Supporting Information

Unloading and reloading colloidal microcapsules with apolar solutions by controlled and reversible buckling

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Movie S1: This movie shows the increase in the depth of the dimple in a capsule with d/R_t = 0.05 in time, due to the solubilization of *PDMS* oil from its interior by the surfactant micelles. The movie was captured soon after addition of P123 surfactant (3.5%v/v) and it took about 20 min for the depth of the dimple in the capsule to become stable. The acquisition time for 1 frame was 1.28 s with a delay of 1.6 s between subsequent frames and the movie is displayed at 50 fps. All capsules show the same increase in dimple depth, but the circled capsule is stuck to the wall at a fixed orientation so that the process can be observed.

Movie S2: This movie shows the sudden shape transition of thin capsules, d/R_t = 0.006, from bowl to coffee bean, during the buckling of shells in the presence of surfactant. The circled areas focus on areas where particles make the transition. The movie was acquired and displayed at 24 fps.

Movie S3: This movie shows the evolution of the morphology of a capsule (circled) of a low value of d/R_t< 0.005, when *PDMS* oil was released from their interior. The shell initially had multiple dimples which later evolve into a single dimple and then quickly collapses into a coffee bean shape. The movie was acquired at 24 fps and it is displayed at 500 fps. **Figure S1 a,b,c** shows the optical snapshots of the capsule marked in the movie in different shapes during the release of *PDMS* oil.

Movie S4: This movie shows the loading and subsequent elastic recovery of a capsule from a bowl shape to spherical shape in the presence of *OMCTS* oil dyed with Pyrromethene 546. The capsule was made to stick to the capillary wall by coating the wall with *APS*. It took around 4–5 h for the shell to be completely loaded with oil. The acquisition time for 1 frame was 1.28 s with a delay of 15 min between subsequent frames and the movie is displayed at 10 fps.

Morphology changes in extremely thin microcapsules:

Figure S1 shows the sequence of changes in extremely thin ($d/R_t < 0.005$) microcapsules upon buckling. First, a number of indentations were observed (Figure S1b). At a later time only a single large depression was left (Figure S1c). Finally, the shell collapsed to a coffee bean shape (Figure S1d,e)

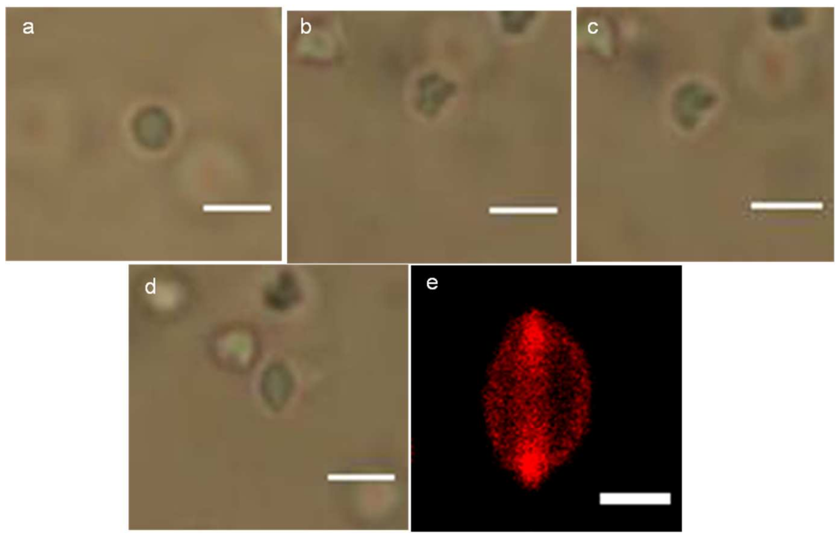

Figure S1. Optical microscope images of the morphology of extremely thin microcapsules, $d/R_t < 0.005$ during the release of oil at (a) t = 0 sec, (b) t = 120 sec, (c) t = 125 sec and, (d) t = 163 sec. (e) Confocal picture of a coffee bean particle. All scale bars represent 2μm.

Swelling of spherical capsules:

Figure S2a,b,c shows the swelling and subsequent formation of oil droplets after addition of fluorescently labeled cyclohexane into a suspension of spherical microcapsules. The initial average size of the microcapsule was 3.92 μm, measured from image Figure S2a. Five minutes after addition of cyclohexane fluorescence was detected from inside the capsule, which indicated that the swelling process had started. We measured a maximal average increase in the size of the capsule by 0.8 μm in diameter about 30 min after addition (Figure S2b). Later, about 1.5 h after addition, we could see an oil droplet partly enclosing the microcapsule (Figure S2c). The size of the capsule at this stage had returned to its initial value of 3.92 μm. The fluorescence profiles (Figure S2d) across the diameter of the capsule before and after addition of cyclohexane clearly show the changes in capsule size. The contact angle of $22.6^{\circ} \pm 3.5^{\circ}$ between the oil and the capsule is much smaller than it was in the cyclohexane overloaded microbowl (Figure 7a), for the same size oil droplet, probably due to the absence of surfactant this time. Interestingly, the part of the shell at the oil–water interface was also found to take on the curvature of the oil droplet, making the shell slightly nonspherical (Figure S2c). This kind of deformation of a soft elastic surface by liquid drops onto which they are placed was reported in reference.[1] It was shown that this deformation of the elastic surface is due to the combined action of Laplace pressure inside the drop and the interfacial tension at its periphery.

