Supplementary Material (ESI) for Chemical Communications

Supporting information

Janus non-spherical colloids by asymmetric etching

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Experimental

Monodispersed silica colloids were synthesized according to Stöber process.[1] A representative colloid about 320 nm in diameter was modified with APTMS by reflux in toluene for 12 h forming a silica-NH_2 colloid, and used to emulsify wax in water forming a Pickering emulsion.[2] In brief, 0.8 g of silica-NH_2 colloid, 40 ml of water and 3.5 g wax (melt point: 50-52 ℃, from Shanghai Huayong Wax Ltd.) was mixed under stirring at 80 ℃ for 1 h. After the system was cooled to room temperature, those solidified wax/silica composite spheres were separated by filtration. 4.2 g of the composite spheres were dried naturally at room temperature, and were immersed into 20 ml of 22 wt.-% aqueous NH_4F for 21 h. The Janus colloids were separated by centrifugation after the wax was dissolved with chloroform. In another procedure, the wax/silica composite spheres were repeatedly immersed/etched in 20 ml of fresh aqueous NH_4F (22 wt.-%) and filtered every 6 days. Mushroom-like Janus silica colloids were obtained after prolonged etching cycle and time for example the seventh cycle after 42 days. Afterwards, the wax/silica composite spheres were further immersed into another 20 ml of fresh aqueous NH_4F (22 wt.-%) for additional 50 days, in order to investigate the final morphology. Those Janus colloids with vinyl corona (silica colloids modified with 3-acryloxypropyl trimethoxysilane) were prepared along the similar procedure.

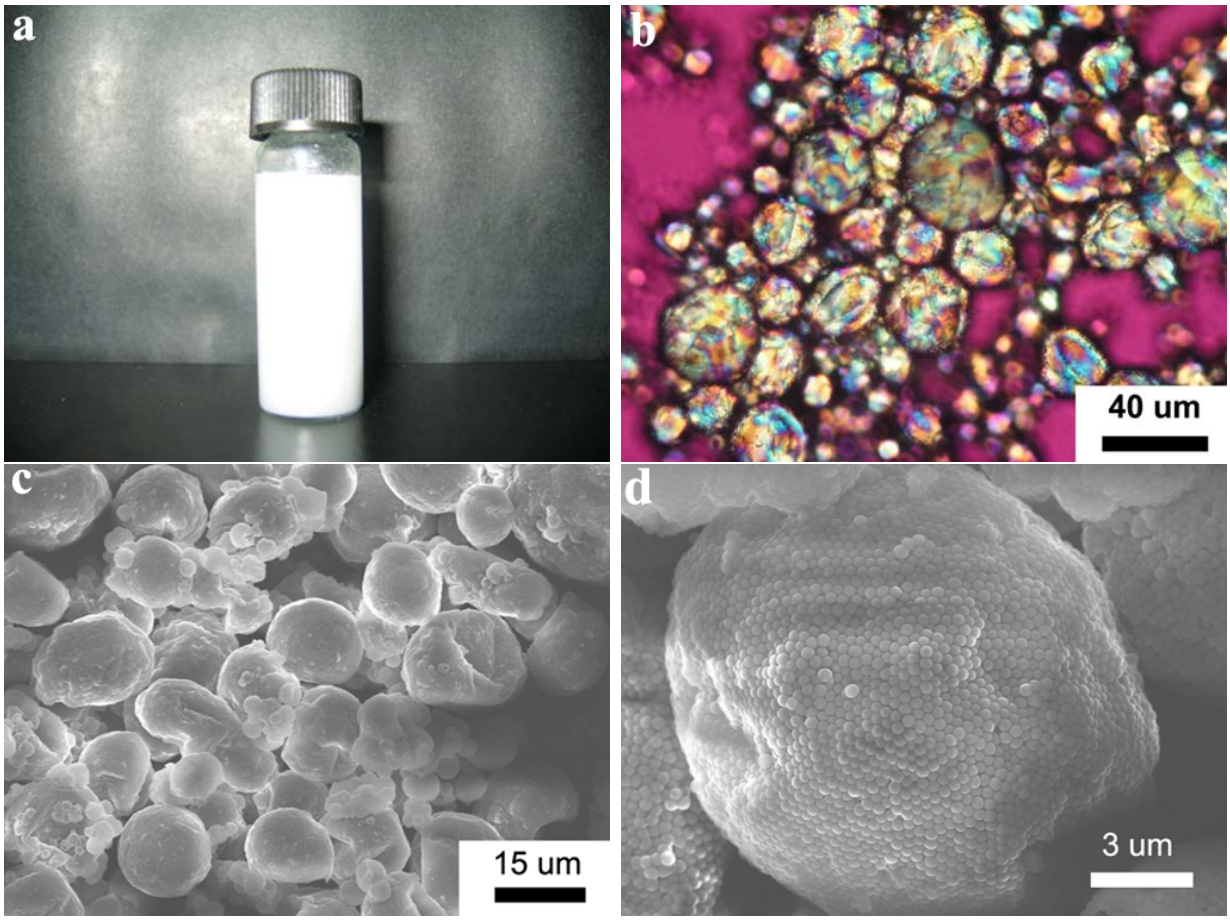
The Janus SiO_2/PS composite colloids with varied PS volume fraction and morphologies were synthesized by emulsion polymerization onto the vinyl corona side of the corresponding Janus silica colloids. 1) Janus SiO_2/PS colloids with PS caps: 1 mg of the Janus colloid was dispersed into 1 ml of water containing 0.4 mg of sodium dodecylbenzenesulphonate (SDBS) and 2.4 mg of $NaHCO_3$, then 50 μl of aqueous potassium peroxysulphate (KPS) (1 wt.-%) and 75 μl of styrene were added. The mixture was purged with nitrogen to remove oxygen. The mixture was gently stirred for a polymerization at 70 ℃ for 1 h. The product was separated by centrifugation at 7000 rpm and washed with water twice, then with ethanol for three times. PS colloids were completely separated, confirmed by the absence of such colloids under SEM. 2) Janus SiO_2/PS dimers: The other parameters were the same as 1) but 2 mg of the Janus silica colloid and 75 μl of KPS (1 wt.-%) were used instead of 1 mg and 50 μl, respectively. In another formulation, the amount of KPS (1 wt.-%) and St were both increased to 100 μl in order to increase the PS volume fraction. 3) Janus SiO_2/PS colloids with PS nano-flowers: 2 mg of the Janus silica colloid was dispersed into 1 ml of water containing 0.5 mg of SDBS and 2.4 mg of $NaHCO_3$. The mixture was purged with nitrogen to remove oxygen, then heated to 70 ℃. The mixture containing 85 μl of aqueous KPS (1 wt.-%), 85 μl of St, 0.5 ml of water, 0.25 mg of SDBS, and 1.2 mg of $NaHCO_3$ was emulsified under ultrasonication, and then was added dropwise at a rate 50 μl every 5 min. After completion of the dropping, the polymerization was performed for additional 10 min.

