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

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A facile synthesis strategy for generating two types of highly uniform amphiphilic polymer Janus particles, the spherical seeds and half-cauliflower particles, is first presented. Both of the submicron particles possessing pH-switchable emulsifiabilities can change their amphiphilicities/shapes and induce phase inversion of emulsions in response to pH values of solution.

Research on Janus particles with contrasting chemistry and wettability has been thriving over the past few years, focusing both on novel synthesis methods and on investigations of their unique properties, manifold shapes and applications.[1] One of the most potential and practical applications of polymer Janus particles (PJPs) is in the stabilization of multiphasic mixtures as polymer surfactants for emulsions and as compatibilizers for immiscible polymers, because theoretical and experimental studies have shown that these amphiphilic PJPs have significantly higher interfacial activity than their homogeneous counterparts. They can effectively lower the interfacial tension between oil and water, and lead to a strengthened adsorption at the interface.[2] Very important contributions for applications of PJPs were for instance published by Müller and coworkers.[3] Amphiphilic PJPs as stabilizers containing two hemispheres, polystyrene (PSt) and poly(methacrylic acid) (PMAA), have been applied to emulsion polymerization of different monomers such as styrene (St) and n-butyl acrylate (BA). The resulting latex dispersions showed very well-controlled particle sizes with extremely low polydispersities. Combined reaction and separation could be achieved in the presence of Pd-containing Janus particles as interfacial catalysts/emulsifiers in a single reaction vessel.[4]

Due to unique advantages in structure and property, stimuli-responsive PJPs have been becoming a highly attractive research topic as solid surfactants, interfacial catalysts, drug delivery and microreactors.[5] Responding to very specific changes in their environments such as temperature, pH value and light, these stimuli-responsive PJPs could dramatically change their properties, morphologies and even induce phase inversion emulsification.[6] The shape-changing and amphiphilicity-reversing PJPs (St/AA) via polymerization-induced phase separation and seeded emulsion polymerization were recently studied, which could stabilize different types of emulsions and induce phase inversion of emulsions in response to changes of pH value.[7] However, most of methods and techniques for preparing PJPs based on microfluidic technique,[8a] toposelective surface modification,[8b] phase separation strategy[8c] and multiple dispersion polymerization[8d] still have some limitations, ranging from complicated process,[8e] time-consuming[8f] to environmentally-unfriendly strategy[8g] of using volatile organic solvents (VOC), which are very undesirable characteristics for industrial production and application. Therefore, it is still a great challenge to prepare PJPs, particularly stimuli-responsive PJPs, through an easy, time-saving and green method.
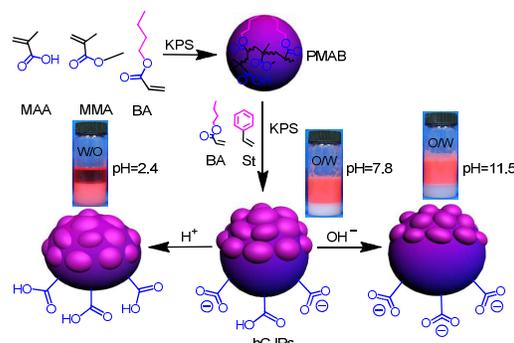
Scheme 1 Synthesis process of the hCJPs with pH-switchable emulsifiabilities.

Recently, we have demonstrated a facile one-step synthetic strategy for the preparation of thermosensitive nanogels based on highly cross-linked poly(ionic liquid)s.[9a] Acorn-like/dumbbell-like amphiphilic PJPs and hollow colloidal particles could be synthesized by controlling multistage emulsion polymerization and varying mass ratios of monomers.[9b] The hydrophilic seeds were only partially encapsulated with hydrophobic PSt therefore forming amphiphilic

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acorn-like particles via conventional emulsion polymerization. They could be fully encapsulated with the hydrophobic PSt by adding moderate polarity polymethylmethacrylate (PMMA) interlayer. The shapes and properties of synthetic particles have been evidently influenced by choosing types of monomers.

