Journal of Saudi Chemical Society (2017) **xxx**, xxx–xxx

King Saud University

Journal of Saudi Chemical Society

www.ksu.edu.sa
www.sciencedirect.com

ORIGINAL ARTICLE

Controlling morphology and particle size of hollow poly(styrene-divinylbenzene) microspheres fabricated by template-based method

Cheng Chen, Liping Zhang, Min Li, Anli Tian, Chunxia Wang, Shaohai Fu *

Jiangsu Engineering Research Center For Digital Textile Inkjet Printing, Key Laboratory of Eco-Textile, Jiangnan University, Ministry of Education, Wuxi, Jiangsu 214122, China

Received 9 November 2017; revised 26 November 2017; accepted 27 November 2017

KEYWORDS

Hollow poly(styrene–divinyl benzene)microspheres;
Template-based method;
Sol-gel method;
Dispersion polymerization;
Chemical etching

Abstract Hollow poly(styrene–divinylbenzene) (P(S-DVB)) microspheres were fabricated via template-based method including synthesis of silica particles by sol-gel method, preparation of silica/P(S-DVB) particles by dispersion polymerization and chemical etching of silica cores by NaOH solution. TEM, FTIR and TG analyses confirmed that the hollow P(S-DVB) microspheres were successfully obtained. The morphology of hollow P(S-DVB) microspheres could be controlled by adjusting the amounts of DVB, AIBN and VTES, and the round-ball-like hollow P(S-DVB) microspheres were fabricated when the amount of DVB, AIBN and VTES was 30.0 wt%, 5.0 wt % and 30.0 vol% respectively. Both the size of silica particles and amount of monomers were regarded as the two key factors to control the particle size of the round-ball-like hollow P(S-DVB) microspheres.

1. Introduction

The hollow microspheres have some potential applications in catalysis, protection of biologically active agents, fillers, micro reactors, waste removal, and controlled drug-release [1–7]. Therefore, fabrication of hollow microspheres in varying shapes and sizes is currently one of the fastest growing fields of materials science and engineering. Recently, a variety of methods for fabrication of hollow microspheres have been developed, such as polymerization [8,9], sol-gel process [10,11], self-assembling [12,13]etc.

Template-based method was usually applied to prepare hollow microspheres, the typical procedure was that the templates were coated by controlled surface deposition of precursors or by surface chemical reactions utilizing functional groups on the templates to create core-shell composites, and subsequently the templates were removed by chemical etching in an appropriate etchant or by calcination at elevated temperatures in air to generate hollow microspheres [14–16]. Obviously, the hollow polymer microspheres were prepared by selective removal of template particles from core-shell particles, thus the morphology and the particle size

* Corresponding author.
E-mail address: shaohaifu@hotmail.com (S. Fu).
Peer review under responsibility of King Saud University.

Production and hosting by Elsevier

https://doi.org/10.1016/j.jscs.2017.11.004
1319-6103

of hollow polymer microspheres were determined by the size of template particles and the total amount of monomers. Nowadays, the studies regarding the fabrication of hollow polymer microspheres are less than those of hollow inorganic microspheres, and the fabrication of hollow polymer microspheres with controllable structure becomes an attractive topic [17–19]. For the past few years, researches on fabrication of hollow P(S-DVB) microspheres were few. Li et al. [20] reported that hollow P(S-DVB) microspheres were fabricated by selectively dissolving uncross-linked PS cores of PS/P(S-DVB) particles prepared by two-stage soap-free emulsion polymerization. Unfortunately, although the above work was interesting, the preparation seemed to be time-consuming; for example, multistep processes were needed for the synthesis of PS/P(S-DVB) particles. Moreover, to obtain the hollow microspheres from the core-shell microspheres, removing the PS cores by lengthy dissolution using carbon tetrachloride was required. Therefore, developing a highly-effective and feasible method to fabricate hollow P(S-DVB) microspheres continues to be an immediate area of research focus.

The method developed in this study for fabrication of hollow P(S-DVB) microspheres was different from two-stage soap-free emulsion polymerization and seed swelling polymerization. Hollow P(S-DVB) microspheres could be obtained by etching silica cores of silica/P(S-DVB) particles, and the morphology was controlled by changing the amounts of DVB, AIBN and VTES during the dispersion polymerization on the silica surface. Furthermore, the hollow P(S-DVB) microspheres with different particle sizes were fabricated successfully by adjusting the size of silica particles or by changing the amount of monomers. Thereby, fabrication of hollow P(S-DVB) microspheres with controllable structure could be realized.