The as-prepared wax/silica composite spheres were observed under a microscope Olympus BX51. Morphology observation and energy-dispersive X-ray (EDX) analysis of the samples were preformed with a HITACHI S-4800 scanning electron microscope (SEM) equipped with an EDX analyzer operated at an accelerating voltage of 15 KV. The samples were dispersed in ethanol and dropped onto carbon-coated copper grids for transmission electron microscope (TEM) characterization (JEOL JEM-1011).

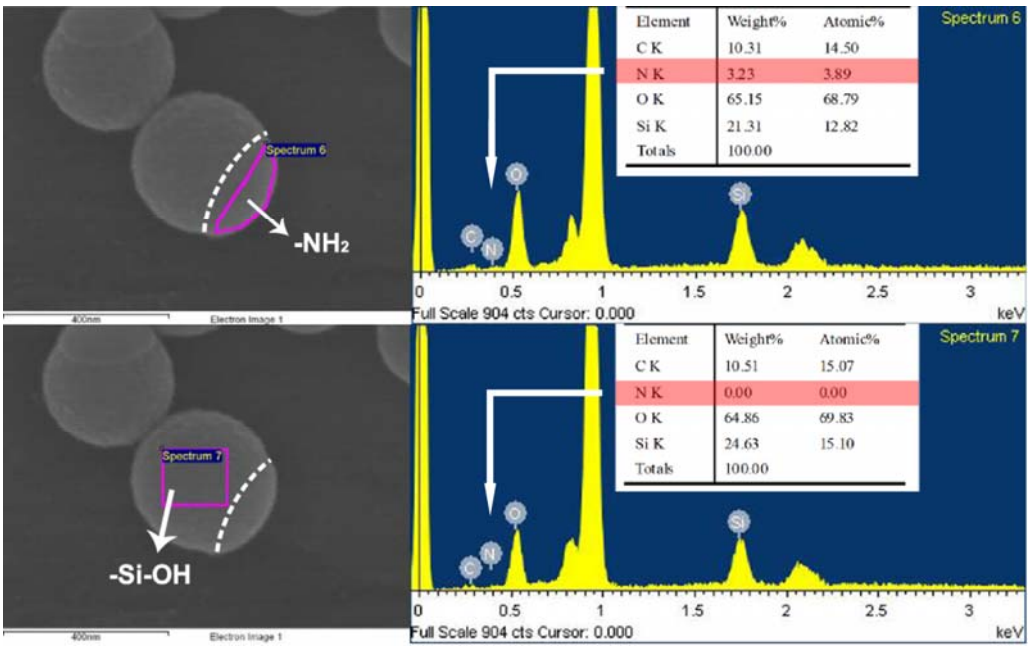
References:

