Surfactant-Free Fabrication of SiO₂-Coated **Negatively** Charged Polymer Beads and Monodisperse Hollow SiO₂ Particles

Author Names: Wanghui Chen, Chika Takai, Hadi Razavi, Masayoshi Fuji*, Takashi Shirai

Author Affiliation: Advanced Ceramics Research Center, Nagoya Institute of Technology,
Honmachi 3-101-1, Tajimi, Gifu, 507-0033, Japan

***Corresponding Author** E-mail address: fuji@nitech.ac.jp

Abstract: SiO₂ coating on the surface of negatively charged polymer beads (n-PBs) succeeded in a typical stöber process with tetraethyl orthosilicate (TEOS). The core-shell structure of the resulting particles was confirmed by TEM observation and EDS mapping. Hollow SiO₂ particles (HSPs) with monodisperse size and high dispersibility were further fabricated by calcining the obtained SiO₂-coated n-PBs in air at 600°C. Two advantages of using n-PBs for the fabrication of SiO₂-coated polymer beads and HSPs were revealed as (1) lower cost with respect to positively charged polymer beads (p-PBs) and (2) improving the dispersibility of the obtained HSPs. According to our observations, there are two prerequisites for the formation of SiO₂ shells on n-PBs, as (1) the high surface charge density of n-PBs and (2) low water concentration in reaction system. A mechanism was proposed for explaining the coating of SiO₂ on the like-charged polymer beads. In that mechanism, the adsorption of NH₄⁺ ions on the surface of n-PBs played a critical role for SiO₂ coating, as it not only screened the surface charge of n-PBs to reduce the energetic barrier for

SiO₂ deposition, but also caused the accumulation of OH⁻ ions to restrict the location where SiO₂ nucleated to the surface of n-PBs.

Keywords: SiO₂ coating; Hollow SiO₂ particles; Negatively charged; NH₄⁺; Stöber process; P(St-co-AA)

1. Introduction

In recent years, there has been an increasing interest in SiO₂-coated colloid particles, because of their potential applications in spectroscopic, magnetic, catalytic, coating, and biological [1, 2]. Among them, SiO₂-coated polymer beads (PBs) can be further used to fabricate hollow SiO₂ particles (HSPs), since the polymer beads (i. e., cores) are easy to be removed by either heating or organic solvent, while the SiO₂ shells are much more stable. HSPs is a kind of novel material owning much lower bulk density and higher specific surface area with respect to solid SiO₂ particles [3, 4]. Besides, SiO₂ shells and their surrounding hollow space also bring out the potential applications of HSPs in optical [5, 6], loading- releasing ability [7], heat insulation [8] and so on. Since the process of SiO₂ coating on PBs determines the properties of SiO₂ shell (e. g. thickness, surface roughness, porosity) to a considerable degree, it should be intensively investigated.

Stöber process [9], in which the rate of SiO₂ nucleation and growth can be well controlled, is usually adopted for SiO₂ coating. A typical Stöber process conducts in the reaction system that contains Tetraethyl orthosilicate (TEOS) as the precursor, ammonia solution as the catalyst, and ethanol as the solvent. On the other hand, with considering that the SiO₂ generated in the Stöber process has a negative surface, positively charged polymer beads (p-PBs), such as the polystyrene beads with their surface terminated by NH₂ groups [10], are usually used as the cores for SiO₂ coating. On contrary, it was believed that negatively charged polymer beads (n-PBs) were not so

