

One-pot facile synthesis of half-cauliflower amphiphilic Janus particles with pH-switchable emulsifiabilities

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Supporting Information

Experimental section

Methacrylic acid (MAA, 98.0%), methyl methacrylate (MMA, $\geq 99.5\%$), butyl acrylate (BA, $\geq 99.0\%$), styrene (St, $\geq 98.0\%$) and toluene ($\geq 99.5\%$) were purchased from Tianjin kaixin chemical industry co., LTD. China. Potassium persulfate (KPS, AR), sodium hydroxide (NaOH, AR), hydrochloric acid (HCl, AR) and the above reagents were used as received. Distilled water (pH=7.04) was used throughout.

Synthesis of half-cauliflower Janus particles (hCJPs)

The hCJPs were synthesized by one pot emulsifier-free seeded emulsion polymerization. Firstly, 40 mL distilled water was added into a 250 mL three-necked flask equipped with a reflux condenser, a mechanical stirrer and dropping funnels. After heated to 80 °C with stirring, the system was introduced into 6 mL KPS solution (0.003 g/mL) and stirred for 20 min. Then, the residual 14 mL KPS solution (0.003 g/mL) and monomer mixture comprising 1.2 g of MAA, 2.8 g of MMA and 2.0 g of BA were simultaneously added into the reaction flask. The feeding rates were 10 drops per minute, and the whole process took more than 1 h. The reaction system was stirred at 80 °C for a further 2 h to ensure complete monomer conversion, affording PMAB latex. Subsequently, 12 mL KPS solution (0.0025 g/mL) was firstly introduced into the above seed latex. Immediately, the residual 12 mL KPS solution (0.0025 g/mL) and hydrophobic monomers (5.0 g of St and 1.0 g of BA) were

simultaneously dropwise added into the reactor for 1 h. Finally, the reaction was finished after another 2 h to obtain hCJPs latex.

Synthesis of Ag-PMAB and Ag-hCJPs

For the formation of Ag-PMAB (or Ag-hCJPs), 10 g of 0.1 wt% PMAB (or 0.1 wt% hCJPs) particle dispersion was mixed with 9.8 mg of silver nitrate ($\geq 99.8\%$) and stirred gently for 24 h at room temperature. After that, 42.2 mg of urotropine ($\geq 99.0\%$) and 1.4 mg of poly(N-vinylpyrrolidone) ($\geq 95.0\%$) were added to the dispersion and stirred for another 5 h at 80 °C. Finally, the particles were washed with distilled water three times by centrifugation at 4500 rpm for 30 min.

Emulsification and pH-switchable emulsifiabilities

Firstly, the pH values of 10 wt% PMAB latex and 10 wt% hCJPs latex were respectively adjusted to ~ 8.0 and ~ 9.0 using 1 mol/L NaOH solution, while stirring for 1 h at room temperature. Then, the colloidal particles were washed with distilled water five times by centrifugation at 4500 rpm for 30 min. 3 mL of aqueous latex containing 0.3 wt% alkali treated PMAB (or hCJPs) (the gravimetric method) was added in a glass vial. Subsequently, the pH of aqueous latex was changed to 2.4 (or 11.4) by adding 20 μL of 1 mol/L HCl solution (or 20 μL of 1 mol/L NaOH solution). To explore their emulsification, 3 mL of toluene (oil) containing 0.01 wt% Sudan Red III was also added in the glass vial, followed by shaking for 1 min with hand. To explore their pH-switchable emulsifiabilities, the pH of o/w emulsion was changed from 11.4 to 2.4 by adding 40 μL of 1 mol/L HCl solution. Meanwhile, the pH of w/o emulsion was changed from 2.4 to 11.4 by adding 40 μL of 1 mol/L NaOH solution. All emulsions were vigorously shaken with hand, then samples were more than 30 min at a standstill prior to imaging.

Characterization

Fourier transform infrared spectroscopy (FT-IR) spectra were recorded on Digital FTS3000 spectrometer (America). Scanning electron microscopy (SEM) was

performed on a ULTRA Plus microscope (at 5 kV, Germany). The samples were prepared by placing a drop of diluted PMAB dispersion (or hCJPs dispersion) of pH 7.4, pH 2.4 or pH 10.4 on hydrophilic cover glass (or hydrophobic teflon thin film), which were dried at room temperature (except special instructions). After that, the samples were sputtered with Au prior to imaging. Transmission electron microscopy (TEM) was performed on a JEOL JEM 1230 microscope (Japan) with an acceleration voltage of 200 kV. Sample specimens were prepared by placing a drop of diluted PMAB dispersion (or hCJPs dispersion) on carbon-coated copper grids. The grids were finally air dried and analyzed without further treatment. The Optical microscopy was performed on a OPTEC MIT 500 (China) microscope. The samples were prepared by placing a drop of emulsions of o/w (or w/o) on glass slide, followed by imaging.

