

## Aqueous Core Polystyrene Microspheres Fabricated via Suspension Polymerization Basing on a Multiple Pickering Emulsion

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**ABSTRACT:** Multi-hollow or hollow polymer particles are of great interest in many fields. Here we successfully fabricate polystyrene microspheres with aqueous cores through w/o/w Pickering emulsion stabilized by modified SiO<sub>2</sub> nanoparticles. The final structure and constituents of the microspheres is investigated via SEM, X-ray photoelectron spectra, and thermo-gravimetric analysis. The results demonstrate that the size and amount of aqueous cores in the microspheres can be tuned by the original structure of the multiple emulsions: when the volume fraction of inner water is 0.2, the inner structure of the microspheres obtained is porous and each pore is not interconnected; when the volume fraction of inner water is increased to 0.7, the resulting products are hollow microspheres and when 0.3% wt/vol of salt is added to the inner aqueous phase, the inner pores of the resulting microspheres enlarge or even coalesce. The multi-hollow or hollow polystyrene microspheres with aqueous cores are expected to be candidates for encapsulation in biotechnology. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 39761.

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### INTRODUCTION

Recently, multi-hollow or hollow polymer particles have attracted considerable interest<sup>1–8</sup> because of their potential application in many fields such as inks, coatings, cosmetics, weight-saving thermal insulations, sound absorption materials, scaffolds in tissue engineering, and controlled release of drug. Conventional hollow or multi-hollow particles have been achieved by the alkali swelling procedure,<sup>9</sup> the dynamic swelling method,<sup>10</sup> seed emulsion polymerization,<sup>11</sup> suspension polymerization,<sup>12</sup> phase inversion technique,<sup>13</sup> the concentrated emulsion template method,<sup>14</sup> and so forth. Compared with many other methods, the method of water-in-oil-in-water (w/o/w) multiple emulsions polymerization is much more convenient and effective,<sup>15</sup> because no template is needed to be fabricated in advance and only water droplets are used as porogen, which are cheap and clean.

W/o/w multiple emulsions are emulsion systems where small water droplets are entrapped within larger oil droplets which in turn are dispersed in a continuous water phase.<sup>16</sup> If the oil droplets are polymerizable, multi-hollow or hollow polymer particles can be fabricated. Conventional multiple w/o/w emulsions system need at least two kinds of surfactants to stabilize the primary w/o emulsion and the secondary o/w emulsion, respectively, so the final multi-hollow or hollow polymer particles inevitably contain surfactants that will cause adverse

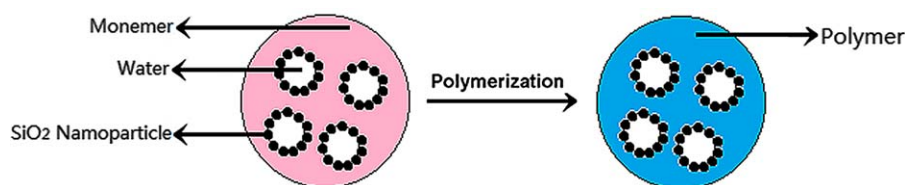
effects in some cases such as irritancy, interactions with living matter, and so on. Particle-stabilized emulsions, so called Pickering emulsions, have attracted much interest recently.<sup>17–22</sup> In Pickering emulsion, particles are irreversibly adsorbed at the oil–water interface because of their high energy of attachment, which make them good emulsifiers.<sup>23</sup>

Herein, multi-hollow or hollow polystyrene microspheres with aqueous cores have been prepared via multiple w/o/w emulsions based on Pickering emulsion. Modified SiO<sub>2</sub> nanoparticles are applied to stabilize the water-in-styrene Pickering emulsion, which is subsequently dispersed in a continuous water phase and the styrene in oil droplets is polymerized to fabricate water core polystyrene microspheres. The final structure and constituents of the microspheres is investigated and the effect of inner water volume and salt in inner aqueous phase is discussed. The volume fraction of inner aqueous phase is tuned from 0.2 to 0.7, to our knowledge, which is far higher than previously reported. Because of noncontact with harsh solvents, this kind of aqueous multi-core microspheres is well-suited for use as encapsulation in biotechnology.

