Electronic Supplementary Information

Preparation of monodisperse hybrid gel particles with various morphologies via flow rate and temperature control

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Experimental procedure

Preparation of monodisperse PNIPAM gel particles by using a flow-focusing microfluidic device

A round glass capillary tube (inner diameter: 500 μm, outer diameter: 900 μm, SANSYO Co.) was tapered to an inner diameter of 250 μm using a capillary puller (Sutter Instrument Co., P-1000IVF) and a microforge (Narishige, MF-900). The interior of the tube was coated with a hydrophobic reagent (Tokyo Chemical Industry Co., Ltd., triethoxy-1*H*,1*H*,2*H*,2*H*-tridecafluoro-*n*-octylsilane). The tube was then inserted into a square glass capillary (inner dimension: 1.0 mm, VitroCom), and they were fixed and sealed on a slide glass by a transparent epoxy resin where required.

An aqueous solution of a gelation reagent containing *N*-isopropylacrylamide (NIPAM, 1 M, Wako Pure Chemical Corp.) and *N*,*N*′-methylene-bis-acrylamide (BIS, 5 mM, Sigma-Aldrich Co.) was used as the water phase. The oil phase used was silicone oil (50 cSt, Shin-Etsu Polymer Co., Ltd.) containing a photoinitiator (0.2 wt%, Ciba, DAROCUR 1173) and a surfactant (2 wt%, Dow Corning, RSN-0749). The solutions were filtered with 0.45-μm filters to remove particulate impurities, and they were infused into the microfluidic device through polyethylene tubing attached to syringes that were driven by positive displacement syringe pumps (Chemyx Inc, Fusion 200). Formation of droplets was monitored with a high-speed camera (Photron Ltd., FASTCAM-SA5), attached to an inverted optical microscope (Olympus, GX-71). After collection, they were irradiated by a UV lamp (AS ONE Corp., SUV-16) for 2 h on a cold plate (AS ONE Corp., SCP-125) at 15 °C

to polymerize the gelation reagent. The obtained PNIPAM gel particles were removed from the silicone oil, and then washed and stored in isopropyl alcohol.

Preparation of monodisperse PNIPAM-PAAM hybrid gel particles

The monodisperse PNIPAM gel particles were dried and put into an aqueous solution of a gelation reagent containing acrylamide (AAM, 4 M, Sigma-Aldrich Co.) and *N*,*N*′-methylene-bis-acrylamide (BIS, 100 mM, Sigma-Aldrich Co.) so that the PNIPAM gel particles absorbed the solution. A wire with a diameter of 100 μm was inserted into the one end of the round glass capillary (outer diameter: 600 μm, inner diameter: 200 μm, SANSYO Co.), and the PNIPAM gel particles together with the solution were injected into the capillary from the opposite end. After at least 100 gel particles were accumulated in the capillary, the wire was removed. The capillary was then fitted into a square glass capillary (inner dimension: 600 μm, VitroCom) fixed on a slide glass. The gap between the capillaries was sealed with a plastic paraffin film (Bemis Company, Inc., Parafilm). The silicone oil (50 cSt, Shin-Etsu Polymer Co., Ltd.) containing a photoinitiator (0.2 wt%, Ciba, DAROCUR 1173) and a surfactant (2 wt%, Dow Corning, RSN-0749) was used as the oil phase, filtered with a 0.45-μm filter. Water and oil phases were pumped to the square capillary by positive displacement syringe pumps (Chemyx Inc, Fusion 200). The formation of droplets containing PNIPAM gel particles was monitored with a high-speed camera (3000 fps, Photron Ltd., FASTCAM-SA5) attached to an inverted optical microscope (Olympus, GX-71). After collection, the temperature was controlled by using a thermal stage (AS ONE Corp., KM-1). The sample was then irradiated by a UV lamp (AS ONE Corp., SUV-16) for 20 min to polymerize the gelation reagent in the water phase. The obtained PNIPAM-PAAM hybrid gel particles were washed with silicone oil (0.65 cSt, Shin-Etsu Polymer Co., Ltd.) and dried. The particles were then put into water. The temperature of the sample was controlled using a thermal stage (AS ONE Corp., KM-1).