

Electronic Supporting Information

Synthesis of Janus particles via kinetic control of phase separation in emulsion droplets

Bing Liu^{*a}, Helmuth Möhwald^a, Dayang Wang^{*b}

^a *Department of Interfaces, Max-Planck Institute of Colloid and Interfaces, 14476, Potsdam, Germany.*

E-Mail: liubing@iccas.ac.cn

^b *Ian Wark Research Institute, University of South Australia, Mawson Lakes, SA 5095, Australia.*

E-Mail: dayang.wang@unisa.edu.au

Experimental Section

Materials. All chemicals were purchased from Sigma-Aldrich unless claimed differently. Methanol, ethanol, ammonia aqueous solution, toluene, styrene, octadecyltrimethoxysilane (ODTS), azobisisobutyronitrile (AIBN), cetyltrimethyl ammonium bromide (CTAB, 99%, Fluka) and polystyrene (PS, Mw = 40000, Polymer Source Int.) were used as received. Deionized water with a resistivity of 18.2 MΩ cm was prepared by a MiliQ system.

Experimental section

Preparation of PS – SiO₂ Janus particles:

1) Polymerization-induced phase separation. 11.25 mg of AIBN was dissolved in 0.45 mL of styrene, and then was mixed homogeneously with 0.05 mL of ODTS. The mixture was added into 20 mL of 1 wt % of CTAB aqueous solution and then homogenized at a speed of about 25000 rpm for 180s to form an oil-in-water emulsion. The emulsion was deoxygenated by bubbling with argon for 5min. Then the emulsion was sealed and placed into an oil bath at 80 °C. After polymerization was performed for 16 h, 3 mL of ammonia was added. The reaction was performed for another 6 h. Finally, the product was collected by centrifugation and washed with water for two times. The experiments were performed along the similar procedure except different feeding ratio of St/ODTS.

2) Solvent evaporation-induced phase separation. 0.45 ml of polystyrene toluene solution (10 w/v %) and 0.05 mL of ODTS were mixed and then added into 12 mL of 1 wt.- % of CTAB aqueous solution. The mixture was homogenized at a speed of about 25000 rpm for 180s to form an oil-in-water emulsion.

Then the emulsion was placed into an oil bath at 70 °C, and a hole was made on the cap with a 0.45 mm of syringe needle. Toluene evaporated during heating for 24 h. Afterwards, an equal volume of ammonia aqueous solution was added. The reaction was performed for another 6 h. Finally, the product was collected by centrifugation and washed with water for two times. The experiments were performed along the similar procedure except different feeding ratio of PS/ODTS.

The separated PS phase was obtained after detachment of the SiO₂ domains of as-prepared Janus particles via incubation in a mixture of octanol and ethanol (5/1, v/v) under sonication for 2 h. The separated SiO₂ phase was obtained after decomposition of the PS domains of as-prepared Janus particles using N, N'-dimethylformamide (DMF).

3) Prepration of PS – SiO₂ core shell particles. 11.25 mg of AIBN was dissolved in 0.45 ml of styrene, and then was mixed homogeneously with 0.050 mL of ODTS. The mixture was added into 20 mL of 1 wt.-% CTAB aqueous solution and then homogenized at a speed of about 25000 rpm for 180s to form an oil-in-water emulsion. The emulsion was deoxygenated by bubbling with an argon inset for 5 min. Then 3 mL of ammonia was quickly added. The emulsion was sealed and stirred at room temperature at least 6 h. Then the reaction vessel was transferred into an oil bath at 80 °C. The polymerization was performed for another 16 h.

All the experiments were performed along the similar procedure except different addition time of ammonia.

Characterization. SEM imaging was performed by using field-emission scanning electron microscopy (Gemini LEO 1550) operated at 3 kV. Optical images in fluorescence and transmission modes were obtained by CLSM (Leica DM IRBE).

