Supporting Information

Bi-Continuous Emulsion by Janus Particle

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1. Experiment

1.1 Materials

Divinylbenzene (DVB) was purchased from Aldrich and purified over Al₂O₃ column. 3-Methacryloxypropyltrimethoxysilane (MPS), cumene hydroperoxide (CHP) and acrylamide (AA) were purchased from Alfa Aesar. Aqueous ammonia (28 wt%), toluene, ethanol, paraffin (Tm=52-54 °C), ferrous sulfate heptahydrate (FeSO₄·7H₂O), potassium peroxydisulfate (KPS), sodium dodecyl sulfate (SDS) and azobisisbutyronitrile (AIBN) were purchased from Sinopharm Chemical Reagent. Polystyrene (PS) hollow particle HP-433 was purchased from the former Rohm & Haas.

1.2 Synthesis of silica@PDVB/PS Janus particles

5.0 g of freeze-dried powder of PS hollow particle HP-433 was dispersed in 160.0 g of water containing 0.048 g of SDS as a seed emulsion. 3.0 g of DVB and 0.03 g of AIBN were mixed and emulsified in the presence of desired amount of SDS under ultrasonication for 3 min forming a monomer emulsion. The seed emulsion and the

monomer emulsion were mixed under stirring at ambient temperature for 8 h to swell the PS hollow particle with the monomer/initiator mixture. The system was heated to 70 °C allowing the seeded emulsion polymerization for 12 h. The example PDVB/PS hollow particle was synthesized after centrifugation and vacuum dried at 40 °C. 0.6 g of freeze-dried powder of the PDVB/PS hollow particle was dispersed in 20.0 g of water under stirring at 70 °C. 0.6 g of MPS, 0.6 g of KPS aqueous (1 wt%), 0.02 g of SDS and 10.0 g of water were mixed under ultrasonication at room temperature for 2 min to form a monomer emulsion. After the monomer emulsion was dropped into the dispersion at 70 °C within 30 min, the mixture stood for the polymerization for 24 h. After the polymerization, 1.0 ml of aqueous ammonia (28 wt%) was added under stirring at 70 °C for 1 h to induce a further sol-gel process of polyMPS (PMPS). The example silica@PDVB/PS Janus particle was obtained after centrifugation and washing with water and ethanol.

1.3 Emulsions stabilized by the silica@PDVB/PS Janus particle

After the silica@PDVB/PS Janus particle was dispersed in water, a given amount of toluene was added under stirring at 25 °C for 3 min. The mixture weight was fixed at 3.00 g, and the Janus particle was fixed at 0.01 g. In the case of water-paraffin (Tm=52-54 °C) emulsions, the emulsions formed at 70 °C for 3 min.

1.4 Interfacial polymerization of the emulsions

4 mg of AA was added in a given amount of water as the aqueous phase. 4 mg of DVB and 2 mg of cumene hydroperoxide (CHP) were added in toluene as the oil phase. The aqueous and oil phases were mixed under stirring for 3 min to form the emulsions. Afterwards, 2 mg of FeSO₄·7H₂O was added into the emulsion at 30 °C and stood for polymerization for 3 h. Interfacial polymerization of the emulsions was performed. One composite was achieved after removal of liquids by washing with ethanol/water and vacuum freeze-drying.

1.5 Characterization

Morphology of the samples was observed with SEM (FEI QUANTA FEG 250) operating at 15 kV. Ethanol was used as the dispersant in order to avoid aggregation of the silica@PDVB/PS Janus particle. The samples were ambient dried and vacuum

sputtered with Pt. Morphology of the Janus particles was observed with TEM (JEOL 1011) operating at 100 kV. Fluorescence microscopy images were recorded on Olympus IX-71. Polarizing microscopy images were recorded on Leica DM LP. The emulsified (turbid) parts of emulsion were measured by AC impedance and viscosity. AC impedance measurement was performed on insulation resistance tester MASTECH MS5205. Viscosity of the emulsions was measured with MAYZUN MZ-NDJ-8S viscometer. Thermogravimetric analysis (TGA) was performed on PerkinElmer Pyris 1 thermogravimetric analyzer in air at a scanning rate of 10 °C/min. Type of the emulsions was determined via confocal laser scanning microscope (CLSM) FV1000 and confocal fluorescence microscope with IX-81 inverted base and PMT detector.

a) = 0

2. Results and Discussion

Figure S1. (a) SEM and (b) TEM images of the PS hollow particle; (c) SEM and (d) TEM images the crosslinked PDVB/PS hollow particle.



Figure S2. Fluorescence microscopy images of the emulsions at varied water/oil weight ratio: (a) 0.90/2.10; (b) 1.80/1.20. Water soluble dye FITC was added into water phase for easy observation.



Figure S3. Polarizing microscopy images of the emulsions at varied water/paraffin weight ratio: (a) 1.00/2.00; (b) 1.90/1.10.



Figure S4. Cross-section SEM images of the emulsions and magnified SEM images of the paraffin spheres surface from the emulsions at varied water/paraffin weight ratio: (a, b) 1.00/2.00; (c, d) 1.90/1.10.



Figure S5. TGA curves of the silica@PDVB/PS Janus particle (curve 1) and the bicontinuous Janus network (curve 2).



Figure S6. (a) Prussian blue dyed water (left) and Sudan red dyed toluene (right); (b) Top toluene phase and bottom Prussian blue dyed water phase (left), top Sudan red dyed toluene phase and bottom water phase (right).