Electronic Supplementary Information 1: The PDMS microfluidic device

Microfluidic Synthesis of Janus Particles by UV-directed Phase Separation

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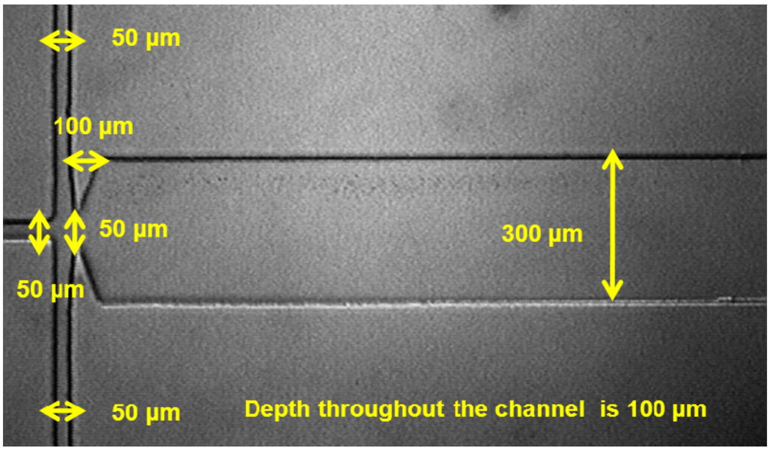


Figure S1. Optical micrograph of the cross-junction microfluidic channel.

The master molds were fabricated by conventional photolithography using SU-8 photoresist on a silicon wafer. A mixture of PDMS prepolymer and curing agent (10: 1 ratio) was thoroughly stirred and then degassed in a vacuum oven. The degassed PDMS mixture was then poured onto the silicon master and cured at 65 °C. After curing, the PDMS replica containing the microchannel pattern was lifted off the silicon master. After cooling, holes were punched in the replica to accommodate the reagent lines. The PDMS replica and glass slide were then exposed to oxygen plasma for 40 s, and bonded to each other. The dimensions of the final assembled microfluidic channels were 50 μm × 100 μm (width × height) for the injection and junction section and 300 μm × 100 μm (width × height) for the main reaction channel.

Electronic Supplementary Information 2: Effect of flow rate of continuous phase on the diameter of resultant droplets and effect of polymer concentration on phase-separated protruded head

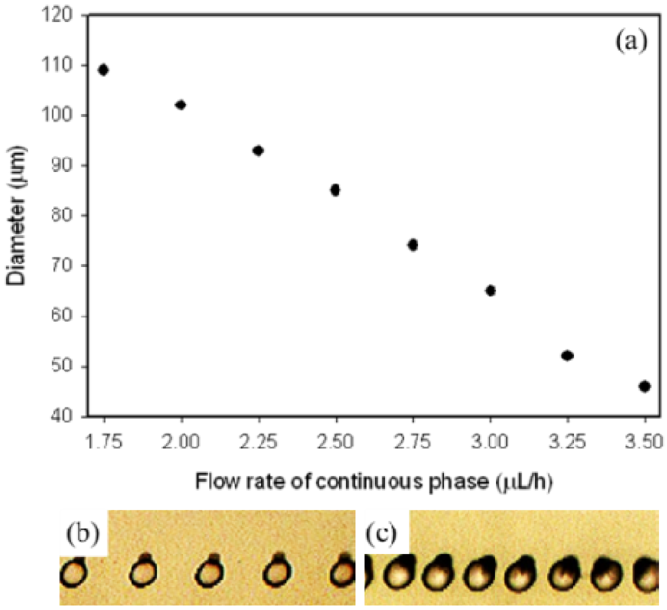


Figure S2. The effect of the flow rate of continuous phase on the diameter of resultant droplets: (a) a plot of droplet diameter as a function of the flow rate for the continuous phase when the flow rate for the discontinuous phase is fixed at 0.5 µL/h, (b) and (c) optical images of Janus particles prepared at two different concentrations of PNIPAAm-*co*-SPO-*co*-fluorophore in the aqeous mixture, 2.5 wt % and 5 wt %, respectively.

The average diameter of the aqueous droplets can be controlled by varying the flow rate of continuous phase. This effect is examined by keeping the flow rate of aqueous phase constant and changing the flow rate of continuous phase as shown in Fig. S2 (a). Additionally, by tuning the concentration of PNIPAAm-*co*-SPO-*co*-fluorophore in the aqueous mixture, the fraction of phase separated protrusion can be controlled. The portion of aggregated polymer increases with the increase in the concentration. At low concentration (2.5 wt %) of PNIPAAm-*co*-SPO-*co*-fluorophore in the aqueous phase, the size of phase separated polymer is almost half (Fig. S2 (b)) as compared to (5 wt %) (Fig. S2 (c)).

Electronic Supplementary Information 3: Color change of SPO moiety

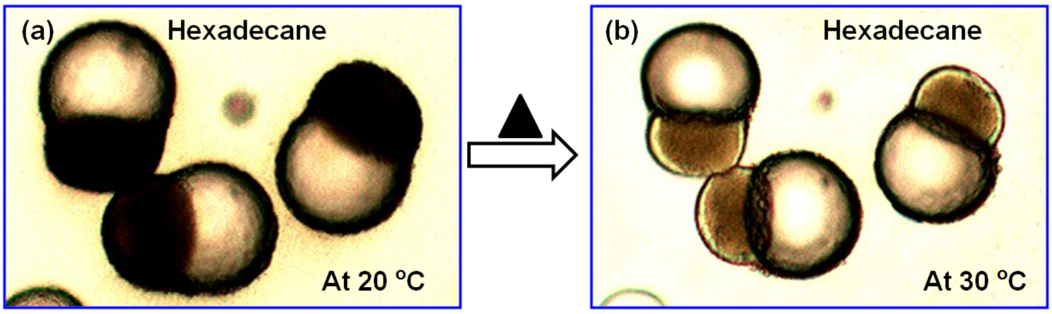


Figure S3. Optical images for thermo-chromism of the SPO in Janus particles: (a) merocyanine (open) form of SPO at 20 ^{o}C and (b) spiro (closed) form of SPO at 30 ^{o}C.