In a typical one-step emulsion polymerization, only non-amphiphilic particles are produced. Meanwhile, in the conventional two-step emulsion/dispersion polymerization, highly cross-linked seeds, suspended in a suitable solvent, are swollen with monomers. The following polymerization induces phase separation, leading to a variety of PJPs.[10] Herein, we first reported a facile and novel method for the bulk synthesis of uniform amphiphilic seeds (PMAB) with pH-switchable emulsifiabilities via one-step emulsifier-free emulsion copolymerization (EfEP) of MAA, methyl methacrylate (MMA) and BA (Fig. S1, ESI†). Then, based on selective phase separation of hydrophobic copolymer of St and BA in the hydrophobic sides of amphiphilic PMAB as seeds, the half-cauliflower PJPs (hCJPs) could be synthesized via one-pot EfEP in water without swelling processes or using crosslinking agents and any VOC (Scheme 1). A surprising finding was that the PMAB particles and the hCJPs with hydrophobic curds of dozens of nanometers could change their amphiphilicities/shapes and induce phase inversion of emulsions by hydrophilic sides with enriched MAA repeating unit in response to pH values. Therefore, our results present a facile and simple approach for bulk synthesis of two types of uniform amphiphilic PJPs. They will further widen the functionalities and applications of the PJPs as promisingly pH-switchable surfactants to stabilize both oil-in-water (o/w) and water-in-oil (w/o).

Here, owing to forming hydrophilic hemispheres possessing enriched carboxyl groups by hydrogen bonding interaction, the amphiphilic PMAB particles were simply synthesized by one-step EfEP in water. In the experiment, we also observed that amphiphilic PMAB particles did not possess pH-switchable emulsifiabilities when MAA content was more than 30 wt% with respect to monomers. The amphiphilic particles could not be obtained in the present of complex emulsifier (sodium dodecyl sulphate and OP-10) (Fig. S2, ESI†). Due to the emulsifiability of amphiphilic PJPs greatly depending on the surface wettability and shape of the particles, the shape changes of the PMAB particles with pH-switchable emulsifiabilities in aqueous phases of pH 2.4, 7.4 and 10.4 were characterized (Fig. 1a-f). The monodisperse PMAB particles (~ 450 nm in diameter) could be structurally divided into the up and down hemispheres because of different chemical compositions (Fig. 1a-c). Meanwhile, they appeared different morphologies and aggregations under different pH conditions. Under pH 2.4, the spherical particles gathered in many different clusters (Fig. 1d) on hydrophilic cover substrate, which was consistent with average particle size of 3530 nm in water (DLS). In contrast, the non-spherical particles at pH 7.4 and 10.4 were discretely dispersed (Fig. 1e, f). It is well-known that carboxyl groups are protonated in acid conditions (~ pH 2) and deprotonated in alkaline (~ pH 9), respectively.[11] The protonation of the carboxyl groups from hemi-spheres in acid conditions could make PMAB particles have low positive charges. Therefore, the surfaces were relatively hydro-phobic, then they tended to gather in many large clusters, and stayed the spherical morphology. Upon increasing the pH value to
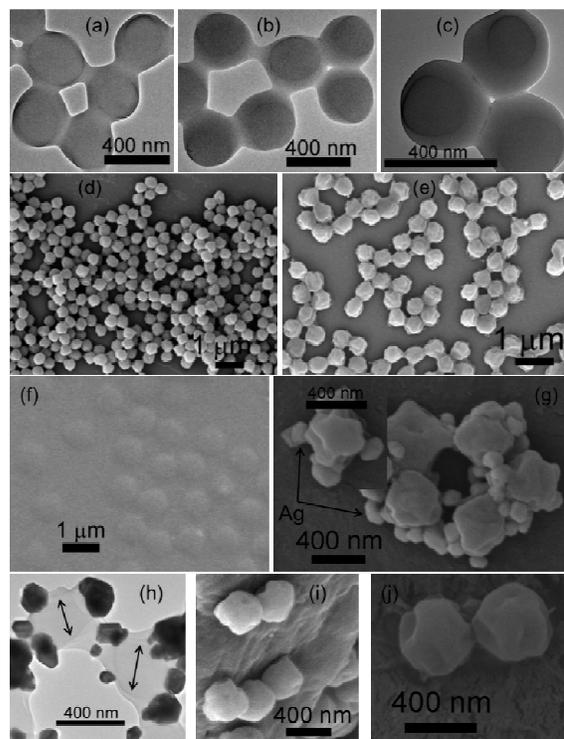

