Electronic Supplementary Information

S1. O/W/O double-emulsion drops

**Fig. S1** (a) Schematic illustration of the microfluidic device for preparation of O/W/O double-emulsion drops with an ultra-thin shell. (b, c) Optical microscope images showing generation of O/W/O double-emulsion drops in the continuous dripping mode and the resultant monodisperse double-emulsion drops.

S2. Description of Movies

- **Movie S1**: Effect of degree of confinement of interface. The plug-like drops are generated in the injection capillary with inner diameter of 580 μm, which produce double-emulsion drops in the discontinuous dripping mode, where Q₁, Q₂, and Q₃ are
maintained at the values of 4000 µl/h, 1000 µl/h, and 5500 µl/h, respectively. The stable jet is prepared in the injection capillary with inner diameter of 200 µm, which produces double-emulsion drops in a continuous dripping mode, where Q₁, Q₂, and Q₃ are maintained at the values of 2500 µl/h, 500 µl/h, and 8000 µl/h, respectively.

- **Movie S2**: Effect of Q₁. For Q₁ of 1200 µl/h, a stable jet in the injection capillary with an inner diameter of 200 µm is emulsified in the continuous jetting mode. For Q₁ of 800 µl/h, by contrast, the stable jet produces double-emulsion drops in the continuous dripping mode. For Q₁ of 400 µl/h, plug-like drops are emulsified in the discontinuous dripping mode. In all three cases, Q₂ and Q₃ are maintained at the values of 100 µl/h and 4500 µl/h, respectively.