Electronic Supplementary Information (ESI)

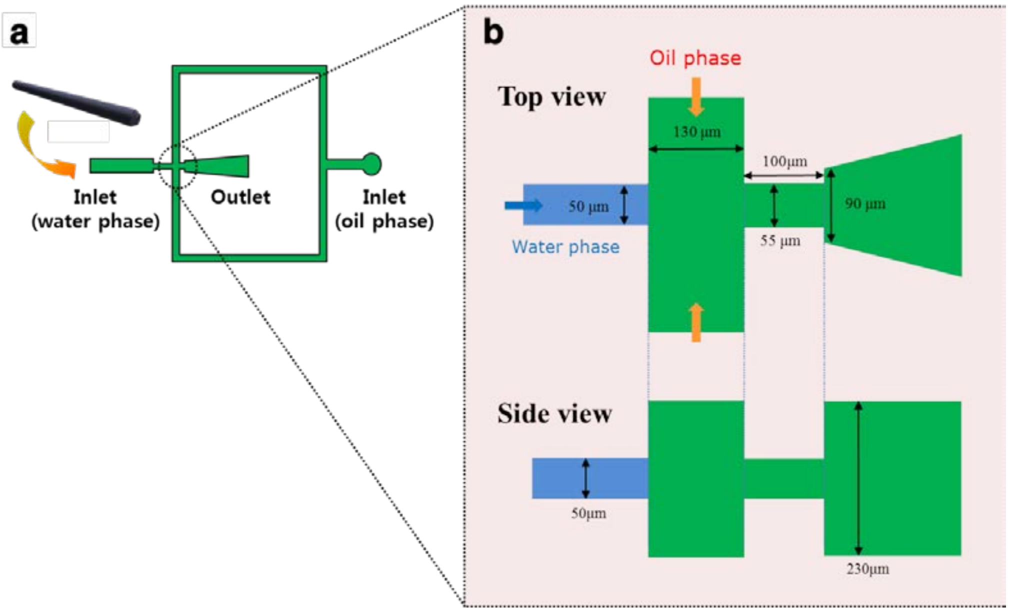

Fig. S1 Schematic diagram of a 3-D microfluidic flow-focusing device. (a) Overview of the device. The glass capillary was inserted into the dispersed (water) phase channel, which is open on one end. (b) Top and side views of the orifice region enclosed by the circle in (a).

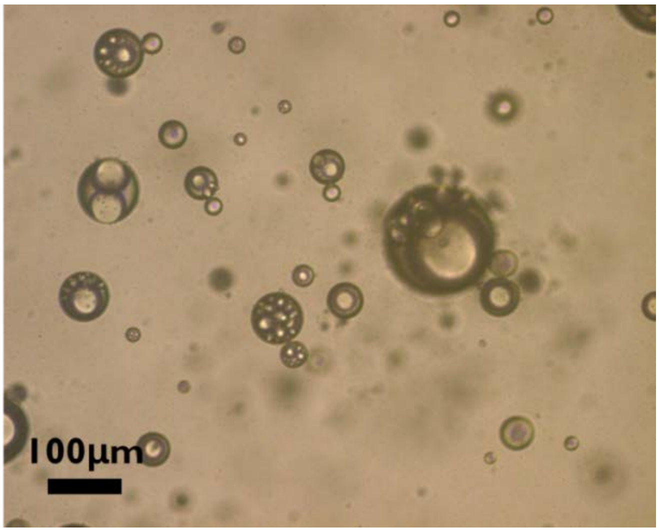

Fig. S2 Optical micrograph image of double emulsion droplets prepared under a high-shear mixing. Both internal and external droplets have highly polydisperse size distributions.