(1) W. Stöber, A. Fink, E. Bohn, *J. Colloid Interface Sci.*, 1968, **26**, 62.

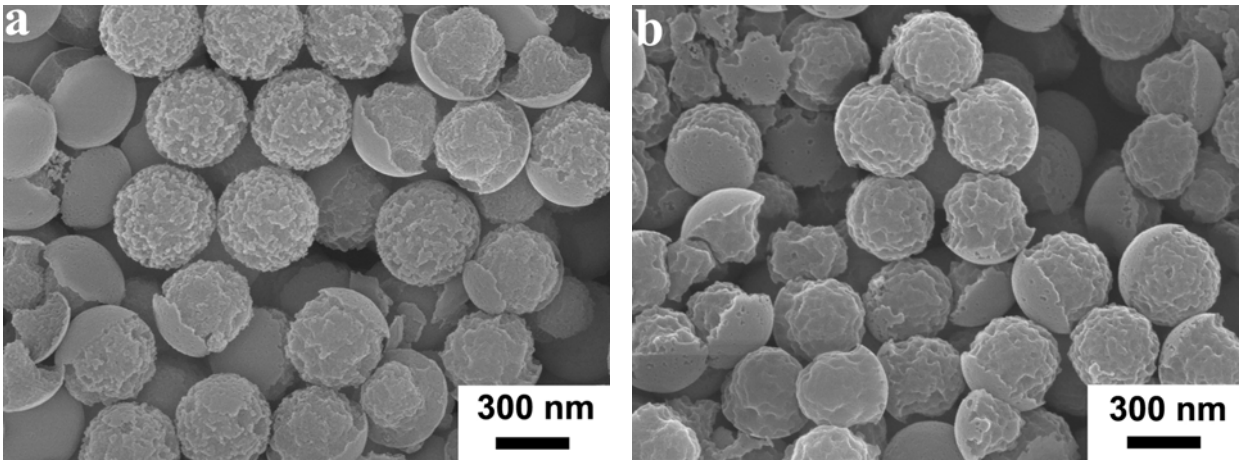
(2) L. Hong, S. Jiang, S. Granick, *Langmuir*, 2006, **22**, 9495.