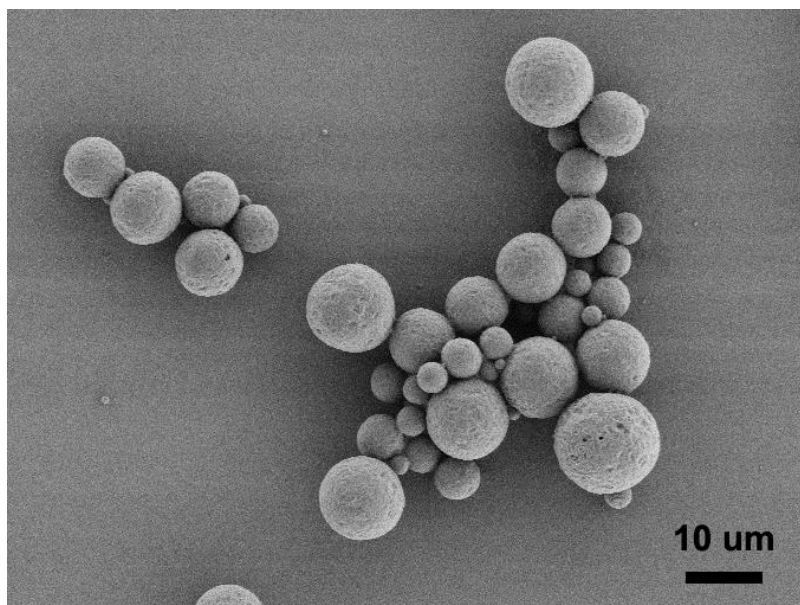
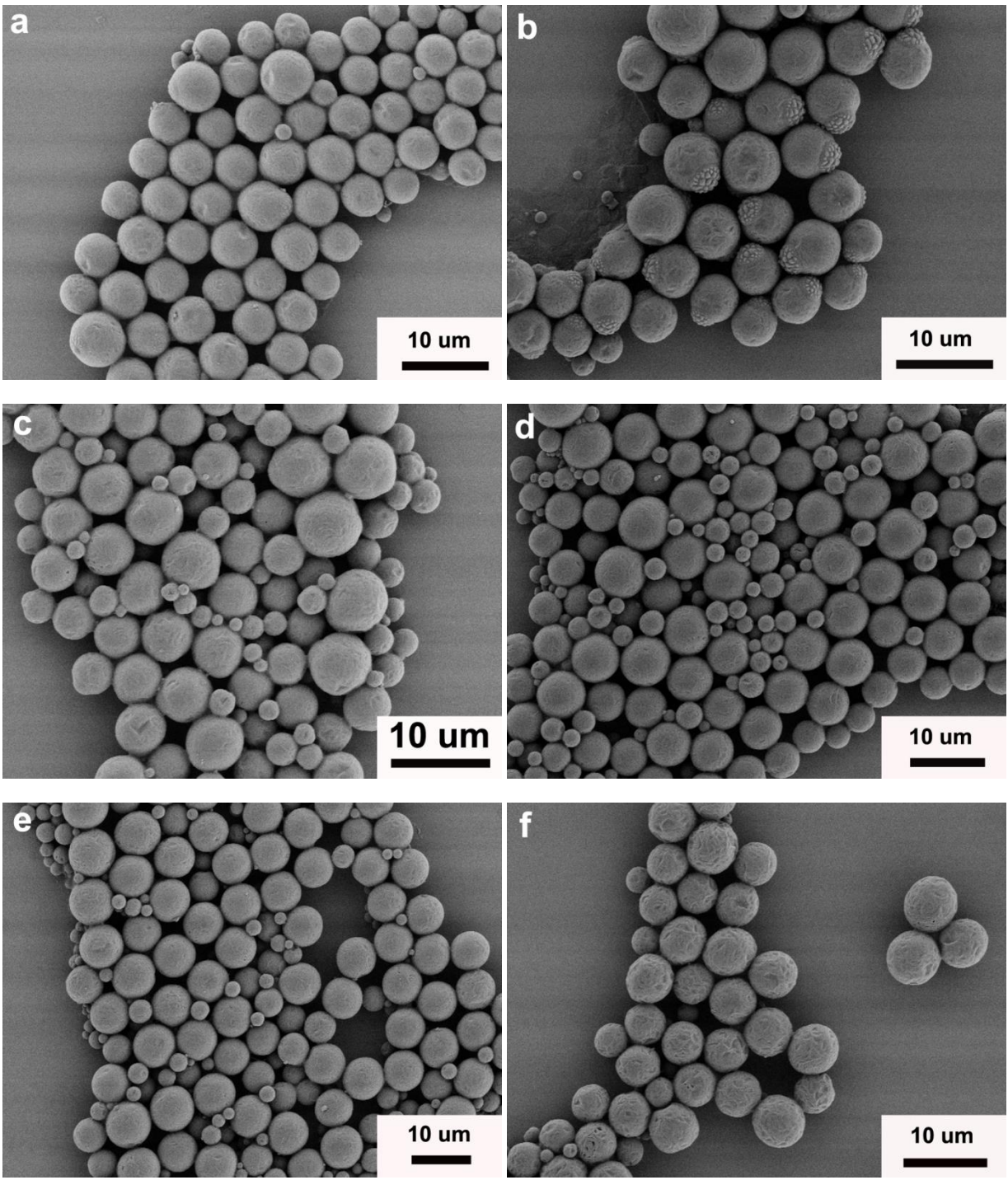


Figure S1 SEM image of SiO₂ particles derived via hydrolysis of ODTs droplets emulsified by CTAB in water.



