Electronic supplementary information

Evaporation driven liquid-liquid phase separation for Janus droplets fabrication

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Materials and instruments

NOA61 was from Norland company. Paraffin oil (PO) was from Tianjin Damao Chemical Reagent Factory (Tianjin, China). Poly(ethylene glycol) diacrylate (PEGDA, M_n=700) was from Sigma. Hexadecane, and 1H,1H,2H,2H-perfluorooctyltrichlorosilane were from J&K Scientific Ltd (Beijing, China). Ethyl acetate (EA), ethanol, dimethyl formamide (DMF) and acetone were purchased from Xilong Chemical Engineering Co., Ltd. (Guangdong, China). Octanol was from Wuxi City Yasheng Chemical Co., Ltd (Wuxi, China). Methylene blue was obtained from Shanghai Chemical Reagent Co., Ltd. (Shanghai, China). Span 80 was acquired from TCI Development Co., Ltd. (Shanghai, China). Rhodamine B (RhB), Fc40 was obtained from 3M company, Krytox®FSL157 was obtained from DuPont. Sylgard 184 PDMS oligomer and curing agent were from Dow Corning (Midland, MI). SU-8 (3035) photoresist was purchased from Micro Chem. UV source HY-UV003 was from Zhuhai Da Yang Technology Co., Longer syringe pump L0107-3A was purchased from Baoding Longer Precision Pump Co., Ltd. (Hebei, China). An inverted microscope (Olympus IX71) was from Olympus (Tokyo, Japan), and an Evolve 512 electron-multiplied charge-coupled device was from Photometrics (EMCCD; Tucson, USA). All the micrographs were captured by the inverted microscope except the photos in figure S1A and figure S2 which were taken by an iPhone 4S. Ltd. SEM images were taken by a JSM-5600 scanning electron microscope (JEOL, Japan).

Evaporation induced phase separation in macroscope

We added 2 mL 0.1 % (wt) methylene blue water solution and 2 mL octanol into a sample bottle. A clear liquid interface were formed between octanol and water solution. Then, we added 4 mL ethanol slowly. The mixture became homogenous and the liquid interface disappeared. After that, we placed the homogenous mixture in a fume hood for 8 hours. The ethanol evaporated from the mixture. Water and octanol were separated into two layers again.

Microfluidic emulsification

The microdevice with T-junction structure was fabricated by standard soft microlithography process and pretreated by our previously proposed method [1]. The dimension of microchannel was shown in figure S1C. We used water-octanol-ethanol ternary mixture as disperse phase and FC-40 oil containing 2 % (wt) FSL-157 as continuous phase. The flow rate of continuous phase and disperse phase were set as 1.5 μL/min and 0.5 μL/min respectively. Homogenous ternary droplets were generated stably. To observe the dynamic phase separation processes induced by ethanol

evaporation, we cut off the injecting tube of continuous phase and disperse phase, and ternary droplets were stopped in microchannel. After that, we toke the images until the homogenous ternary droplets evolved into final Janus droplets. By setting the time of droplets stopping as 0 minute, the whole evolution process in microchannel needed about 20 minutes.

Conventional bulk emulsification

5 mL FC-40 oil containing 2 % (wt) FSL-157 was put in a glass bottle. Under the vigorous stirring, 0.4 mL water-octanol-ethanol mixture (V_{water}:$V_{octanol}$:$V_{ethanol}$ = 1:1:2) was pipetted into FC-40 oil drop by drop. Then, the emulsion was stirred for 20 minutes to ensure the completely evaporation of ethanol. After that, the formed emulsions were observed by an inverted microscope.

The morphology regulation of Janus droplets

To get the tri-component phase diagram of water, octanol, and ethanol, we prepared a series of mixtures with exactly volume ratio of octanol and ethanol. The mixtures were first clear. Then, we gradually added water into these mixtures until the solution became turbid. After that, we calculated the volume ratio of three components and drawn the pseudo-phase diagram. The pseudo-phase diagrams of PO-DMF-EA and PO-PEGDA-EA were also obtained by the same method.

