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Fabrication of monodisperse anisotropic silica hollow microspheres using polymeric cave particles as templates

Hailin Cong [a,b,*], Jilei Wang [a], Bing Yu [a,b,*], Jianguo Tang [a,b], Wei Cui [a]

[a] Qingdao University, Qingdao 266071, China
[b] Laboratory for New Fiber Materials and Modern Textile, Growing Base for State Key Laboratory, Qingdao University, China

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ABSTRACT

Monodisperse anisotropic poly(styrene-co-divinylbenzene) (PS-DVB) particles with single cavity structures were synthesized using a modified dispersion polymerization method. The effects of DVB adding modes and speeds on the particle morphologies were studied. Using the PS-DVB cave particles as templates, monodisperse anisotropic silica (SiO_2) hollow microspheres were fabricated facilely. The obtained anisotropic silica hollow spheres had a potential application in rapid waste removal and detoxification extraction with a very simple procedure.

1. Introduction

In recent years, monodisperse anisotropic particles with novel structure and properties have attracted considerable attention [1–3]. A wide variety of anisotropic particles with diverse anisotropy in size, shape, and chemical functionality have been explored, and many of them have potential applications in fabricating photonic crystals, sensors, and biomaterials [4–7].

Monodisperse anisotropic particles can be synthesized by a few methods such as spray drying, lithography, and microfluidics [8–10]. For example, Park et al. obtained monodisperse "red blood cell-like" polyurethane (PU) particles via consolidation of charged droplets in electrospraying process [11]. Rolland and co-workers fabricated monodisperse polyethylene glycol (PEG) particles with controllable size and shape using photocurable templates [12]. Wang et al. prepared monodisperse toroidal polysulfone (PSF) particles by controlled solidification of polymer solution in microfluidic device [13]. Tanaka and co-workers synthesized pH-responsive "mushroom-like" poly(methyl methacrylate) (PMMA) based copolymer particles using a solvent evaporation method [14].

Another important application of the monodisperse anisotropic particles is to make hollow spheres with special structures via template method [15–17]. For example, Nagao and co-workers fabricated asymmetrical silica hollow dumbbells containing a movable inner core using PS–PMMA Janus particles as templates [18]. Liu et al. synthesized anisotropic Co_3O_4 hollow nanocapsules using $CoCO_3$ precursor particles as templates [19]. For the great control over hollow sphere morphology they afford, as well as the wide array of hollow spheres that they can be used to synthesis, template method represents an excellent means for hollow sphere synthesis. While direct synthesis methods tend to involve fewer steps, and are versatile as well, they are often unable to produce hollow spheres with high degrees of complexity and anisotropy [20,21]. As special derivates of core–shell materials, anisotropic hollow spheres have novel prospects, particularly in areas such as molecular catalysis, medicine release, chromatography separation, microreactor, coatings, photonic and electronic devices [22–25]. It is believed that the asymmetrical shapes and structures of the hollow spheres have important influence on their properties [26–28].

In this paper, we reported the preparation of monodisperse anisotropic SiO_2 hollow spheres with single cavity structures through template method. The effects of DVB adding modes and speeds on the template synthesis were investigated. The formation mechanism of the single cavity structures of the templates and application of the obtained anisotropic hollow spheres in rapid waste removal and detoxification extraction were researched and discussed preliminarily.

2. Materials and methods

2.1. Materials

Styrene (St, 99%), divinyl-benzene (DVB, 99%), 2,2-azobis(isobutyronitrile) (AIBN, 98%), ammonium hydroxide ($NH_3{\cdot}H_2O$, 28%),

* Corresponding authors. Address: College of Chemical Engineering, Qingdao University, Qingdao 266071, China (H. Cong and B. Yu). Fax: +86 532 8595 5529.
E-mail address: hailincong@yahoo.com (H. Cong).

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ethanol (99.5%) and hexadecyl trimethyl ammonium bromide (CTAB, 99%) were purchased from Tianjin Chemical Company. Tetraethyl orthosilicate (TEOS, 98%) and poly(N-vinylpyrrolidone) (PVP, Mn = 10,000) were provided by Sinopharm Chemical Reagent Company and Fluka, respectively. Iodine (I, 99.8%) was purchased from Shanghai Yindian Chemical Company. DVB and St were distilled under vacuum before use. AIBN was recrystallized from ethanol before use. The other reagents were used as received.

2.2. Synthesis of monodisperse PS-DVB cave particles

Monodisperse anisotropic PS-DVB cave particles were synthesized with a modified dispersion polymerization. The typical procedure can be described as follows: 25.0 g of St, 2.0 g of PVP, 0.75 g of AIBN, and 82.0 mL of ethanol were added into a three-necked bottle under mechanical stirring at a speed of 350 rpm. Polymerization was carried out at 70 °C for 4 h under nitrogen protection. Then a DVB containing mixture consisting of 5.0 g of St, 1.0 g of DVB, 26.4 mL of ethanol, and 17.6 mL of distilled water was added dropwise using a syringe pump at different speeds (0.3 0.45, or 0.6 mL/min) into the bottle, and the polymerization was continued for an additional 24 h. After polymerization, the PS-DVB cave particles in the dispersion liquid were separated by centrifuge and washed with distilled water for several times. Finally, the purified products were dried at 40 °C for 12 h.

