Supporting Information

Large Scale Synthesis of Janus Submicron Sized Colloids by Wet Etching Anisotropic Ones

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Experimental Section:

***Synthesis**:* Monodisperse silica colloids were synthesized along with Stöber method (Stöber, W.; Fink, A.; Bohn, E. *J. Colloid Interface Sci.* **1968**, *26*, 62-69.). One example colloid with about 400 nm diameter was used. Vinyl was introduced onto the silica colloid surface by modification with a silane coupling agent [3-(methacryloyloxy) propyl] trimethoxysilane (MPS) (The mixture of 0.1 g silica colloids/0.4 g MPS/2 g ethanol was stirred at 25 °C for 12 h, afterwards removing residual MPS by centrifugation and wash with ethanol). 0.1 g of MPS modified silica colloid was dispersed in 3 g of water. At 80 °C under stirring, an example monomer emulsion (0.025 g of styrene (St), 0.025 g of divinylbenzene (DVB), 0.025 g of sodium dodecyl benzenesulfonate (SDS), 0.05 g of 1 wt.-% potassium persulfate (KPS) aqueous solution, and 10 g of water) was added dropwise into the silica dispersion in 2 h, polymerization occurred onto the silica surface. Afterwards, the system was held at 80 °C for 6 h. The composite colloids were obtained after centrifugation and wash with ethanol and water to remove surfactant.

***Etching**:* A fresh silica surface was generated by etching weak part of composite colloids, forming the corresponding Janus colloids. 0.1 g of composite colloid was dispersed in 10 g of dilute aqueous hydrofluoric acid (HF) solution in ethanol of varied concentration. The mixture was stirred at room temperature for 12 h, afterwards refining the resultants by centrifugation and wash with ethanol and water.

Emulsification: The PS/silica Janus colloids were washed with DMF to remove the surfactant and linear polymers. 0.015 g of freeze-dried powder of PS/silica Janus colloids was dispersed in 2.5 g of water, followed by adding 2.5 g of toluene. The emulsion stabilized with Janus colloids was formed after the mixture was emulsified by ultrasonic for 5 min.

Characterization:

Structure and morphology of colloids were characterized using transmission electron microscopy (JEOL 1011 and JEOL 100CXII at 100 KV) and scanning electron microscopy (HITACHI S-4300 at 15 KV). The samples for SEM characterization were prepared by vacuum sputtering with Pt on the ambient dried samples. TEM samples were prepared by spreading very dilute colloid dispersions in ethanol onto carbon-coated copper grids. FT-IR spectroscopy was performed using a BRUKER EQUINOX 55 spectrometer with the samples/KBr pressed pellets. Pyrolysis Gas Chromatography-Mass Spectrometry (SHIMADZU GC-MS 2010S) was used to detect the presence of polymer in the etching supernatant. Thermogravimetic Analysis (TGA) was performed from 25 °C to 800 °C in air by EXSTAR TG/DTA 6300 (Seiko Instruments Inc.). Dynamic Laser Scattering (DLS) was performed using Zetasizer NanoZS (Malvern Instruments Inc.). The morphology of emulsions stabilized with Janus colloids was characterized using Olympus BX51 microscope.