### EXPERIMENT

#### Materials

Tetraethoxysilane (TEOS), ethacryloxypropyltrimethoxysilane (MPTMS) and methanol are obtained from Tianjing Damao Chemical Reagent (China). Azobisisobutyronitrile (AIBN) is



**Figure 1.** A schematic representation of suspension polymerization based on a multiple Pickering emulsion for preparing aqueous core polymer microspheres. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

purchased from Sinopharm Chemical Reagent (China). Styrene (St) is supplied by Tianjing Damao Chemical Reagent (China) and treated with 1M NaOH solutions to remove the inhibitor prior to polymerization. Other reagents are analytical grade and used as received. Deionized water is used throughout the work.

#### Preparation of MPTMS-Modified SiO<sub>2</sub> Nanoparticles

SiO<sub>2</sub> nanoparticles are prepared through the hydrolysis and condensation of TEOS. A typical preparation procedure is detailed as follows: methanol (60 mL), water (8 mL), and ammonium hydroxide (NH<sub>3</sub> 25%) (7.5 mL) are mixed together to form a solution. TEOS (20 mL) and methanol (60 mL) are also mixed together. Subsequently, two solutions are rapidly mixed and stirred for 8 h at 40°C. Then the mixture of 3 mL MPTMS and 10 mL methanol is added dropwise into the reactor and stirred for 24 h. The obtained white turbid suspension is centrifuged to separate the SiO<sub>2</sub> nanoparticles and the collection is washed with water and ethanol respectively. After being dried at 50°C for 24 h, MPTMS-modified SiO<sub>2</sub> nanoparticles are obtained.

#### Preparation of Multihollow Polystyrene Spheres

Multiple w/o/w Pickering emulsions with styrene as the oil phase are prepared in a two-step procedure. The primary and simple w/o emulsion is prepared by using water and a dispersion of modified SiO<sub>2</sub> nanoparticles in styrene with AIBN via ultrasonification. In the second step, the w/o emulsion prepared is re-emulsified into an aqueous dispersion of PVA by stirring. Subsequently, the produced w/o/w emulsion is polymerized for 24 h at 60°C and multi-hollow polystyrene spheres are obtained as shown in Figure 1 and the recipe is shown in Table I.

#### Characterization

Light microscopy images are collected with an optical microscope (Beijing TECH Instrument, China) equipped with a digital camera (Panasonic WV-CP460/G) and image analysis software (Beijing TECH Instrument, China). The three-phase contact angle of SiO<sub>2</sub> nanoparticles and MPTMS-modified SiO<sub>2</sub> nanoparticles is measured by using the compressed disk method.<sup>24</sup> SiO<sub>2</sub> particles are compressed into a 2-mm-thick disk at the pressure of 400 kgf/cm<sup>2</sup> and the disk is placed at the bot-

tom of an open, transparent glass vessel. Then styrene is poured into the vessel and a drop of water is placed on the particle layer. The appearance of the water drop on the SiO<sub>2</sub> layer is immediately photographed and the contact angle is directly measured by using a protractor. X-ray photoelectron spectra (XPS) is recorded by employing thermo ESCALAB 250 system with Al K $\alpha$  ( $h\nu = 1486.6$  eV) as X-ray source. Field emission electron microscope (FE-SEM) observations are conducted on a FEI Sirion200 system with an accelerating voltage of 5 kV. Thermo-gravimetric analysis (TGA) curves of the dry products are collected with a thermo-analyzer (TG209F3 NETZSCH) within a temperature range of 20–800°C and with the rate of increasing temperature of 10°C/min.

## RESULTS AND DISCUSSION

#### Modification of SiO<sub>2</sub> Nanoparticles

Figure 2 is the SEM image of SiO<sub>2</sub> nanoparticles modified with MPTMS. As estimated from SEM, the average size of SiO<sub>2</sub> nanoparticles is about 50 nm.

The survey scan XPS spectra of SiO<sub>2</sub> nanoparticles and SiO<sub>2</sub> nanoparticles modified with MPTMS is shown in Figure 3. The curve for SiO<sub>2</sub> nanoparticles [Figure 3(a)] confirms a substantial amount of Si and O existence and no C existence. For SiO<sub>2</sub> nanoparticles modified with MPTMS, the appearance of the peak belonging to the C element indicates the existence of organic groups, as shown in Figure 3(b), which demonstrates that the surface of SiO<sub>2</sub> nanoparticles is grafted by MPTMS.

