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pH responsive Janus polymeric nanosheets

Peng Zhou, Qian Wang *, Cheng-Liang Zhang, Fu-Xin Liang, Xiao-Zhong Qu, Jiao-Li Li, Zhen-Zhong Yang *

State Key Laboratory of Polymer Physics and Chemistry, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

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ABSTRACT

pH responsive polymeric Janus nanosheets with poly(maleic acid) moiety and crosslinked PS onto the corresponding sides have been synthesized by free radical polymerization. The Janus nanosheets can serve as solid emulsifier to stabilize an oil/water emulsion, whose stability is easily triggered by changing pH across pKa of the poly(maleic acid).

1. Introduction

Janus materials with two different compositions compartmentalized onto the same surface, have gained growing academic and industrial concerns [1–7]. Their anisotropic characteristics in composition or (and) shape endow the materials additional performances of such as amphiphilic [8,9], magnetic [10–12] and catalytic [12,13]. They can serve as building blocks toward complex structures [14–17]. Those Janus particles with polar and apolar sides integrated have been extensively investigated as solid surfactants [18–21]. They are capable to stabilize emulsions more effectively than the homogeneous counterparts arisen from the Pickering effect [22,23]. Responsive Janus particles are becoming attractive since the Janus performances can be triggered by external stimuli such as pH [24–26], temperature [27], electric [28,29] and ion [30]. In comparison with the spherical shape, Janus nanosheets are more advantageous in stabilizing emulsions since their rotation at an interface can be greatly restricted owing to highly anisotropic characteristic in shape [31,32]. It is important to precisely tune thickness of the nanosheets. Lower amount of the Janus nanosheets is required to emulsify oil/water mixture using thinner nanosheets [33]. It becomes a key concern to develop methods to synthesize the responsive Janus nanosheets with tunable thickness. Multiple-step etching silicon substrate has been reported to achieve inorganic Janus nanosheets, which can stabilize liquid droplets more effectively even in air [34]. However, yield of the Janus nanosheets is extremely low. We have previously reported on the synthesis of inorganic Janus nanosheets and the corresponding inorganic-polymer bi-layered composite ones by crushing the corresponding polymeric hollow spheres [35,36]. The Janus hollow spheres are prepared based on materialization of an emulsion interface using self-organized sol–gel process of silane precursors in the oil phase. Although the inorganic composite nanosheets can tolerate organic solvents, they are usually rigid and difficult to fold. Alternatively, polymeric Janus nanosheets are more flexible and foldable. Some guest species can be encapsulated thereby. Self-assembly approach from block copolymers is proposed to synthesize polymeric Janus nanosheets [37–41]. The block copolymers should possess sufficiently narrow molecular weight distribution in order to form uniform lamellar structure. Controlled polymerization methods are usually employed to synthesize such copolymers, which should be carried out under strict conditions. The polymeric Janus nanosheets lack of responsive performance. It is highly required to develop a general and facile approach toward Janus polymeric nanosheets which are responsive.

Herein, we report a facile approach to synthesize pH responsive Janus polymeric nanosheets as illustrated in Scheme 1. Four key steps are involved: (1) Maleic anhydride (MA) forms a self-assembly layer onto a sucrose particle template. MA is preferentially adsorbed onto the sucrose particle surface *via* hydrogen bonding between MA and hydroxyl group onto sucrose particle surface. Meanwhile, the particles become dispersible in toluene. (2) A polymer layer is subsequently grown onto the MA layer. Since MA is not self-polymerizable, a polymer layer for example

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* Corresponding authors.
E-mail addresses: wangqian@iccas.ac.cn (Q. Wang), yangzz@iccas.ac.cn (Z.-Z. Yang).

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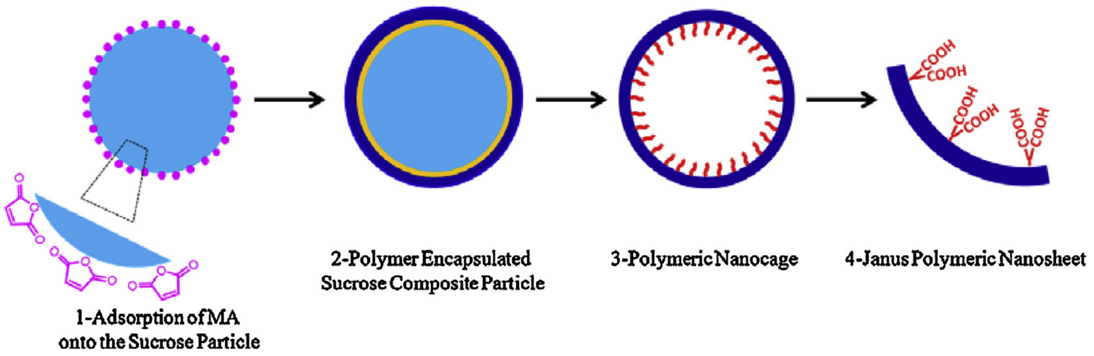