suitable for using, as the SiO₂ deposition on them would possibly be suppressed by the electrostatic repulsive force. As reported [10, 11], when n-PBs were used for SiO₂ coating, SiO₂ particles independently generated in the bulk solution instead of depositing on the surface of n-PBs, and the corresponding HSPs also couldn't be obtained. Nevertheless, those studies may be more reasonable if the surface charge density of n-PBs and reaction parameters for SiO₂ coating have been varied. In fact, there have been some works indirectly demonstrated the possibility of SiO₂ coating on n-PBs. Graf et. al. [12] found SiO₂ shell could be constructed on the surface of n-PBs under the assistance of a nonionic surfactant (i. e., PVP) that couldn't change the surface charge of n-PBs. Deng et. al. [13] most recently obtained n-PB@Vinyl-SiO₂ core-Shell particles with using a special precursor (i. e., VTMS) of SiO₂, and proved the high yield of SiO₂ coating on n-PBs. Therefore, much more experiments should be carried out for addressing whether one can realizing SiO₂ coating on the surface of n-PBs in a typical Stöber process or not, and more facts (e.g., surface charge density of n-PBs, reaction parameters) should be considered for an appropriate conclusion.

In this paper, we demonstrate the SiO₂ coating on the surface of n-PBs can be realized in a typical stöber process, once certain prerequisites have been met. For the credibility of our results, surfactants were not used in the whole process and the n-PBs were also synthesized in an emulsifier-free polymerization [14]. Correspondingly, we propose a mechanism for the SiO₂ coating on n-PBs. We also confirm the feasibility of using the obtained SiO₂-coated n-PBs to fabricate HSPs. According to our studies, the advantages of using n-PBs to obtain SiO₂-coated PBs and HSPs are: (1) the lower cost with respect to p-PBs, since n-PBs could be obtained with using cheap anionic initiators (e. g., KPS), while expensive cationic initiators (e. g., 2,2'-azobis(2-methylpropionamide) dihydrochloride) or some certain surface modifications were necessary for the synthesis of p-PBs [10, 11, 15, 16]; (2) improving the dispersibility of the obtained

SiO₂-coated PBs and HSPs, since there was no “surface charge reversal” phenomenon in the process of SiO₂ coating on n-PBs.

2. Experimental

2.1 Materials.

Styrene (St) was from Kanto Chemical Co., Inc. Japan. Before using, St was first washed with 5.0 wt. % NaOH (Wako Pure Chemical Industries, Ltd. Japan) solution for 4 times and DI water for 4 times respectively, followed by distilling under reduced pressure. All the following chemicals were used as received without further purification: Acrylic acid (AA, 98.5%), K₂S₂O₈ (KPS, 98.0%) from Kanto Chemical Co., Inc. Japan; Tetraethyl orthosilicate (TEOS, 95.0%), Ethanol (99.5%), Ammonia solution (25.0 %) from Wako Pure Chemical Industries, Ltd. Japan. DI water was produced by RFD250NB distilled water system (Toyo Roshi Kaisha, Ltd. Japan).

2.2 Synthesis of n-PBs

Three kinds of n-PBs (i. e., PS, P(St-co-2.5%AA) and P(St-co-5.0%AA) beads) have been synthesized by a reported emulsifier-free polymerization ^[14] with using an anionic initiator KPS. For the as-synthesized P(St-co-AA) beads, the percentage in name denotes the volume ratio of AA to St before polymerization (see **Table 1**). For the emulsifier-free polymerization, briefly, 170mL DI water, 15mL St and a certain volume of AA were first poured into a 4-neck flask equipped with a condenser, a thermometer, a gas inlet pipe and a PTFE stirrer. Then N₂ was bubbled into the monomer/water mixture for 20min. Afterward, the system was closed and heated to 70°C. During the heating, stirring was started and controlled at 340rpm. The polymerization was initiated by

pouring 10mL 1.5 wt. % KPS aqueous solution (pre-heated to 70°C) in, and then lasted for 24h at 70°C with continuous stirring. After the reaction, n-PBs were collected by centrifugation at 6000rpm and washed with DI water for several times. Finally, the well cleaned n-PBs were dried in vacuum at 40 °C for 24h.