Fig. 1 Transmission electron microscopy images (TEM; a-c,) and scanning electron microscope images (SEM; d-f, i, j) of PMAB particles in aqueous phases of pH 2.4 (a, d) and pH 7.4 (b, e, i, j), pH 10.4 (c, f); SEM (g) and TEM (h) images of Ag-PMAB particles. Inserts: SEM images of the Ag-PMAB particles.

be neutral or basic, the deprotonated carboxyl groups were negatively charged and became very hydrophilic, resulting in being discretely dispersed and destroying their spherical structure on hydrophilic cover glass. The results above showed the surfaces of latex particles possessed enriched carboxyl groups. In order to prove only hemispheres containing enriched carboxyl groups, the water contact angles (CA) of the PMAB crystal film prepared by drying suspension of pH 7.4 at 80 °C on hydrophilic cover glass were observed. The wettability of about 62° showed that the up hemispheres possessed enriched butylgroups, because Wang et al[12] demonstrated the water CA of films from the particles with hydrophilic carboxyl groups were 16° ~ 20°. Ag-carrying PMAB Janus particles (Ag-PMAB) were in-situ reduced as reported method.[13] As a result of coordination effect between organic carboxyl groups and silver ions, silver nanoparticles were only selectively formed on the down hemispheres with carboxyl groups as we would expect them to (Fig. 1g, h). Besides, the PMAB particles could attach to the surface of solid paraffin (Fig. 1i), and stayed well round on hydrophobic Teflon thin film (Fig. 1j), which showed evidently their contrasting sides and amphiphilicity.

To explore emulsification and pH-switchable emulsifiabilities of the PMAB particles, 3 mL of toluene containing 0.01 wt% Sudan Red dye and 3 mL of aqueous emulsion containing 0.3 wt% PMAB were studied under different pH conditions (Fig. 2). After being vigorously shaken with hand, the mixtures stood there forming toluene-in-water (o/w) emulsions at pH 7.4 (Fig. 2b, e) or pH 10.4 (Fig. 2d), whereas the mixture formed water-in-toluene (w/o) emulsion at pH

2.4 (Fig. 2c). More importantly, when pH value of the mixture was adjusted from 10.4 to 2.4 with 1 mol/L aqueous HCl solution, the o/w emulsion changed quite rapidly to w/o emulsion (Fig. 2g). After adjusting pH value from 2.4 to 10.4 with 1 mol/L NaOH solution, the mixture reversibly changed to o/w emulsion (Fig. 2f). The reversible process could be repeated several times. The phenomena are due to the drastic changes in their wettability and shape of PMAB particles by swelling and deswelling in high and low pH conditions, respectively. Similar results were also reported by Lee et al,[7] the amphiphilic Janus particles were synthesized by seeded emulsion polymerization followed by acid hydrolysis. Here, the anisotropic PMAB particles with pH-switchable emulsifiabilities were facilely synthesized by one-step EfEP. The selected optical micrographs of forming emulsions at different pH were investigated (Fig. 2B). The emulsions were imaged clearly as round spherical droplets, and the smaller droplets showed better emulsification in high pH conditions.
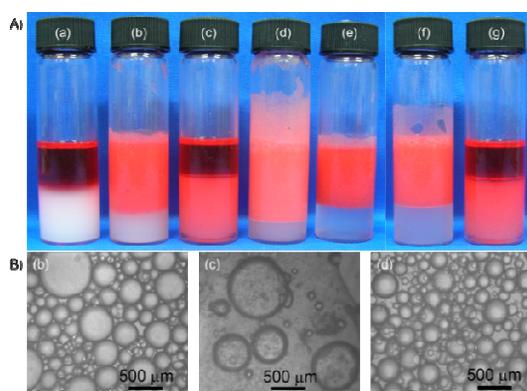

Fig. 2 Digital photographs and selected optical micrographs of emulsions, which are stabilized by PMAB (0.3 wt%); The pH values of aqueous phases from (a) to (g) are 7.4 (Before emulsification), 7.4, 2.4, 10.4, 7.4 (Containing 20 µL, 0.5 mol/L NaCl solution), 10.4 (Inverted from c), 2.4 (Inverted from d), respectively.

