Anisotropic Particles Templated by Janus Emulsion

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Supporting Information

1. Materials.

Ethoxylated trimethylolpropane triacrylate (ETPTA, > 99 %) was obtained from Aldrich. Tripropyleneglycol diacrylate (TPGDA, > 90 %) was Tokyo Chemical Industry products. Methacryloxypropyl dimethylsiloxane (DMS) was purchased in Gelest, Inc. Fluorocarbon oil (HFE 7200) was 3M company products and used as received. Ethyleneglycol dimethacrylate (EGDMA, 98%) and 1-Hydroxycyclohexylphenyl ketone (HCPK, 99 %) obtained from Sun Chemical Technology (Shanghai) Co., Ltd. Pluronic F127 of average composition $EO_{97}PO_{68}EO_{97}$ and surfactant (Tween 80, > 97 %) was obtained from Sigma and used without further purification. The acetone was the Sinopharm Chemical Reagent Co., Ltd. Deionized water.

2. Emulsion preparations.

A series of samples with certain amount of ETPTA solubilized with 4 wt % of HCPK as initiator, HFE 7200, and 0.25 wt % $F127_{(aq)}$ were weight into 10 mL test tubes. The weight fraction of aqueous phase was kept constant at 0.33. The samples were mixed using the Ultra-turrax T 18 basic (IKA Co., Ltd., Germany) at certain speeds for 3 min until the emulsion appeared homogeneous. For nano-emulsion, further emulsification was endowed by sonication with 21 kHz Ultrasonic processor (Scientz-IID, Ningbo Scientz Biotechnology Co., Ltd., China) equipped with 6 mm diameter probe. The probe was symmetrically placed in the coarse emulsion, and the

process was carried out at applied power range of 20 % of the maximal equipment power (950 W) for 20 min. Work time and rest time for sonication were set at 1 s and 2 s. During emulsification, the difference in temperature from initial coarse emulsions to final emulsion was not more than 15 ^{o}C. The weight fraction of aqueous phase for nano-emulsion is 0.92. Each experiment was performed in triplicate.

3. Particle preparations.

A series of emulsion samples were exposed to UV-irradiation (500 W, λ=330-380 nm) by XPA-photochemical Reactor (XPA-7, Xujiang Electromech-anical plant, China) for 10 min. The anisotropic polymer particles templated from homogenous photo-polymerizable emulsion were obtained by washing with acetone for five times to remove HFE 7200, and dried at room temperature.

4. Size distribution measurements.

The size distributions of emulsions and particles were performed by Laser diffraction particle size analyzer (Mastersizer 3000, Malvern Instruments Ltd., United Kingdom) instrument equipped with a Hydro LV sample dispersion unit. The emulsion was slowly added into Millipore water with gentle stirring at the speed of 2400 rpm to avoid multiple scattering. The diluted sample was then pumped into detector at 1500 mL/min. The size distribution of each sample was measured at least three times. Average size reported was volume-averaged diameter, and the polydispersity of the powder was expressed by the Span value.

$$Span = \frac{[D_{(v,90)} - D_{(v,10)}]}{D_{(v,50)}}$$

Where $D_{(v, 90)}$, $D_{(v, 10)}$ and $D_{(v, 50)}$ were the equivalent volume diameters at 90%, 10%, and 50% cumulative volume.

5. Characterization.

Optical microscopy images of emulsion were recorded with microscope (DMLM/P, Leica Instrument Co., Ltd., Germany) with a magnification of 50 ×. Scanning electron microscopy (SEM, S-4800 II, Hitachi, Japan) was performed at an accelerating voltage of 10 kV. Transmission electron microscopy (TEM, JEM 2100F Microscope, JEOL, Japan) analysis was at an accelerating voltage of 200 kV. The

energy-dispersive X-ray elemental mapping was obtained on High-resolution transmission electron microscopy (HRTEM, Tecnai G2 F30, FEI, United States) at an accelerating voltage of 300 kV.

