Supplementary Material (ESI) for Journal of Materials Chemistry

Polymer Microcapsules as Mobile Local pH-Sensor

O. Kreft[1$], A. Muñoz Javier[2$], G. B. Sukhorukov[1,3*], W. J. Parak[2*]

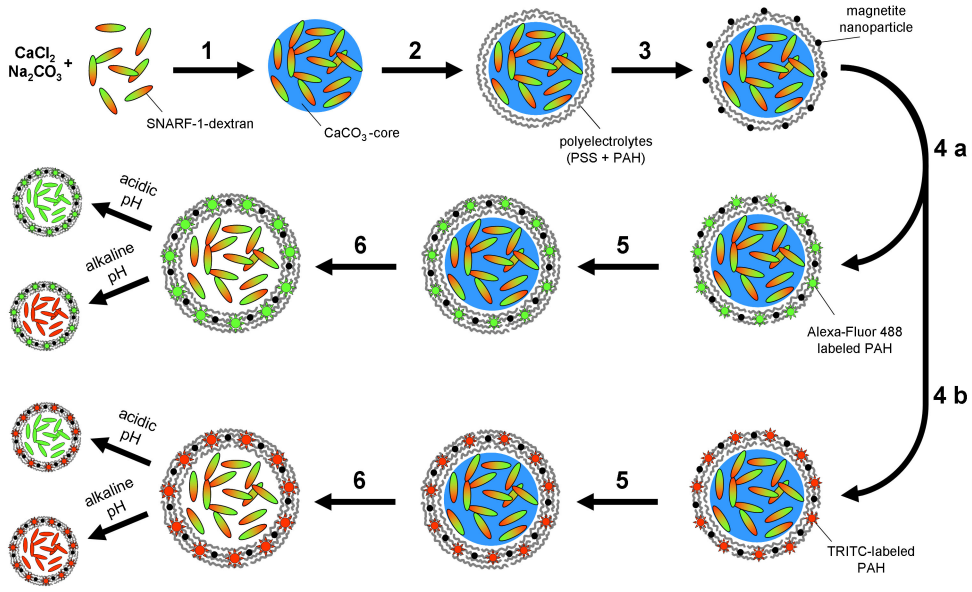
[1]Max-Planck-Institute of Colloids and Interfaces, Potsdam-Golm, Germany

[2]Center for Nanoscience, Ludwig Maximilians Universität München, Munich, Germany

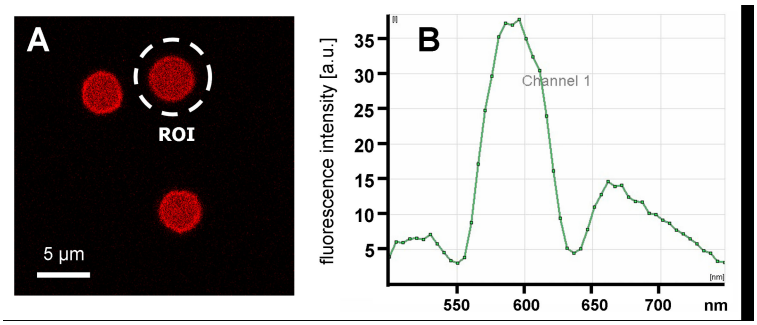
[3]Department of Materials, Queen Mary University of London, London, UK