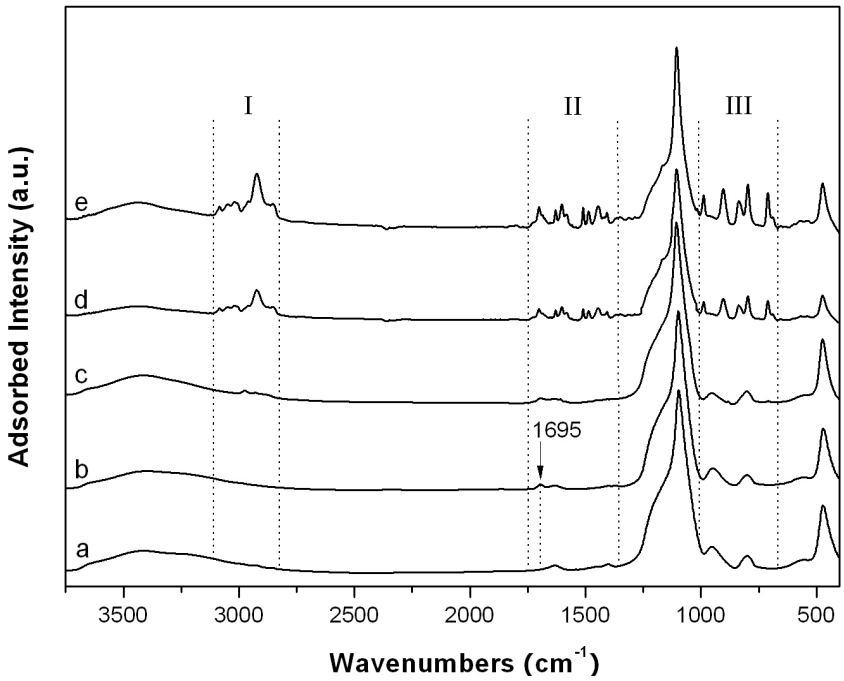


Fig. S1 FT-IR spectra of some representative samples: a, b) silica colloids before and after being modified with MPS; c-e) anisotropic composite colloids with increased monomer/silica weight ratio: 0.1:1, 0.5:1 and 6:1 respectively (as shown in Figures 1b-d). The St/DVB weight ratio in the monomer mixture is kept at 1:1. The 1695 cm^{-1} peak indicates the C=O group of MPS. I, II and III areas correspond to the characteristic bands of crosslinked PS.

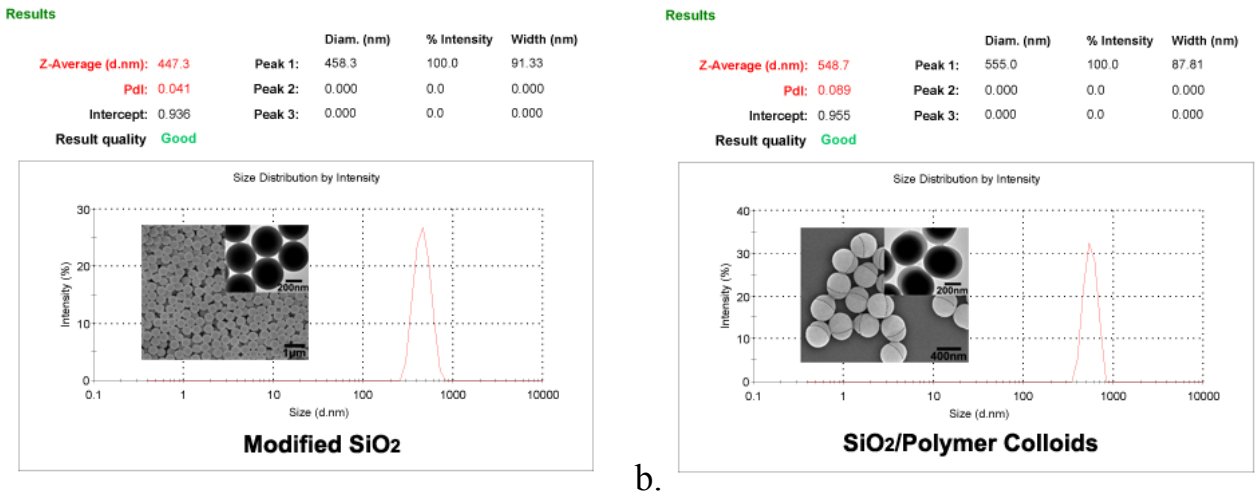


Fig. S2 Dynamic light scattering (DLS) data of two representative samples: a) the modified silica colloids (as shown in Figure 1a); b) the PS/silica anisotropic colloids (as shown in Figure 1c).