It was reported that the "confetti" particles possessing multiple lobes from single seed particle could form because of the absorption of multiple radical oligomers onto the larger seeds.[14] Wu et al[15] demonstrated the raspberry-like colloidal particles with both smaller corona particles and larger core particles could be prepared based on the second nucleation on the core surfaces. To date, it has not been reported that the hCJPs could be synthesized via one-pot EfEP in the present of amphiphilic seeds. The gradually increasing process of curds was monitored in second-step polymerization time (Fig. S3, ESI†). Surprisingly, the hCJPs had the same amphiphilicity and pH-switchable emulsifiabilities. Owing to the hydrophobic copolymer of St with BA without carboxyl groups via second-step EfEP, the hydrophobic copolymer of curds was synthesized in hydrophobic side of amphiphilic PMAB seeds based on phase separation[10] thereby forming amphiphilic hCJPs. We found that the amphiphilic PMAB particles could not be synthesized by one-step EfEP because of forming a large amount of coagulum, when BA was replaced by St. The reason is that St has higher reactivity and hydrophobicity than that of BA. Hence, main advantages of one-pot method are that it does not need complicated procedures from masking step and can apply to various functional monomers such as

thermo-responsive and fluorescent monomers.

To further confirm the carboxyl groups being not from hydrolysis of carboxylic ester groups of the PMAB and the hCJPs, they were tracked by Fourier transform infrared spectroscopy (FT-IR) analysis (Fig. S4, ESI†). The absorption peaks at 1157 cm^{-1} and 1261 cm^{-1} can be assigned to antisymmetric and symmetric stretching vibrations of the (C-O) groups of carboxylic ester groups. The characteristic peak at 1731 cm^{-1} can be assigned to the (C=O) groups. That means carboxylic ester groups of the hCJPs do not undergo hydrolysis. The peaks at 698 cm^{-1} and 756 cm^{-1} can be ascribed to flexural vibrations (δ_{C-H}) of benzene ring, which confirms the presence of polystyrene chains in the hCJPs.
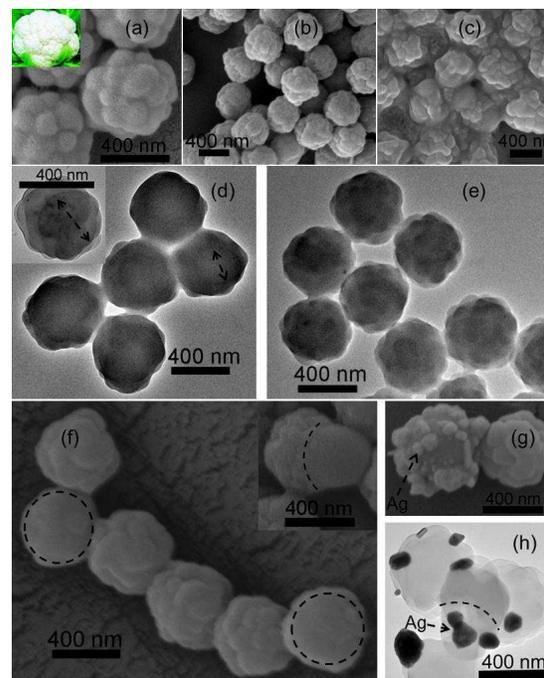

Fig. 3 SEM (a, b) and TEM (d, e) images of hCJPs in aqueous phases of pH 7.8 (a, d) and pH 2.4 (b, e); SEM (c, f) images of hCJPs (pH 7.8, drying in a vacuum oven at 80 °C for 2 h); SEM (g) and TEM (h) images of Ag-hCJPs. Inserts: Photo of cauliflower (a), TEM (d) image of hCJPs, SEM (f) image of hCJPs.

