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Nanoporous Hybrid Core-Shell Nanoparticles for Sequential Release

Supporting Information

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KEYWORDS: core-shell nanoparticles, organosilica, periodic mesoporous organosilica, nanoporous silica, sequential release, controlled delivery

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1 Sorption experiments

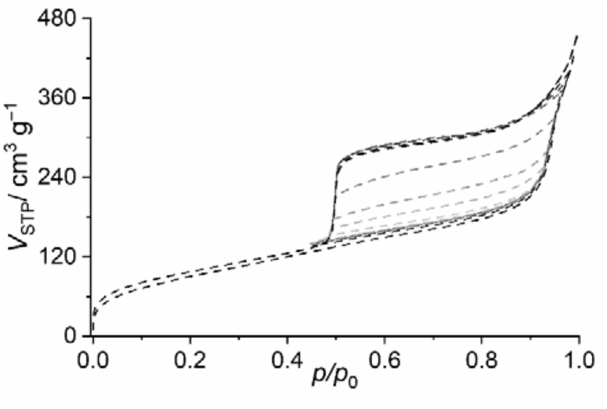

Figure S1: Hysteresis desorption scan of CSNPs with nitrogen at 77 K, proving a cavitation-induced desorption mechanism.

2 Scanning electron microscopy

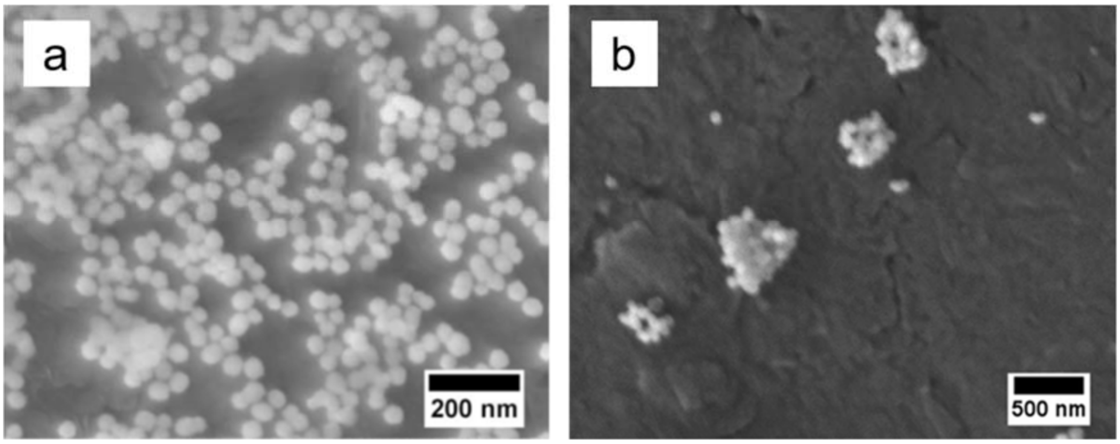

Figure S2: Scanning electron micrographs of NPSNPs (a) [1] and core-shell nanoparticles (b). Scanning electron microscopy (SEM) was performed using a JSM-6700F instrument with a 2 kV field emission gun. For the preparation of the samples, the nanoparticles were dispersed in ethanol via ultrasonication, dropped on a carbon specimen and dried in vacuum.

3 IR measurements

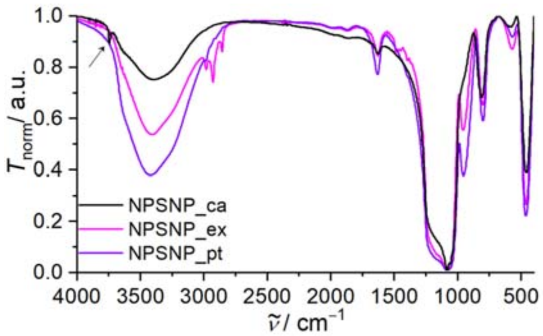

Figure S3: Comparison of normalized FT-IR spectra for NPSNP_ca (black), NPSNP_ex (pink) and NPSNP_pt (violet). The band characteristic for isolated silanol groups at 3740 cm^{-1} is marked by an arrow.

To substantiate the influence of the different treatments of the NPSNPs on the density of silanol groups present on the nanoparticle surface, FT-IR spectra were measured (Figure S3). A significant change in comparison to the freshly calcined nanoparticles resulted for NPSNP_ex as well as for NPSNP_pt for the broad band around 3400 cm^{-1}. This region is characteristic for O-H stretching vibrations of hydrogen-bonded silanol groups and water molecules. The increasing intensity suggests a higher amount of silanol groups and water molecules, which become adsorbed to a larger extent when the intrapore environment becomes more hydrophilic because of additional silanol groups. A similar trend – increasing water adsorption ongoing from NPSNP_ca via NPSNP_pt to NPSNP_ex – can also be discerned from the intensity of the bending vibration of water molecules located at 1650 cm^{-1}. Furthermore, the NPSNP_ca show a signal for isolated silanol groups at 3740 cm^{-1}, which disappears after the pretreatment with hydrogen peroxide and ammonia and is also not present for NPSNP_ex. With increasing water adsorption these groups become hydrolyzed as described by Warring et al.[2]. Therefore, more vicinal silanol groups are present at the surface, which results in O-H stretching bands at 956 cm^{-1} for NPSNP_ex and NPSNP_pt.