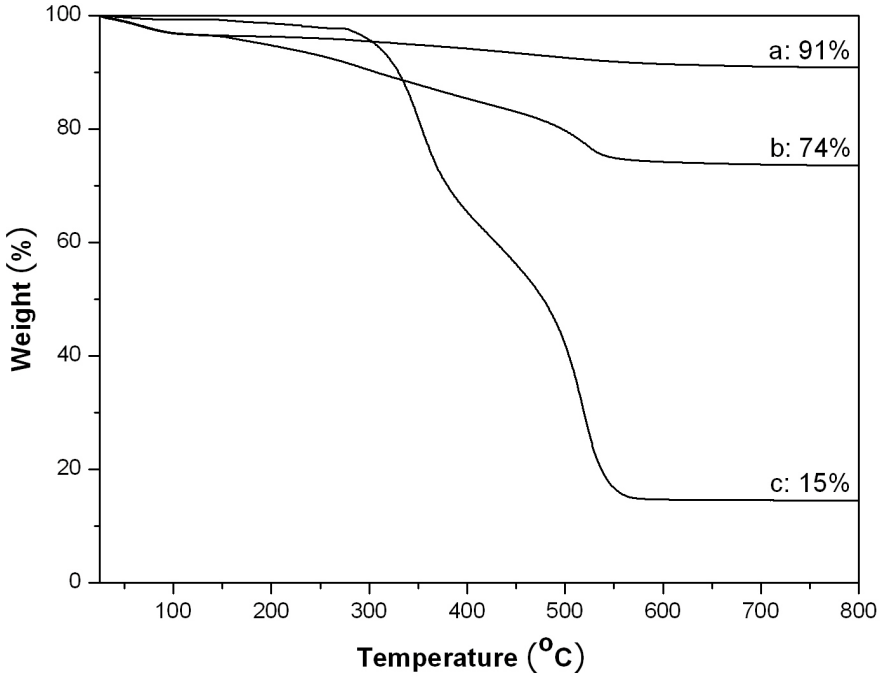


Fig. S3 Thermogravimetic analysis (TGA) curves in air of representative samples with increased PS/silica ratios (as shown in Figures 1b to 1d).

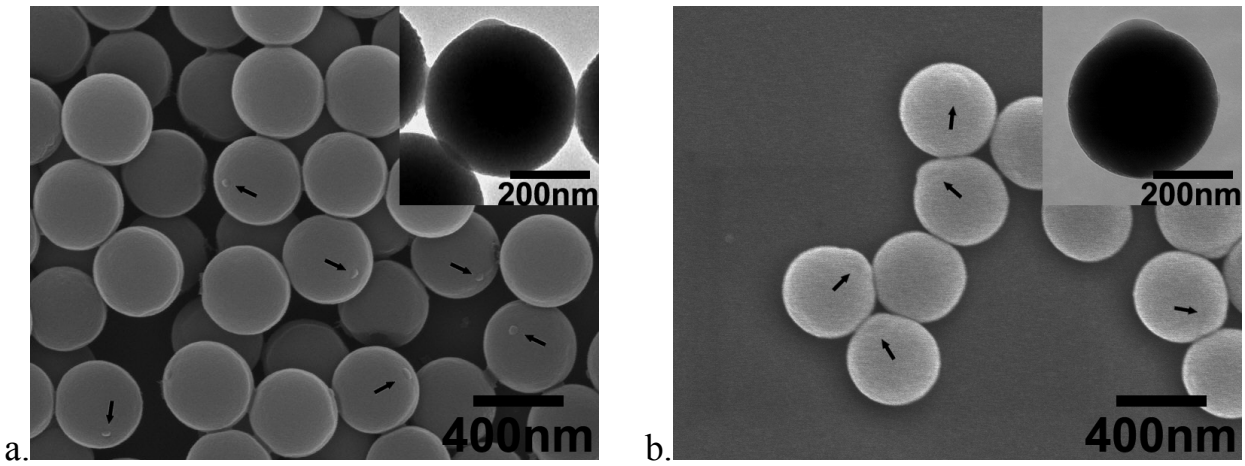


Fig. S4 Morphological evolution of PS/silica colloids at the early stage with different reaction time: a) 20 min; b) 40 min.

