

Electronic Supporting Information

“The Surface Morphology Controlled Growth of Hollow Titania Microspheres: Microfluidic droplets as soft template”

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Experiment setup:

We fabricated microfluidic reactor with PDMS by using soft-lithography technique. The microfluidic reactor has 5 inlets and a long serpentine flowing channel. Width of the channel as labeled in Figure. 1b is about 150 μm , and the total length is 7.5 cm. We can make 12 reactors in one batch on a 10 \times 10 cm square master. Three syringe pumps were used to inject chemicals. Outlet of the reactor is connected to a special tygon tubing (ID 50 μm , Cole-Parmer Company) and immersed into sealed quenching container which is put on a magnetic stirring apparatus. Outlet of the tygon tubing was immersed into a quenching solution which was slowly stirred.

Materials preparation:

Phase 1 is composed of 10% (v/v) DI water dissolved in glycerol (Sigma); phase 2, 2% (w/v) TBT (Fluka Analytical) in hexadecane (Sigma); phase 3, paraffin (Sigma) with no, 1% (v/v) or 2% (v/v) butanol (Sigma). The quenching solution is 0.5% (v/v) oleic acid in hexane (Sigma). **The quench step is: after the formation of gel-like microspheres, they were diverted into quenching solution by immersing the outlet of the chip into solution, the butanol and unreacted TBT being diluted by the solution to slow down the reaction. Slow stirring is applied to disperse the gel microspheres from**

the outlet, after which they are filtered and washed with hexane and isopropyl alcohol, and then put into a freeze drying machine. For fluorescence labeled microspheres, 0.2% (w/v) FITC (95% isomer, International Labrotary, USA) is dissolved into phase 2; 0.2% (w/v) rhodamine (Sigma) is dissolved into phase 1. For droplets generation, the flow rate for phase 1, phase 2, and phase 3 is 0.01 ml h⁻¹, 0.04 ml h⁻¹, and 0.01ml h⁻¹ respectively. Phases 1, 2 were loaded into 3 ml syringes and phase 3 was loaded into 5 ml syringes. There syringe pumps were used to push the syringes and control the flow rates.

Measurement and characterization

The contact angle of phase 2 on the PDMS substrate was measured by a contact angle goniometer (Rame-hart); scanning electron micrograph (SEM) was performed on a JEOL 6390 machine with an acceleration voltage 15kV which was equipped with energy-dispersive X-ray spectroscopy device (EDX, Bruker AXS); the crystal structure was characterized by powder X-ray diffraction (XRD, PANalytical) using Cu K α radiation.

Fluorescence detection:

The FITC and rhodamine labeled titania gel microspheres were imaged by an inverted fluorescence microscope (Axiovert 200M, Zeiss) equipped with a cooled CCD camera (Diagnostic Instruments). The image data acquired from the CCD camera were further processed and analyzed by MetaMorph (Universal Imaging Corp.). Quantitative analysis was carried out with the help of Excel (Microsoft), and refined images were done by Confocal Assistant v4.0 (Bio-Rad) and Adobe

Photoshop. Fluorescent 3D imaging was performed on a Leica TCS SP5 system. The number of section to be scanned is 60 between. Each step size is 1.07 μm .