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Synthesis and property of polystyrene particle with smart surface by emulsion polymerization using "giant" surfactant

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ABSTRACT

The colloidal particles with switchable surfaces (i.e. smart surfaces) have attracted great attention for numerous potential industrial applications. We report here a novel approach for the fabrication of polymeric particles with smart surfaces by emulsion polymerization using "giant" surfactant. Specifically, the "giant" surfactant was obtained by incorporating poly(4-vinylpyridine) chains onto the one bulb of snowman-shaped polystyrene particles, and then used as emulsifier for the emulsion polymerization at pH = 2.00. The nearly monodisperse waxberry-like polystyrene particles were prepared with dual-size roughness surfaces, and the particulate film exhibited reversibly pH-switchable superhydrophobic property due to the pH-sensitivity of P4VP chains and the surface topology. This property enabled the particles could be used to effectively sequester hazardous anions from the wastewater.

1. Introduction

The colloidal particles with unusual shapes [1–8] and functionalities [9–14] have attracted great attention of material chemists. The previous research is focused on surface geometrical structures [15–19] and chemical compositions [20,21] of the particles. Among them, the particles with switchable surfaces (i.e. smart surfaces) have been prepared due to their numerous potential applications [22,23], such as promoting the adhesion of particles or molecules [24–28], controlling release of functional molecules [29,30], self-cleaning surfaces [31,32], tunable optical lenses [33,34], and functional coatings [35,36].

Therefore, the synthetic routes have been developed for colloidal particles with smart surfaces. For instance, Rios et al. [28] designed the biochemically responsive smart surface, and the contact angle of aqueous solutions on such surfaces decreased upon streptavidin binding; recently Narain et al. [37] reported that silica nanoparticles with the pH-responsive poly(2-(diethylamino) ethyl methacrylate) shells were synthesized by surface-initiated atom transfer radical polymerization, and the particles could be adhered to or desorbed from the surface by changing pH. However, we notice that the reports on the preparation of polymeric particles with smart surfaces are limited until now, and it still has great significance to develop new methods to fabricate polymeric particles with smart surfaces for some desired applications.

More recently, we reported a facile approach for fabrication of walnut-like polymeric particles using a "giant" surfactant with monomethoxy poly(ethylene glycol) (MPEG) hairs, and after removing the hydrophilic MPEG chains, the particulate films exhibited superhydrophobic property with a static water contact angle as high as 151° [38]. This method may enable a wide variety of molecular designs to afford novel types of tailored particles with controlled surface morphology and chemistry for the applications. However, this is still an area remained to be explored. In this paper, we expend this method to prepare the polymeric particles with smart surfaces, i.e. the polystyrene particles are prepared with pH-switchable superhydrophobic property by emulsion polymerization using a new "giant" surfactant.

Specifically, the snowman-shaped particles (OCPS-PS) were first prepared with a cross-linked polystyrene bulb containing epoxy groups (OCPS), and then carboxyl terminated poly(4-vinylpyridine) (P4VPC) was grafted onto the OCPS bulb to give the "giant" surfactant (PS-OCPS-P4VP) for the emulsion polymerization (Scheme 1). The "giant" surfactant has a special structure consisting

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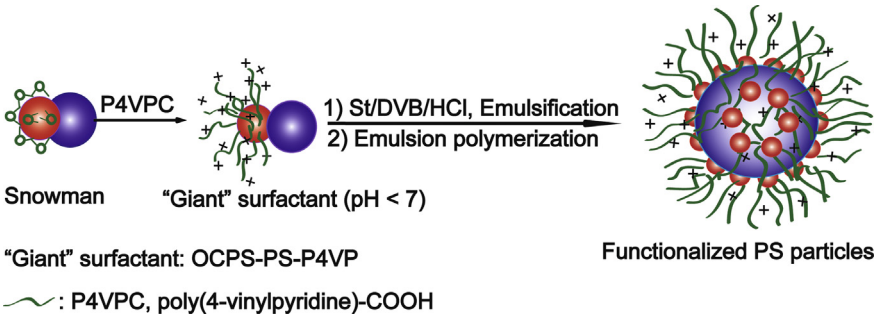

Scheme 1. The schematic for synthesis of polystyrene particles with smart surfaces.

of a hydrophobic head and a hydrophilic P4VP tails at pH = 2.00. It is expected that surface morphology and chemistry of the obtained particles could be controlled, and would be smart to exhibit a reversible superhydrophobic property due to the pH-sensitivity of P4VP chains. This property may enable the particles to effectively separate hazardous ions from the wastewater.

