Electronic Supplementary Material (ESI) for Chemical Communications


# One-pot Facile Synthesis of Janus Particles with Tailored Shape and Functionality

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## 1. Materials

Polyvinylpyrrolidone (PVP, molecular weight 40 kg/mol), tetraethylorthosilicate (TEOS), 3-aminopropyltriethoxysilane (APS), hexadecyltrimethoxysilane (HDTMOS, >85%), mercaptopropyltrimethyoxysilane (MPTMOS, 95%), *n*-pentanol, ammonium hydroxide (28-30 wt%), sodium citrate tribasic dihydrate and anhydrous ethanol were purchased from Sigma-Aldrich and used as received. Deionized water (Millipore Milli-Q grade) with resistivity of 18.0 MΩ was used in all the experiments. All chemicals were used as received.

## 2. Synthesis of silica Janus particles

*2.1 Synthesis of Janus particles with asymmetric shapes*

Using "moon-like" JPs as an example, the detailed synthetic procedure is as follows.[1] In a 20 mL glass vial, 1 g of PVP was dissolved in 10 mL of *n*-pentanol by ultrasonication for 2 hr. Subsequently, 350 μL of deionized water, 100 μL of sodium citrate solution (180 mM in water) and 170 μL of ammonium hydroxide (28 wt%) were added to the above solution. The reaction mixture was vortexed for 1 min. After placed steady for 5 min to remove the gas bubbles, 50 μL of TEOS was added and the solution was then slightly shaken for 30 s. The hydrolysis was allowed to proceed without stirring for 20 hr. After that, 20 μL of TEOS was added and followed by gently shaken again. The hydrolysis of TEOS was preceded for another 20 hr. The solution was then centrifuged at 6000 rpm for 10 min and the particles were washed by ethanol for 5 times at 1000 rpm. In order to further purify the sample, additional centrifugation cycles were performed: 700 rpm for 15 min to remove the supernatant,

300 rpm for 15 min to remove the sediment and 700 rpm for 15 min again to remove the supernatant. By varying the water and TEOS concentrations, “dumbbell-like” and “rod-like” JPs were synthesized, as well. For the “dumbbell-like” particles, 340 μL of deionized water was added; while for the “bullet-like”, 330 μL of deionized water were used.

*2.2 Synthesis of JPs with asymmetric functionality*

The typical synthesis of amphiphilic Janus particles with asymmetric functionality is similar to the procedures above. 1 g of PVP, 350 μL of deionized water, 100 μL of 180 mM sodium citrate solution and 170 μL of ammonium hydroxide were dissolved in 10 mL of *n*-pentanol. Then, 50 μL of TEOS was added to grow the first hemisphere in Janus particles for 20 hr. Then, 1 mL of ethanol was added to the reaction mixture and followed by adding 10 μL of TEOS and 20 μL of HDTMOS for amphiphilic JPs and 40 μL of APS for the TEOS-APS JPs. While for MPTMOS, 5 μL of MPTMOS was added and 10 μL of TEOS was added after another 12 hr. The reaction was set for another 20 hr to get the JPs. The same purification procures were used as described above.

## 3. Self-assembly of amphiphilic Janus particles

*3.1 Self-assembly in selective solvents*

Amphiphilic JPs were dispersed in ethanol to obtain a solution with a particle concentration of 2 mg $mL^{-1}$. A predetermined amount of water was slowly added to 1 mL of the solution of silica JPs in ethanol under shaking at room temperature. The solution was kept shaking gently overnight. The self-assembly of amphiphilic Janus particles was examined by SEM on silicon wafer or polypropylene substrate. In the case of polymer substrate, the sample was coating with gold under high vacuum, after drying the self-assembly solution.

*3.2 Self-assembly at the liquid-liquid or liquid-air interface*

To prepare foams stabilized by the amphiphilic Janus particles, we first re-dispersed 40 mg JPs in 5 mL water by sonicating the mixture for 30 min to obtain a homogeneous particle solution. A 5 mL of the solution was immediately shaken for 20 min to obtain foams in a 20 mL glass vial. After kept steady for 5 min, the foams floated on top of the water phase. A droplet of the foams was then placed on a piece of glass slide and imaged under optical microscopy. To prepare water-in-oil emulsions stabilized by the amphiphilic JPs, a dispersion of particles with a concentration of 8 mg $mL^{-1}$ was prepared by sonicating a mixture of 40 mg particles in 5 mL water for 30 min. A 0.5 mL solution of the particles in water was added into 5 mL toluene in a glass vial, and immediately shaken for 10 min to obtain emulsions stabilized by the particles. After kept steady for 5 min, the emulsions precipitated at the bottom of the glass vial. The emulsions can store in the sealed glass vial for months without aggregation. The particle-stabilized emulsions were imaged under optical microscopy by dropping a 20 μL of the solution on a piece of glass slide.

## 4. Characterizations

The self-assemblies and morphologies of JPs were imaged by using a Hitachi SU-70 Schottky field emission gun Scanning Electron Microscope (SEM) at an operation voltage 5 kV. Samples for SEM were prepared by casting a 10 μL of ASR solution on the silicon wafers (or other substrates) and dried at room temperature. Transmission Electron Microscope (TEM) images were taken by using a JEOL 2100 LaB6 TEM. Optical and fluorescence microscopic images were obtained by using a Nikon Eclipse Ti-S microscope. The solution of JPs was casting on a glass substrate. The size of amphiphilic JPs was measured by a Photocor-FC dynamic light scattering (DLS) at a scattering angle of $90^{o}$, equipped with a 633 nm laser (5 mW).

