Electronic Supplementary Material (ESI) for ChemComm.


Supporting Information

# One-pot synthesis of micron partly hollow anisotropic dumbbell shaped silica core-shell particles

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## Experimental section

### Materials

All chemicals are commercial available and were used without further purification. Cetyltrimethylammonium bromide (99%), (CTAB) was purchased from Fluka, ammonia solution (29% in $H_2O$) from Sigma-Aldrich. Spherical 1.5 µm silica particles (**M0**) (99,9%) where either prepared according to literature[1,2] procedures or purchased from Exmere Ltd, *n*-Tridecane (98%) and ammonium fluoride (96%) are available from ABCR.

### Methods

Nitrogen adsorption and desorption isotherms were measured at 77.35 K using an ASAP 2020 V instrument from Micromeritics. The morphology and size of the particles were characterized by scanning electron microscopy with SU8030 from Hitachi with STEM capabilities. Powder X-ray diffraction (PXRD) patterns were recorded on a Bruker D8 ADVANCE instrument.
Dyeing experiments were performed in water solutions with concentrations between $5x10^{-6}$ and $5x10^{-4}$ mol/l of rhodamine 6G and sulforhodamine, respectively. The particles were immobilized by electrostatic interactions on a negatively charged glass surface or on a glass surface covered with polycations.

### Synthesis of M1, M2 and M3

In a typical reaction first the monodisperse non-porous 1.5 micron silica particles (**M0**) (2.1 g) were suspended and homogenized into an aqueous solution (210 mL) containing 5.762 mmol of the cationic surfactant CTAB. The resulting solution was homogenized for 15 min in an ultrasonic bath. After *n*-tridecane (11.6 ml) was added, the solution was homogenized for another 15 min. Under stirring (150, 240 – 250, and 280 rpm for **M1**, **M2** and **M3**, respectively) the homogeneous suspension was heated to 90°C. After that a fluoride containing aqueous ammonium hydroxide solution (1.35 mmol $NH_4F$ in 12 ml of saturated $NH_4OH$) was added. The milky mixture was stirred at the respective rate for 24h at 90°C. The resultant particles were collected by soft centrifugation at 2500 rpm for 5 minutes. The precipitate was washed twice with ethanol and once with diethyl ether. After each washing step the particles was homogenized in ultrasonic bath and centrifuged. The particles were dried at room temperature for 12 h. To remove the CTAB from the shell the particles were calcined at 600°C in air for 18 h.

