Electronic Supplementary Information (ESI)

One-Step Encapsulation and Triggered Release Based on Janus Particle-Stabilized Double Emulsions

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Experimental Section

Particle Synthesis: (Sty50/AA50) Janus particles are synthesized by seeded emulsion polymerization followed by acid hydrolysis as reported previously.[31] Briefly, 20 wt% linear polystyrene (LPS) dispersion is prepared by dispersing LPS particles in 1 wt% poly vinyl alcohol (PVA, Mw 13,000-23,000, 87-89% hydrolyzed) aqueous solution. A 20 wt% monomer emulsion is prepared by vortexing a mixture consisting of styrene, *tert*-butyl acrylate (*t*BA, 98%), 1 vol% divinylbenzene (DVB, 55%) and 0.5 wt% initiator 2,2'-Azobis(2.4-dimethyl valeronitrile) (V-65B) (Wako) with 1 wt% PVA aqueous solution. LPS particles are swollen with the monomer mixture by mixing the LPS dispersion and the monomer emulsion. The volume ratio of the LPS and the monomer mixture is 20:80. The particle-monomer mixture is mounted on a rotator (Glas-Col®) and rotated for 8 hours at 60 rpm. Seeded emulsion polymerization is performed by tumbling the particle-monomer mixture in an oil bath at 70 °C at 100 rpm for 10 hours. After seed emulsion polymerization, the particles are washed with DI water for least 6 times by centrifugation to remove PVA and unreacted monomer. The particles from seeded emulsion polymerization are then stirred in an acid mixture consisting of 80 vol% trifluoroacetic acid (TFA, 99%) and 20 vol% formic acid (FA, ≥95%) at 1200 rpm for 24 hours for hydrolysis of *t*BA. The volume ratio of particles and acid mixture is 1:40. The hydrolyzed particles are washed with DI water for 10 times by centrifugation.

Emulsion Stabilization and Triggered Release: The emulsions stabilized by Janus particles were prepared by homogenizing toluene and Janus particle dispersion in aqueous solution using a homogenizer (Ultra-Turrax T25 basic) at 9500 rpm for 60 seconds unless otherwise noted. The total emulsion volume was kept at 6 mL for all samples. The oil phase may contain 0.01 wt% nile red (technical grade) and the water phase may contain 1.5×10^{-4} wt% calcein (Sigma) to facilitate the characterization of emulsion. The agitation to multiple emulsion are done by tumbling the glass vial containing the multiple emulsion with a tumbler (IKA RW16 basic) at 120 rpm for 2 minutes. Triggered release is done by injecting 400 μL 1M NaOH solution into multiple emulsion followed by agitation. Evolution of multiple emulsions during increasing pH is done by injecting multiple emulsion into a petri dish (containing 9 mL deionized water) covered with a glass slide and 1 mL 1M NaOH to increase the pH. Snapshots of one multiple emulsion droplet are taken at different times using an upright microscope (Zeiss).

Morphology of (Sty50/AA50) Janus particles

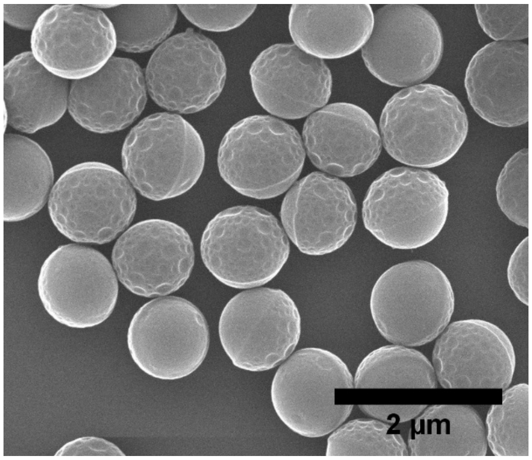


Figure S1. SEM image of (Sty50/AA50) Janus particles. The scale bar is 2 μm.

