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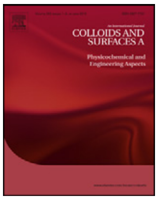

Synthesis of additive-free cationic polystyrene particles with controllable size for hollow template applications

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ABSTRACT

Studies on the synthesis of organic particles for template applications for facilitating the production of hollow particles have attracted tremendous attention. The unavailability of the commercial templates with a positive zeta charge is the main reason for this demand of study. The purpose of this study was to spotlight the synthesis of pure and cationic polystyrene (PS) particles with controllable size (from 30 to 300 nm) using a single step and relatively simple and cheap process and to demonstrate their application as the template in the production of hollow inorganic particles. Different from other methods, the synthesis method was based on the polymerization of styrene monomer in an aqueous solution system in the absence of any additional components (polymers, surfactants, chemicals, etc.) under 2,2-azobis (isobutyramidine) dihydrochloride (AIBA) as a cationic initiator to facilitate the creation of PS with a positive zeta charge. Precise control of the PS particle size in the nanometer range was achieved by the adjustment of reaction parameters (i.e. temperature, and styrene and AIBA concentrations). The size of the PS particles was proportional to the composition of styrene and the amount of initiator but had an inverse-proportional trend to the temperature. In addition, we also found that the styrene amount had more effect than the initiator (more than 4 times) on controlling PS size. Since an FTIR pattern and a micro-Raman spectrum results detected that the prepared PS particles had pure composition and homopolymer in spite of varying reaction parameters, the change of the particle size was due to changes in nucleus formation and particle growth rates. Flexibility of the process in the nanometer size control also drove to the devise of an equation to predict the particle size, which would be important for further scale-up development. Finally, the loaded positive zeta charge in the PS made it possible to assist the production of hollow inorganic particles (e.g. tungsten oxide, zirconia, and silica), in which this production could not be achieved when using commercial PS particles, verified by the particle formation mechanism hypothesis.

1. Introduction

Recently, hollow-structured particles have attracted tremendous attention due to their excellent performances: larger surface area, lower density, lower dielectric, etc. Excellent performance makes this material potential for many applications: catalysts, coating and composite materials, fillers, and drug delivery uses [1–3].

Several approaches for the synthesis of hollow particles have been reported, in which most of them use an organic template-driven self-assembly technique. One of the template candidates is polystyrene (PS). PS is effective because it is easily removed (either with heat treatment or solvent dissolution) [4] and available as a homogeneous sphere. Due to its homogenous sphere, its removal results in the formation of a spherical hole in the host material [5]. This replication phenomenon also offers the possibility in the control of hole size by changing the PS size [6], driving the need of further study in the synthesis of PS particles with controllable size.

Effectiveness of the assistance of PS on the synthesis of hole-structured material in different forms (i.e. film, particle, fiber, etc.) has been reported, informing that the PS is compatible with many self-assembly techniques and various host materials. However, when using PS as the template, several problems have been still noted: (i) most of the reports do not consider the existence of additives in the PS solution (i.e. surfactant, salt, polymer, etc.). These additives can give undesirable effects on the structure of holes [7,8]. The exist of additive also causes the formation of mesoporous structure in shell [2]. This mesoporous structure is avoided for some applications (i.e. lens and optical-related uses) because it can absorb some chemicals [9], leading to change material structure and performance (e.g. refractive index); (ii) most do not concern on the charge of PS. In fact, the charge allows the formation of different hole configurations (i.e. porous and hollow structure) [10]; (iii) most of the current PS particles are synthesized by employing an anionic initiator that typically consists of inorganic component

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(K, Na, etc.) [11], affecting to the purity of the PS itself. Further, this type of initiator allows the synthesis of PS with a negative zeta charge [10], in which this charge creates conflicts for some PS coating processes [12]; and, (iv) current PS particles that available in the market are typically expensive (10 mL (10 wt%) ≈ 100–500 USD) [13], making problems when employing a large volume of template.

To circumvent the above problems, studies on the synthesis of PS particles that are pure and have a positive zeta charge are important, especially when the PS is purposed to assist the production of hollow materials. Although several researchers reported the possibility in the use of negatively zeta charged PS for the production of hollow particles [1–3,12], the assistance of additive for changing the PS charge and pasting the material shell onto template surface could not be avoided. Several methods to the synthesis of pure and cationic PS particles have been developed. Ramos et al. [14] and Covolan et al. [15] reported the preparation of PS particles by the use of cationic initiator that was free of inorganic component. However, their methods cannot be separated from the use of surfactant to stabilize the PS particles. Against to the surfactant problems, Goodwin et al. [16] reported the synthesis of PS particles under the surfactant-free condition and the use of cationic initiator. Control of PS size can be effectively achieved by adjusting several parameters only. However, their methods have limited to the production of submicrometer particles, which is far from the demand of current technologies: the preparation of nanometer-sized particles. Nano-sized template is important because it would presumably create smaller hole in the host material than submicron template, which would be effective to increase material performance (higher surface area and porosity, lower density, etc.) [6]. Moreover, although it has been known that the use of cationic initiator could produce PS particle with a positive zeta charge [10], in the above reports, there is no information about the confirmation of zeta charge and applications of the synthesized PS (e.g. template).