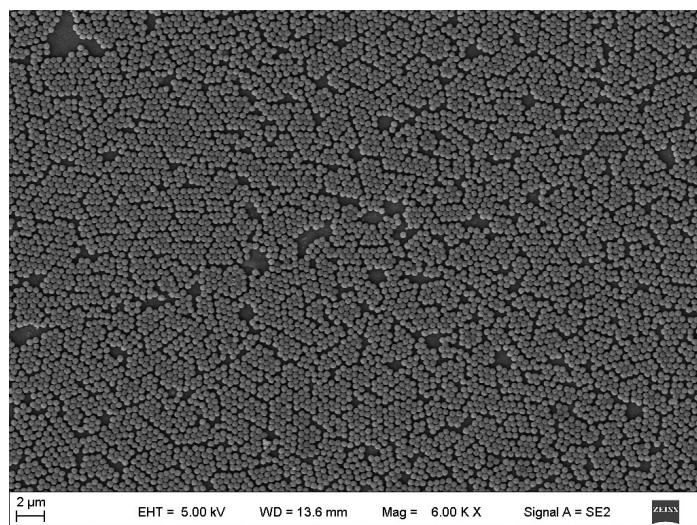


Figure S1. SEM image of PMAB in aqueous phase of pH 7.4 on hydrophilic cover glass.

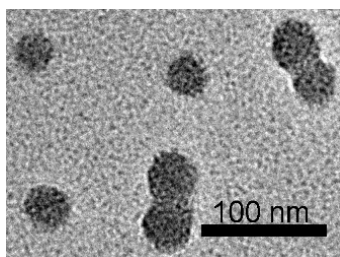


Figure S2. TEM image of colloidal particles prepared by conventional emulsion polymerization

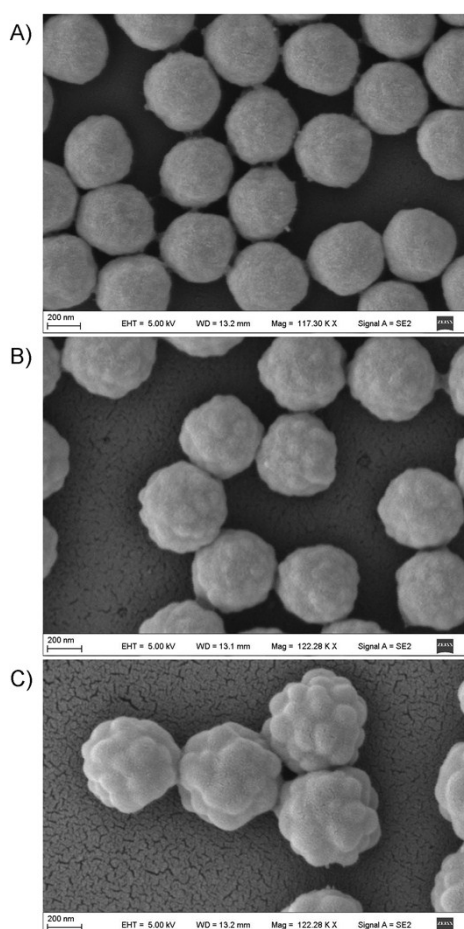


Figure S3. SEM images of hCJPs shape changes in the second-step polymerization time; 20 min (A), 40 min (B), 70 min (C).