4 Thermogravimetric measurements

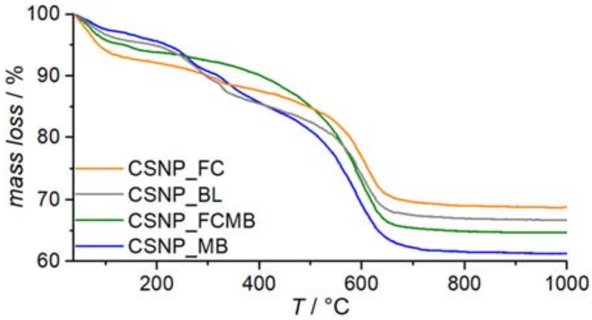

Figure S4: TG curves for CSNP_FCMB and CSNP_BL as well as for the reference samples CSNP_MB and CSNP_FC, measured in argon/air (80:20 v:v). The first mass loss results from the loss of water adsorbed by the nanoparticles. At higher temperatures, combustion of the organic bridging units as well as of the organic dyes takes place, finally resulting in a residue of silicon dioxide. The difference in the masses of the residues corresponds to the amount of dyes present in the loaded CSNP samples.

5 Release studies

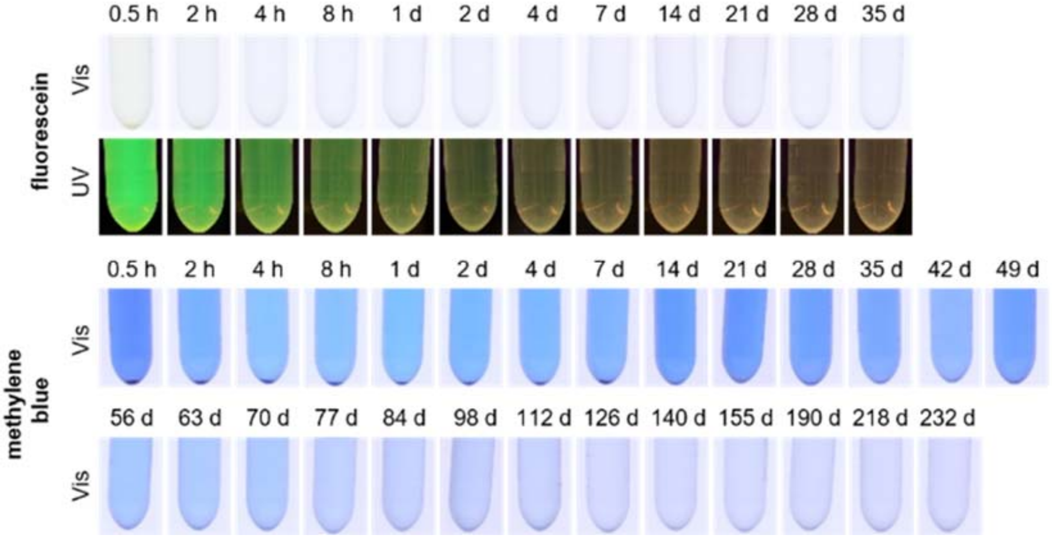

Figure S5: Results from release experiments of CSNPs loaded with a single dye. Upper rows: Supernatants of CSNP_FC in visible and under UV light; at the first time points, these show a subtle yellow color (Vis) and a strong green fluorescence (UV), respectively, both of which quickly fade. Lower row: Supernatants of CSNP_MB in visible light; the supernatants exhibit a strong blue color for several weeks before it starts to fade, but is still visible after 232 d. Measurement of these samples gave rise to the release curves presented in Figure 6.

6 Transmission electron microscopy

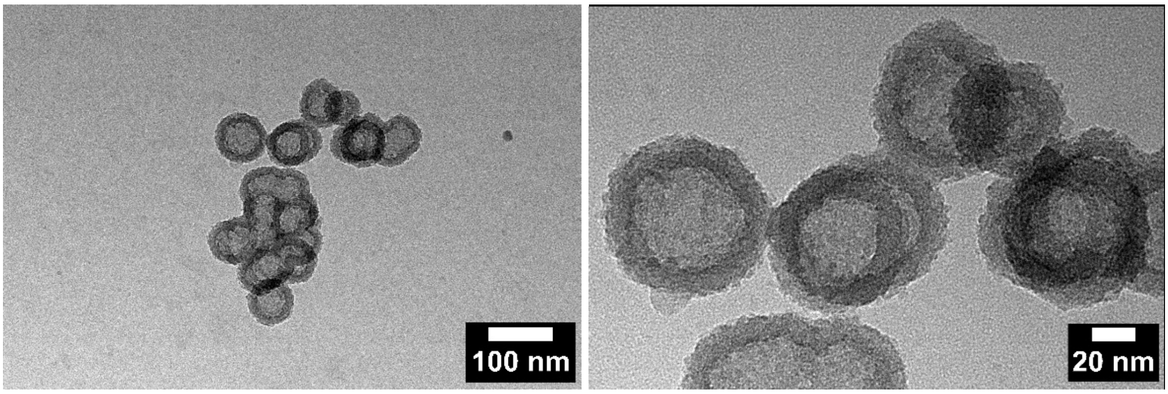

Figure S6: Transmission electron micrographs of core-shell nanoparticles after the release studies, i.e. after one year of exposure to aqueous solutions. The particles appear to be basically intact, at least the shell giving the particles their outer shape is still present.

7 References

[1] Heemeier, T., Biomaterialien im Ohrbereich, doctoral thesis, Gottfried Wilhelm Leibniz University Hannover, **2016.**

[2] Warring, S. L.; Beattie, D. A.; McQuillan, A. J. Surficial Siloxane-to-Silanol Interconversion during Room-Temperature Hydration/Dehydration of Amorphous Silica Films Observed by ATR-IR and TIR-Raman Spectroscopy. Langmuir 2016, 32, 1568–1576.