As shown in Figure S1, (Sty50/AA50) Janus particles have very clear asymmetric morphology: one rough side and one smooth side. The rough and smooth sides are rich in styrene and acrylic acid, respectively.[1]

Emulsion type as a function of emulsion composition

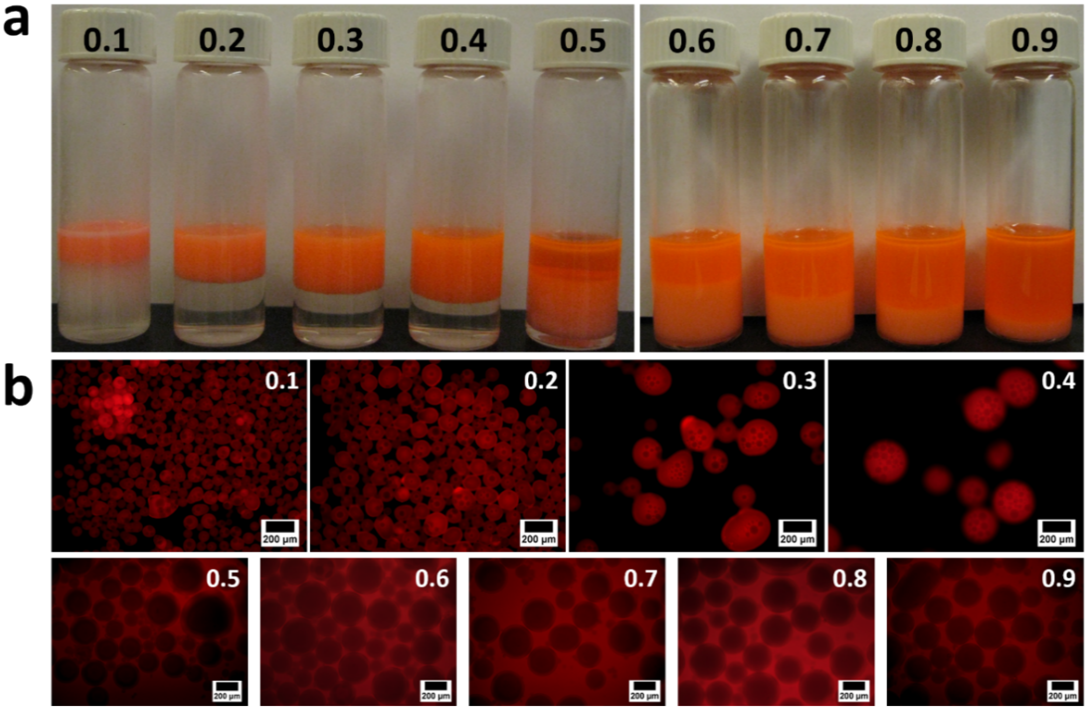


Figure S2. (a) Photo and (b) fluorescent microscopy images of emulsion stabilized by 0.5wt% (Sty50/AA50) Janus particles at pH5.0 with different volume fraction of oil phase (ϕ_o). The scale bar for fluorescent images is 200 μm.

Nine emulsions are generated with different volume fraction of oil phase (ϕ_o) as shown in Figure S2 (a). The water phase has a pH of 5.0 and contains 0.5% (Sty50/AA50) Janus particles. The oil phase is toluene with 0.01wt% Nile Red. When $\phi_o \geq 0.5$, emulsion type is W/O emulsion as confirmed by fluorescent microscopy as shown in the second row of Figure S2 (b). The red fluorescence of these emulsions is coming from the continuous phase and dark droplets are observed indicating that these are W/O simple emulsions. When $\phi_o < 0.5$, W/O/W multiple emulsions are formed. As shown in the first row of Figure S2 (b), the continuous phase is dark indicating that water is continuous phase. Red fluorescence is coming from the emulsion droplets with black spots indicating the formation of W/O/W multiple emulsions.

Adsoprtion of Janus particles at both outer oil-water and inner water-oil interfaces

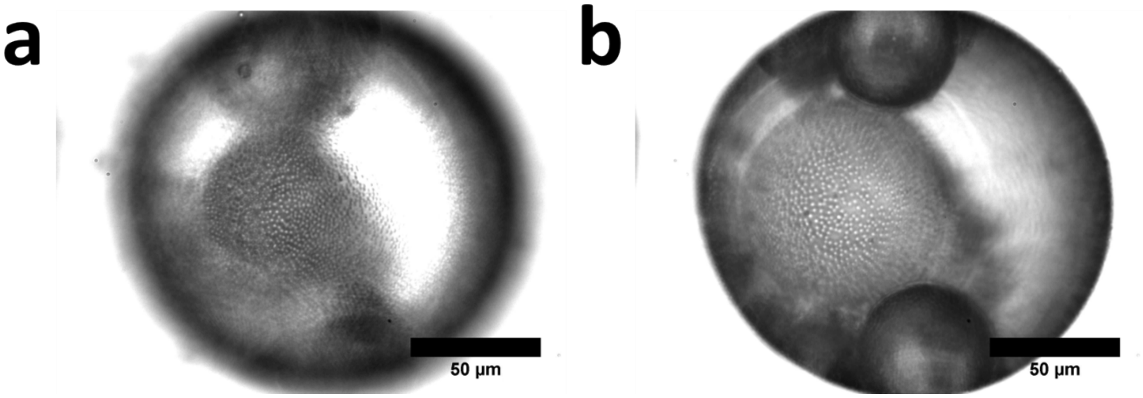


Figure S3. Microscopy images of a multiple emulsion droplet showing Janus particles adsorbed at both (a) outer and (b) inner oil-water interfaces.

