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Role of surface functionality on the formation of raspberry-like polymer/silica composite particles: Weak acid–base interaction and steric effect

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ABSTRACT

The surface functionality of polymer microspheres is the crucial factor to determine the nucleation and growth of silica particles and to construct the organic/inorganic hierarchical structures. The objective of this work was to evaluate the surface functionality and hierarchical morphology relationship via in situ sol–gel reaction. Carboxylic-functionalized poly (styrene-*co*-maleic anhydride) [P(S-*co*-MA)], poly(ethylene glycol)-functionalized poly(styrene-*co*-poly(ethylene glycol) methacrylate) [P(S-*co*-PEGMA)], and hybrid functionalized poly(styrene-*co*-maleic anhydride-*co*-poly(ethylene glycol) methacrylate) [P(S-*co*-MA-*co*-PEGMA)] microspheres were synthesized by emulsifier-free polymerization and used as templates. The morphologies of the composite particles were observed by transmission electron microscopy (TEM) and scanning electron microscopy (SEM). The results showed that core–shell structure was obtained with P(S-*co*-MA) as templates; raspberry-like structure was observed by using P(S-*co*-MA-*co*-PEGMA) as templates; and no silica particles were attached onto the surface of P(S-*co*-PEGMA) microspheres. These results indicated that the carboxylic groups on the surface formed by hydrolysis of anhydride groups were the determinate factor to control the nucleation of silica nanoparticles, and the PEG chains on the surface can affect the growth of silica particles. In addition, the particulate films were constructed by assembling these composite particles on glass substrates and modified with dodecyltrichlorosilane, the contact angles of water on the dual-sized structured surface were up to 160°.

1. Introduction

Nowadays, organic–inorganic composite particles have attracted increasing attention due to the combination of the advantageous properties of polymers and inorganic nanoparticles. Great efforts have been devoted to the design and preparation of organic–inorganic composite particles with different structures or morphologies (e.g., core–shell [1–4], mulberry-like [5], daisy-shape [6], multipod-like [6], snowman-like [7–9], dumbbell-like [8,9], and raspberry-like [10–20,22–33]). Among them, raspberry-like composite particles have been pay more attention due to its wide applications, such as super-hydrophobic surface [10,11], wettability surfaces [12], super-hydrophilic coatings [13], drug delivery [14], self-cleaning coatings [15], antireflective and antifogging coatings [5,15], etc.

Different methods have been established to construct the raspberry-like composite particles and synthetic strategies toward raspberry-like particles mainly include: (1) self-assembly of two different types of particles [16,17], (2) in situ polymerization technique (such as seeded emulsion [18], seeded dispersion [19], pickering emulsion [20,25], emulsifier-free [22,23], and miniemulsion [26–28] polymerization) and (3) in situ growth on the templates surface via sol–gel process [17,24]. The method based on sol–gel process is an effective approach because of its mild reaction conditions (e.g., low temperature and pressure) and simplicity.

The formation of raspberry-like particles was driven by chemical interaction or physical interaction (electrostatic interaction [29], hydrogen bond [30–32], acid–base interaction [23,33]). Based on

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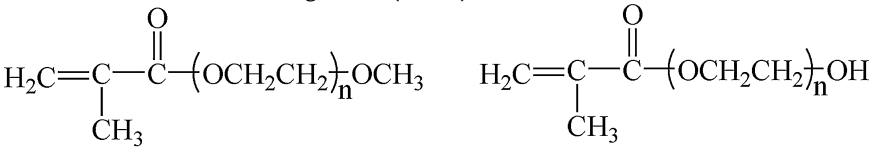
aforementioned methods, many polymer/SiO_2 composite particles with raspberry-like morphology have been reported [34–38]. In our previous study [39], monodispersed carboxyl-functionalized polystyrene (PS) spheres were used as cores and nano-sized silica particles were then assembled at the PS surface to construct the raspberry-like particles. It has been observed that the poly(acrylic acid)-rich chains were the key factor to the formation of raspberry-like PS/SiO_2 microspheres. The effect of the polyelectrolyte [poly(methacrylic acid)] on the formation of the raspberry-like particles has been studied in our group [40] and the result indicated that with the increasing of poly(methacrylic acid) brushes molecular weight, uniform raspberry-like silica particles were obtained. However, when the average number molecular weight was above 136,100, the morphologies of polymer/silica composite particles became complicated. The formation of raspberry-like structure was contributed to the weak acid–base interaction between the carboxyl groups, amine catalyst, and hydrolyzed tetraethoxysilane (TEOS) molecule (—COO^-/—N^+/—SiO^-) [41] and this mechanism has been further proved in our recent work [42]. At the same time, we have immobilized poly(ethylene glycol) (PEG) onto the surface of polymer spheres, and the result showed the steric-effect to inhibit the adsorption of silica in the in situ sol–gel process [43]. It has been reported that PEG-based macromonomers with different numbers of ethylene oxide units have been used to construct raspberry-like composite particles via hydrogen bond interactions between the silica nanoparticles and PEG chains [7,44]. However, hydrogen bond interaction is less stable and easily affected by pH values of the reaction system leading to desorption behavior of silica nanoparticles. It was unsatisfactory to control the adsorption silica particles on the surface of modified with PEG functionality. Further investigation is required to verify the role of nonionic hydrophilic PEG chains on the formation of raspberry-like polymer/silica composite particles. All the studies indicated that the surface chemical composition or functionality could affect the nucleation and growth of silica particles on the templates surface.