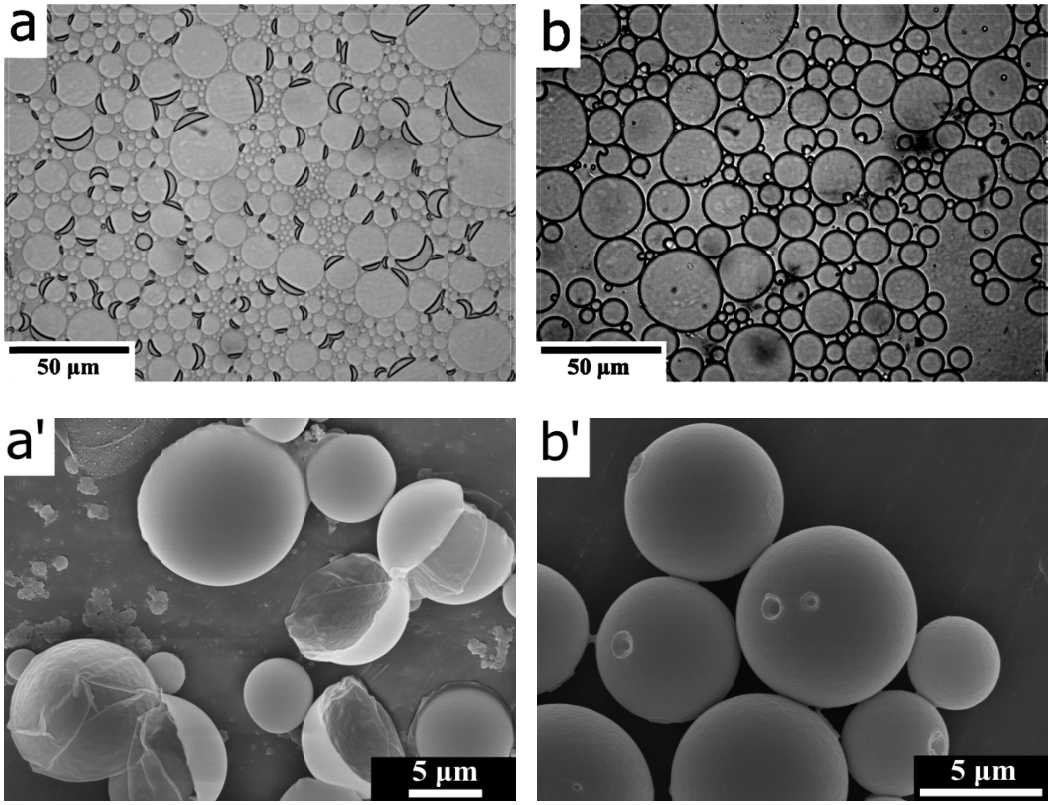

Figure S1. Micrographs of Janus emulsions (a, b), and SEM images of the resultant polymer particles (a', b') at mass ratios of ETPTA/HFE 7200: a-1/16; b-8/1. The weight fraction of 0.25 wt%F127 aqueous solutions is 0.33. The stirring rate of emulsification is 15500 rpm.

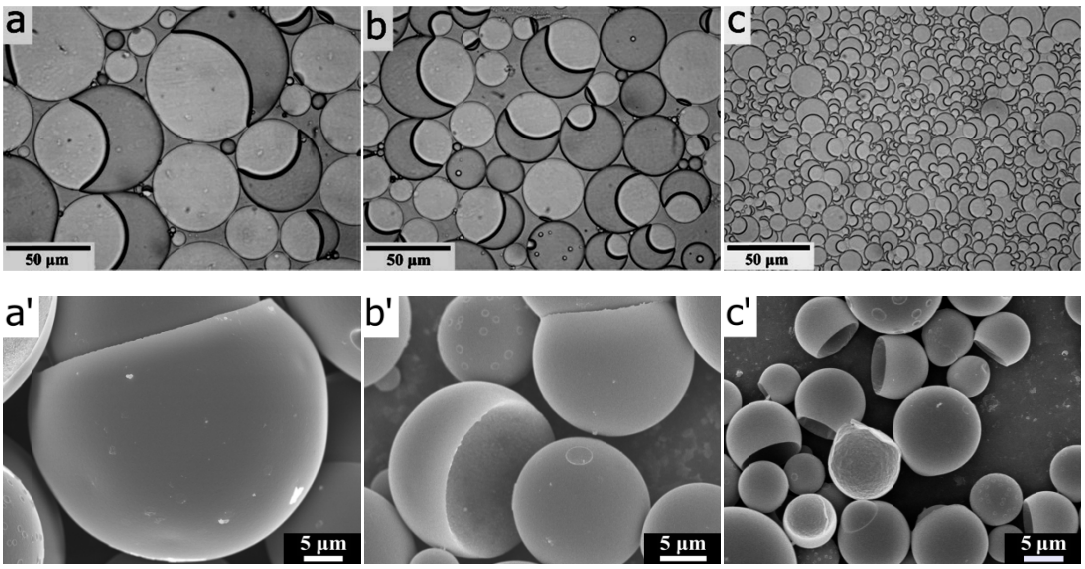

Figure S2. Micrographs of Janus emulsions (a-c), and SEM images of the resultant polymer particles (a'-c') at emulsification rates: a-3500 rpm; b-7000 rpm; c-24000 rpm. The weight fraction of 0.25 wt%F127 aqueous solutions is 0.33, and the mass ratio of ETPTA/HFE 7200 is 1/1.