2.3. Fabrication of monodisperse anisotropic SiO_2 hollow spheres

A typical procedure for synthesizing the monodisperse anisotropic silica hollow spheres was carried out as follows: 3 mL of $NH_3{\cdot}H_2O$, 0.625 g of CTAB and 2.0 g of PS-DVB cave particles were dispersed in 30 mL of ethanol and 25 mL of distilled water, and 2 mL of TEOS was added quickly into the mixture and stirred for 2 h at room temperature. Then the products in the dispersion liquid were centrifuged and washed with distilled water for several times. Finally, the purified products were dried at 40 °C for 12 h, followed by a calcination process in air at 300 °C for 2 h and 550 °C for 5 h to remove the PS-DVB templates completely.

2.4. Characterization

Surface morphology and structure of the anisotropic PS-DVB templates and SiO_2 hollow spheres were investigated by scanning electron microscopy (SEM, JEOL JSM-6309LV) and transmission electron microscopy (TEM, JEOL JEM-1200). X-ray diffraction (XRD) measurement was performed on a Rigaku D/Max2500PC X-ray diffractometer at room temperature. Thermogravimetric analysis (TGA) data were recorded using a Mettler Toledo TGA/DSC1/1600LF simultaneous thermal analyzer at a heating rate of 10 °C/min. Monodispersity and size of the products were measured on a Nanotrac NPA-253 particle size analyzer. UV–Vis absorbance of all liquid samples was detected with a Puxi TU-1810 UV–Vis spectrometer at a wavelength of 365 nm.

3. Results and discussion

3.1. Synthesis of monodisperse PS-DVB cave particles

Monodisperse anisotropic PS-DVB cave particles are synthesized using a modified dispersion polymerization method. As illustrated in Fig. 1, DVB crosslinker is added dropwise after the polymerization of St for 4 h. The DVB containing droplet is absorbed by PS sphere, and under the initiation of free radicals in the dispersion polymerization, the PS sphere is crosslinked partly by the absorbed DVB containing droplet to from a highly crosslinked "hard region" during the merging diffusion process of DVB. In the subsequent polymerization for 24 h, the hard region of the sphere grows slowly for having a high degree of crosslinking, while the adjacent less crosslinked "soft region" grows very fast. Therefore, a single cavity structure is formed in the hard region side of the PS-DVB particle.

Our experimental results verify the delayed addition mode of DVB is the key to the formation of cave particles. As shown in Fig. 2a, when DVB is added at the beginning of the reaction in a normal dispersion polymerization, uniformly crosslinked PS-DVB microspheres with smooth surface will be obtained. However, in the modified dispersion polymerization, when DVB is added after the polymerization for 4 h, PS-DVB cave particles will be formed (Fig. 2b).

The adding speeds of DVB containing droplets have great influence on surface topography of the obtained cave particles. As show in Fig. 3, when a low adding speed of 0.3 mL/min is used, particles with multi-cavity structures will be formed. Increasing the adding speed to 0.45 mL/min, monodisperse particles with single cavity structures will be obtained. Further increasing the adding speed to 0.6 mL/min will result in irregular shaped particles with a broad size distribution. The possible reason for this phenomenon is that the different feeding speeds of DVB containing droplets affect the spatial distribution of the crosslinking density across the spheres to minimum Gibbs interfacial free energy [29–34]. Too fast or too slow introduction of DVB containing droplets is not beneficial for DVB accumulating in one location of the spheres. Moreover, the average diameter of obtained particles increases with increased adding speeds of DVB containing droplets, which may be caused by the aggregation of the latex particles during this process [29]. Additionally, we have investigated the relationship between the

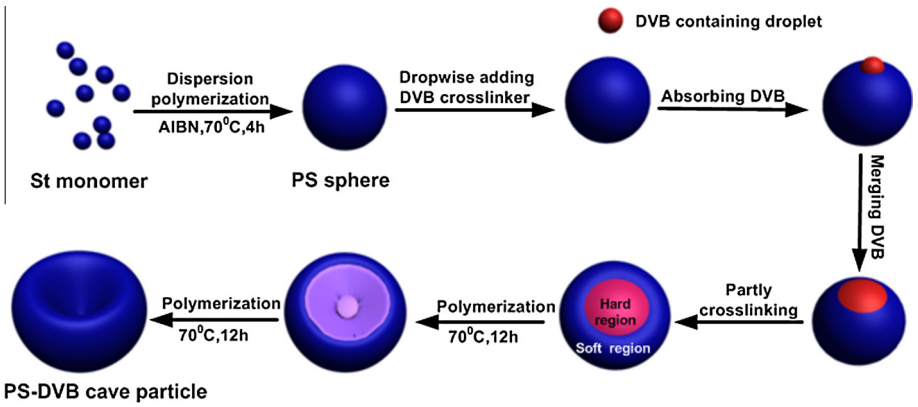

Fig. 1. Schematic illustration of the formation of PS-DVB cave particles.