2.3 Fabrication of SiO₂-coated n-PBs and HSPs

SiO₂-coated n-PBs were synthesized in a typical stöber process [9]. Briefly, 0.414g n-PBs were first added into a mixture of 30ml ethanol, 0.5ml water and 1mL 25.0 wt. % ammonia solution, followed by a 30min ultrasonic treatment. Then the above suspension was stirred by a magnetic stirrer (600rpm). Meanwhile, 18.5mL TEOS solution (5.4 vol. % in ethanol) was poured in. The reaction was allowed to proceed for 12h at room temperature with continuous magnetic stirring. The resulting particles were collected by centrifugation at 6000rpm, and washed with ethanol and DI water for several times. Finally, particles were dried in vacuum at 40 °C for 24h. HSPs were obtained after calcining the SiO₂-coated n-PBs in air at 600°C for 5h. The heating rate for calcination was 5°C/min.

Two supported experiments were carried out only for the purpose of investigating the mechanism of SiO₂ coating. In supported experiment (I), we compared the concentration of NH₄⁺ (c(NH₄⁺)) in the original solution and that in the bulk solution of n-PBs suspension to reveal the adsorption of NH₄⁺ on the surface of n-PBs. The pH of the original solution containing 30ml ethanol, 0.5ml water and 1mL 25.0 wt. % ammonia solution was first measured. Because of the following ionic equilibrium formed in the mixture,

the concentration of NH₄⁺ (c(NH₄⁺)) can be calculated as:

$$\log_{10}c(\text{NH}_4^+)=\log_{10}c(\text{OH}^-)=\text{pH}-14 \quad (2)$$

Then an amount of 0.414g n-PBs was dispersed in the above mixture, followed by a 30min ultrasonic treatment. The resulting suspension was centrifuged at 6000rpm for 2h to separate n-PBs from the solution. The pH of supernatant was measured as soon as the centrifugation finished. The calculated $c(\text{NH}_4^+)$ could be approximately seen as the $c(\text{NH}_4^+)$ in the bulk solution of the former suspension. In supported experiment (II), an amount of 0.414g P(St-co-5.0%AA) beads was first immersed in 50ml KCl solution (5.0 wt.%) for 12h and then dried without washing. The modified P(St-co-5.0%AA) beads was further used for the SiO₂ coating. The production was named as “S-KCl”.

2.4 Characterizations

Scan electron microscopy (SEM) and scanning transmission electron microscope (STEM) images were taken by a JSM-7600F (JEOL Ltd. Japan). Transmission electron microscopy (TEM) images and Energy dispersive X-ray spectroscopy (EDS) mapping were taken by a JEM-z2500 (JEOL Ltd. Japan). Thermogravimetric (TG) curves were recorded by a thermo plus TG-8120 (Rigaku. Co. Japan). Zetasizer nano-ZS (Malvern Ltd. UK) was used to measure the Zeta potential and particle size. FT-IR spectra were retrieved from a FT/IR-6000 (Jasco Co., LTD. Japan). pH was measured by a SG8 SevenGo pH meter (Mettler-Toledo GmbH).

3. Results and Discussion

3.1. SiO₂ coating on n-PBs with different surface charge density

Three kinds of n-PBs (i. e., PS, P(St-co-2.5%AA) and P(St-co-5.0%AA) beads) have been

successfully synthesized by emulsifier-free polymerization. Their zeta potentials (in water) and size are listed in **Table 1**. As seen, all the obtained PBs were negatively charged, though the PBs synthesized without the comonomer AA (i. e., PS beads) were only slightly charged (zeta potential = -1.1mV). The low surface charge density of PS beads was due to the low ratio of initiator-to-monomer (0.011 w/w), since all the charges of them (i. e., SO_3^- groups) were from the initiator KPS. **Table 1** also indicates the low surface charge density of PS beads was significantly improved by using AA as the comonomer, as the zeta potentials of P(St-co-2.5%AA) and P(St-co-5.0%AA) beads increased to -23.7mV and -45.6mV respectively. This improvement can also be proved by the negative shift of zeta potential distribution histograms (**Figure 1a**). It's believed the negative charges on the surface of P(St-co-AA) beads were not only from SO_3^- end-groups but also from additional COO^- groups brought by co-monomer AA. Therefore, the surface charge of P(St-co-AA) beads was much higher than that of PS beads, and it increased with the increasing of the volume of comonomer AA. The existence of COO^- groups in P(St-co-AA) beads has been proved by FTIR spectra (**supplementary material**). Moreover, it's also found that the size of n-PBs reduced with the increasing of the volume of comonomer AA. An explanation for this phenomenon is given as follows. Since the adopted polymerization system was emulsifier-free, the growth of n-PBs could be seen as a process, in which small beads merged to larger beads. Meanwhile, since more and more polymer chains with charged groups had been contained in every bead, the surface charge density of n-PBs also increased along with the increasing in particle size. Therefore, n-PBs would not merge anymore after their surface charge density was high enough to supply sufficient repulsive force between particles. For the P(St-co-AA) beads, since the additional COO^- groups had been introduced into their polymer chains, the number of the polymer chains that they needed to contain for stabilization was much smaller than that of PS beads. Consequently, the