The comprehensive studies on the preparation of cationic PS polymer particles (positive zeta charge) with size of down to the nanometer range and controllable size in the nanometer scale under an additive-free condition is virtually non existence, especially related to the particle charge and the detailed explanation and comparison between experimental result and theoretical analysis. Moreover, most of the papers reported the synthesis of PS particles only but included no mention of the application of PS itself. For this reason, the purpose of our study was to spotlight the synthesis of pure cationic PS particles with controllable size in the nanometer scale using a single step and relatively simple and cheap process under the additive-free condition and to demonstrate their application as the template for facilitating the production of hollow inorganic particles.

Based on our studies on the synthesis of porous silica nanoparticles (namely Hiroshima Mesoporous Materials (HMM-series)) [9], CaF_2 nanoparticles [17], and MgF_2 nanoparticles [18] with controllable size and morphology using a liquid-phase synthesis, here, we reported the synthesis of cationic PS particles with controllable size for hollow template applications. Different from other methods, the synthesis was based on the polymerization of styrene monomer in the absence of any additional components (polymers, surfactants, chemicals, etc.) and in an aqueous solution system. A single step and relatively simple and cheap process could be achieved using the present method. A cationic initiator (i.e. 2,2-azobis (isobutyramidine) dihydrochloride (AIBA)) was used to produce cationic PS particles with a positive zeta charge. Besides, free of inorganic compound was also the advantage of the use of this type of initiator. In addition, we purified the styrene using a basic solution instead of a vacuum distillation method [19], which is simpler and more cost effective for the total synthesis process. Spherical-shaped and well-controlled particle size from 30 to 300 nm in the nanometer scale using the present method was achieved by the adjustment of several reaction parameters (temperature and monomer and initiator concentrations), in which to the best of our knowledge, this is the first documented synthesis of well-controlled size in the nanometer scale under the additive-free condition. The size of the PS particles was proportional to the composition of styrene and the amount of initiator concentrations but had an inverse-proportional trend to the temperature. In addition, we also found that the styrene amount had more effect than the initiator (more than 4 times) on controlling PS size. Due to use of neither surfactant nor other additives, pure and homopolymer PS particles could be obtained, confirmed by an FTIR and a Raman spectrum analysis. Derivation of an equation from experimental scaling law to predict particle size control was also added in this paper. We believe that this novel equation would be useful for further applications, especially related to the scaling-up process.

The ability of our PS as the template to assist the production of hollow particles was also reported along with the hole-structured particle formation mechanism, based on our experiences in the preparation of porous particles using a spray-drying method [5,6,20,21]. Comparison of our prepared and commercial available PS was investigated. The result showed that our PS was compatible to support the production of various hollow-structured particles (i.e. tungsten oxide, zirconia, and silica), in which this production could not be obtained when using commercial PS particles.

2. Experimental method

2.1. Synthesis of PS particles

PS particles were synthesized using a liquid-phase synthesis method, involving a simple polymerization of styrene monomer (styrene, Aldrich, USA) in an aqueous solution (ultrapure water, generated by Millipore, USA) and in the absence of additives (polymers, surfactants, chemicals, etc.) under AIBA (Sigma–Aldrich, USA) as the initiator. The polymerization was conducted in the batch-process reactor-system, which was similar to our previous works [9,18]. The reactor system itself consisted of a batch-glass reactor (300 mL of a four-necked reactor), a magnetic stirrer, a mantle heater, a condenser, and a nitrogen gas inlet.

Firstly, an aqueous solution was put into the reactor system, vigorously stirred (600 rpm), and heated at a specific temperature under a nitrogen atmosphere. The heating process was then kept for 15 min to remove diluted oxygen in the solution. After the oxygen-free condition was reached, styrene monomer was added to the reactor subsequently. The system was then maintained for another 10 min to ensure that the styrene was dispersed homogenously in the aqueous solution. In addition, prior to adding into the aqueous solution, purchased styrene was previously washed by a base solution (NaOH (2.5 M)) to remove its inhibitor. In order to start the polymerization process, AIBA that previously dissolved in water was added to the mixed styrene–water solution. The mixtures were subsequently kept at this temperature for 10 h under a nitrogen atmosphere. The reacted solutions were then cooled to room temperature.

2.2. Application of PS particles as a template

To confirm application of our PS, the preparation of hollow inorganic particles using a spray-drying method and employing our prepared PS as the template was reported. The hole-structured inorganic particles were prepared from a precursor, which was a mixture of colloidal nanoparticles (i.e. tungsten oxide (WO_3; Nishin Engineering Inc., Tokyo, Japan; an average size of 7 nm), silica (SiO_2; Nissan Chem. Ind., Ltd., Japan; an average size of 5 nm), and zirconia (ZrO_2; Sumitomo Osaka Cement Co., Ltd., Japan; an average size of 7 nm)) and our synthesized PS particles (an average size