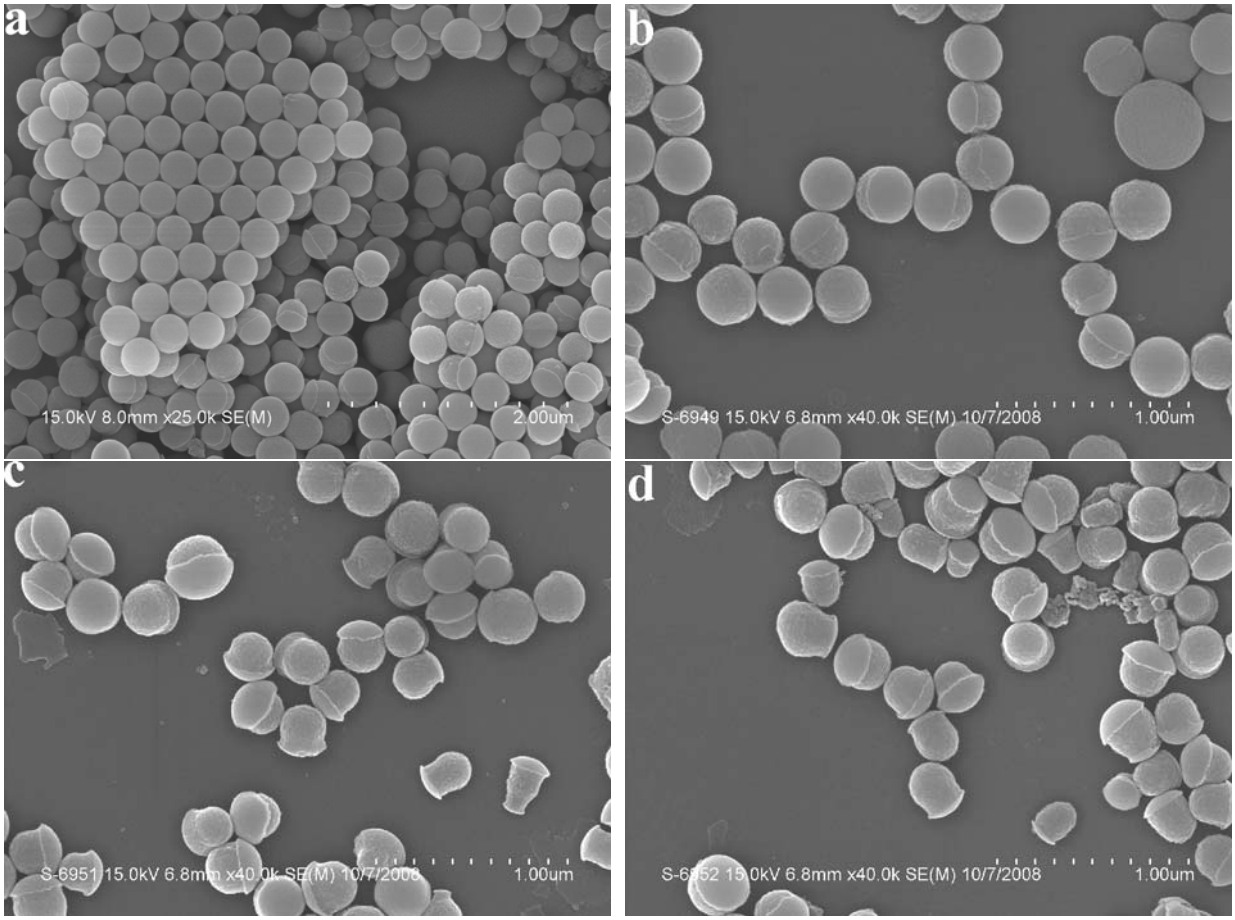
SI Fig. 1. The solidified wax/water Pickering emulsion stabilized by the silica-NH_2 colloid at room temperature: a) optical picture; b) polarizing optical microscopy image; c, d) SEM images of the solidified wax/silica-NH_2 composite spheres at two magnifications.