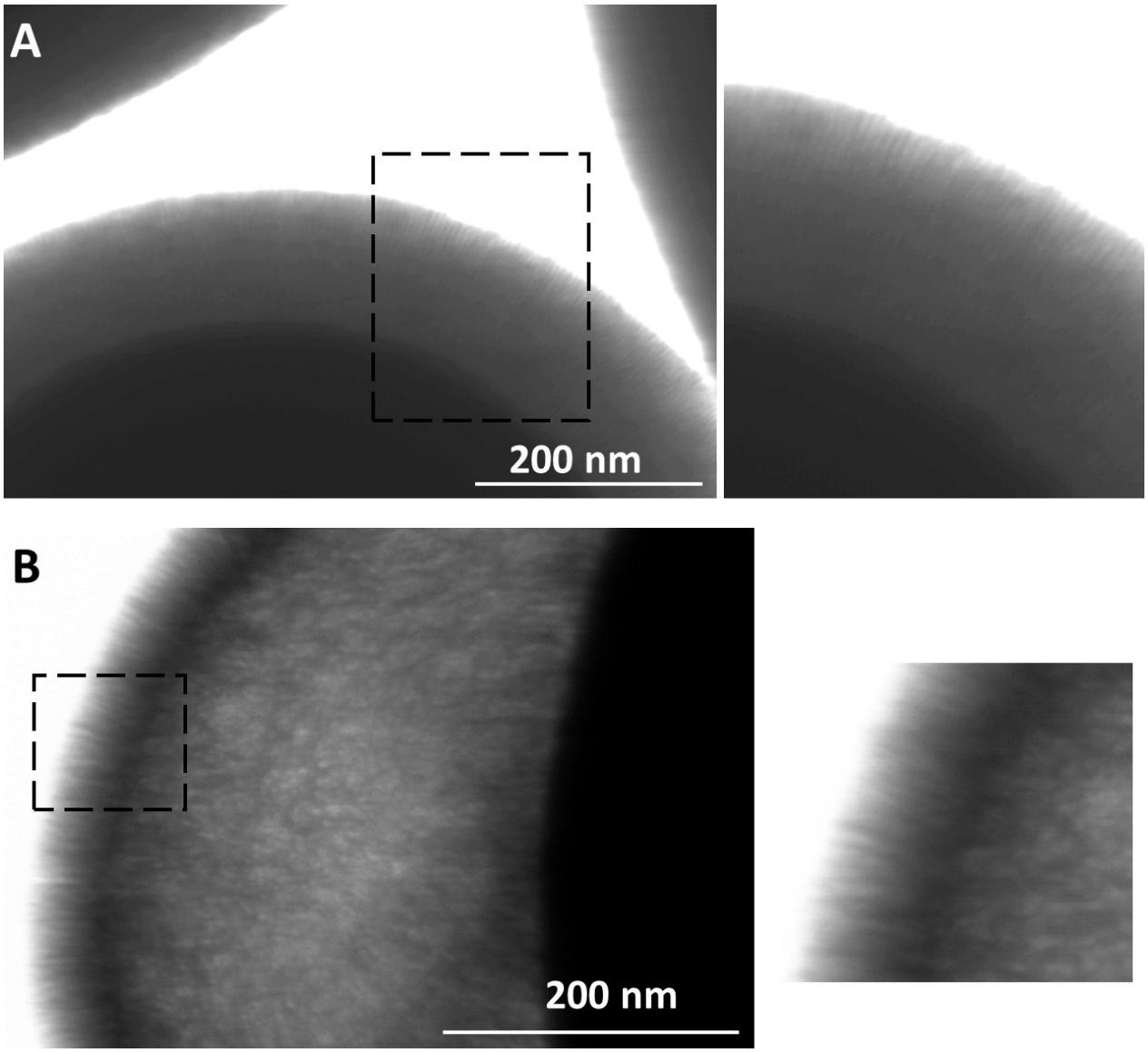


**Figure S1** STEM images of radially ordered pore structure of **M2** on the main particle (A) and on the lobe (B).

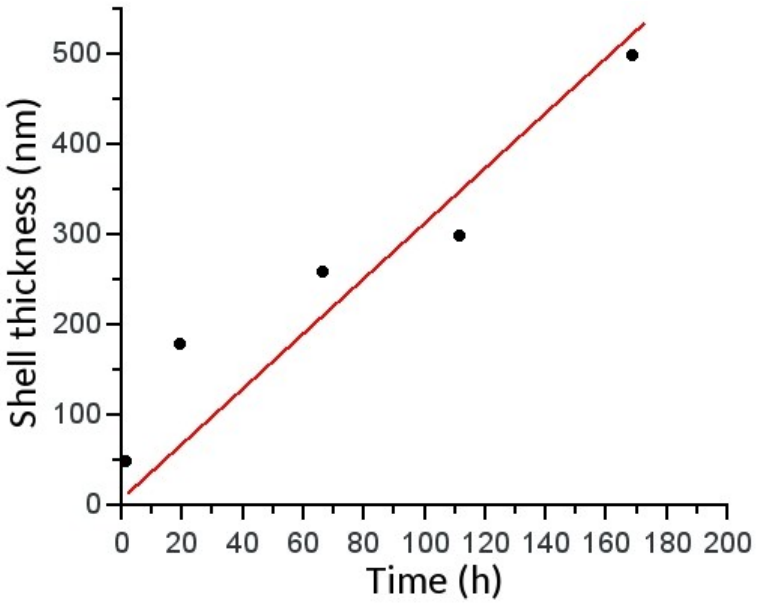


**Figure S2** Growth of the shell of the **M1** particles in dependence on the reaction time.

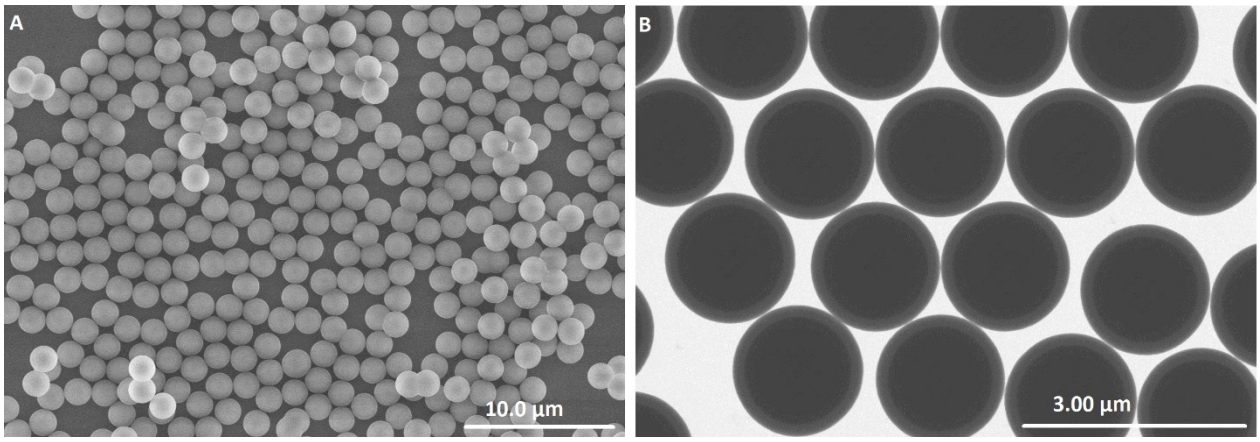


**Figure S3** SEM a) and STEM b) Images of **M3**.

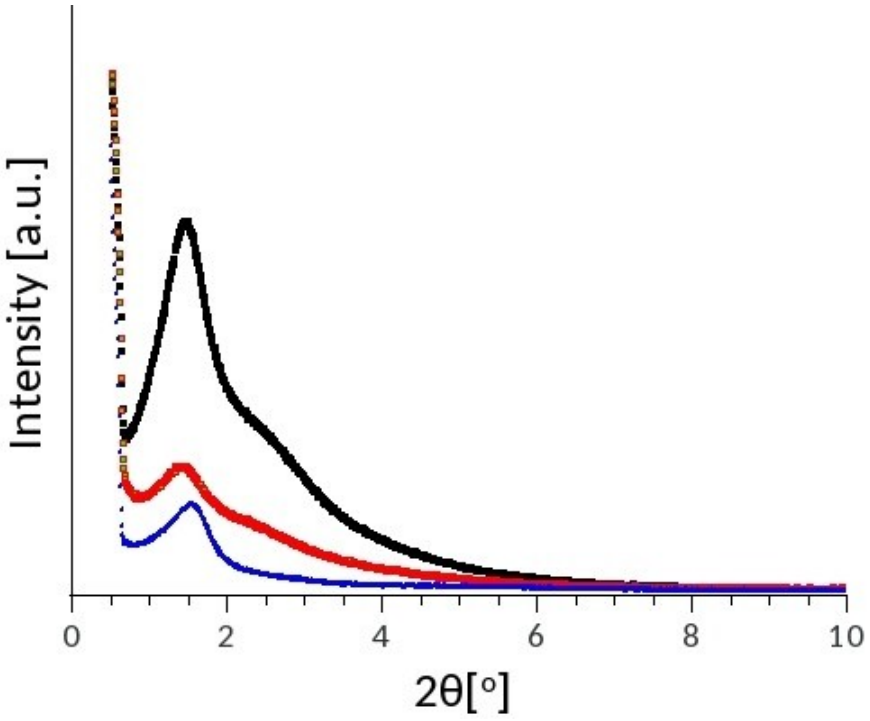


**Figure S4** Small angle X-ray of **M1** (●) **M2** (■) and **M3** (▲).

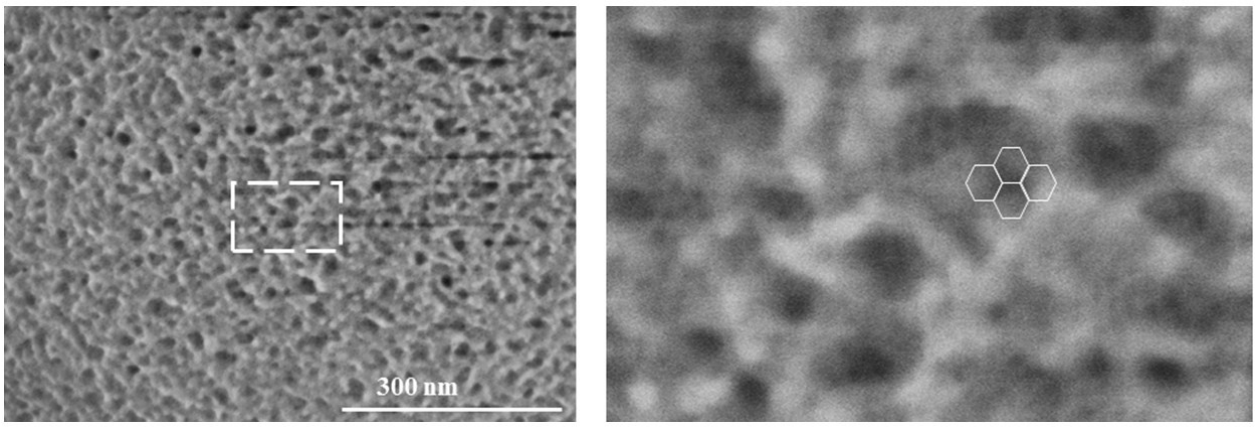


**Figure S5** SEM image of hexagonal pore structure.

**Confocal imaging and spectroscopy**[3,4]

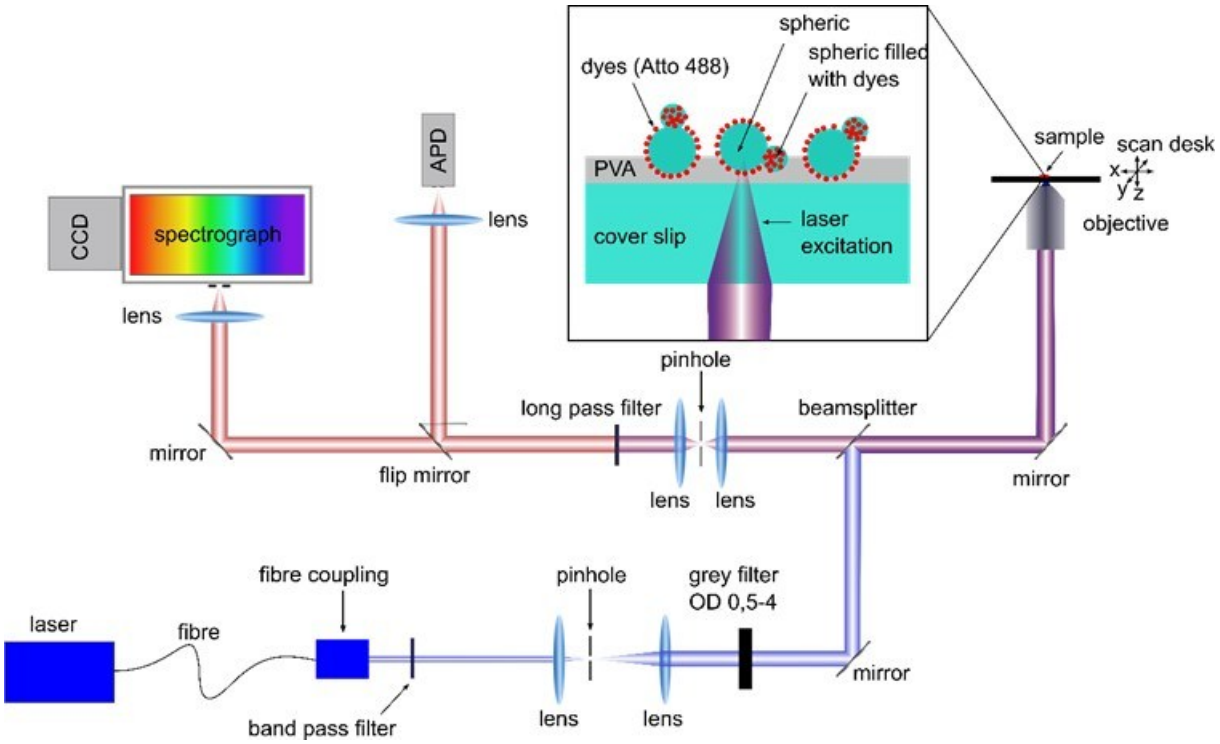


**Figure S6**: Scheme of the setup for confocal imaging and spectroscopy. In the inset the distribution of the sample and the dye molecules are illustrated. The thin PVA-film prevents movements of the silica particles **M1** and **M2** and provides a random