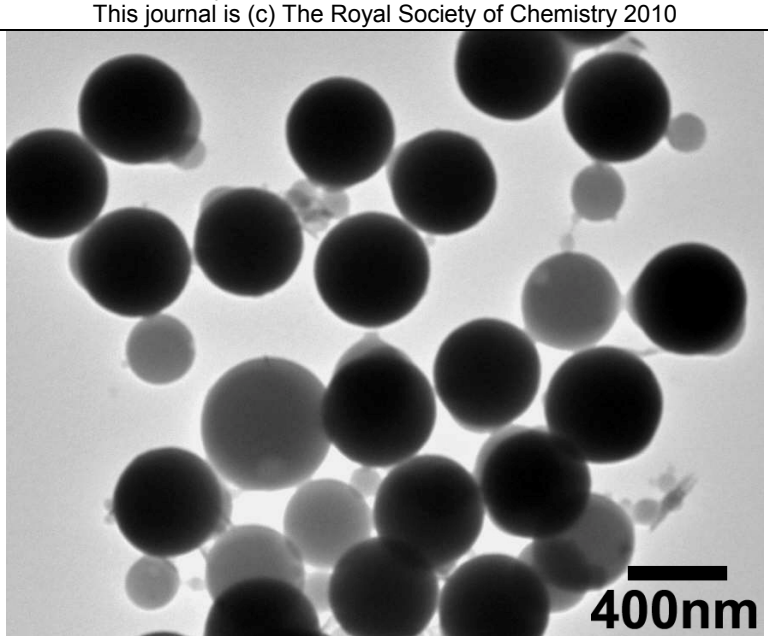
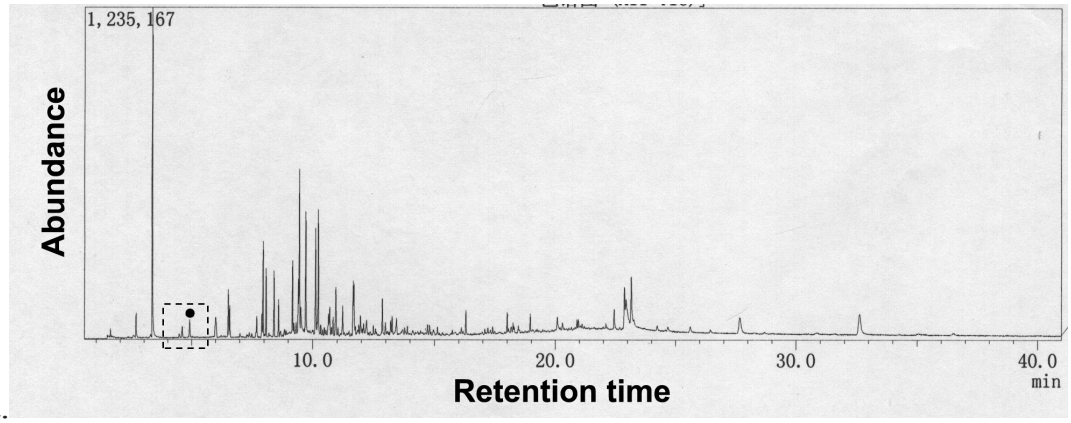
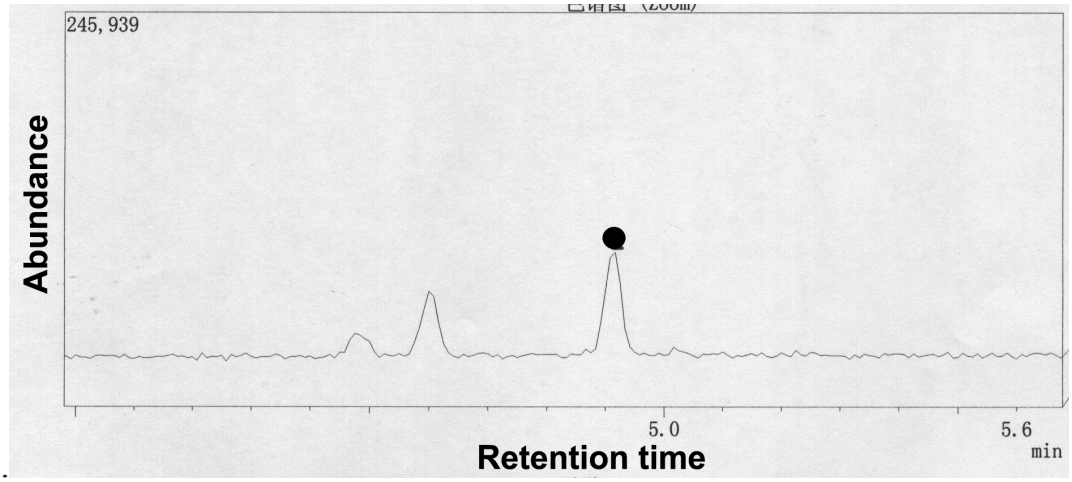