### References

1. A. Kuijk, A. van Blaaderen, A. Imhof, *J. Am. Chem. Soc.* 2011, **133**, 2346.

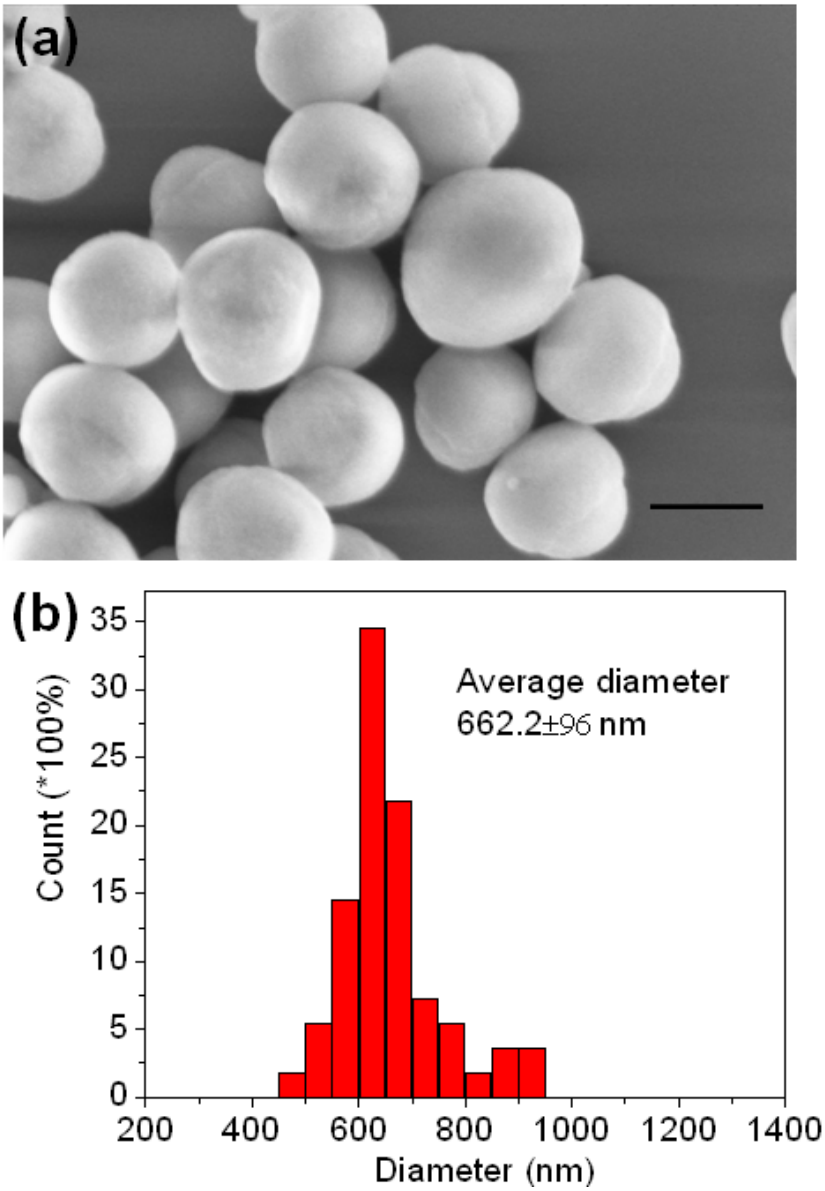


**Figure S1**. (a) Low magnification SEM image of "moon-like" JPs made from TEOS. Scale bar: 500 nm. (b) Size and size distribution of "moon-like" JPs by counting 100 nanoparticles. A 50 μL of TEOS was used as the first precursor and a 20 μL of TEOS was used for the second precursor. Water content in the reaction was 35.0 mg/mL.