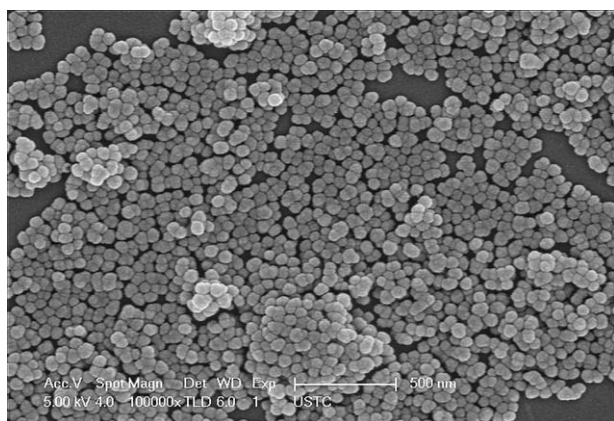
Because of the abundant hydroxyl on the surface, SiO<sub>2</sub> nanoparticles are hydrophilic and the three-phase contact angle is about 30° as shown in Figure 3(a). When SiO<sub>2</sub> nanoparticles are modified with MPTMS, they are translated into hydrophobic and the three-phase contact angle is increased to about 145° [Figure 3(b)], which is suitable to stabilize w/o Pickering emulsion.

#### Formation of Multiple w/o/w Emulsion

Light microscopy images of the primary water-in-styrene (w/o) emulsion with different volume fractions [Figure 4(a,b)] and

**Table I.** Recipe of Water Core Polystyrene Microsphere

Entry	Inner aqueous phase		Oil phase		External aqueous phase		
	Water (mL)	NaCl (%)	St (mL)	AIBN (g)	SiO <sub>2</sub> (g)	Water (mL)	PVA (g)
SM1	2.5	-	10	0.1	0.5	100	0.2
SM2	11.5	-	5	0.05	0.25	100	0.2
SM3	2.5	0.3	10	0.1	0.5	100	0.2

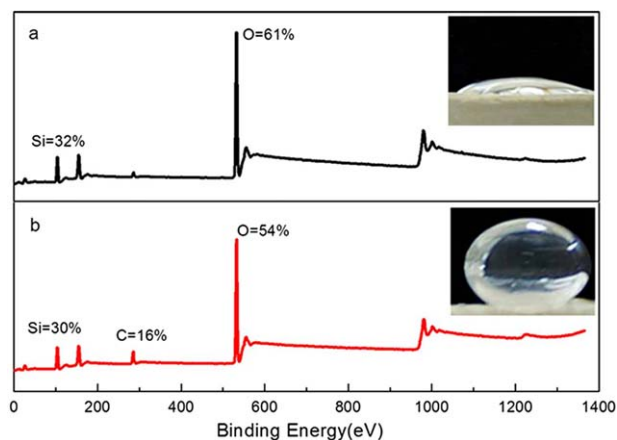


**Figure 2.** SEM image of MPTMS-modified SiO<sub>2</sub>.

the multiple water-in-styrene-in-water (w/o/w) emulsion [Figure 4(c)] are shown in Figure 4. It is shown that the average size of water droplets in the primary w/o emulsion increases when volume fraction increases from 0.2 to 0.7. In the re-emulsification process, the original structure of the primary is kept and it is obvious that many water drops exist inside styrene globules [Figure 4(c)]. The size of styrene globules in multiple w/o/w emulsion mainly depends on stirring rate and it is controlled to make the size of globules range from tens to hundreds micrometers. The major instability in surfactant multiple emulsions results from the diffusion of surfactant from inner to outer interfaces or vice versa. In Pickering emulsion, the solid particles are irreversibly adsorbed at the oil–water interface, which act as the mechanical barriers against coalescence, so the migration of particles is minimal after emulsion formation and the multiple Pickering emulsion prepared has good stability which is necessary for the subsequent suspension polymerization