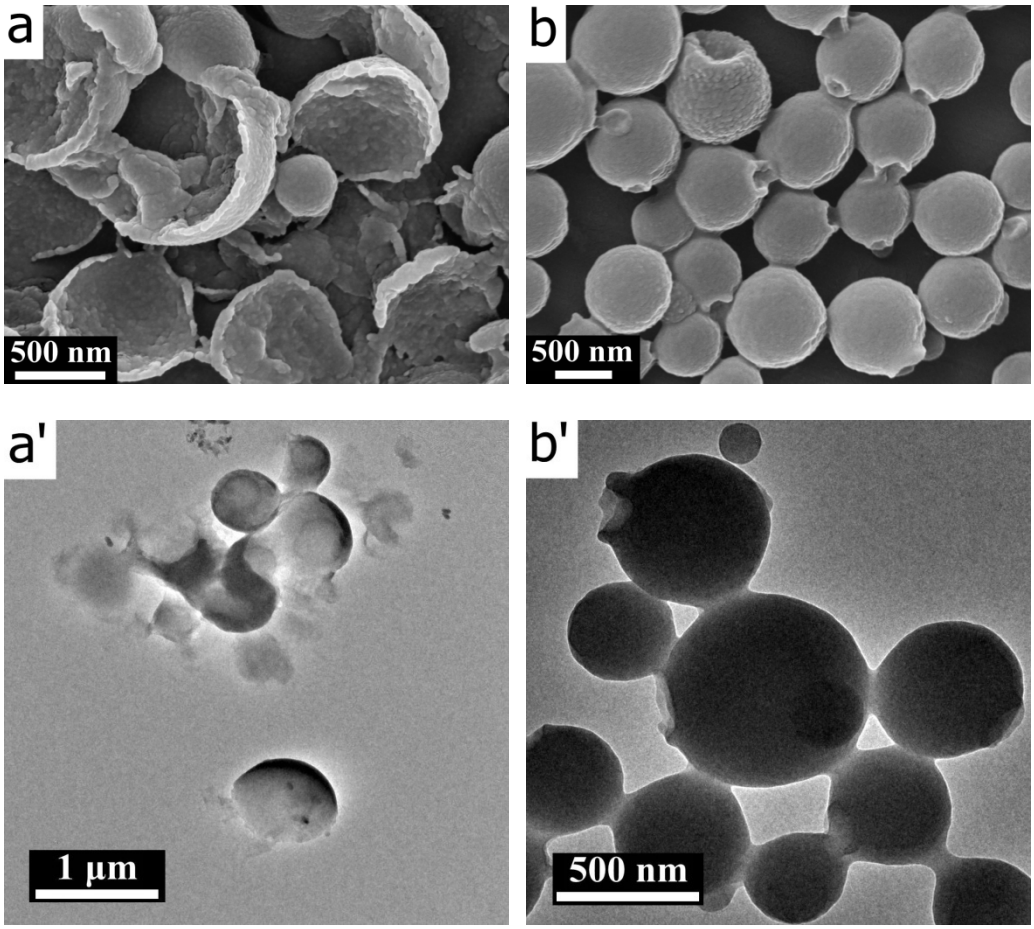

Figure S3. SEM (a, b) and TEM (a', b') images of polymer particles prepared from emulsions obtained by sonicate at mass ratios of ETPTA/HFE 7200: a-1/16; b-8/1. The weight fraction of 0.25 wt%F127 aqueous solutions is 0.92.

Table S1 The Span value of Janus emulsions and Janus particles corresponding to size distribution curves in Figure 1 a, a'.

	Janus emulsions		Janus particles	
ETPTA/HFE 7200	D(v, 0.5)*	Span*	D(v, 0.5)*	Span*
1/0	9.61 (0.48)	2.23 (0.11)	-	-
1/16	6.33 (0.01)	1.44 (0.01)	8.70 (0.11)	2.24 (0.18)
1/8	6.59 (0.01)	1.13 (0.01)	7.36 (0.07)	1.53 (0.01)
1/1	8.18 (0.08)	1.32 (0.02)	7.37 (0.02)	1.27 (0.01)
6/1	11.55 (0.35)	2.08 (0.06)	8.37 (0.04)	1.19 (0.01)
8/1	9.77 (0.23)	1.72 (0.04)	8.37 (0.08)	1.42 (0.02)
0/1	6.10 (0.09)	1.15 (0.03)	-	-

*Note: D (v, 0.5) means equivalent volume diameters at 50%; Span= (D (v, 0.9) - D (v, 0.1)) / D (v, 0.5)

Table S2 The Span value of Janus emulsions and Janus particles corresponding to size distribution curves in Figure 1 b, b'.

	Janus emulsions		Janus particles	
Stirring speed	D(v, 0.5)*	Span*	D(v, 0.5)*	Span*
3500	25.85 (2.15)	1.46 (0.03)	26.05 (1.98)	1.55 (0.11)
7000	16.05 (0.35)	1.23 (0.02)	20.61 (0.12)	1.01 (0.02)
11000	7.74 (0.14)	1.32 (0.03)	11.55 (0.05)	1.19 (0.08)
15500	8.68 (0.13)	1.38 (0.03)	6.35 (0.03)	1.47 (0.02)
20000	7.06 (0.11)	1.11 (0.03)	6.23 (0.01)	1.25 (0.01)
24000	7.13 (0.13)	1.17 (0.01)	6.98 (0.07)	1.01 (0.05)

*Note: D (v, 0.5) means equivalent volume diameters at 50%; Span= (D (v, 0.9) - D (v, 0.1)) / D (v, 0.5)