The hCJPs with one smooth side and the other cauliflower-like side in aqueous phases of pH 2.4 and pH 7.8 were characterized (Fig. 3a-f). Compared with the PMAB seeds, the curds of dozens of nanometers from the monodisperse hCJPs (~ 550 nm in diameter) were clearly observed on cover glass (Fig. 3a). Interestingly, the smooth hemispheres could be observed, when the hCJPs at pH 7.8 were dried carbon-coated copper grid (Fig. 3d), which was different from the morphology at 2.4 (Fig. 3e). And furthermore, the particles at pH 2.4 still gathered in many different clusters (Fig. 3b; Fig. S5, ESI†). The morphology was evidently destroyed, when the hCJPs crystal film with CA of about 72° were dried quickly at 80 °C on hydrophilic cover glass (Fig. 3c) because of comprising the carboxyl groups on down surface and phenyl/butyl groups on up surface. To identify straightforward the shapes and chemical natures of the two sides, we subjected the hCJPs to rapid drying on hydrophobic teflon

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thin film in a vacuum oven at 80 °C. As expected, the smooth sides from partially turning particles could be clearly observed (Fig. 3f). In fact, the hCJPs were snowman-like in aqueous phase because of swelling behavior of hydrophilic sides. However, during the evaporation of water in the period of samples drying, upright particles seemed to be spherical, while only reclining particles looked like snowman-like. The amphiphilicity and half-cauliflower shape were further confirmed by selectively forming silver nanoparticles on the smooth faces with carboxyl groups (Ag-hCJPs), on the contrary, they were not formed on the cauliflower-like hemispheres (Fig. 3g, h).
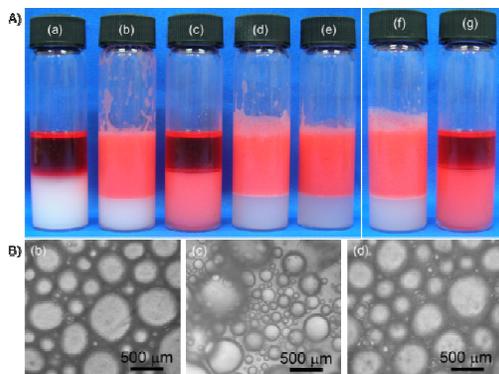

Fig. 4 Digital photographs and selected optical micrographs of emulsions, which are stabilized by hCJPs (0.3 wt%); The pH values of aqueous phases from (a) to (g) are 7.8 (Before emulsification), 7.8, 2.4, 11.5, 7.8 (Containing 20 μL, 0.5 mol/L NaCl solution), 11.5 (Inverted from c), 2.4 (Inverted from d), respectively.

The emulsification and pH-switchable emulsifiabilities of the hCJPs were also observed (Fig. 4). Likewise, the pH-switchable emulsifiabilities could be attributed to the reversible deprotonation/protonation of the carboxyl groups on the hemispheres under alkaline/acidic conditions. As a result, the hydrophilic property of the hCJPs would be enhanced greatly under alkaline condition, forming o/w emulsion. The particles would become relatively hydrophobic under acidic condition, forming w/o emulsion. In addition, it was evident that the emulsification of the hCJPs increased greatly in low pH conditions because of adding hydrophobic copolymer in comparison to that of the PMAB particles, whereas their emulsification decreased in high pH conditions from selected optical micrographs. The similar results were also observed without oil phase, and a large number of bubbles stabilized by amphiphilic PMAB and hCJPs gathered in the interface between water and air in two latexes under alkaline condition (Fig. S6, ESI†).

In summary, we present a facile synthesis strategy for generating highly uniform amphiphilic PJPs, PMAB and hCJPs with hydrophobic curds of dozens of nanometers, and investigations of their emulsifications and pH-switchable behaviors. The switchable Pickering emulsions stabilized by the special particles can be prepared by changing pH values of the solution. The hCJPs can be synthesized in the hydrophobic side of amphiphilic PMAB seeds via one-pot EfEP without masking step. These polymer Janus particles not only evidently change their shapes/amphiphilicities but also completely reverse emulsions of w/o and o/w systems in response

to pH value. This promising fact is significant for the use of these structures in biphasic system, pH-responsive polymer reagents and polymeric-inorganic Janus particles functionalized with metals.

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