Supporting Information

Nanosized core-shell bio-hybrid microgels and their internal structure

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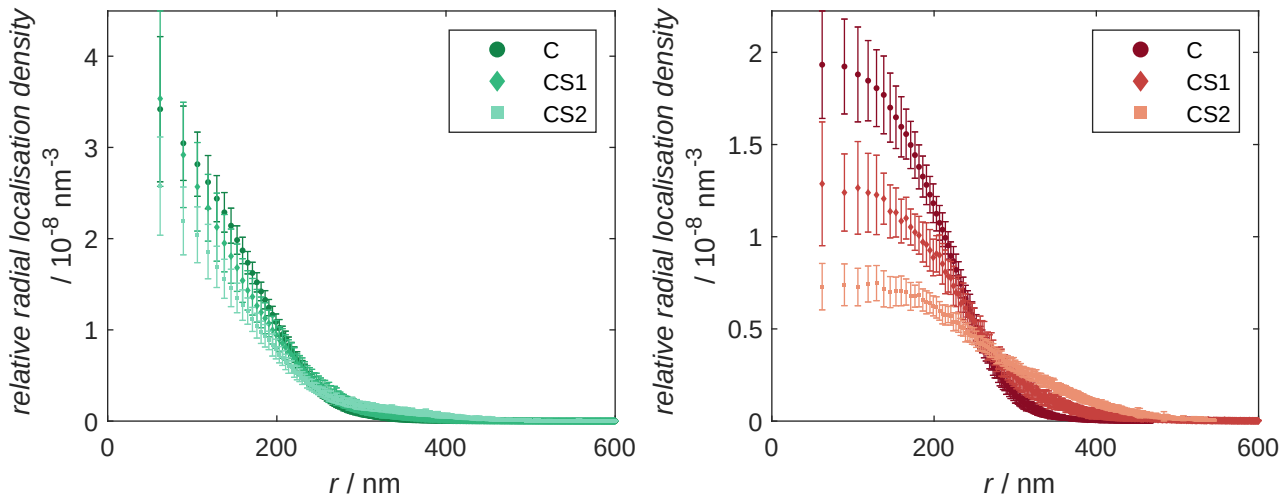
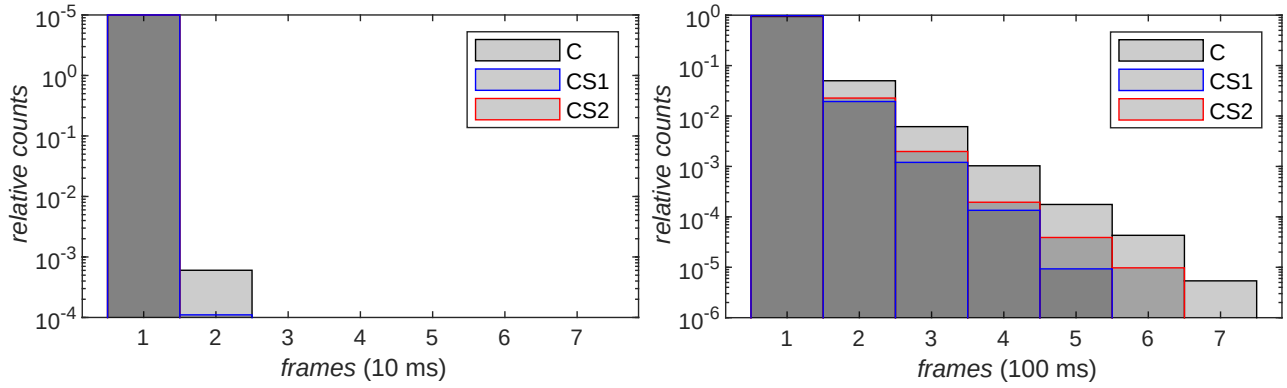
1 Additional super-resolution fluorescence microscopy information



(a) dSTORM (b) DNA PAINT

Figure S1: Radial localization density from microgels in dSTORM (a) and DNA PAINT (b). Visualized is the same data as in the main text, but sorted to highlight the differences between the microgel types.



(a) Duration of blink events in dSTORM. (b) Duration of blink events in DNA PAINT

Figure S2: Duration of blink events from dSTORM and DNA PAINT measurements. The histograms visualize the duration with logarithmic count scale and in number of frames in which the blinking event was observed. One frame equals 10 ms exposure time for dSTORM and 100 ms exposure time for DNA PAINT. In a) dSTORM, the data mainly overlaps and for CS2 no events of 2 or more frames were detected, thus the histogram bars are hidden behind each other.

2 Dynamic light scattering

For non-functionalized microgels, DLS was measured at the Zetasizer ZS (Malvern) with a HeNe-Laser (633 nm, 4 mW,) at a scattering angle of 173°, using UV-microcuvettes (Brand). The hydrodynamic diameter at temperatures from 10 (or 20) to 70 °C in 1 °C increments is fitted with a sigmoid function, where the point of inflection defines the VPTT. The data is plotted along with the obtained PDI in Figure S3.