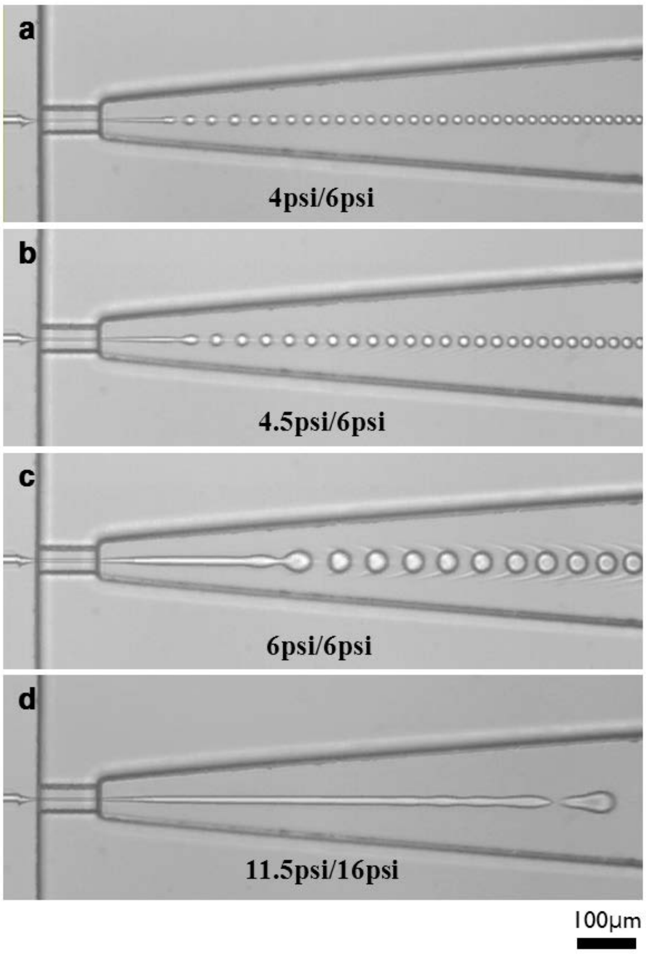

Fig. S3 Representative still images of the droplet breakup process at the indicated pressure ratios (P_w/P_o). Double emulsions and triple emulsions with a single internal droplet were obtained from (a, b) and (c), respectively. (d) The elongated jet produced double emulsions with multiple internal droplets, as shown in Fig. 3d.

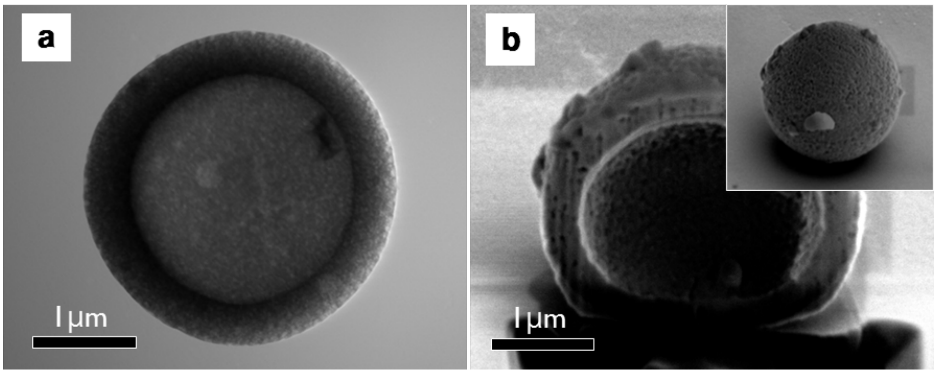

Fig. S4 STEM (a) and SEM (b) images of silica particles (HMS-2) prepared with 0.93% mass concentration of F127 surfactant in water (%w/v). The insets of b shows the surface topography of particles before focused ion beam (FIB) milling.

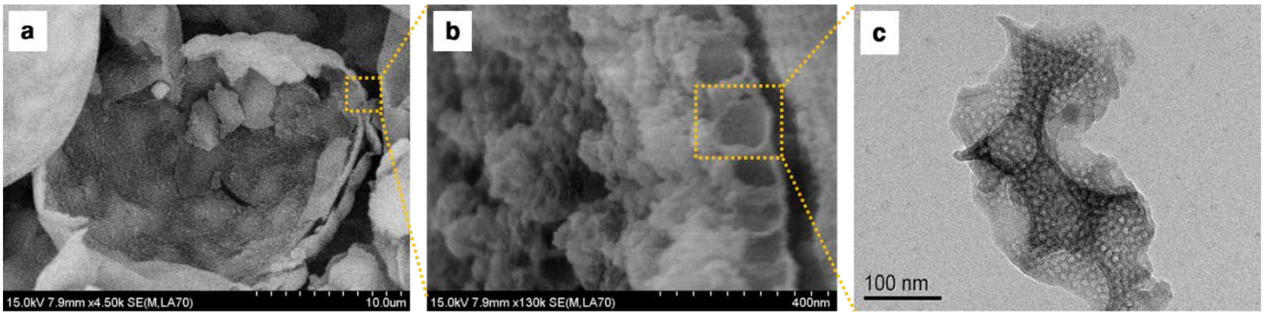

Fig. S5 SEM (a, b) and HR-TEM (c) images of a fractured silica particle (HMS-3) showing the hierarchical trimodal (i.e., giant, macro, and meso) porous structure.