size of obtained P(St-co-AA) beads was smaller than that of PS beads, and could be further decreased by increasing the usage amount of AA. It should be point out the addition of AA didn't affect on the dispersibility, as DLS measurements (**supplementary information**) have indicated all the obtained n-PBs were monodisperse and aggregates-free.

Table 1. Zeta potentials and size of the as-synthesized n-PBs.

Sample name	AA/ vol. % ¹	Zeta potential ² / mV	Size ³ / nm
PS	0	-1.1	599±9
P(St-co-2.5%AA)	2.5	-23.7	392±6
P(St-co-5.0%AA)	5.0	-45.6	350±6

¹ AA to St before polymerization; ² in water; ³ by DLS measurements

All the obtained n-PBs with different surface charge density were used for SiO₂ coating under the same condition. **Figure 1b~d** show SEM images of PS, P(St-co-2.5%AA) and P(St-co-5.0%AA) beads after SiO₂ coating respectively. As seen, when PS beads were used, immobilized SiO₂ and freestanding SiO₂ particles coexisted in the as-obtained production (**Figure 1b**). Even worse, the yield of the latter was much higher than the former, indicating the PS beads could hardly be coated by SiO₂. When P(St-co-2.5%AA) beads were used, freestanding SiO₂ particles still existed in the production, but the number of immobilized SiO₂ particles significantly increased (**Figure 1c**). Different with the above two cases, the surface of P(St-co-5.0%AA) beads was fully occupied by the immobilized SiO₂ particles after reaction, while freestanding SiO₂ particles were absent in the production (**Figure 1d**). In addition, the low-magnification SEM image in **Figure 1d** indicates the high dispersibility of the SiO₂-coated P(St-co-5.0%AA) beads.

The core-shell structure of SiO₂-coated P(St-co-5.0%AA) beads was further confirmed by TEM observation EDS mapping. As seen in **Figure 2**, carbon element only distributes inside of the obtained composite particles while the content of silicon and oxygen elements is maximal at the edge. Meanwhile, the TEM image in **Figure 2** indicates the SiO₂ shell formed on the surface of P(St-co-5.0%AA) beads was uniform and 15nm in thickness.

Figure 1. (a) zeta potential (in water) distribution histograms of the as-synthesized n-PBs; SEM images of PS (b), P(St-co-2.5%AA) (c) and P(St-co-5.0%AA) (d) beads after SiO₂ coating; inserts in (b)~(c) are high-magnification SEM images.

Figure 2. (a) TEM image of SiO₂-coated P(St-co-5.0%AA) beads; (b)~(d) are EDS mappings showing the distribution of C, Si and O, respectively.

3.2. The mechanism of SiO₂ coating on n-PBs

In order to have a better understanding of the SiO₂ coating on n-PBs, intermediate productions at different coating times were collected sequentially for SEM observations and zeta potential measurements. SEM images of the un-coated P(St-co-5.0%AA) beads and intermediate productions collected at 10min, 90min, 3h, 6h, and 9h are shown in **Figure 3**. As seen, SiO₂ particles appeared on the surface of n-PBs at the beginning of reaction, and the number of them increased with the time elapsing. After reacted for 3h, the surface of n-PBs was completely occupied by SiO₂ particles (**Figure 3d**). From then on, immobilized SiO₂ particles merged with each other, and the size of the SiO₂-coated beads started to increase. It's noteworthy that there were no freestanding SiO₂ particles generated in the whole course, implying the SiO₂ particles directly formed on the surface of n-PBs.