The stabilization of multiple emulsion is achieved by the adsorption of Janus particles to both outer and inner oil-water interfaces. Images of one multiple emulsion droplet taken at different focal planes are shown in Figure S3; Janus particles adsorbed at the two oil-water interfaces can be clearly observed.

Orientation of Janus particles at oil-water interface

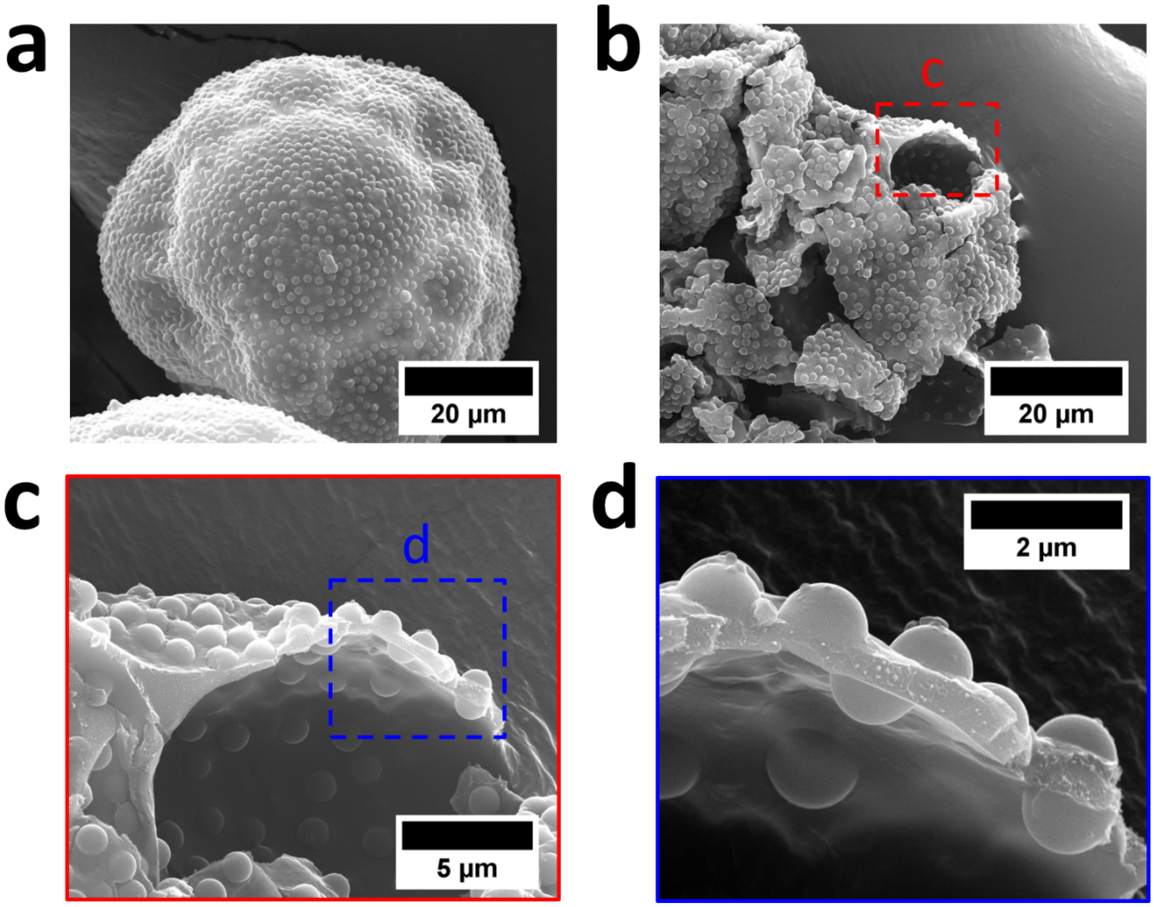


Figure S4. SEM images of (a) intact and (b-d) broken multiple emulsion stabilized by (Sty50/AA50) Janus particles. (c) and (d) are taken from the red and blue dashed areas in (b) and (c), respectively. The scale bars are 20 μm for (a) and (b), 5 μm for (c) and 2 μm for (d).