To further understand the relationship between the surface functionality and the morphology of PS/SiO_2 composite particles, carboxylic-functionalized, PEG-functionalized, and hybrid-functionalized polymer microspheres were synthesized via emulsifier-free polymerization method and used as templates to prepare polymer/silica composite particles via in situ sol–gel reaction. This is the first step in our efforts to clarify the relationship between the hybrid functionality of templates and the hierarchical structure of polymer/silica composite.

2. Experimental

2.1. Materials

The styrene (S) (Sinopharm Chemical Reagent Co., Shanghai, China) was distilled under vacuum to remove inhibitor before use. Maleic anhydride (MA) (Tianjin City Guangfu Technology Development Co., China) and potassium persulfate (KPS) was recrystallized before use. Poly(ethylene glycol) methyl ether methacrylate (PEGMEMA$_{475}$, M_w = 475 g/mol) and poly(ethylene glycol) methacrylate (PEGMA$_{360}$, M_w = 360 g/mol) were purchased from Sigma–Aldrich Co. and used without purification. Dodecyltrichlorosilane (97%) was supplied by Tokyo Chemical Industry Co. and used as received. Anhydrous ethanol, tetraethoxysilane (TEOS) and diethanolamine (DEA) were purchased from Sinopharm Chemical Reagent Co. (China) and used as received.



PEGMEMA(n=~8) PEGMA(n=~6)

2.2. Preparation of functionalized-polystyrene microspheres

Functionalized polystyrene (PS) copolymer microspheres were prepared by emulsifier-free polymerization method [41]. The standard recipes for emulsifier-free polymerization are listed in Table 1. The following procedure was used: all the ingredients were added into a 100 mL three-neck reaction flask equipped with a mechanical stirrer, a condenser and a nitrogen gas inlet. After the mixture was deoxygenated by bubbling with N_2 gas at room temperature for 30 min, the mixture was heated to 70 °C with a water-bath for 24 h. The functionalized PS microspheres were collected by centrifugation and then washed with ethanol for three times. The final product was dried in vacuum oven at 35 °C for 24 h.

2.3. Preparation of PS/SiO_2 composite particles and particulate films

The preparation of polymer/SiO_2 composite particles has been reported [45] and fabricated as follows: the functionalized PS microspheres were firstly dispersed into the mixture solution of 40 mL ethanol and 5 mL water under magnetic stirring. Then 0.2 mL TEOS was added and 1 g DEA was dripped into to catalyze the hydrolysis of TEOS. The reaction was carried out at 30 °C for 8 h. Finally, the composite particles were collected by centrifugation and washed with ethanol for three times. The pH values of reaction solution and morphology of the prepared composite particles are listed in Table 2.

To examine the wettability of PS/SiO_2 composite particles, the prepared composite particles were dispersed in ethanol and sonicated for 5 min, and then, the deposition process was conducted by spin-coating method on 1 cm × 1 cm × 0.1 cm glass substrate at 23 °C (Before using, the glass substrates were immersed in piranha solution for 12 h at 80 °C). A substrate with PS/SiO_2 composite film was obtained by repeating the deposition process three times. Finally, the films were chemically modified by dipped in solution of 1 wt% dodecyltrichlorosilane in hexane for 30 min.

2.4. Characterization

FT-IR spectra were recorded on a NEXUS-870 FT-IR spectrometer. The average zeta potential (minimum three specimens) of functionalized PS microspheres (dispersed in water) was measured by Zetasizer Nano ZS90 (Malvin Co. Ltd.). The morphology of composite particles was observed by TEM (JEOL, JEM-2100) and FESEM (JEOL JSM-6700). Thermogravimetric analysis (TGA) of composite particles was recorded on Germany Netzsch STA449F3 analyzer with a 50–800 °C temperature range at 20 °C/min heating rate under nitrogen. The surface wettability of the particulate films was expressed in terms of the contact angles (CAs) of water. The static CA was measured with Contact Angle Meter SL200B (Solon Tech.