2. Experimental section

2.1. Materials and reagents

2,3-Epoxypropyl methacrylate (GMA, 96%, J&K Chemical Co., Ltd.) was purified to remove the inhibitors under reduced pressure. 4-Vinylpyridine (4VP, 95%, Acros Organics, USA) was purified by column chromatography (basic Al_2O_3) and stored in darkness at −20 °C prior to use. Styrene (Sinopharm Chemical Reagent Co., Ltd., CP) was successively washed with a 5% NaOH aqueous solution and deionized water until neutralization, and after being dried with anhydrous sodium sulfate overnight, they were distilled under reduced pressure and stored at −20 °C prior to use. OCPS-PS particles were prepared according to a modified method reported by Weitz et al. (Supporting Information) [39]. P4VPC was synthesized by reversible addition-fragmentation chain transfer polymerization according to the literature method (Supporting Information) [40]. All other chemicals were used as received.

2.2. Synthesis of "giant" surfactant

(PS-OCPS-P4VP). P4VPC was grafted onto the surface of OCPS-PS particles by reacting with the epoxy groups according to the modified method [41]. 0.50 g of OCPS-PS and 1.00 g of P4VPC were mixed in 20 ml of aqueous solution of HCl (1%), and then the mixture was stirred at the speed of 60 rpm for 12 h at 50 °C. The obtained "giant" surfactants (PS-OCPS-P4VP) were dried in vacuum at 40 °C and were stored in desiccator prior to use. The structures of the "giant" surfactants were confirmed by EDX spectra and FT-IR spectra.

2.3. Synthesis of polystyrene particles with "giant" surfactants

The polystyrene particles were prepared via emulsion polymerization with "giant" surfactant (PS-OCPS-P4VP) according to the literature method [38], and a typical procedure is described as follows: the polymerization was performed in a 150 mL one-necked round-bottomed flask with a magnetic stir bar. Initially, 50 mL of HCl aqueous solution (pH = 2.00) was used as solvent to dissolve 0.05 g of "giant" surfactants, then the solution was stirred to swell for 30 min and dispersed under ultrasonic irradiation for 20 min, and then St (2.50 g) and DVB (0.05 g) were introduced to the flask under stirring. The mixture was dispersed under ultrasonic irradiation, and purged with argon gas for 20 min to get rid of oxygen. After the temperature was raised to 70 °C, 2 mL of an aqueous solution of ammonium peroxydisulfate (APS) initiator (0.025 g/mL) was added to the mixture to initiate the polymerization under inert atmosphere. The polymerization was carried out for 24 h to ensure complete conversion, and the reaction mixture was then slowly cooled to room temperature. Finally, the latex particles were diluted in water (v/v = 1:100) for the measurements of HPPS and SEM.

Further experiments were conducted to investigate the influence of different concentration of "giant" surfactant on the emulsion polymerizations.

2.4. Anion adsorption with colloidal particles

A stock solution of Cr(VI) was prepared by dissolving $K_2Cr_2O_7$ in deionized water, and the main specie of Cr(VI) is $HCrO_4^-$ at pH = 2.00 [42]. 5 mL of colloidal particle (solid content = 0.85%) was dialyzed (MWCO = 3500) in 200 mL dilute aqueous solutions with 2×10^{-4} mol/L of Cr(VI) (pH = 2.00). 1.0 mL of the solution was removed to record ICP spectrometry at the pre−set interval times. After adsorption, the colloidal particles were dialyzed in water (pH = 9.00) to investigate the package of the hazardous anions.

2.5. Characterization methods

Fourier transform infrared (FTIR) spectra were performed using a Varian-1000 spectrometer with the KBr pressed pellets. ^{1}H nuclear magnetic resonance (^{1}H NMR) spectra were obtained on a Varian INVOA-400 instrument at 300 MHz. The Z-average size distribution and zeta potential of the microspheres were measured using a Malvern Zetasizer with irradiation from a 632.8 nm He−Ne laser. Field-emitting scanning electron microscopy (SEM) images were taken by a HITACHI S-4700 microscope operated at an accelerating voltage of 15 kV after depositing the particles on the surface of the silicon slice coating with gold. Transmission electron microscopy (TEM) images were obtained on a FEI Tecnai G20 electron microscope with an accelerating voltage of 160 kV. The sample solution (5 ml) was put on 400 mesh Ultrathin Type-A TEM Grid (Ted Pella, Redding, CA) and allowed to dry before analysis. Energy-dispersive X-ray (EDX) analysis was carried out by a Hitachi S570 scanning electron microscope with an EDAX-PV 9100 energy dispersion X-ray fluorescence analyzer. Contact angle was measured with a Contact Angle Meter Alpha-SE (J. A. Woollam Corporation): the glass substrates were covered with the monolayer PS colloidal particles film by spin coating. Water droplets (2 ml) were dropped carefully onto the films, and three measurements at different locations were used to calculate the average contact angle value. The anion concentrations were determined by

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