orientation of the small spheres of **M2**. Additionally the spatial intensity distribution of the excitation source is indicated compared to the size of the particles (note: for simplicity reasons a much smaller numerical aperture NA was used).

The sample preparation was done by mixing 0.2 mg of the sample particles with 50 µl fluorophore solution, which is the rhodamine derivate Atto488 (with concentration of $10^{-7}$ mol/l) and 50 µl aqueous 4% polyvinyl alcohol (PVA) solution. This solution was homogenized for 10 minutes in an ultrasonic bath to guarantee adsorption of the dye molecules in the mesopores of the shells of the **M1** and **M2** silica particles and to diffuse into the hollow lobe of **M2**.
A droplet of these mixtures was spin-coated for 5 min at 350 rpm on a cleaned glass cover slip (Menzel, 22x22 mm) to get single spheres embedded in a thin PVA polymer matrix of several nanometers. The sample was placed on a feedback-controlled three-axis scanning stage (Physik Instrumente P-517.3CL, 100x100x20 µm) of a home-built confocal scanning microscope as sketched in Fig. S3. The thin PVA-film prevents movements of the spheres during the scanning procedure over the fixed excitation focus and yields additionally a random orientation of the **M2** particles relative to the scanning plane (xy-plane).
A 488 nm laser beam (PicoQuant, LDH-P-C-485) with power less than 1 µW exciting the fluorescence dyes was focused to a diffraction limited volume by a high numerical aperture objective lens (Zeiss, plan-apochromat 63x/1.46 immersion oil). In order to record spatially high resolved fluorescence images, the sample was scanned in the xy-plane at various z-positions with nanometer precision. The fluorescence intensities of the dyes with a maximum emission wavelength around 525 nm was collected by the same objective lens and guided back through a pinhole (diameter = 100 µm, focal length after first lens = 50 mm, after second lens 30 mm) and a long-pass filter (AHF, F76-490) on the detectors, an APD (Perkin Elmer, SPCM-AQRH) and

a spectrograph (Princeton Instruments, Acton SP2500) equipped with a CCD-camera (Princeton Instruments, ProEM).
With the above described settings of our confocal microscope we can reach a maximum lateral resolution of around 170 nm and an axial resolution of around 390 nm, allowing us to accurately localize the position of the fluorophores attached to the large **M1** and **M2** particles and those embedded in the hollow lobe of **M2** in all three space dimensions.


1. J. Maisch, PhD thesis, University of Tübingen, 2016.
2. N. Plumeré, A. Ruff, B. Speiser, V. Feldmann and H. A. Mayer, J. Colloid Interface Sci., 2012, 368, 208–219.
3. M. Minsky, *Scanning* 1988, **10**, 128–138.
4. L. Novotny and B. Hecht, Principles of Nano-Optics, 2nd edition, Cambridge New York, 2012