We modify a previously reported gel trapping method to directly visualize the orientation of Janus particles at the two oil-water interfaces of multiple emulsions.[2] The SEM samples are prepared by emulsifying chloroform containing 5 wt% linear polystyrene (M_w=45k) together with deionized water containing 0.5wt% (Sty50/AA50) Janus particles. The volume fraction of oil phase is 0.2. The multiple emulsions solidified by evaporating chloroform, which traps Janus particles at the oil-water interfaces. As shown in Figure S4 (a), the outer interface is densely covered with Janus particles. Samples in Figure S4 (b-d) are prepared by breaking the solidified multiple emulsions between two glass slides. As shown in Figure S4 (b-d), we can clearly see that Janus particles are adsorbed on both the inner and outer interfaces of the multiple emulsion. As shown in Figure S1, the smooth side of (Sty50/AA50) Janus particles is rich in acrylic acid and thus is hydrophilic.[1] The exposed sides of Janus particles adsorbed at the both inner and outer interfaces of multiple emulsion shown in Figure S4 (d) has very smooth surfaces, indicating that the exposed sides are rich in acrylic acid. These results clearly demonstrate that the Janus particles adopt the so-called upright orientation (*i.e.*, each side is exposed to its preferred fluid phase) at the surface.

Stability of multiple emulsion stabilized by (Sty50/AA50) Janus particle

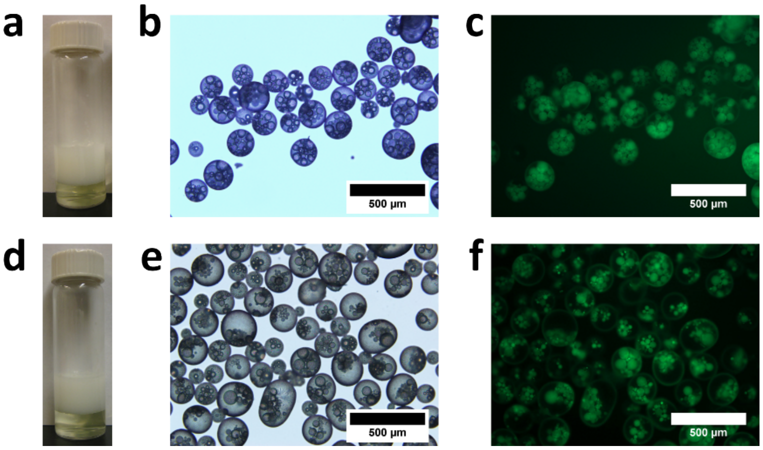
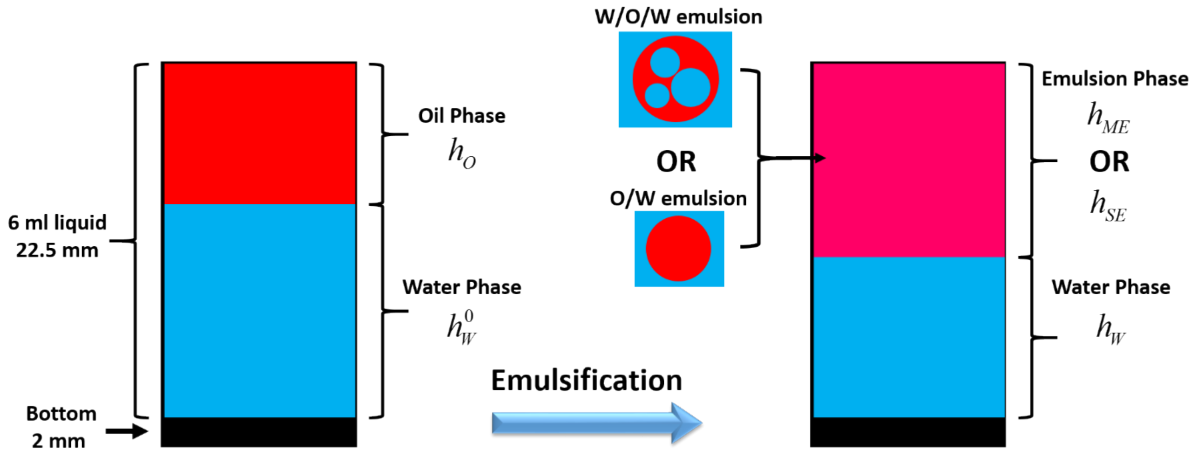


Figure S5. Photos and microscopy images of multiple emulsion (a-c) two hours and (d-f) more than three months after emulsification. Multiple emulsions are made from 1 wt% (Sty50/AA50) Janus particle dispersed in deionized water and toluene with ϕ_o = 0.4. 1.5×10-4 wt% calcein added in the water phase. The scale bar is 500 μm.

