Supporting Information

Double Emulsions from Capillary Array Injection Microfluidics

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I Experimental Section

Materials. The surfactant ethylene oxide–propylene oxide–ethylene oxide triblock copolymer (Pluronic F108), photocurable, ethoxylated trimethylolpropane triacrylate (ETPTA) resin, photoinitiator 2–hydroxy–2–methylphenylpropanone and the hydrophobic reagent octadecyltrichlorosilane (OTS) were all derived from Sigma-Aldrich Co. In order to achieve a better mixing, ETPTA was firstly premixed with ethanol in equal volume. HMPP was then added, with volume fraction of 1% (VHMPP/VETPTA). The mixture was placed in an oven to promote complete volatilization of the ethanol. Water soluble pigments Rhodamine B (red), Methyl orange (yellow) and Methylene blue (blue) were all purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Deionized water was used in all experiments.

Microfluidics. The seven-bore annular capillary array and the collection capillary were gained from World Precision Instruments, Inc. The inner and outer diameters of the capillaries were 580 μm and 1 mm, respectively. The square capillary with an inner diameter of 1.05 mm was purchased from VitroCom, Inc. The capillary array was tapered using a laboratory portable Bunsen burner (Honest MicroTorch). The Bunsen burner was set in its median thermal power and after 3s heating time, the capillary array was stretched by hand to reach a diameter of about 300 μm at the orifice. For the treatment of the capillary array, it was immersed in the hydrophobic reagent octadecyltrichlorosilane (OTS) and incubated for 15 min. After this, the solution was blown out. Then it was inserted into a collection capillary inside a square capillary. The connectors of the assembled capillaries were sealed with dispensing needles and transparent epoxy resin (Devcon 5 Minute Epoxy) where necessary.

Emulsification. The inner and middle phases flowed in the same direction via the injection capillaries in an appropriate arrangement as required. The outer phase flowed via the interstices between the square capillary and the injection capillary array, or between the square capillary and the collection capillary. Each fluid was pumped by a syringe pump (Harvard PHD 2000 Series), and was connected through a polyethylene tube(Scientific Commodities Inc., with inner and outer diameters of 0.86 mm and 1.32 mm, respectively.) with a glass syringe(SGE Analytical Science). The double emulsion generation process in the collection capillary of the device

was observed in real time with a stereomicroscope (NOVEL NTB-3A, Ningbo Yongxin Optics Co., Ltd, China) and was recorded by a charged coupled device (CCD, Media Cybernetics Evolution MP 5.0 RTV). The outer radius (R_{outer}), inner radius (R_{inner}), and shell thickness of the double emulsions were all measured by using software AOS Imaging Studio V3.4.2. Shell thickness was calculated from R_{outer} minus $R_{inner.}$ Each set of experiments was repeated five times and the average values were gained. The polymerization of the double emulsion shells was conducted by UV-light (EXFO OmniCure SERIES 1000, 365nm, 100W) for 3s after collection. The optical images of the multicolored microcapsules were observed by a stereomicroscope (Nikon SMZ 745T) and were captured by the same CCD. The core-shell structure of the microcapsules after polymerization of the shell were explored by SEM images using a scanning electron microscope(SEM, Hitachi S3000N).

II The relationship between flow rates and the double emulsion dimensions.

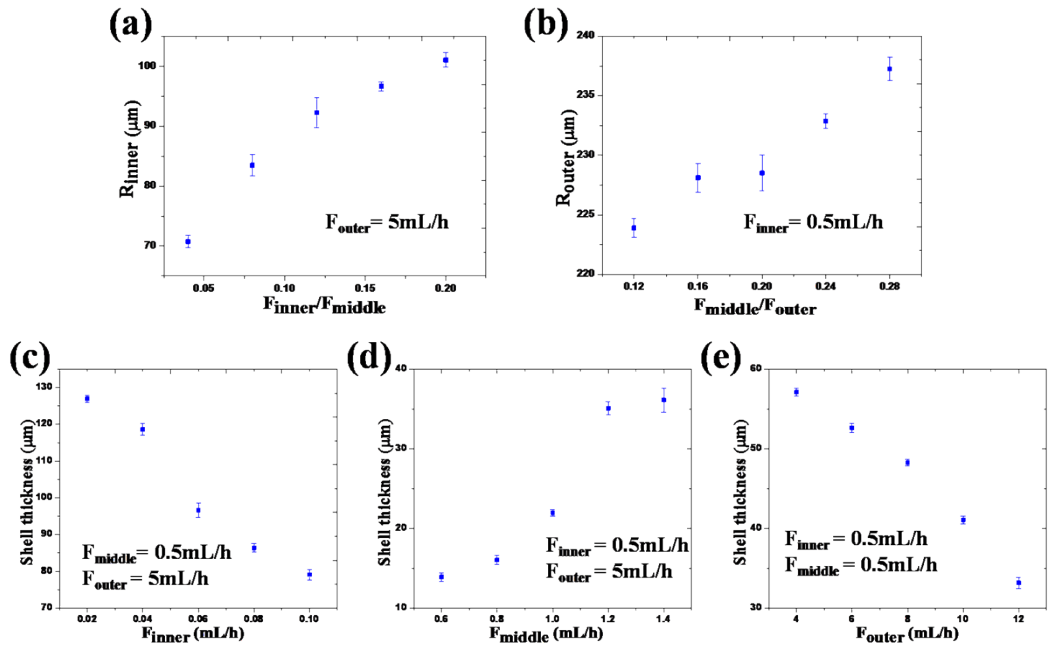

Fig. S1 The relations between flow rates of the different phases and the diameter of both the inner and outer drops as well as shell thickness. (a) The radius of the inner droplets R_{inner} increased with F_{inner}/F_{middle}; (b) The radius of the outer droplets increased with F_{middle}/F_{outer}; (c–e) The shell thickness of the drops decreased with F_{inner} and F_{outer}, while increased with F_{middle}. It was also found that when the value of F_{outer} was kept constant and F_{inner}/F_{middle} was changed, R_{out} showed no regular changes, and when adjusting the ratio of F_{inner} to F_{middle}, none of these parameters (F_{inner}, F_{middle}, $F_{inner}+F_{middle}$) was fixed.

III The SEM images of the microcapsules

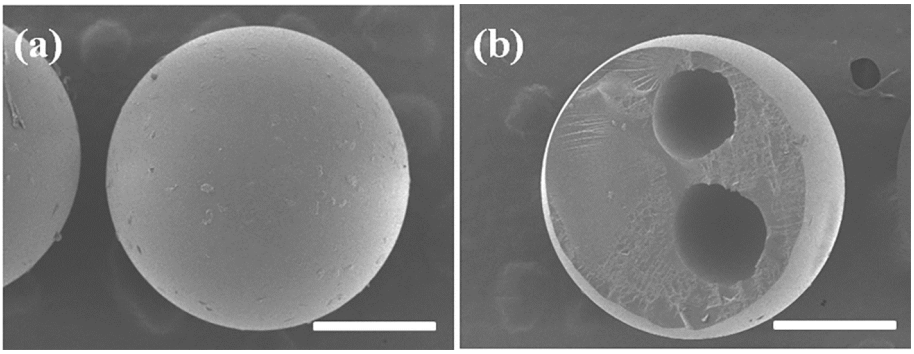

Fig. S2 The SEM images of the microcapsules. (a) The image of the original microcapsule; (b) The cross-sectional image of a microcapsule in the dry state after being cut. Scale bars are 200 μm.