#### Morphology and Properties of Multihollow Polystyrene Microspheres

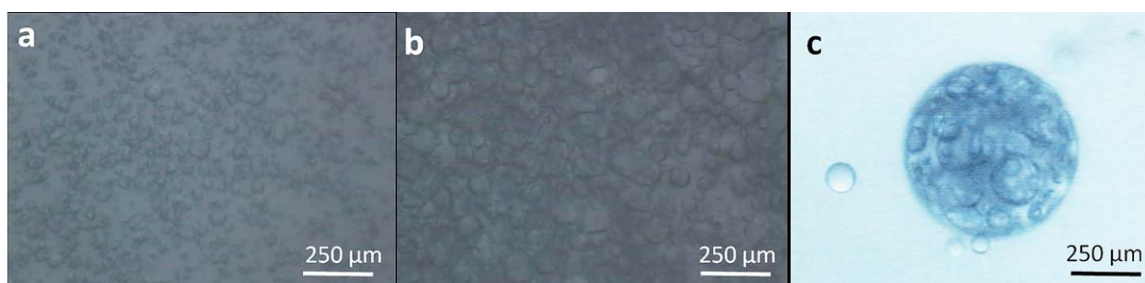
In this work, the inner structure of the microspheres can be tuned by the original structure of the multiple emulsions. As shown in the representative SEM images of SM1 [Figure 5(a)] and SM2 [Figure 5(b–d)], it is observed that all the microspheres are spherical and dispersive. For SM1 with inner water volume fraction of 0.2, it can be clearly seen that the inner structure of the microspheres is porous and each pore is not interconnected [Figure 5(a)]. When inner water volume fraction



**Figure 3.** XPS and three-phase contact angle determination photograph of (a) SiO<sub>2</sub> nanoparticles and (b) SiO<sub>2</sub> nanoparticles modified. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

increases to 0.7, the resulting microspheres of SM2 are hollow as shown in Figure 5(b). In the case of SM1, the inner water fraction is low and SiO<sub>2</sub> nanoparticles are sufficient, so the droplets formed in the primary emulsion are smaller and more stable in the polymerizing process. As a result, there are a lot of droplets wrapped in the microspheres and the multi-hollow structure forms. In the case of SM2, when the inner water fraction is increased, the droplets formed in the primary emulsion enlarge and are apt to coalesce in the polymerization process. It probably arises from the lack of sufficient numbers of SiO<sub>2</sub> nanoparticles. In this work, SiO<sub>2</sub> nanoparticles is 5 wt % with respect to the styrene and less styrene causes less particles if compared to the emulsion with inner water volume of 0.2. As a result, the inner water droplets coalesce to reduce surface area and microspheres with hollow structure are obtained. As estimated from a partial enlarged view [Figure 5(d)] of a broken microsphere of SM1 [Figure 5(c)], the shell thickness is about 4 μm.

Figure 6 shows the XPS spectra of intact microspheres [Figure 6(a)] and sectioned ones [Figure 6(b)]. According to curve a, a large number of C and a small amount of O (probably come from the PVA residual on the surface), but almost no Si is detected. However, for sectioned microspheres, the peak belonging to Si element demonstrates the existence of SiO<sub>2</sub> and it is proved that SiO<sub>2</sub> nanoparticles mainly aggregate in the inner microspheres.



**Figure 4.** OM images of (a) primary w/o emulsion (20 vol %), (b) primary w/o emulsion (70 vol %) and (c) multiple w/o/w emulsion from re-emulsification of primary w/o emulsion. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