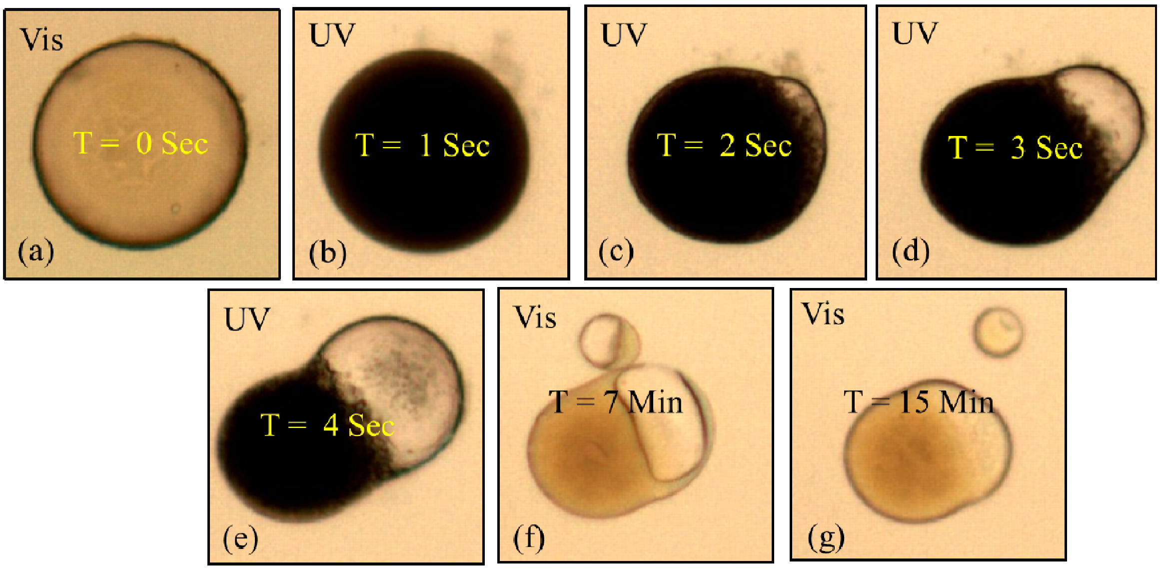
The photo- or thermo-chromism of spironaphthoxazine (SPO) involves the reversible stimuli-induced cyclization between colorless-spiro (closed) form and the colored-merocyanine (open) forms. The SPOs are photochromic compounds analogous to spiropyrans. Due to the presence of SPO group in poly(NIPAAm-*co*-SPO-*co*-fluorophore) copolymer, it undergoes reversible photoinduced heterolytic cleavage of the C (spiro)-O bond under UV irradiation, yielding the colored-open form that has all the chances to return to the colorless form by ring closure when subjected to heat.

During UV irradiation, SPO moiety undergoes spiro-merocyanine transformation, and which leads to deep red color as well as directional clustering of the copolymer. At this moment, Janus particle morphology can be fixed by the free-radical polymerization of MBA in the presence of DEAP (an oil-soluble photo-initiator). This open structure (deep reddish color) can be maintained for a long period of time due to the network structure of crosslinked poly(MBA), but the reverse process (from ‘open’ to ‘close’) can be accelerated by heating.

Electronic Supplementary Information 4: UV-directed phase separation in the absence of oil-soluble photoinitiator

Figure S4. Reversible phase separation of PNIPAAm-*co*-SPO-*co*-fluorophore in W/O droplet to give rise to asymmetric structure in the absence of oil-soluble photoinitiator under the UV-Vis irradiation.

In order to reveal the driving force for the phase separation of copolymer (PNIPAAm-*co*-SPO-*co*-fluorophore) in W/O emulsion, we carried out a separate multistep experiment. The aqueous phase is composed of 5 wt. % of poly(NIPAAm-*co*-SPO-*co*-fluorophore) and 1 wt. % of *N*,*N*′-methylenebisacrylamide (MBA). The continuous phase consists of hexadecane and 5 wt. % Span-80. At first, W/O droplet is produced through microfluidic device. Under visible light the aqueous droplet is homogenous and the polymer is evenly distributed in the droplet. Secondly, when W/O droplet is subjected to UV light, the copolymer poly(NIPAAm-*co*-SPO-*co*-fluorophore) aggregates in the W/O droplet and squeezes out water molecules from the polymer. As the experiment is carried out in the absence of oil-soluble photoinitiator, there is no polymerization in the droplet and aggregated polymer returns back to the homogenous morphology under the action of visible light, but the reverse reaction is slower. The slower rate confirms the intra- and inter-ionic bond formations due to the existence of zwitterions in the



polymer under UV-irradiation. W/O droplet is not stable for long time and therefore loses some material into the surroundings, consequently decreases in size. From above results we conclude that phase separation of polymer is purely UV-directed.