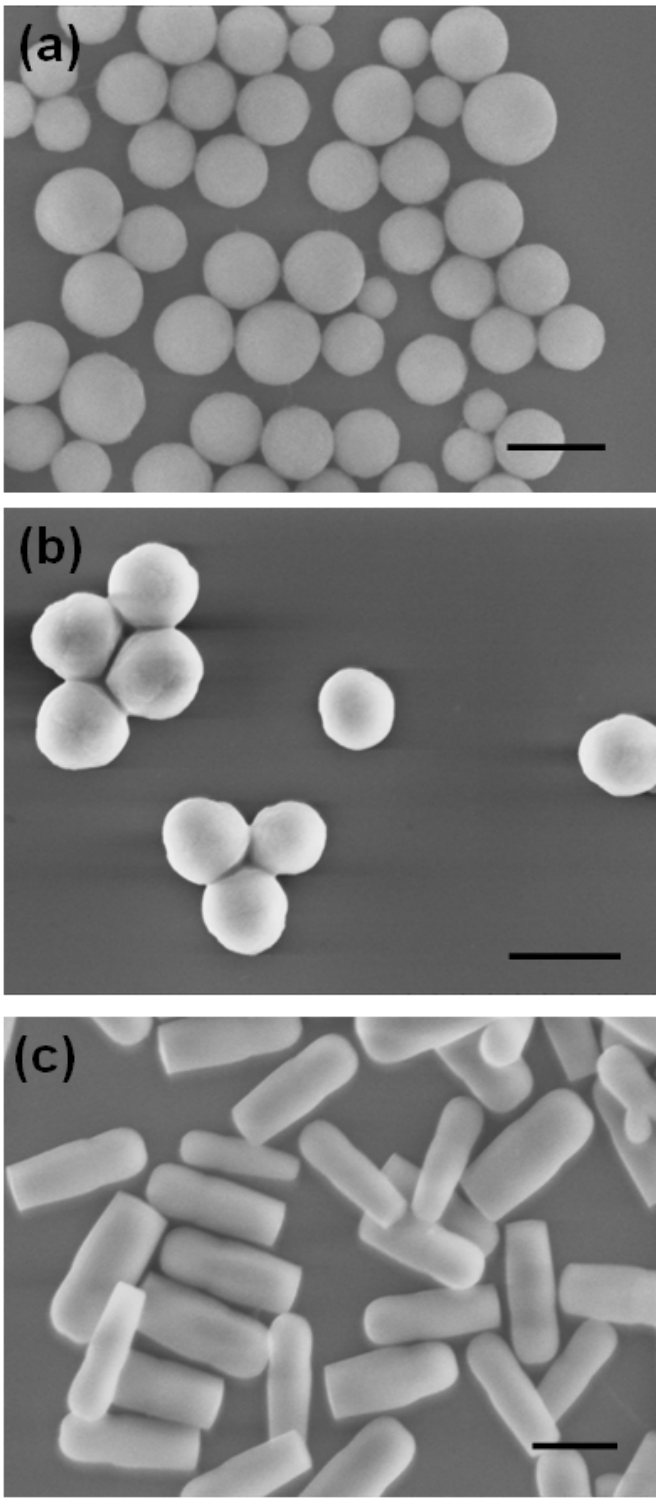


**Figure S2**. The effect of water concentration on the morphology of the synthesized JPs. (a) spherical particles: 38.0 mg/mL water. (b) JP particles: 35.0 mg/mL water. (c) rod-like JPs: 30.0 mg/mL water. The diameter of the JPs along the long axis increased with decreasing water content in the synthesis. Scale bars are 500 nm.

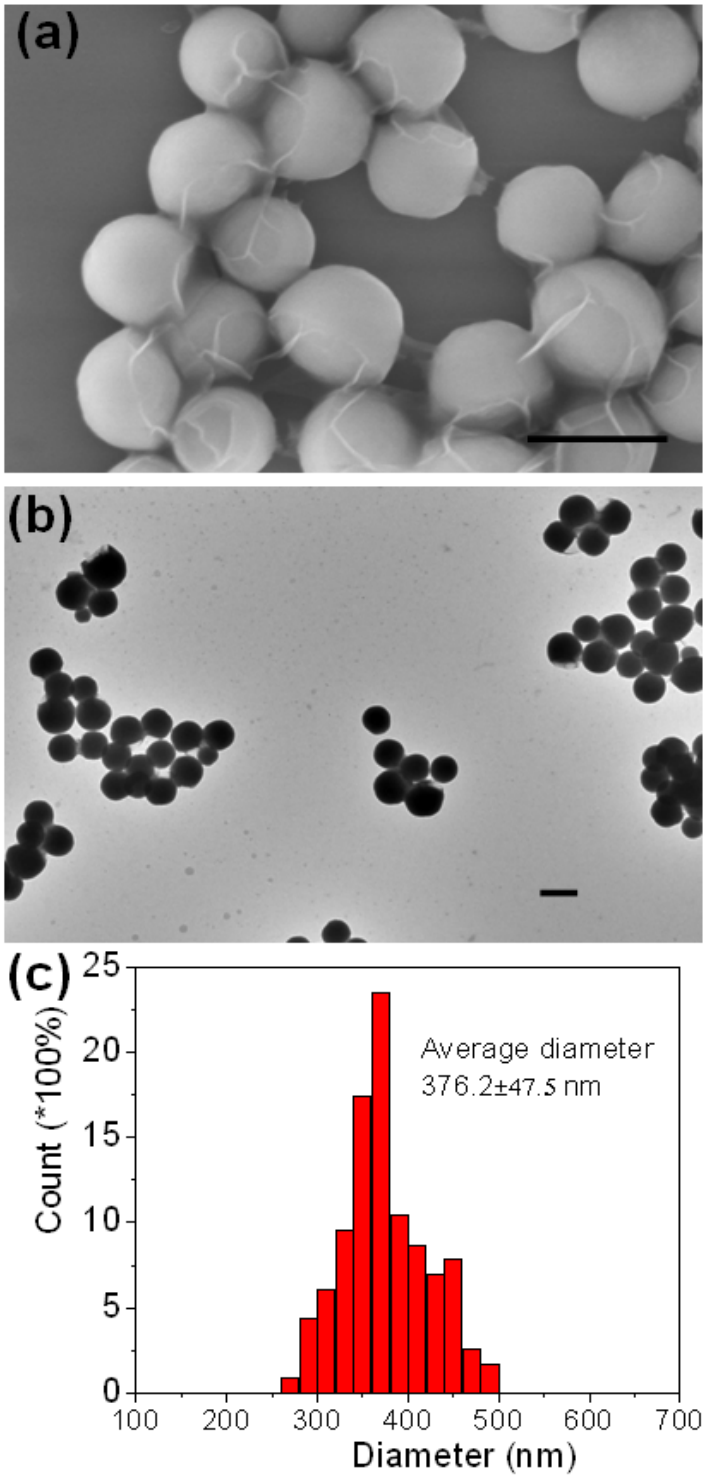


**Figure S3**. (a) SEM and (b) TEM images of amphiphilic JPs made from TEOS-HDTMOS. (c) Size and size distribution by counting 200 nanoparticles. Water concentration used in the synthesis was 35.0 mg/mL. A 50 μL of TEOS was used as the first precursor and 20 μL of HDTMOS was used as the second precursor. Scale bars are 500 nm.