2. Experimental

2.1. Materials

Styrene (St) was purchased from Shanghai Chemical Reagent of China and distilled to remove the inhibitor in a vacuum. Divinylbenzene (DVB, 50%) was supplied by Shanghai Macklin Biochemical (China). Both 2,2′-azobis(isobutyronitrile) (AIBN, 98%) and Poly(vinylpyrrolidone) (PVP, K30) with a molecular weight of 30,000 were supplied by Sinopharm Chemical Reagent of China and used as received. Tetraethyl orthosilicate (TEOS, 98%), vinyl triethoxy silane (VTES, 98%), absolute ethanol, aqueous ammonia ($NH_3{\cdot}H_2O$, 28%) and sodium hydroxide (NaOH) were of analytical grade and purchased from Shanghai Chemical Reagent of China. Deionized water was used throughout the experiment.

2.2. Fabrication of hollow P(S-DVB) microspheres

Fabrication of hollow P(S-DVB) microspheres is shown in Scheme 1, and the whole procedure could be divided into three steps, including synthesis of silica particles as templates via sol-gel method, synthesis of silica/P(S-DVB) particles via dispersion polymerization and obtaining of hollow P(S-DVB) microspheres via NaOH etching.

2.2.1. Synthesis of silica particles via sol-gel method

The silica particles were prepared by sol-gel method. 100 mL of absolute ethanol and 33 mL of deionized water were charged into a 250 mL three-neck flask equipped with a mechanical stirrer, a thermometer with a temperature controller. Then variable amounts of $NH_3{\cdot}H_2O$ and TEOS were added into the above solution under stirring, and then the sol-gel reaction took place and was kept at 30 °C for 12h; subsequently, the corresponding amount of VTES was added to the above system for introducing vinyl groups on the surface of the silica prepared by the sol-gel reaction, the modification was carried out at 30 °C for 12h; finally, the VTES-modified silica particles with various particle sizes were obtained. Various amounts of $NH_3{\cdot}H_2O$, TEOS and VTES are collected in Table 1. In addition, the different volume ratios of VTES to TEOS (10.0 vol%, 20.0 vol%, 30.0 vol%, 40.0 vol%, 50.0 vol %) were also added into the sol-gel reaction system to synthesize the different silica particles for later use.

2.2.2. Synthesis of silica/P(S-DVB) particles via dispersion polymerization

The silica/P(S-DVB) particles were prepared as follows: 3 g of silica particles, 2 g of PVP, various mass ratios of AIBN to St (2.5 wt%, 3.75 wt%, 5.0 wt%, 6.25 wt%), desired amounts of St (2 g, 3 g, 4 g, 6 g), DVB (based on the weight of St, 7.5 wt %, 15.0 wt%, 22.5 wt%, 30.0 wt%, 37.5 wt%, 45.0 wt%, 52.5 wt%) and 5 mL of deionized water were added into 45 mL of absolute ethanol and stirred at high speed for some time, then heated to 80 °C for 6 h to obtain the silica/P(S-DVB) particles in which silica was used as core and P(S-DVB) as shell.

2.2.3. Obtaining of hollow P(S-DVB) microspheres via NaOH etching

50 mL of NaOH aqueous solution (0.5 M) was added into the silica/P(S-DVB) particles, where the silica cores were etched at 80 °C for 4 h.

2.3. Characterization and measurements

2.3.1. Scanning electron microscope (SEM)

The morphologies of samples were characterized using a SEM apparatus (Hitachi su1510, Hitachi Co., Japan). The samples were diluted and dried on a tinfoil and sputter-coated with gold prior to examination.

2.3.2. Transmission electron microscope (TEM)

The samples were diluted with deionized water and then dried onto carbon-coated copper grids before examination. The core-shell, hollow structure and shell thickness of the samples were observed by TEM apparatus (Hitachi JEM-2100, Hitachi Co., Japan).

2.3.3. Fourier transforms infrared spectroscopy (FTIR)

The samples were centrifuged and washed to remove the impurities and then dried at 40 °C for 24 h and finally pressed into KBr pellets. The characteristic functional groups were measured by FT-IR spectrometer (is50, Thermo Scientific, USA).

Please cite this article in press as: C. Chen et al., Controlling morphology and particle size of hollow poly(styrene-divinylbenzene) microspheres fabricated by template-based method, Journal of Saudi Chemical Society (2017), https://doi.org/10.1016/j.jscs.2017.11.004