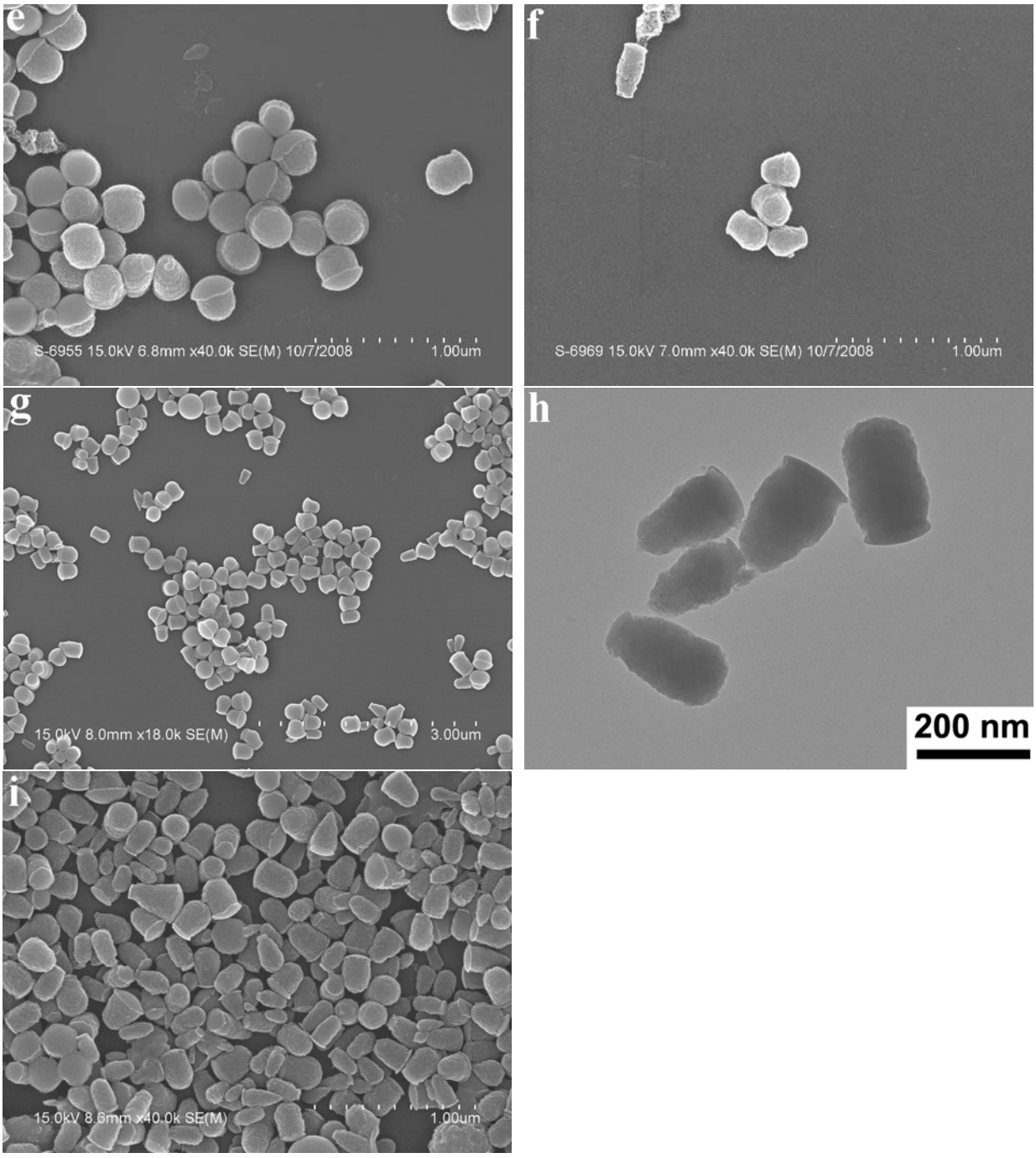


SI Fig. 2. EDX spectrum of as-prepared Janus silica colloids from APTMS modified silica. Spectrum 6: corresponding to the imbedded and protected smooth amino corona side. Spectrum 7: corresponding to the etched coarse silica side. N element is detected on the smooth side, and no N element is detected on the coarse side.