Moreover, as seen in **Figure 4**, there was no “surface charge reversal” occurred in the process of **SiO₂ coating on n-PBs**. In this process, the zeta potential of particles (i. e., n-PB/SiO₂ composites) gradually reduced from -17.2 mV along with the deposition of SiO₂, and then kept steady at around -36.7mV once SiO₂ shells had formed (6h). It’s noteworthy, the zeta potential of n-PBs in pure ethanol (-17.2 mV) was much lower than that in water (-45.6 mV). The zeta potential of n-PBs further reduced to -11.9mV after ammonia solution was added in. This phenomenon can be attributed to the adsorption of NH₄⁺ ions on the surface of n-PBs.

Figure 3. SEM images of un-coated P(St-co-5.0%AA) beads (a) and intermediate productions collected at 10min (b), 90min (c), 3h (d), 6h (e), 9h (f); all scale bars represent 100nm.

Figure 4. The change of zeta potential (in ethanol) before and in the course of SiO₂ coating;

P(St-co-5.0%AA) beads were used.

The adsorption of NH_4^+ ions on the surface of n-PBs was further proved by the supported experiment (I). **Table 2** compares the $c(\text{NH}_4^+)$ in the original solution and that in the bulk solution of n-PBs suspension (see the detail in section 2.3). As seen, the $c(\text{NH}_4^+)$ in bulk solution decreased after n-PBs were dispersed in. Typically, in the suspension of P(St-co-5.0%AA) beads, the $c(\text{NH}_4^+)$ in bulk solution sharply decreased from the original 5.01 to 0.16mM, indicating there had been a large number of NH_4^+ ions adsorbed on the their surface. **Table 2** also indicates the adsorption of NH_4^+ ions was closely related with the surface charge density of n-PBs, as neither P(St-co-2.5% AA) nor PS could attract such a large number of NH_4^+ ions to adsorb on their surface. Moreover, it seems the adsorption of NH_4^+ ions subsequently caused the transferring of OH^- ions to the surface of n-PBs, as the pH also decreased after n-PBs was dispersed in. In fact, we believe there was an electric double layer containing NH_4^+ and OH^- ions formed on the surface of n-PBs.

Table 2. pH and c(NH₄⁺) in the original solution and that in the bulk solution of n-PBs suspension (see the detail in the supported experiment (I))

n-PBs	pH	c(NH ₄ ⁺) / mM	Δc(NH ₄ ⁺) / Mm
Original solution ¹	11.7	5.01	--
P(St-co-5.0% AA)	10.2	0.16	-4.85
P(St-co-2.5% AA)	11.3	2.00	-3.01
PS	11.6	3.99	-1.02

¹ i. e., the mixture of 30ml ethanol, 0.5ml water and 1mL 25.0 wt. % ammonia solution

Based on the above observations, we propose a mechanism for the SiO₂ coating on the surface of n-PBs (**Scheme 1**). In this mechanism, the electrostatic interaction between SiO₂ and carriers is not seen as the driving force for SiO₂ coating anymore, which is different with that for SiO₂ coating on the surface of p-PBs. Meanwhile, the difference between the SiO₂ generation rate on the surface of PBs and that in the bulk solution is emphasized. As we know, the generation of SiO₂ in the stöber process (using TEOS) can be described as:

(3-1) and (3-2) are the hydrolysis of TEOS and the condensation of silanols respectively ^[17]. Both of these two reactions are nucleophilic, in which silicon atom is attacked by OH⁻. Therefore, the generation of SiO₂ can only occur in the location where a considerable number of OH⁻ ions exist. According to our observations, when the n-PBs with high surface charge density were used for SiO₂ coating, almost all the NH₄⁺ ions in the reaction solution adsorbed on the surface of n-PBs. The accumulation of NH₄⁺ ions subsequently caused the accumulation of OH⁻ on/near the same surface