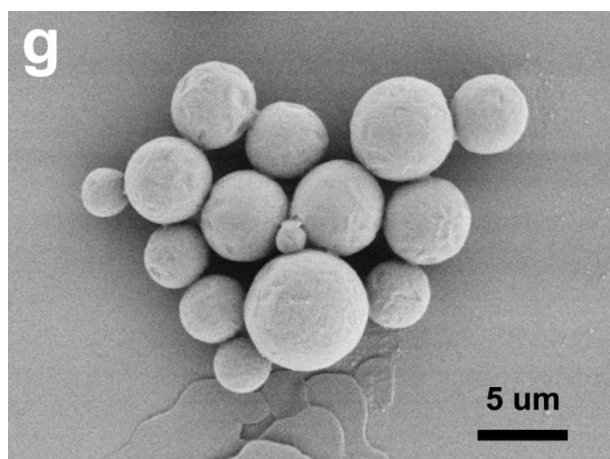


Figure S2. SEM images of PS/SiO₂ particles derived from the St/ODTS droplets emulsified by CTAB in water. The particles shown in Figures a - e are obtained via ODTS hydrolysis after 16 h (a), 3 h (b), 1 h (c), 0.25 h (d) and 0 h (e) St polymerization. The particles shown in Figures f and g are obtained via St polymerization after 6 h (f) and 24 h (g) ODTS hydrolysis.

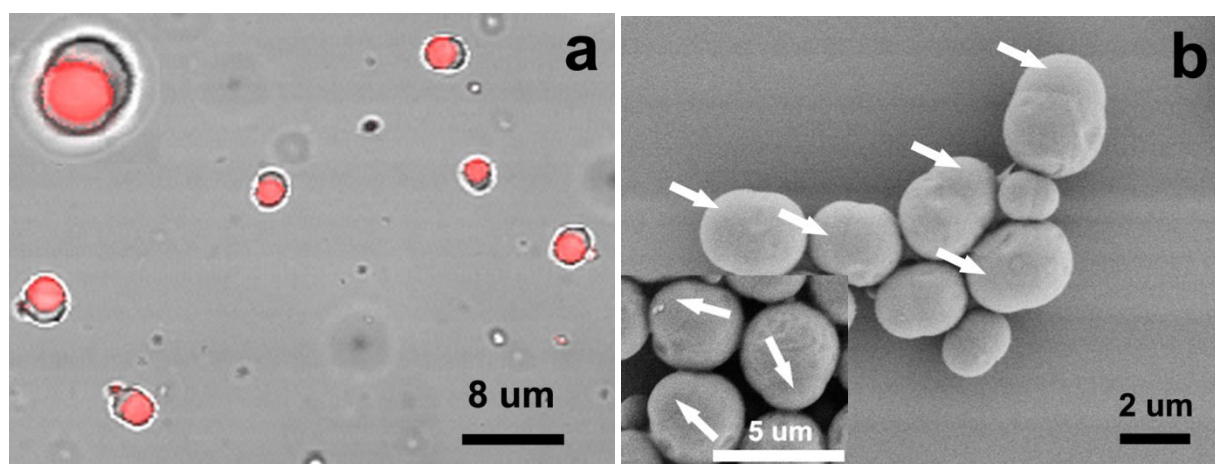


Figure S3. CLSM (a) and SEM image (b) of PS - SiO₂ Janus particles obtained via consecutive St polymerization and ODTS hydrolysis of CTAB-stabilized St/ODTS/toluene droplets in water. The St - to - ODTS - to - toluene volume ratio is 9:1:8. The resulting PS domains are stained by Nile red in Figure a. The PS domains are indicated by white arrows in Figure b. For comparison, the Janus particles obtained under the same time but in the absence of toluene in the emulsion droplets are shown in Figure 1b and the inset of Figure b.