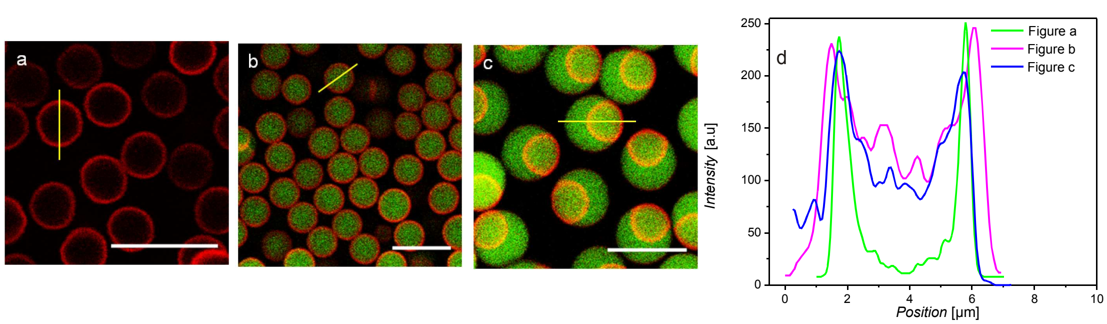

Figure S2. Confocal pictures of spherical *TC-PDMS* microcapsule (d/R_t = 0.04) (a) before addition of cyclohexane and after addition of cyclohexane (b) 0.5 h, (c) 1.5 h. Shells are shown in red and cyclohexane in green. (d) A fluorescence profile across the diameter of typical capsules from all 3 confocal pictures. The intensity is the fluorescence from the capsule wall (red). The slightly larger values of intensity from the interior of the capsules in (b and c) compared to (a) is due to the cross-talk of fluorescence emission signal from the dye in the shell (*RITC*) to that of the emission from the dye in the droplet (Pyrromethene 546). To reduce pixel noise we applied a Gaussian filter (2 pixels) prior to plotting the fluorescence profile. All scale bars represent 10 μm.

Loading of microcapsules with *QD*'s:

The suspension of *QD's* was added to microbowls of $\delta/2R_t$= 0.56 and d/R_t = 0.04 after the buckling experiments and examined under the confocal microscope about 20 min after addition.The *QD*'s were excited with a wavelength of 488 nm and the fluorescent signal was detected setting the detector in the range 550–620 nm. Figure S3a is the confocal image of microcapsules after addition of the *QD* solution. The uniform green sphere in the image is a *QD* loaded toluene droplet. We also observed a weak fluorescence from the shells, although it was labeled with *RITC* whose excitation wavelength is 543 nm. We think the fluorescence from the shell was not caused by the *QD*'s because we could detect the microcapsules even in the absence of *QD*'s with the same settings. In addition to elastic recovery, a toluene droplet formed outside the capsule similar to the case of loading with cyclohexane. This was a clear indication that the oil is loaded by the capsules, but the *QD*'s are not. The droplet or the oil bulge was invisible in the fluorescence image, but could be seen in the optical microscope. The presence of the bulge was confirmed from the slightly nonspherical shape of the microcapsule, where the shell at the oil-water interface was found to take up the curvature of the droplet, which is indicated by a red circle in the confocal image in Figure S3b. Nevertheless, we also confirmed the impermeability of the shell to these *QD*'s by bringing them in direct contact with the microcapsules. For this experiment we added the *QD* solution (50 μL) to *PDMS* filled spherical microcapsules of d/R_t = 0.04 lightly dried in an oven at 50 ^{o}C for 3.5 h to remove the aqueous phase. The capsules got aggregated during drying, but the capsule wall was not permeable for 3 nm *QD*'s. Figure S3c is the confocal image of capsules in direct contact with *QD* solution taken after three days of addition. The black spheres are the capsules and the green background is the fluorescence from the *QD* solution.