1 to form an electric double layer. Consequently, after TEOS was added in, SiO₂ mostly generated in
2 the electric double layer rather than in the bulk solution, as such a low c(OH⁻) in the latter was
3 insufficient to catalyze the hydrolysis of TEOS and related condensations. Meanwhile, because the
4 heterogeneous nucleation of SiO₂ was much easier to occur than the homogeneous one, the
5 generated SiO₂ directly nucleated on the surface of n-PBs. The screening of adsorbed NH₄⁺ ions to
6 the negative surface of n-PBs was also positive for the SiO₂ deposition. Moreover, along with the
7 consumption of the TEOS that on/near the surface of n-PBs, a mass diffusion of TEOS from bulk
8 solution occurred subsequently. Since this mass diffusion ensured the continuity of SiO₂ deposition,
9 a SiO₂ shell would form on the surface of n-PBs in a certain time. Here, we also analysis the reason
10 for the failure SiO₂ coating on the surface of n-PBs that with low surface charge density (i. e., PS
11 and P(St-co-2.5%AA) beads). In that case, there were still a considerable number of NH₄⁺ and OH⁻
12 ions existed in the bulk solution for catalyzing the generation of SiO₂. Therefore, SiO₂
13 simultaneously nucleated both on the surface of n-PBs and in the bulk solution during the reaction.
14 Obviously, the SiO₂ nucleuses that formed in bulk solution couldn't deposit on the surface of n-PBs,
15 and they would possibly grow to freestanding SiO₂ particles.

16 In fact, the importance of the adsorption of NH₄⁺ and OH⁻ ions on the surface of n-PBs has
17 also been demonstrated by the supported experiment (II). In that experiment, the adsorption of NH₄⁺
18 and OH⁻ ions on the surface of n-PBs was suppressed by the pre-existed K⁺ and Cl⁻ ions. As a result,
19 although P(St-co-5.0%AA) beads were used for SiO₂ coating, freestanding SiO₂ particles could still
20 be found in the production "S-KCl" (**supplementary information**).

Scheme 1 SiO₂ coating process on n-PBs with high (up) and low (down) surface charge density.

3.3. Monodisperse HSPs from SiO₂-coated n-PBs

After their core-shell structure was confirmed by TEM observation and EDS mapping, the SiO₂-coated P(St-co-5.0%AA) beads were further used for the fabrication of HSPs. Figure 5a shows FTIR spectra of P(St-co-5.0%AA) beads, SiO₂-coated P(St-co-5.0%AA) beads before and after calcination. All the characteristic peaks of P(St-co-AA) can be seen in the former two spectra, including that for aromatic C=C (1700-1500 cm⁻¹), aromatic C-H (860-680 cm⁻¹), alkyl C-H (2921 cm⁻¹) and carboxylic C=O (1731 cm⁻¹). After SiO₂ coating, the peaks appeared at 465cm⁻¹, 799cm⁻¹, 942cm⁻¹ and 1089cm⁻¹ could be assigned to the O-Si-O bending vibrations, Si-O-Si symmetric stretching vibrations, silanol groups and Si-O-Si asymmetric stretching vibrations of SiO₂, respectively. After calcination, all the characteristic peaks of P(St-co-AA) disappeared, indicating the polymeric cores of SiO₂-coated P(St-co-5.0%AA) beads had been completely burned away. Furthermore, the SEM image in Figure 5b and the STEM image in Figure 5c intuitively indicate the hollow structure and high monodispersibility of the HSPs that obtained from SiO₂-coated P(St-co-5.0%AA) beads. The absence of collapsed hollow particles in the obtained HSPs indicated

1 SiO₂ shells formed on P(St-co-5.0%AA) beads possessed sufficient mechanical strength to sustain
2 their spherical shape during calcination. Moreover, the obtained HSPs showed a low poly-dispersity
3 index of 0.085 in DLS measurements (**Figure 5d**), which indicated their high dispersibility. In
4 addition, because of the high monodispersibility and ultra-thin shells, the obtained HSPs showed a
5 visible Mie scattering phenomenon on a black background with illumination (insert of **Figure 5c**).

