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Fabrication of hierarchical microparticles by depositing the in situ synthesized surface nanoparticles on microspheres during the seed emulsion polymerization

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ABSTRACT

A general strategy for the synthesis of polymeric hierarchical microparticles containing surface nanoparticles through modified seed emulsion polymerization is proposed. This modified seed emulsion polymerization has a character that suitable amount of monomer miniemulsion is added during the polymerization. The in situ synthesized surface nanoparticles which are resulted from the monomer miniemulsion as well as the shell-forming polymer coagulate on the seed particles and therefore hierarchical microparticles are fabricated. Various polymeric hierarchical microparticles containing 20–36 nm poly(styrene-*co*-acrylamide), poly(styrene-*co*-acrylic acid), and polystyrene surface nanoparticles are synthesized following the proposed method. The advantages in the present synthesis including both the well controls in the size, the composition, and the number of the surface nanoparticles and the convenience are demonstrated. The proposed strategy is anticipated to be a general method to fabricate hierarchical microparticles and is believed to have promising application in particle surface modification.

1. Introduction

Hierarchical microparticles such as raspberry-like microspheres have attractive characteristics such as unique morphology, surface roughness, high specific surface area, and high light scattering [1–5]. Generally, the synthesis of hierarchical microparticles is specified by two methods. The first strategy is the "grafting" method, following which small-sized nanoparticles are grafted onto the large-sized microparticles to fabricate hierarchical microparticles [6–11]. The drive force to graft the small-sized nanoparticles onto the large-sized microparticles is ascribed to the interaction between the binary particles, and therefore the covalent bonding [6–9], the hydrogen bonding [10], and the electrostatic interaction [11] between the nanoparticles and microparticles are usually employed. To make a harmonious interaction, surface particle modification before the grafting procedure is usually needed [6–9]. The second methodology to fabricate hierarchical microparticles is based on the coagulation method [12–25]. Compared with the grafting method, employing the pre-prepared nanoparticles and microparticles to fabricate hierarchical microparticles, pre-preparation of the small-sized nanoparticles and/or the large-sized microparticles in the coagulation method is needless. That is, either the small-sized nanoparticles or the large-sized microparticles are in situ synthesized during the deposition or coagulation. Clearly, compared with the grafting method, the coagulation method affords great convenience to fabricate hierarchical microparticles. However, synthesis of polymeric hierarchical microparticles through the coagulation method is rarely reported [23–25], although success in the synthesis of inorganic and polymer/inorganic hybrid hierarchical microparticles is achieved [12–22]. Hitherto, convenient fabrication of polymeric hierarchical microparticles is still a challenge.

Seed emulsion polymerization is a general method to synthesize polymeric core–shell microparticles [26–37]. Following this method, polymerization of the shell-forming monomer is performed on the surface of the seed particles to produce core–shell microparticles. Up to now, synthesis of core–shell microparticles [26–37] through seed emulsion polymerization and the subsequent synthesis of hollow microparticles [38–46] by selectively etching the core of the resultant core–shell microparticles have been extensively discussed by many research groups including ours. Herein, it is supposed, if additional monomer miniemulsion is added during the seed polymerization, the miniemulsion droplets will initially been converted into nanoparticles, and subsequently the resultant nanoparticles deposit onto the seed microparticles to fabricate hierarchical microparticles. Based on this hypothesis, a feasible approach to synthesize polymeric hierarchical microparticles including solid and hollow hierarchical ones through depositing the in situ synthesized nanoparticles on the seed microparticles during the seed emulsion polymerization is reported. The synthesis demonstrates that solid and hollow

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polymeric hierarchical microparticles containing different surface nanoparticles can be fabricated through the modified seed emulsion polymerization. The present synthesis, in which both the pre-preparation of surface nanoparticles and the particle surface modification are needless, has the advantage over the general grafting method [6–11]. Furthermore, compared with the general coagulation method to fabricate hierarchical microparticles [23–25], the size, the chemical composition, and the number of the surface nanoparticles embedded on the resultant hierarchical microparticles can be easily tuned just by changing the content of the monomer miniemulsion.

2. Experimental

2.1. Materials

Styrene (St, >98%), methylacrylic acid (MAA, >99%), and acrylic acid (AA, >99%) were purchased from Tianjin Chemical Company and distilled under vacuum before being used. Acrylamide (AM, >99%, Tianjin Chemical Company) was recrystallized from acetone before being used. The cross-linker of divinylbenzene (DVB, >80%, Alfa) was washed with 5% NaOH aqueous solution and water, followed by dried with $MgSO_4$. $K_2S_2O_8$ (>99.5%, Tianjin Chemical Company) and polyvinylpyrrolidone (PVP, Mw = 60,000 D, BASF) were used as received. The seed particles of the polystyrene-*co*-poly(methylacrylic acid) (PS-*co*-PMAA) microspheres, which contain 84 wt% polystyrene (PS) segment and 16 wt% poly(methylacrylic acid) (PMAA) segment and the average size of which is 220 nm, were synthesized by soap-free emulsion polymerization as discussed elsewhere [47,48]. Other chemical reagents were analytic grade and used as received.