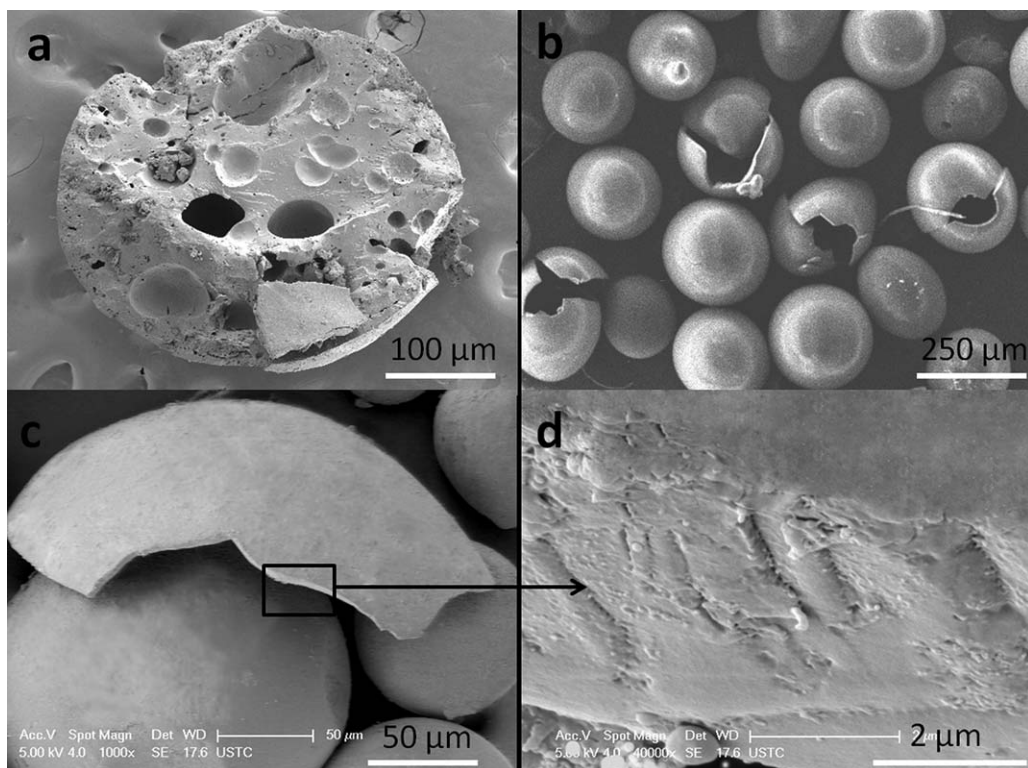


Figure 5. SEM images for (a) SM1, (b, c, d) SM2.

The TGA curves of pure PS microspheres [Figure 7(a)] and the resulting microsphere of SM2 [Figure 7(b)] are shown in Figure 7. The weight loss from 300°C to 450°C in Figure 7(a,b) is obvious because of the degradation of polymer chains. For curve b, there is a weight loss at 100°C because of the evaporation of water. Because all the samples tested are dried in advance, the weight loss demonstrates the existence of water cores in microspheres. According to Figure 7(b), water weight contained in SM2 is 60% and it is calculated to be 66% according to the feed. The decrease of water content is probably because partial inner water escapes under shearing during the

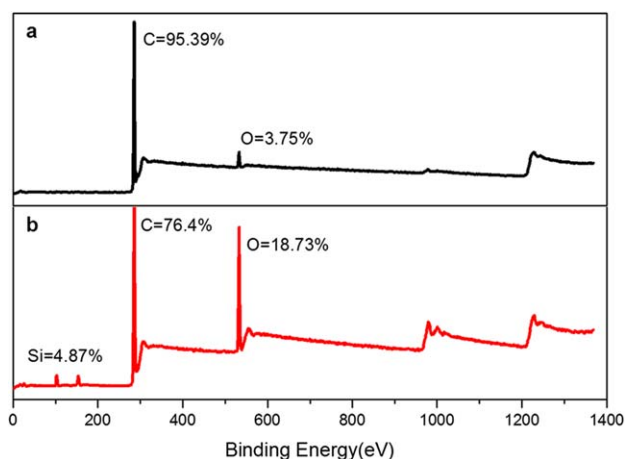


Figure 6. XPS of (a) intact microspheres, (b) sectioned microspheres. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

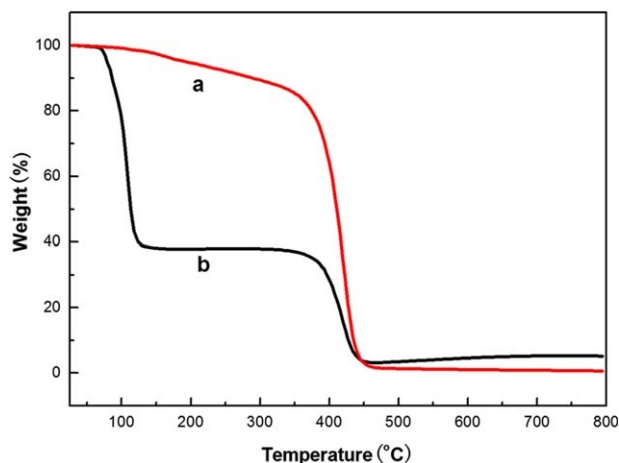


Figure 7. TGA of (a) PS microspheres and (b) microspheres of SM2. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

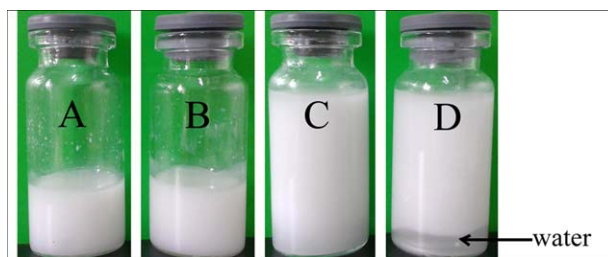


Figure 8. Photograph of water-in-styrene Pickering emulsion stabilized by  $\text{SiO}_2$ : (a) pure water (20 vol %), (b) 0.3% wt/vol salt solution (20 vol %), (c) pure water (70 vol %), and (d) 0.3% wt/vol salt solution (70 vol %). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