[*]corresponding author: Wolfgang.Parak@physik.uni-muenchen.de

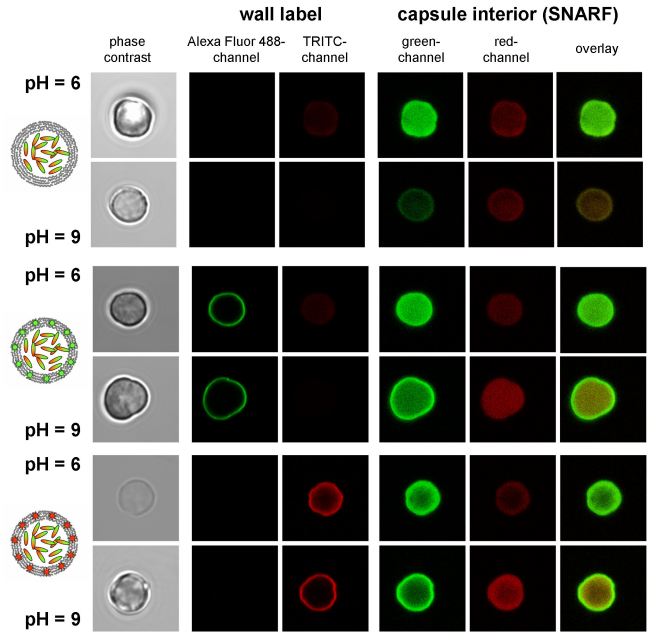
SUPPLEMENTARY INFORMATION



SI-1: General route for the synthesis of multifunctional, pH-sensitive polyelectrolyte capsules. (**1**) Spherical calcium carbonate microparticles (diameter = 4-6 µm, drawn in blue) comprising SNARF-1-dextran were fabricated by precipitation from supersaturated $CaCl_2$ and Na_2CO_3 solution in the presence of SNARF-1-dextran („coprecipitation-method“). After the LbL-self-assembly of 2 double layers of PSS/PAH (**2**) magnetite nanoparticles were adsorbed electrostatically onto the polyelectrolyte multilayer (PEM) (**3**). By adsorbing one bilayer of either PSS/PAH-Alexa-Fluor 488 (**4a**), or PSS/PAH-TRITC (**4b**), a fluorescence label can be introduced to the PEM. The PEM build-up was completed by depositing 2 double layers of PSS/PAH (**5**). The dissolution of the $CaCO_3$-core by EDTA treatment results in the release of SNARF-1-dextran into the inner void of the emerging polyelectrolyte capsule (**6**). Upon acidification or alkalinization of the bulk solution the encapsulated dye exhibits either green or red fluorescence. For simplicity we have only included 4 layers of polyelectrolytes in this figure. The capsules are not drawn to scale. The thickness of the walls is in the nm range, whereas the diameter of the capsules is in the µm range.



SI-2: Fluorescence spectra derived from single capsules. Fluorescence images (**A**) of individual SNARF-1-dextran containing capsules were imaged with Confocal Laser-Scanning Microscopy (for details see Experimental Part). Fluorescence intensities within 4 to 6 micrometer-sized, so-called "regions of interest" (ROI) covering the scope of one single capsule were used for the generation of fluorescence emission spectra. The conversion of such lambda-scans into fluorescence spectra (**B**) was accomplished using the Leica-TCLS-software. The excitation wavelength used for SNARF-1-dextran was 488 nm, whereas emission was scanned between 500 nm to 750 nm in 5 nm steps.



SI-3: Addressable capsules by double-labeling. For demonstrating the addressability of capsules we synthesized SNARF-1-dextran loaded capsules with either no label, Alexa Fluor 488, or TRITC in their walls. The idea is that the label in the wall can be utilized to identify individual capsules, whereas the cavity of the capsule can be independently filled with functional macromolecular species, i. e. sensors. Since there is a spectral overlap between these specific dyes we had to record the fluorescence intensities with 4 different filter sets, matching the Alexa Fluor 488, TRITC, green SNARF, and red SNARF fluorescence.
It can be clearly seen, that the inside of the capsules is sensitive to the pH (see the SNARF-channels: green fluorescence for acidic, red fluorescence for alkaline pH), while the capsules can be clearly distinguished by the wall label (see Alexa Fluor 488 and TRITC channel). Nevertheless, some overlap between the interior- and wall-label occurs.
Fluorescence images of individual SNARF-1-dextran containing capsules were imaged by CLSM. The capsules were immersed in buffer solutions of pH =6 or pH = 9. For all the different conditions 5 images were taken of each capsule: column 1: transmission, column 2: Alexa Fluor 488 fluorescence (used filter sets: λ_{exc} = 488 nm, λ_{em} = 510-530 nm), column 3: TRITC fluorescence (λ_{ext} = 554 nm, λ_{em} = 570-590 nm), column 4: green channel of SNARF fluorescence (λ_{ext} = 488 nm, λ_{em} = 580-600 nm), column 5: red channel of SNARF fluorescence (λ_{ext} = 488 nm, λ_{em} = 640-660 nm) and column 6: overlay of both SNARF channels.