Packing fraction and encapsulation fraction



Scheme S1. Schematic illustration of parameters for the calculation of packing fraction and encapsulation fraction.

To determine the packing fraction of emulsion droplets, simple emulsion is needed. If the emulsion is simple O/W emulsion as shown in Scheme S1, the packing fraction can be calculated as

$$P = \frac{V_O}{V_{SE}} \qquad (1)$$

where V_O and V_{SE} stand for the volume of oil phase and simple emulsion phase, respectively.

Because the height is directly proportional to the volume in a cylindrical glass vial, the packing fraction can also be written as

$$P = \frac{h_O}{h_{SE}} \qquad (2)$$

where h_O and h_{SE} denote for the heights of oil phase and simple emulsion phase, respectively. The height of emulsion phase and that of water phase is related by

$$h_{SE} = 22.5 - h_W \quad (3)$$

because 6 mL liquid in the glass vial corresponds to 22.5 mm in height as shown in Scheme S1.

As shown in Table S1, the average packing fraction P as determined using simple O/W emulsion at pH 11.0 is 0.67 which is consistent with the packing of polydisperse spheres and emulsions.[3] The encapsulation fraction is defined as the volume ratio of encapsulated water phase and original water phase. The volume of encapsulated water phase is calculated with packing parameter as

$$V_{encap} = V_{ME}P - V_O \qquad (4).$$

Therefore the encapsulation fraction can be expressed as

$$\varepsilon = \frac{V_{ME}P - V_O}{V_W^0} \qquad (5).$$

Using the same simplification, the encapsulation fraction can be expressed in terms of the height of each phase in the glass vial as

$$\varepsilon = \frac{h_{ME}P - h_O}{h_W^0} \qquad (6)$$

where $h_{ME} = 22.5 - h_W$ (7).

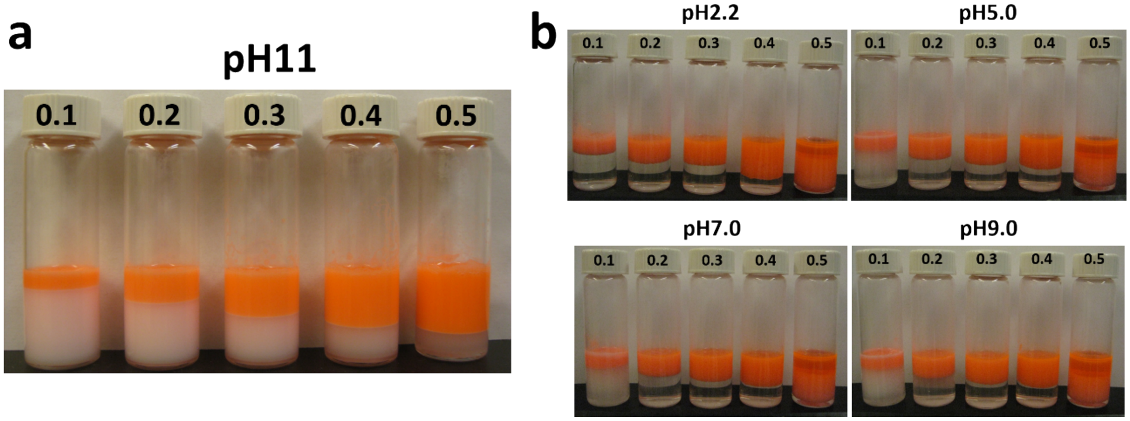


Figure S6. Emulsions made at (a) pH11.0 and (b) pH lower than 11.0 with different ϕ_o for calculating (a) packing parameter and (b) encapsulation fraction, respectively. In all cases, particle concentration is kept as 0.5 wt%.

Table S1. Parameters obtained from O/W emulsion in Figure S5 (a) and packing fraction calculated for each case.

V_O/V_W	10:90	20:80	30:70	40:60	50:50
h_O (mm)	2.25	4.5	6.75	9	11.25
h_W (mm)	19	16	12	9	6
h_{SE} (mm)	3.5	6.5	10.5	13.5	16.5
P	0.64	0.69	0.64	0.67	0.68

1 F. Tu, D. Lee, *J. Am. Chem. Soc*, 2014, **136**, 9999.

2 V. N. Paunov, *Langmuir*, 2003, **19**, 7970.

3 M. Clusel, E. I. Corwin, A. O. N. Siemens and J. Brujić, *Nature,* 2009, **460**, 611.