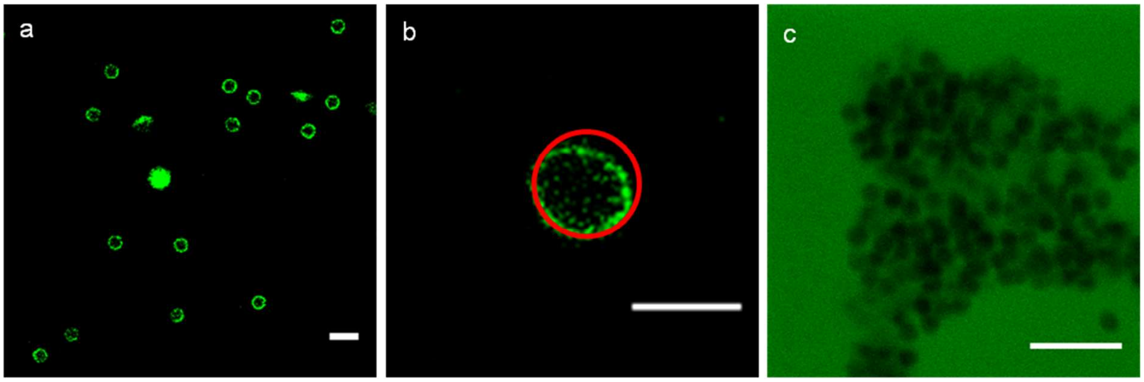

Figure S3. Confocal image of microcapsules (d/R_t = 0.04): (a) 20 min after addition of a *QD*-toluene solution (*CdSe* with an average 3nm size and coated with stabilizer oleic acid), (b) a fully relaxed microbowl ($\delta/2R_t$ = 0.56) with a toluene bulge marked by red circle that run through the perimeter of the shell at oil-water interface, taking the curvature of the oil droplet. (c) Slightly dried shells kept in direct contact with *QD* solution for three days. Scale bars in (a) and (c) represent 10 μm and in (b) 5 μm.

Measurement of the shell thickness with AFM:

Shell thicknesses were measured using Atomic Force Microscopy (AFM). Collapse of the dried shells led to plateaus in the height that corresponded to twice the thickness of the shell (Figure S4).

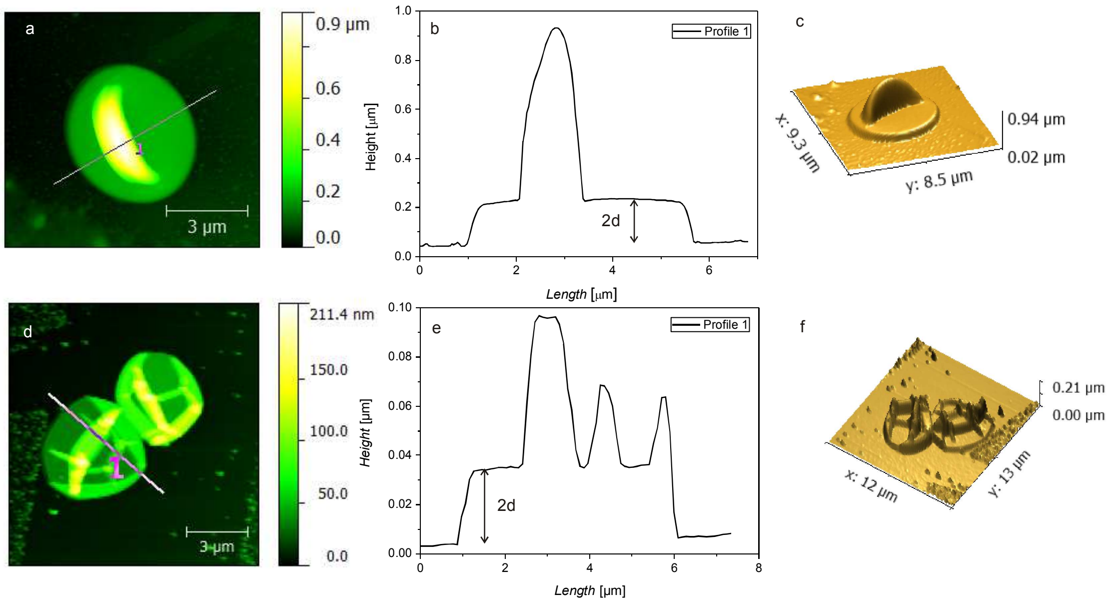

Figure S4. AFM images of typical microcapsules of d/R_t = 0.04 and 0.0075 (a and d) operated in the tapping mode. Shells collapse with creases and folds upon drying. The creases are more prominent for thin shells, d/R_t =0.0075, compared to thick shells. Graphs (b) and (e) show the height profiles taken along the lines drawn through the collapsed capsules. The height of the plateaus (marked with double headed arrow) corresponds to twice the thickness of the shell (d). We measured an average shell thickness of 88 nm and 16 nm for capsules of d/R_t = 0.04 and 0.0075. Graphs (c) and (f) are the 3D views of the collapsed shells.

1. Pericet-Camara, R.; Best, A.; Butt, H. J.; Bonaccurso, E. Effect of Capillary Pressure and Surface Tension on the Deformation of Elastic Surfaces by Sessile Liquid Microdrops: An Experimental Investigation. *Langmuir* **2008,** *24*, 10565-10568.