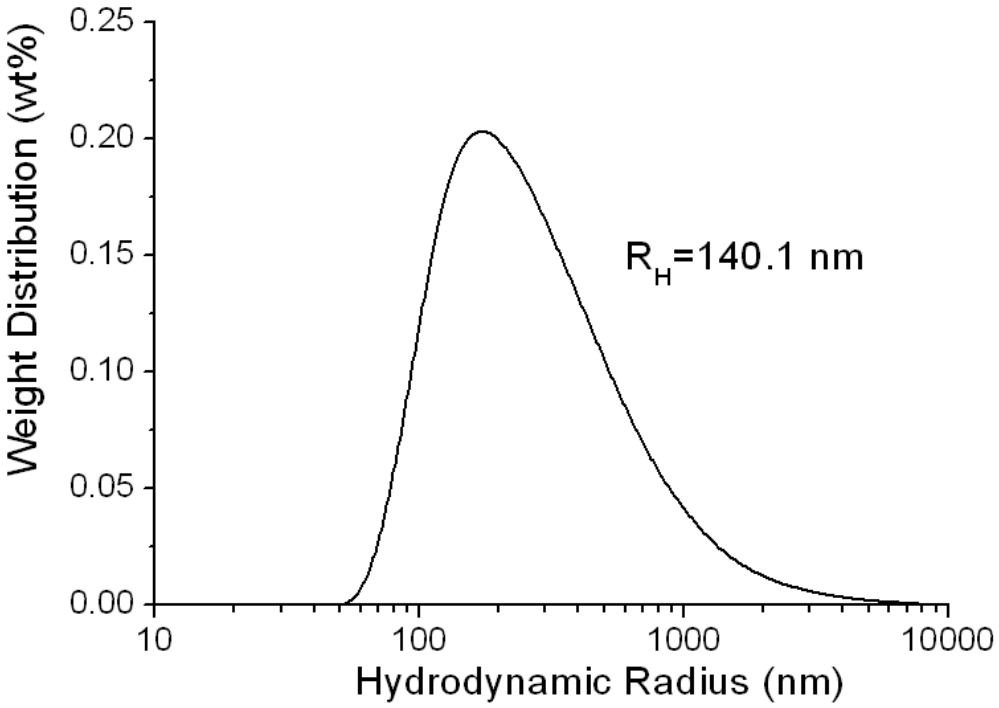


**Figure S4**. Size distribution of amphiphilic JPs measured by DLS. The amphiphilic JPs were dispersed in ethanol with a concentration of 1 mg/mL.

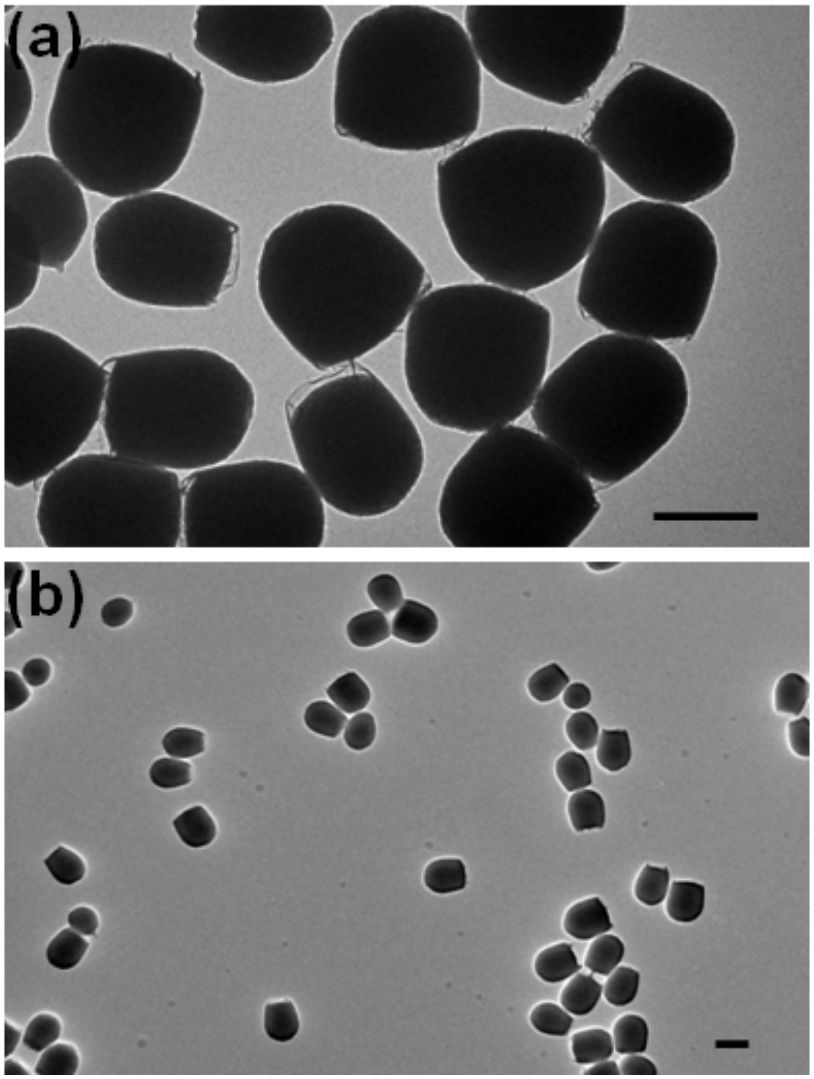


**Figure S5**. TEM images of amphiphilic JPs, showing the effect of relative amount of precursors on the morphologies of amphiphilic JPs (compared with JPs in Figure S3). Experimental condition is identical to that used for the synthesis of amphiphilic JPs in Figure S3, except that a 60 μL of TEOS was used as the first precursor and a 30 μL of HDTMOS was used as the second precursor. Water concentration was 35.0 mg/mL. Scale bars are 500nm.

