SUPPORTING INFORMATION

Reversibly Permeable Nanomembranes of Polymeric Microcapsules

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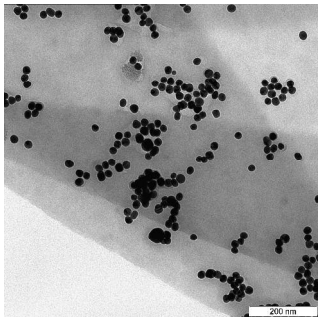

Figure S1. TEM image showing aggregates of nanoparticles in the shell of the microcapsule.

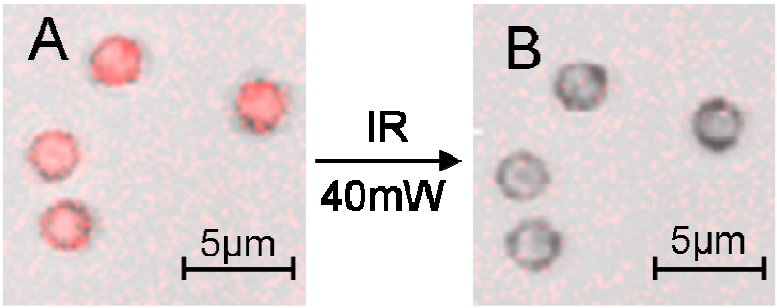

Figure S2. Fluorescence image of microcapsules before release (A) and after release (B). Transmission image of the same capsules is shown in (C).

Remote release. Release experiments were conducted according to the previously described methods[S1,5]. In previous experiments microcapsules were either exploded[S1] or deformed[5,11], which was due to a high concentration of large nanoparticles. In current sequential release accomplished here only small aggregates were assembled, Figure S1. The exposure of these aggregates keeps microcapsules intact, Figure S2, while permitting the release of encapsulated polymers. Release is conducted completely, i.e. emptying microcapsule's content entirely, if the laser beam is constantly kept upon the microcapsule. Sequential release is conducted when the laser was removed immediately after a microcapsules released a portion of encapsulated polymers. Laser intensity of 40 mW was used in the experiments. A homemade laser setup equipped with a CW laser diode operating at 830 nm with intensities of up 90 mW was used[S1].

Photobleaching and water heating. Photobleaching by laser beam is described in the main text. Photobleaching due to the exposure to the white light can be excluded because whereas the emission of the IR irradiated capsule decreases that of the non-irradiated remains unaffected (Figure 1), although both experience the same excitation by visible light. Water heating in the focus of a microscope objective even at higher intensities and similar wavelengths is under 1 degree[S2]. Control experiments were conducted in which microcapsules containing no absorbing nanoparticles were exposed to the laser beam – no release took place in that case. These data confirm that water heating does not affect the release.

Preparation of Silica Templates. The fabrication of $(PDADMAC/Au/PSS)_4$ microcapsules was done on 4.78 μm (Microparticles GmbH, Germany) particles using the Layer-by-Layer deposition technique. Typically, 1 mL of template SiO_2 particles solution were first cleaned from stabilizers in a sonication bath after resuspending them in a 1:1 solution of water and isopropanol.

Layer-by-Layer Assembly of Polyelectrolyte Microshells. Solutions of poly(diallyldimethylammonium chloride) (PDADMAC, Sigma-Aldrich) (2 mg/mL, 0.5 M NaCl), 20 nm colloidal gold (Sigma-Aldrich) and poly(styrenesulfonate, sodium salt) (PSS, Sigma-Aldrich) (2 mg/mL, 0.5 M NaCl) were prepared without further purification. For the capsule sample containing non-aggregated gold nanoparticles, SiO_2 templates with PDADMAC as the outermost layer were re-suspended in a mixture of water and colloid gold solution while gently stirring. Microcapsules with aggregates of nanoparticles, the same mixture of colloidal gold was prepared but in a solution of 0.1 M NaCl and was left to incubate for 60 seconds before re-suspending the PDADMAC coated silica with the solution of now aggregated gold. The templates were further dissolved in HF (0.3 M) solution, and the sample is then washed with water until the pH of the solution reaches above 5.

Thermal Shrinking of Microshells, Permeability and Encapsulation of Fluorescently Labeled Polymer. Capsule diameter and standard deviation (CL = 95%) were determined by averaging the diameter of 30 capsules using a laser scanning confocal microscope. The encapsulation of Alexa Fluor 555 dextran (AF555, 10 kDa, Invitrogen, Germany) was done by heating a mixture of capsules and AF555 (0.1mg/mL) at 54ºC for 20 minutes. The mixture was left to vortex at low speed for 20 minutes before heating in order to allow the fluorescent polymer to diffuse across the multilayer complex. The samples were allowed to cool for 5 minutes and washed thrice with water to remove non encapsulated fluorescent label.

Microshells Characterization. Transmission electron microscopy (TEM) was done using a Zeiss Omega EM 912 at an operating voltage of 120 kV. Confocal laser scanning microscopy (CLSM) was used to visualize the capsules in solution. Images were recorded by means of a 100x/1.4-0.7 oil immersion objective. A CARY 50 conc. (Varian, Germany) UV-Vis spectrophotometer was used for absorption spectra measurements.

References:

S1. Skirtach, A. G.; Antipov, A. A.; D. G. Shchukin; Sukhorukov, G. B. *Langmuir.* **2004,** 12, 6414.

S2. Schönle, A.; Hell, S. *Opt. Lett.* **1998**, *23*, 325.