Morphosynthesis of Star-Shaped Titania-Silica Shells

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Experimental Section

Instrumentation. Single oil droplets of definite size were generated using commercially available microinjection equipment (Eppendorf micromanipulator 5171, Eppendorf transjector 5246). Videomicroscopic investigations were carried out using an inverted stage microscope (Olympus IX70) equipped with a CCD camera (Hitachi HV-C20 3CCD RGB camera with 795×596 (h×v) pixels resolution). Frame capturing and subsequent image processing was performed with a digital imaging system (PC frame grabber “GrabBit” and imaging software “Analysis V3.0”, Soft Imaging System, Germany).

Glass capillaries possessing a front aperture of approx. 35 μm were manufactured with a micropipette puller (DMZ-Universal microelectrode puller). Oil droplets were microinjected through glass capillaries into aqueous solutions (3 mL volume) contained in an open PTFE chamber (Leiden Cover Slip Dish, Harvard Apparatus), the bottom of which consisting of a 25 mm round glass cover slip to allow microscopic observation in transmission mode.

Fluorescence microscopy was performed with a custom-made multibeam multiphoton laser-scanning microscope.[17] Fluorescence is excited by two-photon absorption of a focused titanium-sapphire femtosecond laser (Coherent Vitesse, primary emission wavelength λ = 802 nm, output power P = 30 mW, pulse duration τ = 50 fs). To allow fast scanning the signal strength is increased by employing 4 beams simultaneously. The beams are scanned through the sample by two galvanometer scanners (GSI Lumonics).

As fluorescent probe we used coumarin 153 (Systematic name: 2,3,5,6-1H,4H-Tetrahydro-8-trifluormethylquinolizino-[9,9a,1-gh]coumarin, C_{16}H_{14}NO_{2}F_{3}, purchased from Lambda Physik AG, Göttingen). The emitted fluorescent light is imaged onto a triggered Peltier-cooled monochrome CCD camera (PCO Sensicam, 1280×1024 (h×v) pixels resolution, 12 bit greylevels). To allow real-time image construction, the object field was sampled with 4 laser beams simultaneously and the scanned region of interest (ROI) was limited in size to an area of approx. 320×170 μm (47×44 μm, respectively).

Scanning electron microscopic investigations were performed using a Philips XL30 ESEM-FEG operated at an acceleration voltage of 30 kV in wet chamber vacuum mode (4 Torr) using secondary electron imaging. Air-dried samples were Au-sputtered in an Ar plasma prior to examination. Elemental distribution was determined from uncoated samples at selected areas using an energy-dispersive X-ray fluorescence detector (EDAX New XL30 133-10, Philips EDX controller).
Preparation procedures. All chemicals employed were used without further purification unless stated otherwise. The surfactants arachidic acid (CH$_3$(CH$_2$)$_{18}$COOH) and cetyltrimethylammonium bromide (CTAB, CH$_3$(CH$_2$)$_{15}$N(CH$_3$)$_3$Br) were purchased from Fluka (> 99% purity). Chlorocyclohexane was purchased from Merck (> 98 % purity) and distilled at normal pressure using a short vigreux column. As titania precursor we used tetra-tert-butyl orthotitanate (TBOT, C$_{16}$H$_{36}$O$_4$Ti) purchased from Merck (nominal purity 93% in relation to the Ti content). As silica precursor tetramethoxysilane (TMOS, C$_4$H$_{12}$O$_4$Si) and tetrathioxysilane (TEOS, C$_8$H$_{20}$O$_4$Si) were employed (Fluka, > 98% purity). Doubly deionized water of a resistance of at least 18.2 MΩ·cm (Millipore Simplicity) was used to prepare aqueous solutions.

Spontaneous emulsification in the precursor-free system.
Arachidic acid (26.5 mg) is dissolved in hot (80°C) chlorocyclohexane (2 g). The clear solution (42.4 mM) is cooled to room temperature. A small portion of the freshly prepared (over-saturated) solution is filled into a glass capillary. The tip of the glass capillary is brought into focus by moving the capillary into an aqueous CTAB solution (3 mL, 55.6 µM). The arachidic acid solution then is microinjected into the aqueous phase by applying a definite overpressure such that the droplet rests at the capillary tip. Further movement of the oil droplet is avoided during the course of emulsification which starts after a lag period of a few minutes.

Formation of star-shaped titania particles in the precursor-contained system.
The arachidic acid solution (2.0265 g) is prepared as described above. TBOT (80 mg, 4.0 mass per cent) is added to the organic solution which turns slightly yellow. Droplet microinjection is carried out into a more concentrated aqueous CTAB solution (3 mL, 0.556 mM). It is important to use a freshly prepared organic solution since TBOT hydrolysis occurs in aged stock solutions that are frequently exposed to air humidity, which may alter the emulsification process significantly.

Bulk preparation of robust star-shaped mixed titania/silica particles.
The organic solution is prepared by adding TMOS (120 mg) and TBOT (80 mg) to a supersaturated solution of Chlorocyclohexane (1,80 g) and arachidic acid (26.5 mg) prepared by the above described procedure. An aqueous CTAB solution is prepared (100 mL, 0.556 mM) to which is added TMOS (1.522 g). The emulsion is stirred for 5 minutes upon which a clear solution results. The aqueous solution (5 mL) is filled into a sealable glass vial and a single drop (approx. 15 mg) of the freshly prepared organic solution is transferred to the vial by means of a Pasteur pipette. The vial is closed firmly and shaken gently for a few times. It is observed that the organic phase forms emulation droplets which lead to a cloudy appearance of the solution. The reaction mixture is left to stand quiescent for about a few days upon which the emulsion droplets have settled at the bottom of the vessel. The formation of star-shaped particles takes place within the first hour; after a few hours particle shape is persistent such that the vial may be moved and its content may be examined by light microscopy. After a few days the mineralized particles are mechanically robust and the aqueous CTAB solution can be replaced by deionized water. It is possible to isolate the star-shaped mineralized particles by slowly evaporating the solvent at room temperature.

Samples for fluorescence microscopic investigations were prepared as described above with the fluorescent probe coumarin 153 being added to the organic phase at a conc. of 3.23 mM (1 mg/mL).