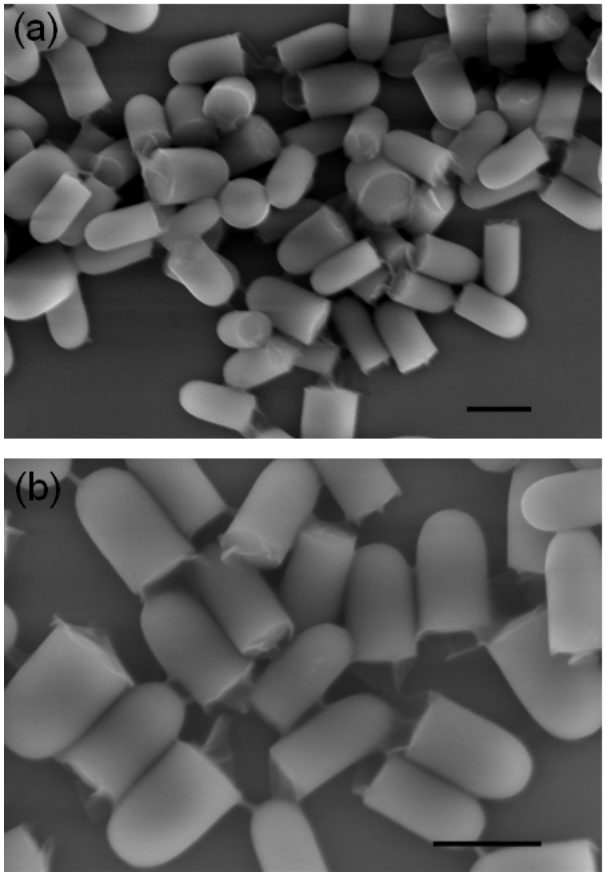


**Figure S6**. SEM images of "rod-like" amphiphilic JPs, showing the effect of relative amount of $H_2O$ (compared with JPs in Figure S5). Experimental condition is identical to that used for the synthesis of amphiphilic JPs in Figure S5, except that water concentration was 30.0 mg/mL. The length of the "rod-like" amphiphilic JPs increased with the decrease of water content in the reaction. Scale bars are 500nm.

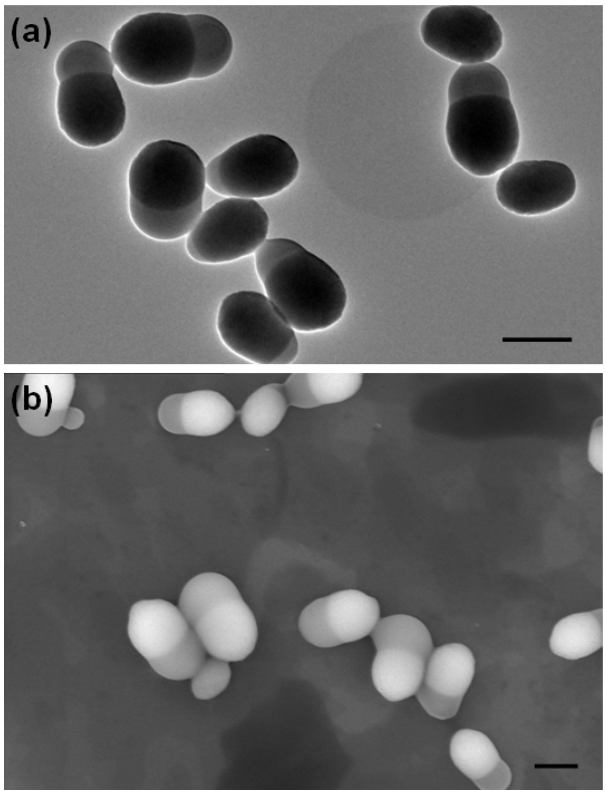


**Figure S7**. TEM (a) and SEM (b) images of JPs having one half made from TEOS and another half made from APS. Scale bars are 500 nm.