FT-IR spectra of the PMAB and the hCJPs are shown in Figure S4. The absorption peak at 3431 cm^{-1} is ascribed to hydroxyl groups $\nu_{\text{O-H}}$ of $-\text{COOH}$ groups. The absorption peaks at 2875 , 2929 , and 2954 cm^{-1} can be attributed to $\nu_{\text{C-H}}$ of saturated ($-\text{C-H}$) groups, whereas those at between 3000 and 3100 cm^{-1} correspond to $\nu_{\text{C-H}}$ of unsaturated (C-H) groups in benzene rings, which confirm the presence of polystyrene chains in the hCJPs. The absorption peak at 1492 cm^{-1} is due to the presence of benzene ring vibrations ($\nu_{\text{C-C}}$). The absorption peaks at 1392 cm^{-1} and 1454 cm^{-1} can be checked to bending vibrations ($\delta_{\text{C-H}}$) of saturated ($-\text{C-H}$) groups. However, the strength of absorption peak at 1454 cm^{-1} increases evidently in the hCJPs when compared with that of in the PMAB, which is due to the presences of

conjugated system of -COO^- groups at pH 7.8.

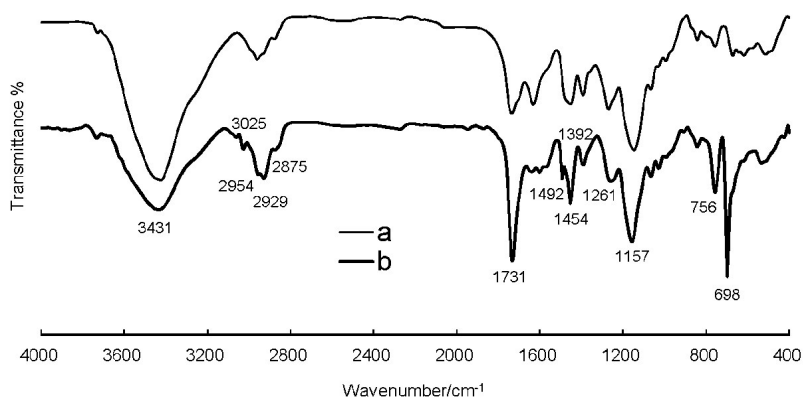


Figure S4. FT-IR spectra of PMAB (a) and hCJPs (b).

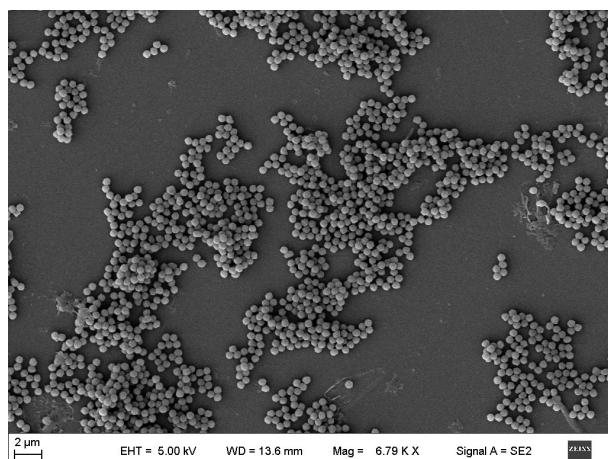


Figure S5. SEM image of hCJPs in aqueous phase of pH 2.4 on hydrophilic cover glass.

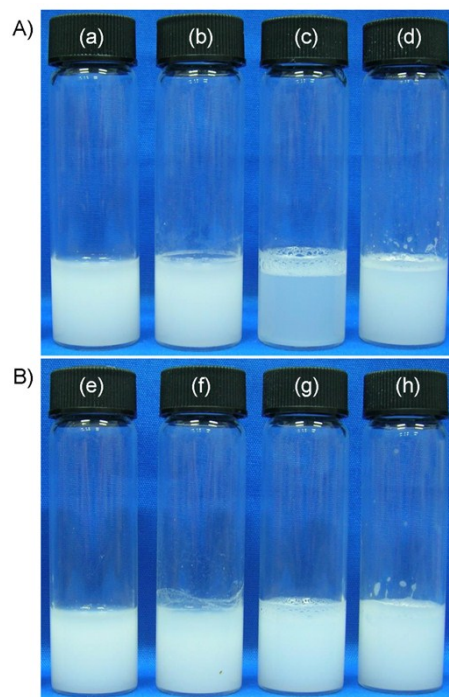


Figure S6. Digital photographs of emulsions containing 0.3 wt% PMAB (A) and 0.3 wt% hCJPs (B); The pH values of aqueous phases from (a) to (h) are 7.4, 2.4, 10.4, 7.4 (Containing 20 μ L, 0.5 mol/L NaCl solution), 7.8, 2.4, 11.5, 7.8 (Containing 20 μ L, 0.5 mol/L NaCl solution), respectively.