To regulate the morphology of Janus droplets, we chose eight kinds of ternary mixture compositions (Point 1-8). The volume ratio of water, octanol and ethanol were 5:1:5 (Point 1), 3:1:4 (Point 2), 2:1:3 (Point 3), 1:1:2 (Point 4), 1:2:3 (Point 5), 1:3:4 (Point 6), 1:5:5 (Point 7) and 1:1:1 (Point 8). Point 1-7 was above the bimodal solubility curve. Point 8 was below the bimodal solubility curve. These ternary mixture was homogenous and transparent except point 8. After microfluidic emulsification, the initial ternary droplets flew out of channel. Then, we observed the evolution of droplets. The whole processes needed about 8-10 minutes. As the environment variation (such as temperature, air flow and moisture) might affect the evaporating rate of co-solvent. To avoid the deviation of environment during experiment, we captured all the final structures after 20 minutes evaporation in the next experiments, which ensure the reproducibility of results

The chemical composition control of Janus droplets

In our method, the chemical compositions of the two parts was determined by the composition of the two immiscible liquids. To regulate the two parts of Janus droplets, we selected four kinds of ternary mixtures. PO, DMF and EA were mixed together to form homogenous solution with a volume ratio of 1:1:3. By using PO-DMF-EA ternary mixture as disperse phase and FC-40 as continuous phase, PO-DMF-EA droplets were generated. After completely phase separation, PO-DMF Janus droplets were formed and captured by an inverted microscope. In the same route, PO-NOA61-EA (V_{PO}:V_{NOA61}:V_{EA}=1:1:5) droplets, NOA61-Water-EA (V_{NOA61}:V_{water}:V_{EA}=5:1:10) droplets, and PO-PEGDA-EA (V_{PO}:V_{PEGDA}:V_{EA}=1:1:6) droplets evolved into PO-NOA61, NOA61-water, and PO-PEGDA Janus droplets.

To encapsulate effective molecules into target part of Janus droplets, 1 mL Rh B water solution with a concentration of 20 g/mL, 1 mL octanol, and 2 mL ethanol were mixed to be employed as disperse phase. After microfluidic emulsification, the ternary droplets with homogenous fluorescence were generated. Accompany with ethanol evaporation, droplets evolved into Janus structure and Rh B molecules were collected into octanol parts.

More complex Janus droplets fabrication

0.1 mL NOA 61, 0.1 mL water, 0.3 mL hexadecane, and 3.6 mL acetone (co-solvent) were mixed to form a quaternary mixture. Then, we pipetted 0.4 μL quaternary mixture into FC-40 oil containing 2 % (wt) FSL-157. The quaternary mixture drop evolved into a final ternary Janus droplet gradually. The whole droplet evolution processes were observed and recorded by an inverted microscope.

By using the same method, the whole phase separation processes of NOA61-water-octanol-EA quaternary mixture droplet (The mixture was formed by mixing 0.2 mL NOA61, 0.2 mL water, 0.4 mL octanol, and 2.7 mL EA) and NOA61-water-PO-EA quaternary mixture droplet (The mixture was composed of 0.1 mL NOA61, 0.2 mL water, 0.2 mL PO, and 6.5 mL EA) were observed and recorded by an inverted microscope. For NOA61-water-octanol-EA quaternary mixture, a final core-shell Janus droplet was obtained. For NOA61-water-PO-EA quaternary mixture, a final multiple Janus droplet was generated.

Besides that, we used the above quaternary mixtures as disperse phase and FC-40 oil as continuous phase to form homogenous droplets on the microdevice. The flow rate of continuous phase and disperse phase were 1.5 μL/min and 0.5 μL/min respectively. After the evaporation, the droplets size was reduced intensively due to the large quantity of co-solvent needed to form homogenous quaternary mixtures. Thus, we could not clarify the structure of core-shell Janus and multiple Janus. Only ternary Janus droplets were distinguished.

Particles synthesis

We prepared a series of ternary mixtures composed of NOA61, PO and EA. The volume ratios of NOA61 and PO in these ternary mixtures were 2:1, 1:1, 1:3 and 1:5 respectively. The EA was slight excess of volume to ensure the mixtures were homogenous during storage. By using these mixtures as disperse phases, and FC-40 containing 2 % (wt) FSL-157 as continuous phase, ternary droplets were generated on the microdevice. After the evaporation of EA, the ternary droplets evolved into NOA61-PO Janus droplets. We used a UV source with 365 nm light to initiate the Janus droplets. The NOA61 parts were polymerized into solid particles. Besides that, we fabricated two other NOA61 particles with sectorial spherical shape and porous hemispherical particles shape through using ternary Janus and multiple Janus droplets as templates.