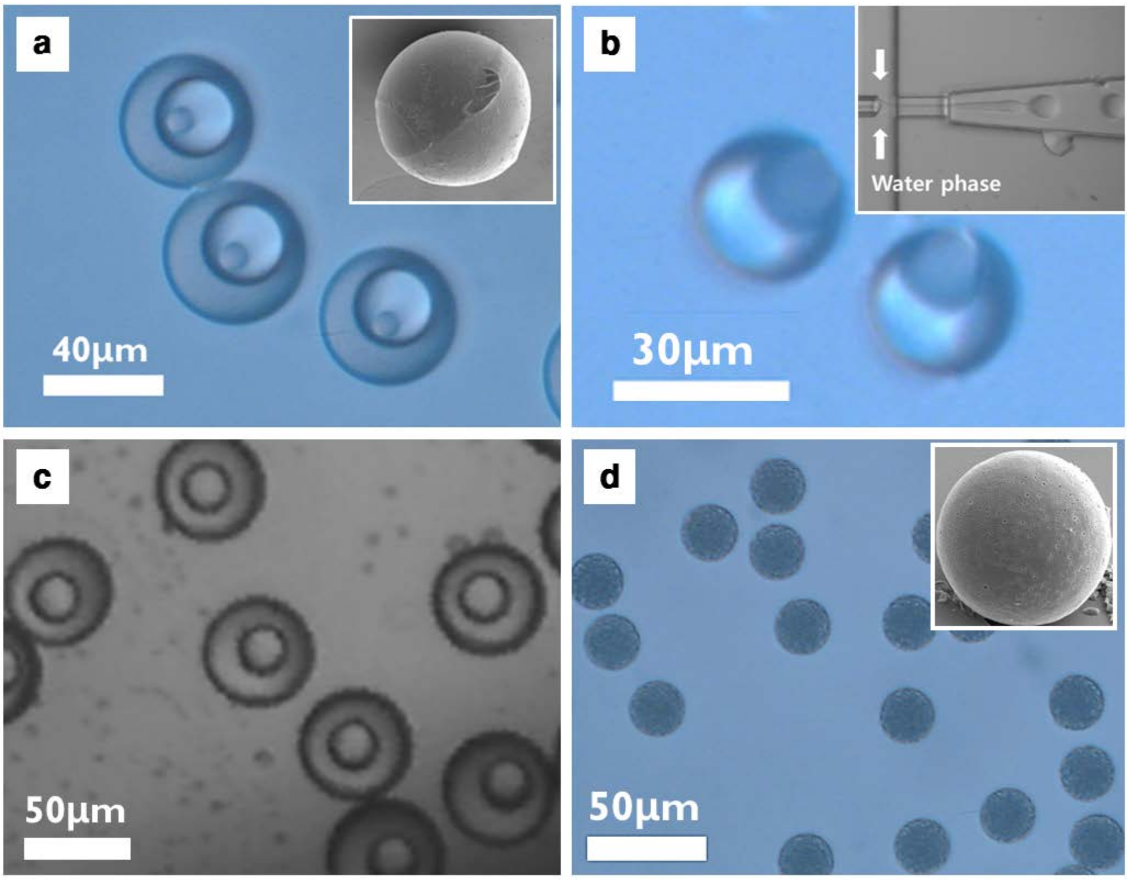

Fig. S6 (a) PEGDA (Mn = 700, Sigma-Aldrich)-in-mineral oil-in-PEGDA-in-mineral oil (W/O/W/O) triple emulsions. The poly(ethylene glycol) microcapsules were produced by UV-polymerization of diacrylated-PEG monomers inside the intermediate phase. Inset: SEM image of a PEG microcapsule. (b) Water-in-toluene-in-water (W/O/W) double emulsions prepared by dispersed phase with toluene-water-THF. In the absence of any added surfactant, the inner water droplets were highly unstable due to the density mismatch between the innermost water and intermediate toluene phases. Inset: still image of W/O/W double emulsion formation. (c) Water-in-dichloromethane (DCM)-in-water double emulsions prepared by dispersed phase with DCM-water-THF. (d) Ethyl cellulose microcapsules prepared by water-in-DCM-in-water double emulsions that contain ethyl cellulose (EC, Sigma-Aldrich) in the intermediate oil phase. Dichloromethane (DCM) inside the emulsions quickly evaporates to a gas at room temperature, producing ethyl cellulose microcapsules which can be used as a drug-delivery carrier.[1] Inset: SEM image of a ethyl cellulose microcapsule.

[1] a) L. Liu, J. P. Yang, X. J. Ju, R. Xie, L. Yang, B. Liang, L. Y. Chu, *Journal of Colloid and Interface Science* **2009**, *336*, 100-106; b) Y. Yoshikawa, A. Kawai, H. Yasui, H. Yoshikawa, K. Takada, *Biopharmaceutics & drug disposition* **1998**, *19*, 333-339.