6 In fact, it was hard to produce aggregates-free HSPs using p-PBs as templates, if the system for
7 SiO₂ coating was surfactant-free ^[16, 18]. When p-PBs were used as the cores for SiO₂ coating, a
8 surface charge reversal occurred while SiO₂ was depositing, as the originally positive surface (of
9 p-PBs) changed to a negative surface (of p-PB@SiO₂). Apparently, there was an intermediate stage
10 in this event, at which the surface of p-PBs were partly coated by SiO₂ and the zeta potential of
11 these PB/SiO₂ composite particles was close to 0. Accordingly, such low electrostatic repulsive
12 force between particles could not prevent the generation of aggregates. Consequently, aggregated
13 SiO₂-coated PBs and hollow particles were observed in productions. On the contrary, since the
14 surface charge reversal didn't occur in the process of SiO₂ coating on n-PBs, as discussed in section
15 3.2, there was always considerable electrostatic repulsive force between particles to sustaining their
16 high dispersibility, even when n-PBs were partly coated. Consequently, the dispersibility of the
17 obtained SiO₂-coated PBs and HSPs was improved.

Figure 5. (a) FTIR spectra of P(St-co-5.0%AA) beads, SiO₂-coated P(St-co-5.0%AA) beads and obtained HSPs; SEM (b) and STEM (c) images of HSPs; the insert of (c) is the digital photograph of the HSPs taken with a dark background. (d) size distribution histograms of P(St-co-5.0%AA) beads, SiO₂-coated P(St-co-5.0%AA) beads and HSPs in water.

3.4. The influence of C_{NH3} and C_{H2O}

In the process of SiO₂ coating on n-PBs, the SiO₂ yield was closely related with the concentration of NH₃ (C_{NH3}) and the concentration of water (C_{H2O}) in reaction system. **Table 3** lists 7 different experimental conditions we used for SiO₂-coating, in which the C_{NH3} and C_{H2O} was varied independently. The n-PBs used in all these experiments were P(St-co-5.0%AA) beads. SiO₂ yields (Y_{SiO2}%) were calculated by using the following equations,

$$Y_{SiO_2}(\%) = \frac{W_{SiO_2}}{W_{thero-SiO_2}} * 100\% \quad (4-1)$$

$$W_{theor-SiO_2} = \frac{V_{TEOS} * \rho_{TEOS} * M_{SiO_2} / M_{TEOS}}{m_{n-PBs} + V_{TEOS} * \rho_{TEOS} * M_{SiO_2} / M_{TEOS}} \quad (4-2)$$

where W_{SiO_2} is the weight percent of SiO_2 in SiO_2 -coated n-PBs calculated from corresponding TG curve (**Figure 6a, 7a**); $W_{theor-SiO_2}$ is the theoretical value of W_{SiO_2} with assuming that the conversion rate of TEOS is 100%; m_{n-PBs} (0.414g) is the weight of n-PBs, V_{TEOS} (1ml) is the volume of TEOS, ρ_{TEOS} is 0.933g/ml, M_{SiO_2} is 60.08g/mol, and M_{TEOS} is 208.33g/mol. The calculated SiO_2 yields are also listed in **Table 3**. By analyzing the plot of Y_{SiO_2} vs. C_{NH_3} (insert of **Figure 6a**), it's clear that the SiO_2 yield increased linearly along with the increasing of C_{NH_3} . For instance, the SiO_2 yield was only 60.6% when the C_{NH_3} was 0.29M, while it increased to 87.5% when the C_{NH_3} reached to 0.49M. Meanwhile, the positive correlation between SiO_2 shell thickness of the obtained HSPs and the C_{NH_3} in SiO_2 coating process was significant. **Figure 6b~d** show STEM images of HSPs with the shell thickness around 15, 20, and 25nm respectively. On the other hand, the SiO_2 yield could also be improved by increasing the C_{H_2O} in reaction system, as shown in **Table 3** (B series). However, it seemed that an excessively high C_{H_2O} would exert a negative influence on the SiO_2 coating. Typically, when C_{H_2O} was 3.06M in reaction system, despite that the SiO_2 yield reached to 90.4%, SiO_2 shells didn't formed on the surface of n-PBs, as the immobilized SiO_2 particles only connected loosely with each other (**Figure 7b**). Correspondingly, HSPs obtained by calcining this kind of SiO_2 -coated n-PBs were so fragile that even couldn't endure the ultrasonic treatment in SEM sampling. Although it needs, of course, further experiments (out of the scope of this paper) to address the incomplete coating of SiO_2 on n-PBs under high C_{H_2O} , we give a probable reason here as follows. Since the surface of n-PBs was hydrophobic, the high C_{H_2O} in reaction system increased the difficulty of the transferring of SiO_2 precursors from bulk solution to the surface of cores. Therefore, SiO_2 precursors preferred to participate in the growth of the immobilized SiO_2 particles,