Fig. S5 TEM image of PS/silica colloids by one-step batch emulsion polymerization (the monomer/silica weight ratio is 0.5:1, and the St/DVB weight ratio is 1:1).

a.



b.



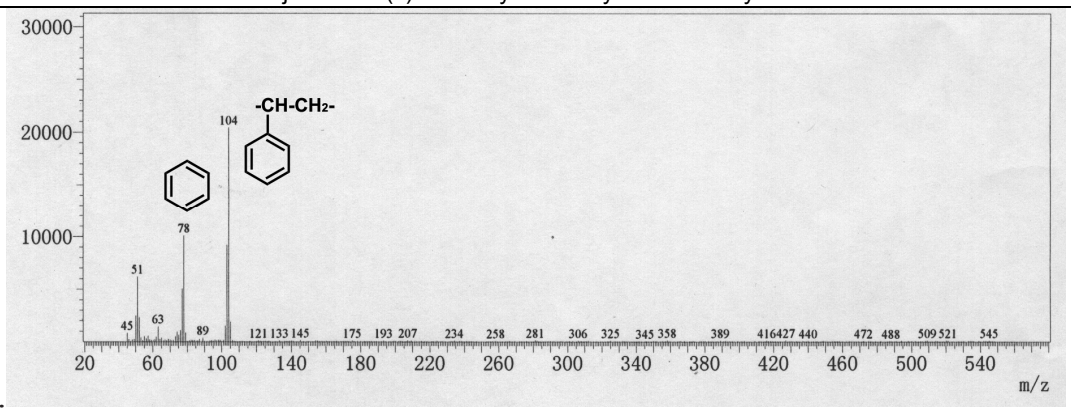
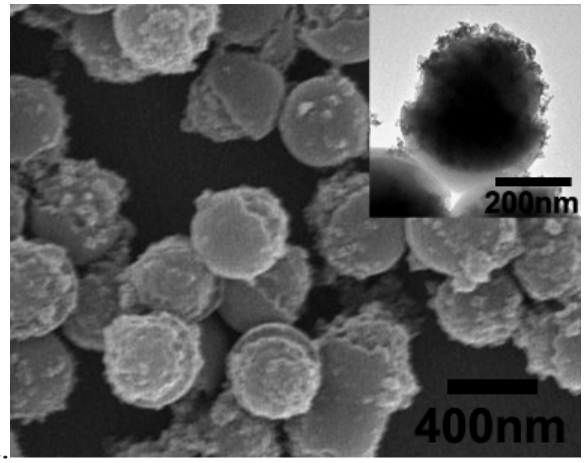
c. 

Fig. S6 Pyrolysis Gas Chromatography-Mass Spectrometry (PyGC-MS) spectra of supernatant after etching the composite colloids with aqueous HF: a) total ion chromatogram; b) magnified image of labeled region in Figure S6a; c) mass spectrum of labeled peak (retention time: 4.9 min) in Figure S6b.

a. 

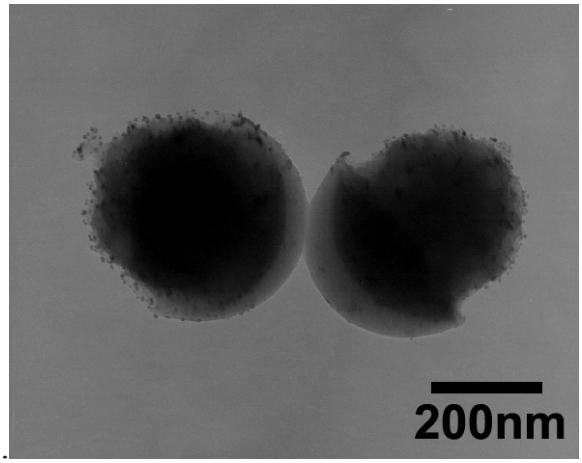
b. 