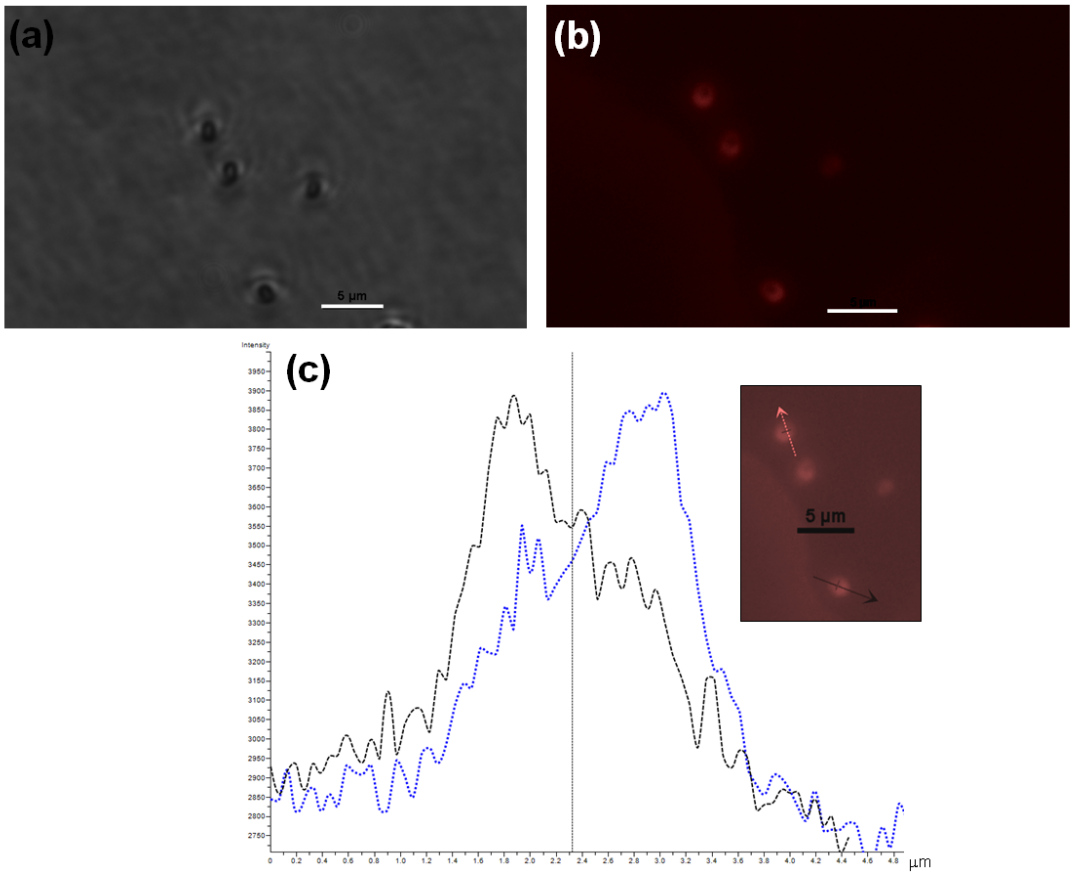


**Figure S8.** Optical (a) and fluorescence (b) microscopic images of JPs made from TEOS and APS (in Figure S7). Scale bars are 5 µm. The JPs were stained with Rhodamine B and the fluorescence was excited by a 550 nm laser. (c) The fluorescence intensity profile over two individual particles. It is clear that fluorescence intensity profiles show two intensity distributions, corresponding to the two compartments of JPs.

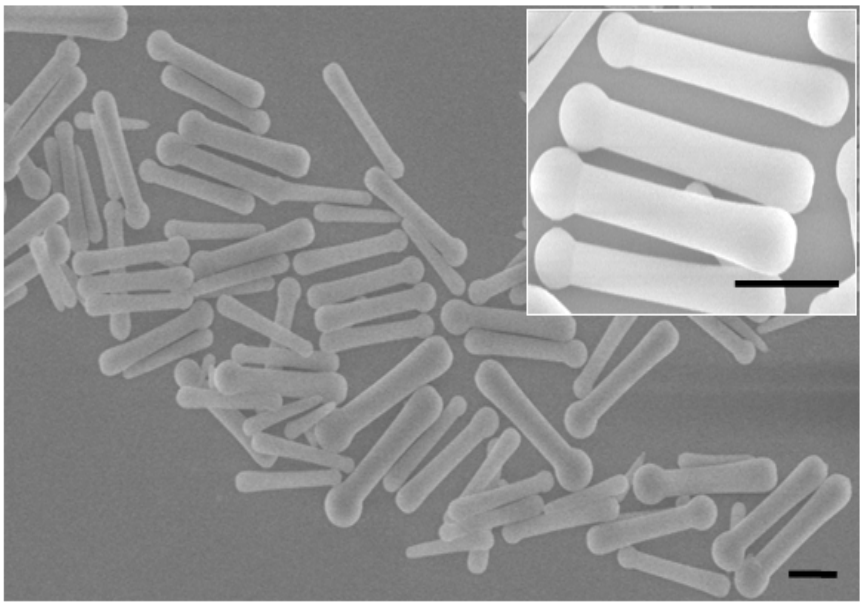

**Figure S9.** SEM images of "rod-like" JPs made from TEOS and APS, showing the effect of solvent. The round head is APS phase, and the rod part is TEOS phase. Water concentration is 28.0 mg/mL and ethanol concentration is 100 mg/mL. The addition of ethanol dramatically increased the aspect ratio of the "rod-like" JPs. A 60 μL of TEOS was used as the first precursor and 30 μL of APS was used as the second precursor in a 10 mL reaction. Scale bars are 1 μm.

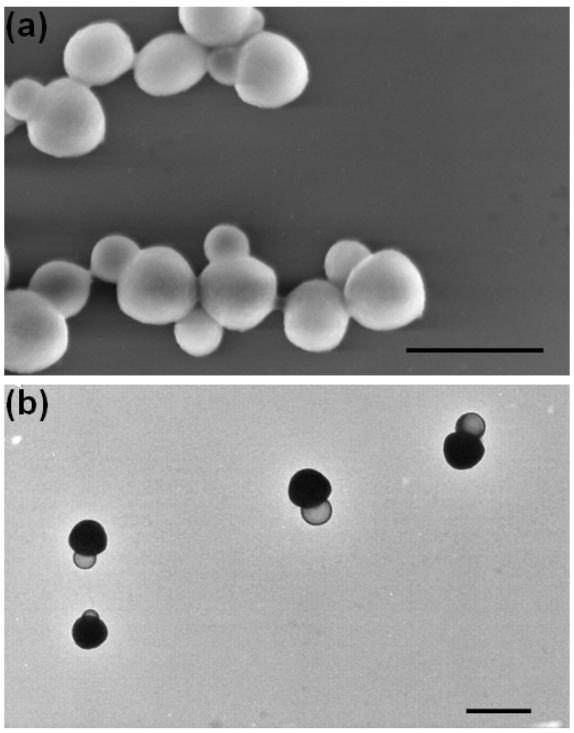


**Figure S10**. SEM (a) and TEM (b) images of JPs having one half made from TEOS and another half made from MPTMOS. Scale bars are 1 μm.