Scheme 1. Illustrative synthesis of the pH responsive Janus polymeric nanosheets. (1) Adsorption of MA (pink dots) onto the sucrose particle (blue droplet) surface. (2) A free radical polymerization of crosslinked PS (blue-black shell) conjugated onto the MA layer forming a PS-PMA bi-layered shell (orange shell). (3) Removal of the sucrose to achieve the polymeric hollow spheres whilst PMA is hydrolyzed into acidic PMa (red chains). (4) Janus polymeric nanosheets derived by crushing the shell into pieces.

polystyrene (PS) is further grown by free radical polymerization after the initial copolymerization between MA and styrene (St). (3) Janus hollow spheres are derived after washing the sucrose particle with water, meanwhile the MA groups is hydrolyzed into maleic acid group (PMa). (4) Janus polymeric nanosheets are achieved after crushing the shell into pieces. Since one side of the nanosheets contain maleic acid group and the other side is composed of PS, the Janus nanosheets should be pH responsive. The PS layer will be strengthened to tolerate organic solvents rather than dissolution when a crosslinker for example divinylbenzene (DVB) is added in St.

2. Experimental

2.1. Materials

Maleic anhydride (MA), styrene (St) and azodiisobutyronitrile (AIBN) were purchased from Sinopharm Chemical Reagent Beijing Co. Divinylbenzene (DVB) was purchased from Sigma–Aldrich. Monomers of St and DVB were purified by passing through Al_2O_3 to remove the inhibitor. Sucrose particles were purchased from Sinopharm Chemical Reagent Beijing Co. and mechanically crushed into small particles. All the other reagents were used as received without further purification.

Synthesis of pH responsive Janus polymeric nanosheets: 4.0 g of sucrose particle was added into 50.0 mL of toluene containing 0.2 g of MA under stirring for 10 min. The sucrose particles were coated with a layer of MA to ensure a good dispersion. Free MA was washed away with 50.0 mL of toluene for three times after centrifugation. The MA coated sucrose particles were dispersed in 50.0 mL of toluene again. After degassing with nitrogen for 30 min, the solution of 0.12 g of St, 0.12 g of DVB and 0.05 g of AIBN was added into the dispersion. The system was heated to 70 °C to initiate the polymerization and stood for 4 h to form the sucrose/polymer core/shell particles. After centrifugation, free polymers were removed from the dispersion. Polymer hollow spheres were obtained after washing the sucrose with water at ambient temperature. After crushing the hollow spheres with ultrasonic cell crusher, the Janus nanosheets were achieved.

2.2. Characterization

Morphology of the samples was characterized using transmission electron microscopy (JEOL 100CX operating at 100 kV) and scanning electron microscopy (S-4800 at 15 kV). The samples for SEM observation were prepared by vacuum sputtering with Pt after being ambient dried. The samples for TEM observation were prepared by spreading very dilute dispersions in ethanol onto carbon-coated copper grids. FT-IR spectroscopy was performed using a Bruker EQUINOX 55 spectrometer with KBr pressed pellets with the horizontal attachment. Morphology of the emulsions was characterized using Olympus BX 51 microscope. Fluorescence microscopy images were taken using confocal laser scanning microscope (CLSM, Leica TCS-sp2, Germany) with an excitation wavelength of 488 nm. The absorption spectra of dispersions were collected in the range of 200–800 nm on a TU-1901 UV–vis spectrophotometer. AFM images were recorded under ambient conditions using a Digital Instrument Multimode Nanoscope IIIA at tapping mode. The Zeta potential of the Janus nanosheets was performed in aqueous dispersion at varied pH using a Zeta-sizer (Nano Series, Malvern Instruments, UK) at 25 °C and repeated for three times.

3. Results and discussion

The sucrose particles are large ranging from 10^0 to 10^1 of micrometers (Fig. 1a). It is easy to separate the particles by simple filtration or low speed centrifugation. The particle surface is smooth. Hydroxyl groups are present on the surface which is conducive to a favorable absorption of MA forming a self-assembly layer by hydrogen bonding. The sucrose particles precipitate from toluene. After coating with a layer of MA, the particles become well dispersible. After the dispersion is heated to high temperature for example 70 °C in the presence of AIBN, no any particles are found after washing with water. This implies that that MA is not self polymerized onto the particle surface. When monomers St and DVB are added in the dispersion, the polymer layer is formed [42,43]. At an initial stage of the polymerization, MA should be copolymerized with the monomers. Upon consumption of MA, St is polymerized forming a crosslinked PS layer. The particle surface remains smooth after the polymerization (Fig. 1b). After washing with water, the particles are achieved which can keep their original shape without collapse (Fig. 1c). TEM image indicates they are hollow (Fig. 1d). This is resulted from removal of the sucrose core. The irregular contour of the hollow spheres is duplicated from the irregular sucrose particles. The polymeric hollow spheres are well dispersible in toluene but not in water. This indicates that the exterior surface is hydrophobic. A water/toluene immiscible mixture is used to demonstrate a selective capture of water by the hollow spheres (Fig. 2a, left). A trace amount of FITC is added into water phase for easier observation. Both top oil and bottom water phases are transparent. After addition of the hollow spheres, the top oil phase becomes opaque (Fig. 2a, middle). Upon stirring, the bottom water is absorbed inside the hollow spheres. As results, the whole system becomes opaque (Fig. 2a, right). CLSM image reveals that cavity of the hollow spheres is filled with the dyed