfrac{1}{\rho_{pol}}\left(\dfrac{\left[\dfrac{r-h}{r}\right]^3}{1-\left[\dfrac{r-h}{r}\right]^3}\right)}$$

wherein m_{hex} is the mass of hexadecane used in g, m_{mon} is the mass of monomer used in g (assuming all in droplets), *r* is the radius of the capsule, ρ_i are the densities of hexadecane, monomer and polymer in g cm^{-3}. The burst raspberry core-shell capsule shown in Figure 2a has an approximate radius of 15 µm. Its average shell thickness had a value of *ca*. 0.35 µm. Input values for the densities of hexadecane, monomer and polymer of 0.77, 0.91 and 1.1 g cm^{-3} and experimental amounts of hexadecane, styrene and divinylbenzene being 4.017, 0.517 and 0.516 g lead to a calculated monomer conversion of *ca*. 46%.

We assume:

1) building block dimensions negligible with respect to size of capsules

The total volume of a raspberry core-shell microcapsule is:

$$V = V_{pol} + V_{mon} + V_{hex}$$

The thickness of the wall is determined by the volume of polymer. Now we can find the following when we assume a perfect hollow sphere with radius *r* and shell thickness *h*:

$$\frac{V_{mon} + V_{hex}}{V} = \left(\frac{r-h}{r}\right)^3$$

We have to relate the individual volumes to monomer conversion. We do take into account the difference in density of polymer and monomer. This results in:

$$\frac{\left(\dfrac{m_{mon}(1-x)}{\rho_{mon}}\right) + \left(\dfrac{m_{hex}}{\rho_{hex}}\right)}{\left(\dfrac{m_{mon}(1-x)}{\rho_{mon}}\right) + \left(\dfrac{m_{hex}}{\rho_{hex}}\right) + \left(\dfrac{m_{mon}(x)}{\rho_{pol}}\right)} = \left(\frac{r-h}{r}\right)^3$$

Isolation of *x* gives the desired equation.