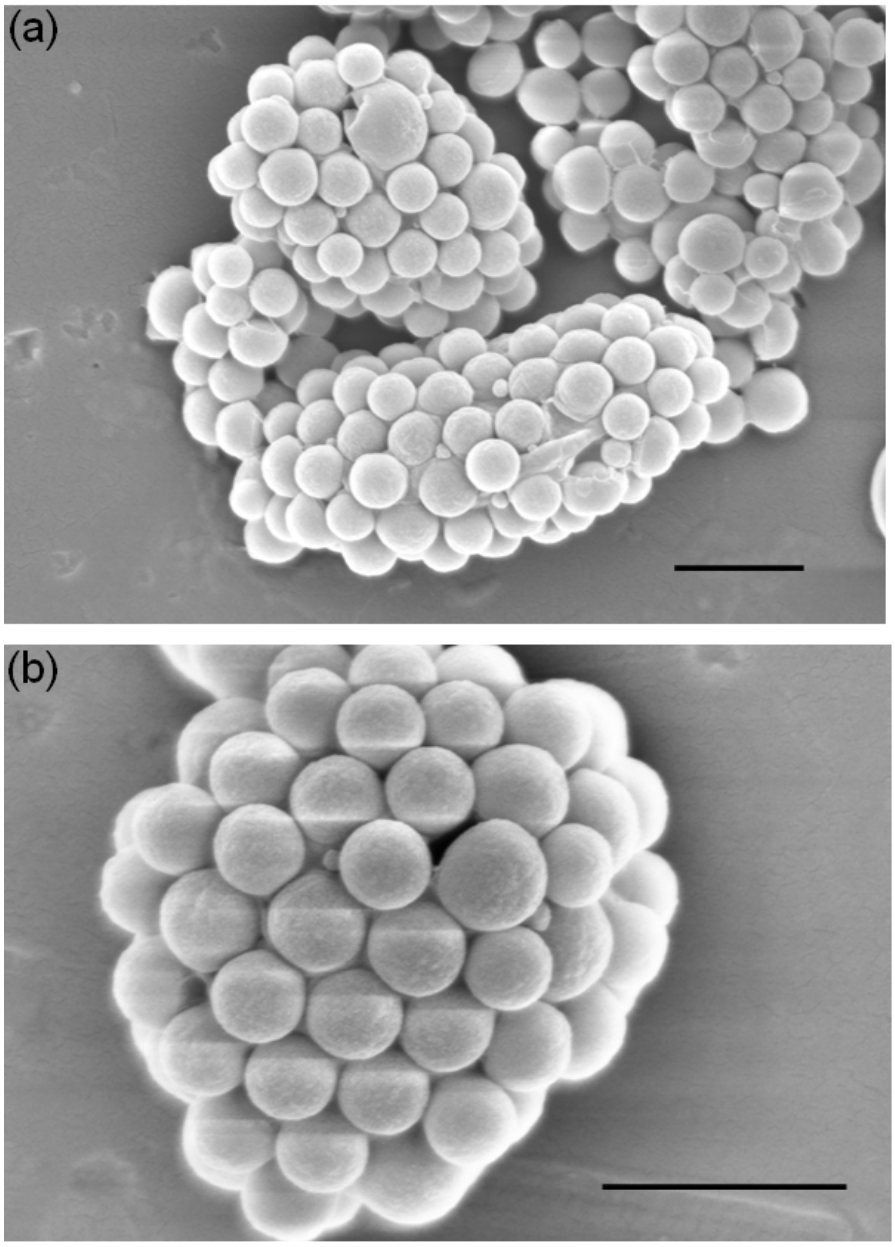


**Figure S11.** SEM images of self-assembled amphiphilic JPs in a mixture of water:ethanol (1:1, vol) at a particle concentration of 2 mg/mL. The SEM sample was prepared by drying a droplet of assembled JPs on a polypropylene substrate and subsequently coating the sample with gold. Scale bars are 1 μm.

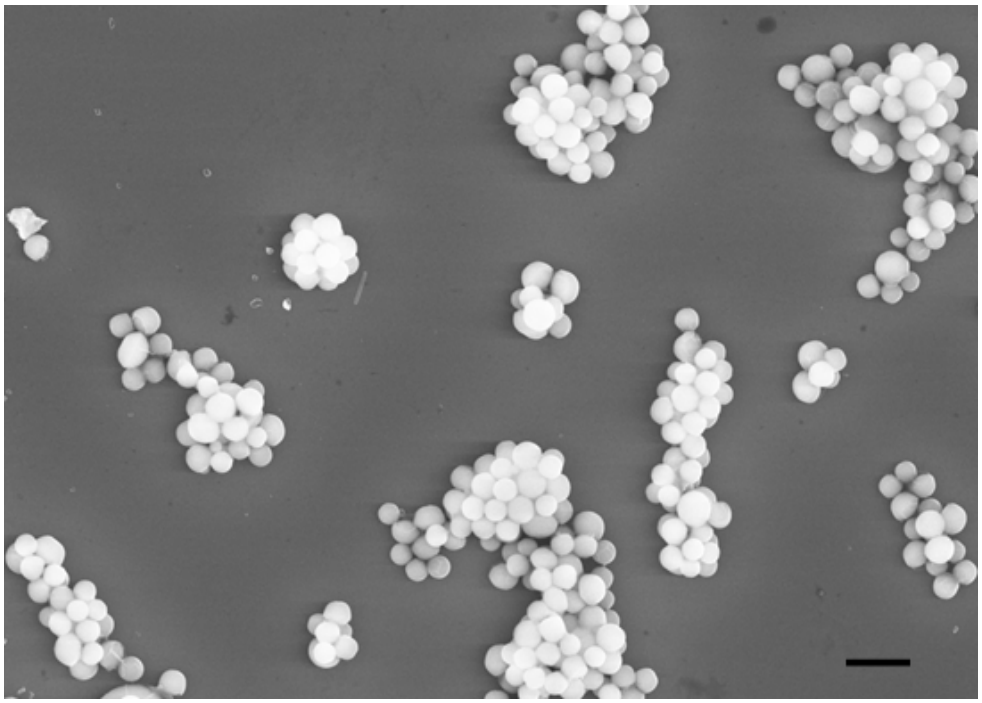

**Figure S12.** Low magnification SEM image of self-assembled amphiphilic JPs in the mixture of water:ethanol (1:1, vol) at a concentration of 2 mg/mL. Scale bar is 2 μm.