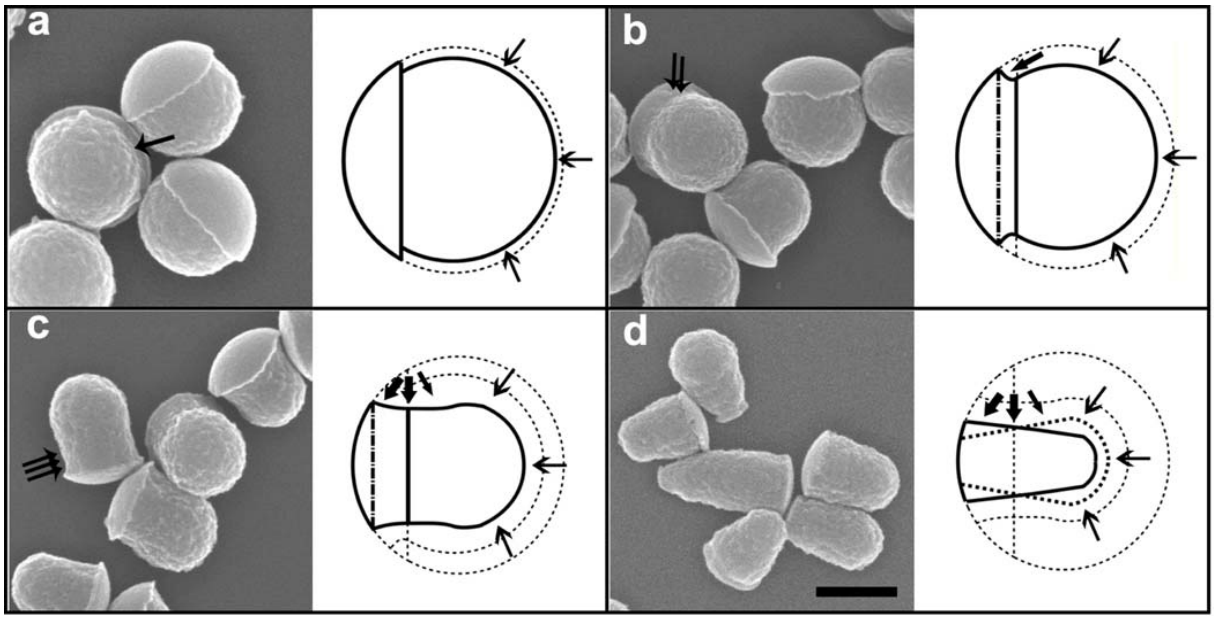


SI Fig. 3. SEM images of the Janus colloids by asymmetrical etching with vigorous stronger etching solution of increasing concentration: a) in a mixture of 10 ml of aqueous NH_4F (22 wt.-%) and 10 ml of aqueous HF (1.0 wt.-%); b) in 20 ml of aqueous HF (1.0 wt.-%). Weight of the wax/silica composite spheres is fixed at 4.2 g.

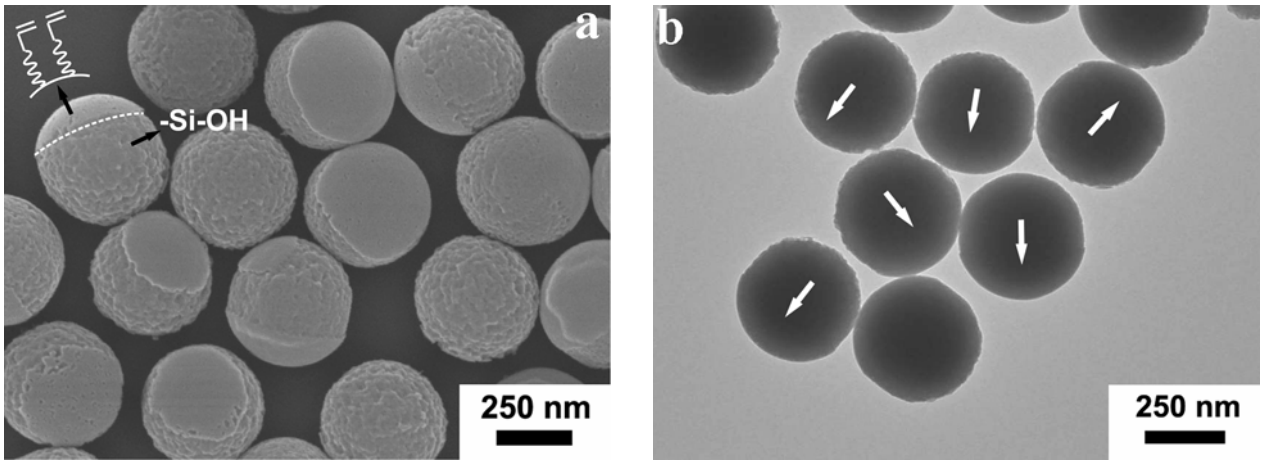




SI Fig. 4. Morphological evolution of the Janus colloids by asymmetric etching after varied cycle and time (days): a) 1st (6); b) 2nd (12); c) 3rd (18); d) 4th (24); e) 5th (30); f) 6th (36); g) 7th (42); h, i) 8th (92).



SI Fig. 5. The morphological evolution from spherical to non-spherical shape of the Janus colloids by repeatedly asymmetric etching for varied cycle (time - days): a) 1 (6); b) 3 (18); c) 7 (42); d) 8 (92). The scale bar represents 250 nm. Black arrows indicate the etching groove in the figures. From SI Fig. 5a to 5c, the groove becomes necking and wider with etching process. In SI Fig. 5d, many shapes coexist. The corresponding inset schemes illustrate the morphological evolution. The thin arrow represents etching mode I, and the thick arrow represents etching mode II.



SI Fig. 6. a, b) SEM and TEM images of the Janus silica colloids from the AcOPTMS modified silica colloids. Vinyl corona on the smooth side and the fresh silica with group Si-OH are indicated by the corresponding arrows. In the TEM image, the vinyl corona smooth side is indicated by the arrow.