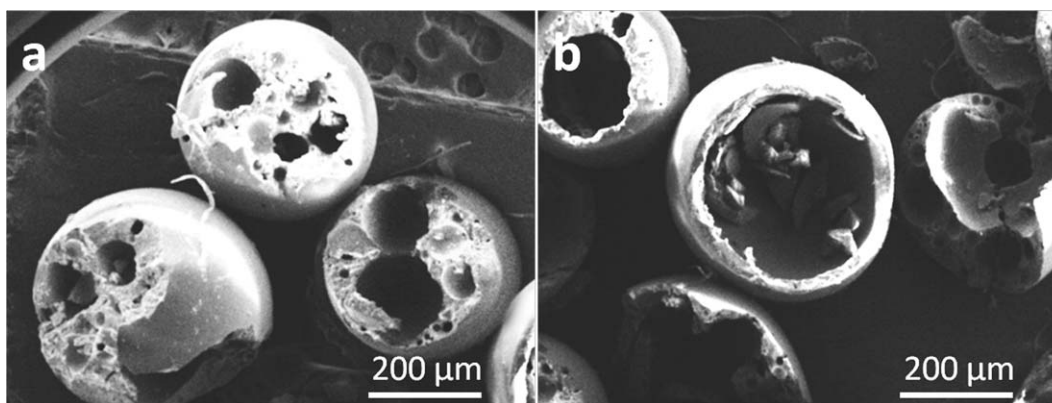


Figure 9. SEM images for (a) SM1 and (b) SM3.

re-emulsification process.  $\text{SiO}_2$  has not lost in the experimental temperature range, so there is a little residue for SM2.

#### Effect of Electrolytes in Inner Aqueous Phase

In order to study the effect of electrolytes in inner phase, pure water and 0.3% wt/vol salt solution are used as dispersive phase, respectively, to form the primary water-in-St Pickering emulsion. The Photograph of the primary Pickering emulsion is shown in Figure 8. When the inner phase fractions are 20%, the emulsion containing salt water [Figure 8(b)] is as stable as the one containing pure water [Figure 8(a)]. When the inner phase fractions are increased to 70%, the emulsion consisting of pure water keeps stable [Figure 8(c)], whereas phase separation is observed in the emulsion containing salt solution [Figure 8(d)]. It seems that the addition of salt reduces the emulsifying capacity of  $\text{SiO}_2$  in primary w/o emulsion, which is probably because of the reduction of the electrostatic repulsion between the particles. As a result, the emulsion containing salt is apt to coalesce during the polymerization process. Besides the reduction of emulsifying capacity of  $\text{SiO}_2$ , water influx under the increased internal osmotic pressure will probably cause rupturing of the inner aqueous droplets and swelling too. SEM images of SM1 [Figure 9(a)] and SM3 [Figure 9(b)] are shown in Figure 9. SM3 had the same inner water content with SM1, but 0.3% wt/vol of salt was added in its inner aqueous phase. It can be observed that the inner pores of SM3 increased or even coalesced, but the microspheres of SM3 are not enlarged obviously compared to SM1. It is probably because of the sharply increasing viscosity of Styrene during the polymerization process, which makes water influx and microsphere swelling difficult.

#### CONCLUSION

In summary, polystyrene composite microspheres with aqueous cores are successfully fabricated via suspension polymerization based on multiple w/o/w emulsion. The size and amount of aqueous cores in microspheres can be tuned by the original structure of the multiple emulsions. When the volume fraction of inner water was 0.2, the inner structure of the microspheres obtained is porous and each pore is not interconnected. On the other hand, when the volume fraction of inner water is increased to 0.7, the resulting products of SM2 are hollow microspheres. When salt was added to the inner aqueous phase,

the inner pores of the resulting microspheres enlarge or even coalesce. Compared with previous routes of fabricating multi-core microspheres, our method is facile, need no surfactant or solvent, and it can also be extended to prepare other multicore polymer microsphere in different system, which might have potential applications in materials science and biotechnology.

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