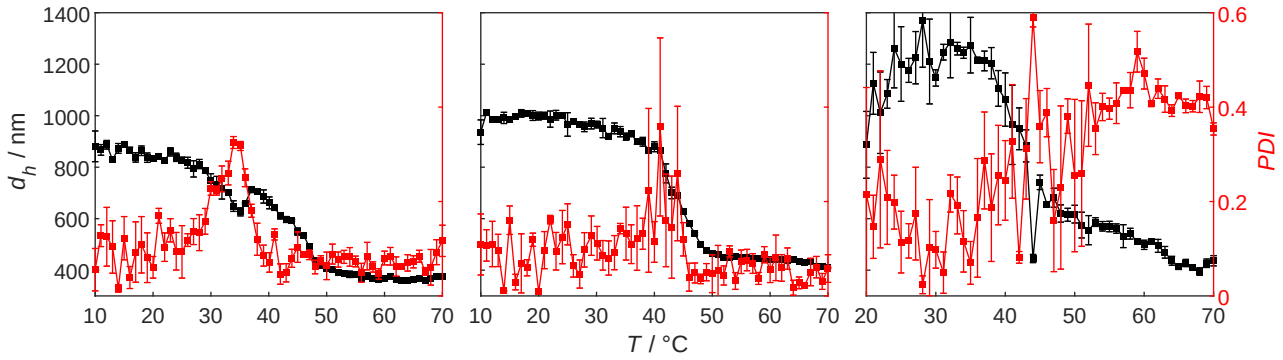


Figure S3: Hydrodynamic diameter plotted against temperature of *C* (left), *CS1* (middle), and *CS2* (right), obtained by DLS measurements.

Table S1: Hydrodynamic radii of microgels above and below the VPTT and the VPTT obtained by temperature-dependent DLS.

microgel sample	$r_\mathrm{h}(T < \mathrm{VPTT})$ / nm	$r_\mathrm{h}(T > \mathrm{VPTT})$ / nm	VPTT / °C
C	350 ± 5	165 ± 5	43 ± 5
CS1	485 ± 15	220 ± 5	43 ± 3
CS2	595 ± 60	240 ± 30	41 ± 3

3 Scanning transmission electron microscopy

Scanning transmission electron microscopy (STEM) images were recorded at a Zeiss LIBRA 200 FE with an acceleration voltage of 200 kV at the Central Facility for Electron Microscopy at RWTH Aachen University. To prepare the sample, larger microgel agglomerates were removed by centrifugation (500 rcf, 10 min). The resulting supernatant was then diluted 1:100 with ultrapure water. A droplet of the diluted dispersion was deposited onto a carbon-supported copper grid (200 mesh, Science Services) and allowed to dry for 1 min. Any remaining liquid was carefully removed using an Eppendorf pipette, and the grid was left to dry overnight.

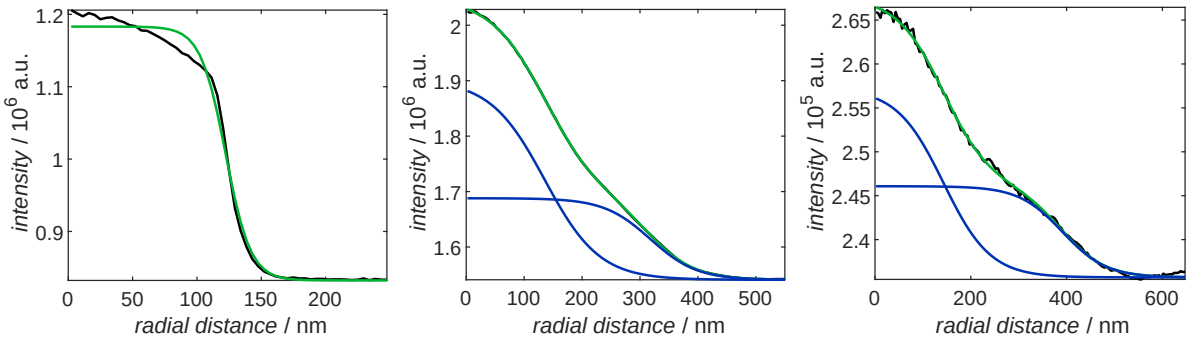


Figure S4: Radial profiles of microgels in STEM (black), (total) logistic curve fit (green), fit components (single logistic curves) for core-shell microgels (blue). Left: *C*, center: *CS1*, right: *CS2*.