Fig. S7 SEM and TEM images of Janus colloids with the nanoparticles selectively absorbed onto the modified silica surface: a) Fe_3O_4, b) Au.

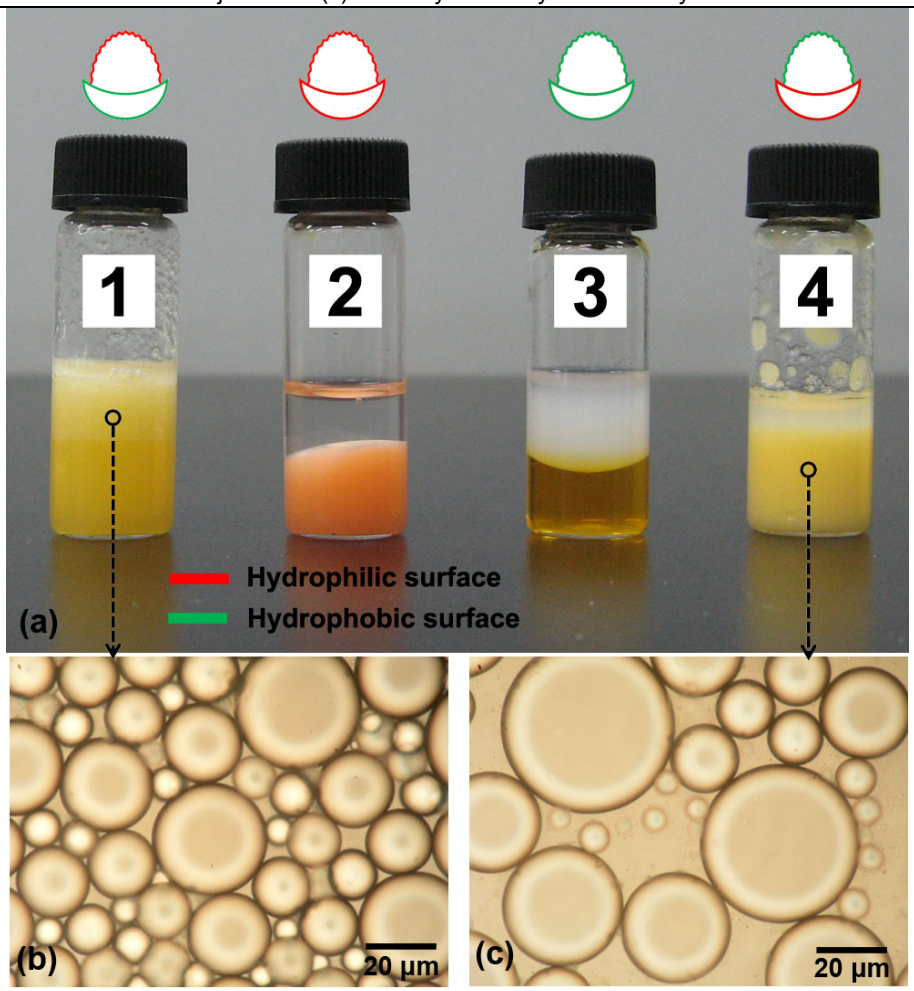


Fig. S8 a) Janus performance of some representative composite colloids: 1) O/W emulsion stabilized by the PS/silica Janus colloids as shown in Fig. 3b; 2) the sulfonated PS/silica colloids dispersible only in the bottom water phase; 3) the PS/OTS modified silica colloids dispersible only in the top oil phase; 4) W/O emulsion stabilized by the sulfonated PS/ OTS modified silica Janus colloids. Optical micrographs of two representative emulsions: b) O/W emulsion in vial 1; c) W/O emulsion of vial 4. The toluene/water weight ratio is 1:1, the colloid solid content is 0.3 wt.-%, and methyl orange is added to water as chromogenic agent.