The additional figures not displayed in the main text

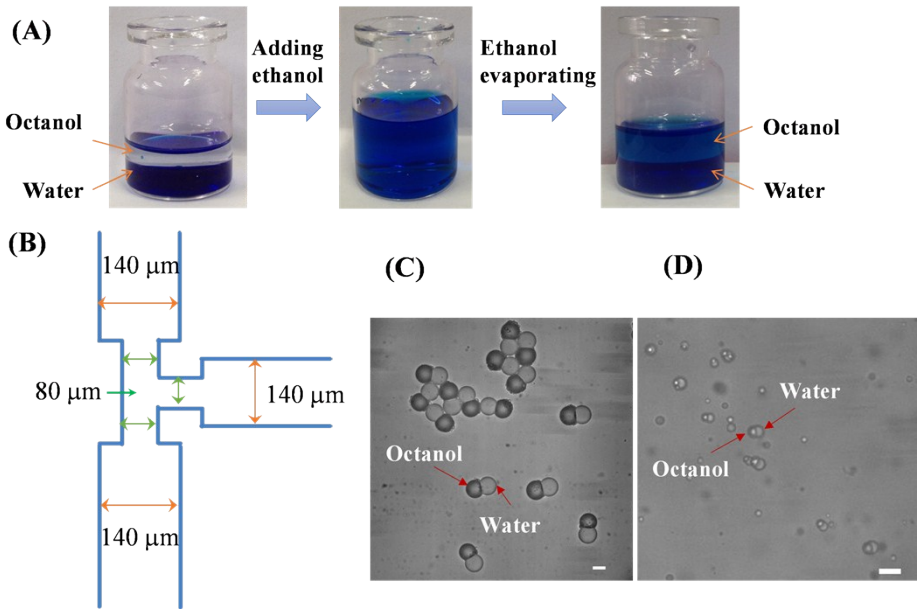

Figure S1 (A) The evaporation of co-solvent induced phase separation in macroscope. (B) The schematic of T-junction microdevice. The formed water-octanol Janus droplets by microfluidic emulsification (C) and bulk emulsification (D). The volume ratio of water, octanol and ethanol is 1:1:2. Scale bar is 40 μm.

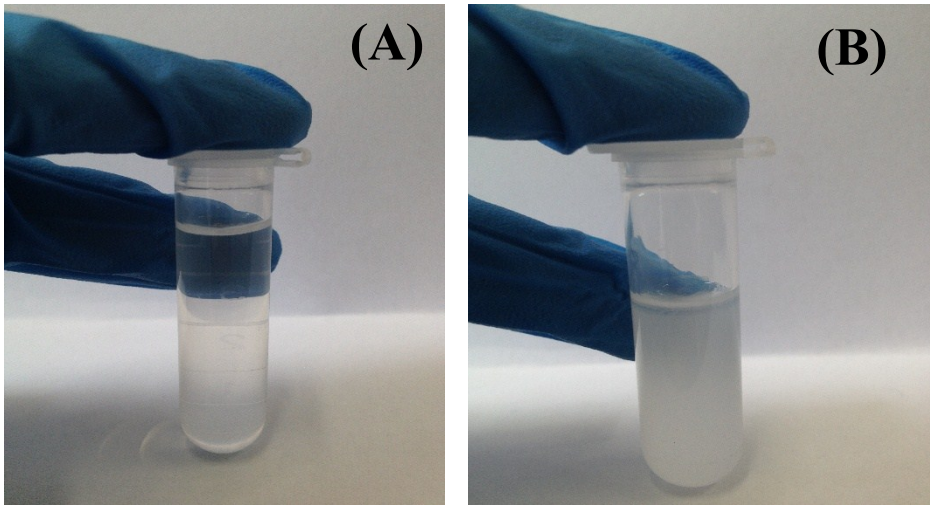

Figure S2 (A) The homogenous and transparent ternary mixture with composition corresponding to point 4. (B) The heterogeneous and opaque ternary mixture with composition corresponding to point 8.