The three different microgel samples were imaged in scanning transmission electron microscopy (STEM). The radial intensity profiles of single microgels were extracted using a custom python script. They were fitted with the following logistic curve function:

$$I(r) = \frac{I_1}{1 + \exp\big(-b_1 \cdot (r - r_1)\big)} + \frac{I_2}{1 + \exp\big(-b_2 \cdot (r - r_2)\big)} + offset$$

with the overall intensity I which can be split into an intensity I_1 related to the core and an intensity I_2 related to core and shell. The corresponding distances r_1 and r_2 at the reflection points can be used as measure for the size of core and shell. The parameter b reflects the smoothness of the transition. For core-only microgels *C*, the shell intensity is set to $I_2 = 0$.

Table S2: Fit parameters of logistic curve fits. Uncertainty ranges: $u_{I_1} = (0.08 - 3) \times 10^5$; $u_{I_2} = (0.3 - 1) \times 10^5$; $u_{b_1} = (0.6 - 4) \times 10^{-2}\,\mathrm{nm}^{-1}$; $u_{b_2} = (3 - 4) \times 10^{-3}\,\mathrm{nm}^{-1}$; $u_{r_1} = 2 - 12\,\mathrm{nm}$; $u_{r_2} = 9 - 20\,\mathrm{nm}$; $u_{offset} = (0.3 - 7) \times 10^4$.

Microgel	I_1	b_1/nm^{-1}	r_1/nm	I_2	b_2/nm^{-1}	r_2/nm	$offset$
C	3.48×10^5	9.2×10^{-2}	121				8.33×10^5
CS1	3.18×10^5	2.1×10^{-2}	134	1.30×10^5	2.6×10^{-2}	317	1.51×10^6
CS2	1.88×10^4	2.0×10^{-2}	141	1.07×10^4	1.8×10^{-2}	377	2.40×10^5

4 Atomic force microscopy

AFM measurements were performed on a NanoScope IIIa-Atomic Force Microscope by Digital Instruments in tapping mode using OMCLAC160TS-W2 probes by Olympus and WSxM 5.0 Develop 6.5.[1] The microgels were deposited on boiled silicon and measured in dry state. The images were treated equally to the STEM images to obtain radial profiles and logistic curve fits.

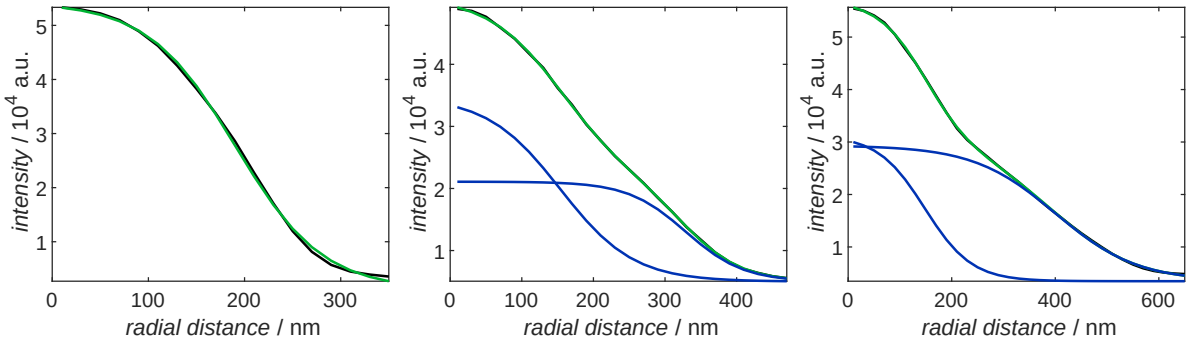


Figure S5: Radial profiles of microgels in AFM (black), (total) logistic curve fit (green), fit components (single logistic curves) for core-shell microgels (blue). Left: *C*, center: *CS1*, right: *CS2*.

Table S3: Fit parameters of logistic curve fits. Uncertainty ranges: $u_{I_1} = (3-5) \times 10^3$; $u_{I_2} = (3-4) \times 10^3$; $u_{b_1} = (0.9-2) \times 10^{-3}\,\mathrm{nm}^{-1}$; $u_{b_2} = 3 \times 10^{-3}\,\mathrm{nm}^{-1}$; $u_{r_1} = 7-15\,\mathrm{nm}$; $u_{r_2} = 6-17\,\mathrm{nm}$; $u_{offset} = (0.7-2) \times 10^3$.

Microgel	I_1	b_1/nm^{-1}	r_1/nm	I_2	b_2/nm^{-1}	r_2/nm	$offset$
C	5.25×10^4	2.2×10^{-2}	184				1.35×10^3
CS1	3.63×10^4	1.9×10^{-2}	170	1.44×10^4	2.7×10^{-2}	339	3.51×10^3
CS2	2.88×10^4	2.1×10^{-2}	150	1.95×10^4	1.7×10^{-2}	406	3.74×10^3

References

[1] I. Horcas, R. Fernández, J. M. Gómez-Rodríguez, J. Colchero, J. Gómez-Herrero and A. M. Baro, *Rev. Sci. Instrum.*, 2007, **78**, 013705.