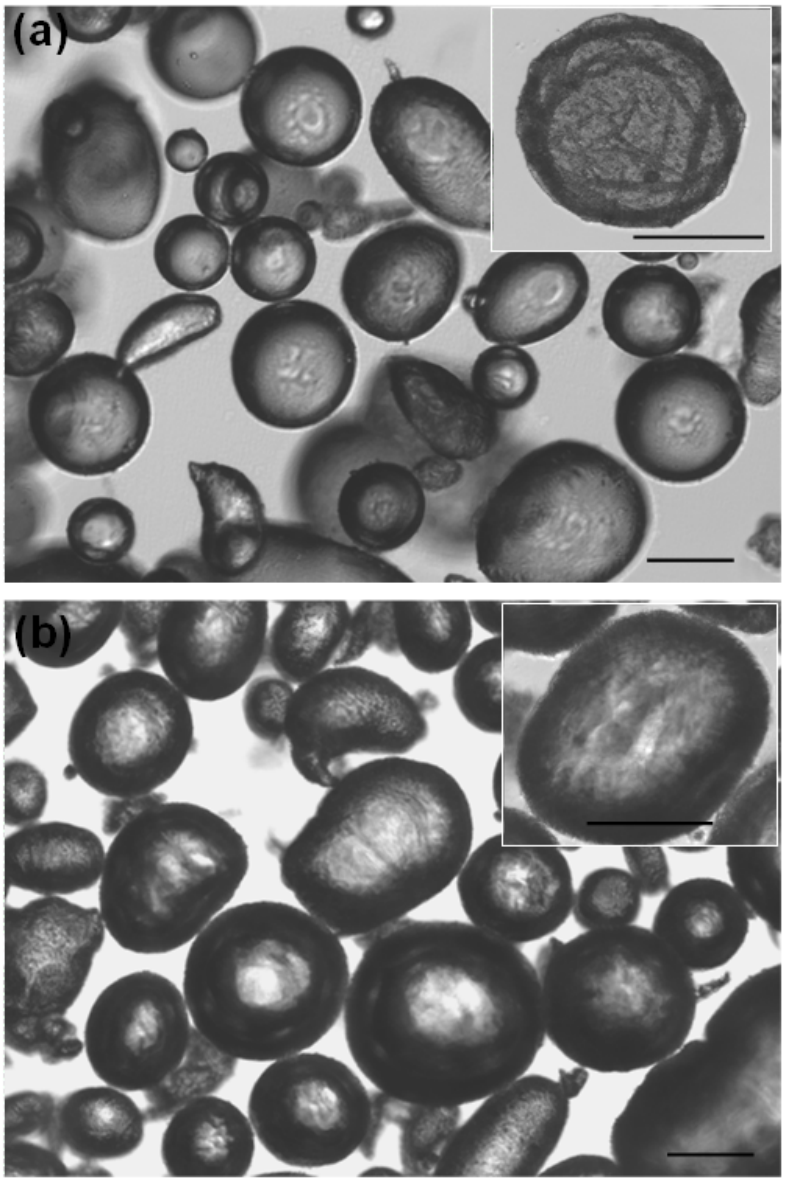


**Figure S13.** The application of amphiphilic Janus particles as colloidal surfactants. (a) Optical microscope image of water-in-oil Pickering emulsions stabilized by amphiphilic JPs. Oil phase is toluene. (b) Optical microscope image of foams stabilized by amphiphilic JPs. Scale bars are 100 μm.

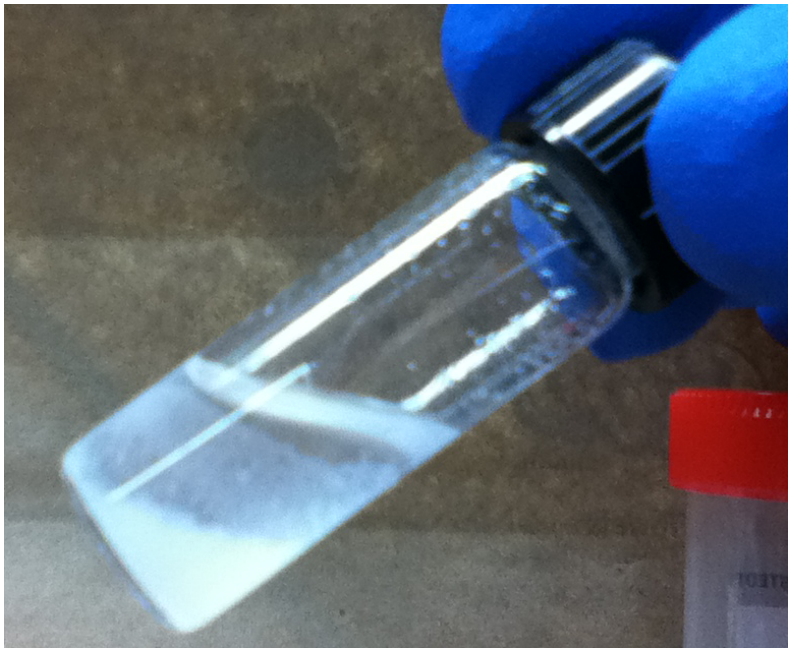

**Figure S14.** A photograph of water-in-oil Pickering emulsions stabilized by amphiphilic JPs. Oil phase is toluene.