2.2. Synthesis of the solid and hollow hierarchical microparticles containing poly(styrene-co-acrylamide) (PS-co-PAM) surface nanoparticles

Into a glass flask, the aqueous dispersion of the seed particles of the PS-*co*-PMAA microspheres (10.0 mL, 0.09 g/mL), H_2O (40.0 mL), and $K_2S_2O_8$ (0.110 g, 0.41 mmol) was added. The flask content was degassed under nitrogen purge at room temperature with vigorously stirring. Subsequently, the flask content was initially held at 80 °C for 5 min and then a mixture of St (0.820 g, 7.9 mmol) and DVB (0.051 g, 0.39 mmol) was added dropwise. After being kept at 80 °C for 30 min, the pre-prepared monomer miniemulsion was added dropwise. The monomer miniemulsion was prepared by initially mixing St (1.04 g, 10 mmol), AM (0.178 g, 2.5 mmol), DVB (0.032 g, 0.25 mmol), PVP (0.10 g), and H_2O (25.0 mL) with vigorously stirring and followed dispersing by means of an ultrasonic bath for 30 min (KQ-200KDE, 40 KHz, 200 W, Zhoushan, China). The polymerization was performed under nitrogen atmosphere with vigorously stirring for 24 h at 80 °C. After completion of the polymerization, the resultant solid hierarchical microparticles of PS-*co*-PMAA@PS/PS-*co*-PAM, in which the PS-*co*-PMAA represents the seed microspheres, the PS represents the coated shell of the cross-linked polystyrene on the seed, and the PS-*co*-PAM represents the surface nanoparticles embedded on the PS shell, respectively, were washed with water (20 mL × 3) and collected by centrifugation.

To fabricate hollow hierarchical microparticles, the collected PS-*co*-PMAA@PS/PS-*co*-PAM hierarchical microparticles were initially dried under vacuum at 40 °C for 24 h and then dispersed in dimethylformamide (DMF, 50 mL) at room temperature for about 12 h to remove the seed-forming polymer. The resultant hollow hierarchical microparticles of PS/PS-*co*-PAM, in which the PS represents the hollow shell of the cross-linked polystyrene and the PS-*co*-PAM represents the surface nanoparticles embedded on the PS hollow shell, were washed initially with DMF (20 mL × 3) and followed with water (20 mL × 2), collected by centrifugation, and finally dried under vacuum at 40 °C.

By changing the weight ratio (M/S) of the monomer mixture of AM/St/DVB (M) in the miniemulsion to the shell-forming monomer mixture of St/DVB (S) from 1.4 to 0.7, two hierarchical microparticles were fabricated.

2.3. Synthesis of the PS-co-PAM nanoparticles

Into a glass flask, H_2O (50.0 mL) and $K_2S_2O_8$ (0.050 g, 0.18 mmol) were added. The flask content was degassed under nitrogen purge at room temperature with vigorously stirring. Subsequently, the flask content was initially held at 80 °C for 5 min and then the pre-prepared monomer miniemulsion containing St (1.04 g, 10 mmol), AM (0.178 g, 2.5 mmol), DVB (0.032 g, 0.25 mmol), PVP (0.10 g), and H_2O (25.0 mL) was added dropwise. After completion of the polymerization at 80 °C for 24 h under N_2 atmosphere, the resultant PS-*co*-PAM nanoparticles were washed with water (10 mL × 3) and collected by centrifugation.

2.4. Synthesis of the solid and hollow hierarchical microparticles containing poly(styrene-co-acrylic acid) (PS-co-PAA) or polystyrene (PS) surface nanoparticles

Besides the hierarchical microparticles containing the PS-*co*-PAM surface nanoparticles, solid and hollow hierarchical microparticles containing the PS-*co*-PAA surface nanoparticles and PS surface nanoparticles, which are called solid PS-*co*-PMAA@PS/PS-*co*-PAA hierarchical microparticles, hollow PS/PS-*co*-PAA hierarchical microparticles, solid PS-*co*-PMAA@PS/PS hierarchical microparticles, and hollow PS/PS hierarchical microparticles, respectively, were fabricated with the similar method as demonstrated above, except the monomer miniemulsion containing AA/St/DVB or St/DVB monomer mixture was employed.

2.5. Characterization

The scanning electron microscopy (SEM) images were obtained with a JEOL JSM-6700F electron microscope. Transmission electron microscopy (TEM) observation was performed using a Philips T20ST electron microscope at an acceleration of 200 kV, whereby a small drop of the aqueous dispersion of the synthesized microparticles was deposited onto a piece of copper grid and then dried at room temperature under vacuum. The FTIR measurement was performed on a Bio-Rad FTS-6000 IR spectrometer using KBr pellets. The X-ray photoelectron spectroscopy (XPS) analysis was performed with a Kratos Axis Ultra DLD spectrometer employing a monochromated Al Kα X-ray source (1486.6 eV) and a delay line detector (DLD). Dynamic laser scattering (DLS) measurements were performed on Nano-ZS90 (Malvern) laser light scattering spectrometer with He–Ne laser at a wavelength of 633 nm.

3. Results and discussion

3.1. General synthesis of the solid and hollow hierarchical microparticles containing PS-co-PAM surface nanoparticles

Scheme 1 shows the strategy to fabricate solid and hollow hierarchical microparticles containing surface nanoparticles. Initially, the hydrophilic initiator of $K_2S_2O_8$ and the shell-forming monomer mixture of St/DVB are added into the aqueous dispersion of the seed particles of the PS-*co*-PMAA microspheres. The shell-forming monomer is initiated by $K_2S_2O_8$, and the resultant shell-forming