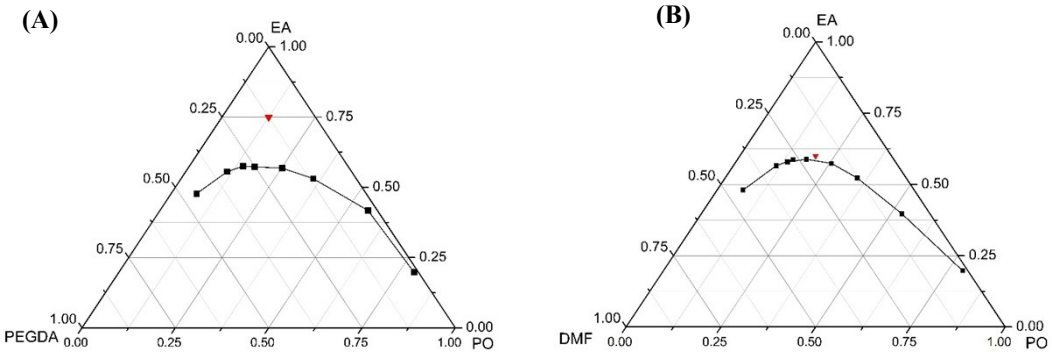

Figure S3 The pseudo-phase diagrams of PO-PEGDA-EA (A) and PO-DMF-EA (B). The red triangles represent the used volume ratios of PO-DMF-EA and PO-PEGDA-EA.

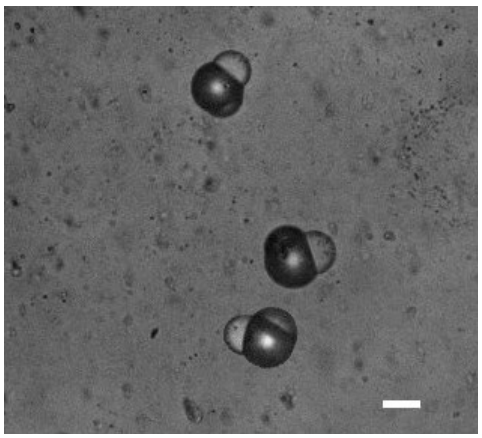

Figure S4 The micrograph of ternary Janus droplets formed by microfluidic emulsification. The disperse phase is NOA 61-water-hexadecane-acetone quaternary mixture. Scale bar is 40 μm.

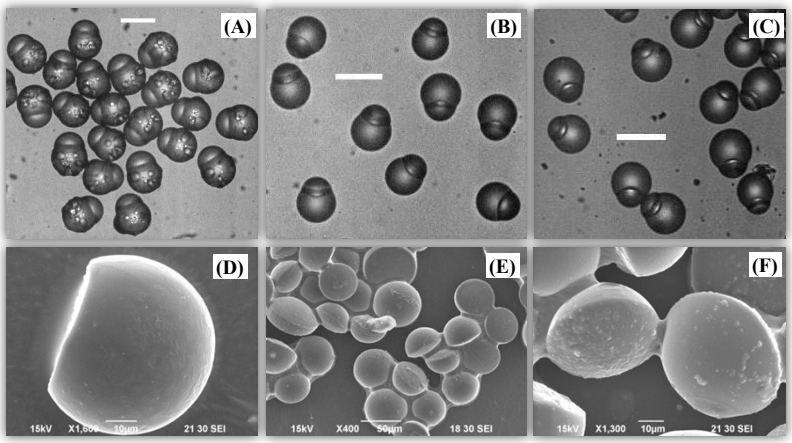

Figure S5 The solid particles synthesis by using NOA61-PO Janus droplets as templates. (A)-(C) Micrographs of Janus droplets generated by microfluidic emulsification. V_{NOA61}: V_{PO} = 2:1 (A), 1:3 (B) and 5:1 (C). Scale bar is 80 μm in (A)-(C). (D)-(F) SEM images of corresponding solid particles.

1. Q. Zhang, X. Liu, D. Liu and H. Gai, Lab on a Chip, 2014, 14, 1395–1400.