which oppositely had a hydrophilic surface, instead of forming new nucleation on the surface of polymer beads. Consequently, the SiO₂ deposition under high C_{H₂O} couldn't yield a complete SiO₂ shell on the surface of n-PBs, though the SiO₂ yield was high under this condition.

Table 3. SiO₂ coating on P(St-co-5.0%AA) beads under different C_{NH₃} and C_{H₂O} ^{1, 2}

Sample	V _{water} / ml	V _{25.0 wt. % ammonia} / ml	C _{H₂O} /M	C _{NH₃} /M	SiO ₂ Yield/%
A1	0.50	1.0	1.4	0.29	60.6
A2	0.27	1.3	1.4	0.38	72.6
A3	0	1.7	1.4	0.49	87.5
B1	0	1.0	0.8	0.29	2.43
B2	1.0	1.0	1.9	0.29	78.7
B3	1.5	1.0	2.5	0.29	87.2
B4	2.0	1.0	3.0	0.29	90.4

¹ The concentration of TEOS in all the reaction was 95mM; ² P(St-co-5.0%AA) beads were used for all the samples.

Figure 6. TG curves of SiO₂-coated n-PBs synthesized under different C_{NH_3} (a); the insert plots Y_{SiO_2} vs. C_{NH_3} ; STEM images of HSPs obtained from the sample A1 (a), A2 (b) and A3 (c).

Figure 7. TG curves of SiO₂-coated n-PBs synthesized under different $C_{\text{H}_2\text{O}}$ (a); the insert plots Y_{SiO_2} vs. $C_{\text{H}_2\text{O}}$; SEM and STEM images of sample B4 synthesized with $C_{\text{H}_2\text{O}}=3.0$ (b); STEM image of HSPs obtained by calcining sample B4 (c).

4. Conclusion

In summary, our studies demonstrated that the SiO₂ coating on the surface of n-PBs can realize in a typical and surfactant-free stöber process, once certain prerequisites have been met. The prerequisites are (1) the high surface charge density of n-PBs and (2) low water concentration in reaction system. Accordingly, a mechanism has been proposed for explaining the coating of SiO₂ on the like-charged polymer beads. In that mechanism, the adsorption of NH₄⁺ ions on the surface of n-PBs played a critical role for SiO₂ coating, as it not only screened the surface charge of n-PBs to reduce the energetic barrier for the deposition of SiO₂, but also caused the accumulation of OH⁻ ions to restrict the location where SiO₂ nucleated to the surface of n-PBs. Furthermore, HSPs with monodisperse size and high dispersibility have been obtained by calcining the obtained SiO₂-coated n-PBs in air at 600°C. There were two advantages of using n-PBs as the templates for the fabrication of HSPs, as (1) lower cost with respect to the use of p-PBs and (2) improving the dispersibility of the obtained HSPs.

This work suggests PBs that suitable for SiO₂ coating can be extended to a wider range, without considering if their surface is positive or negative. We also believe using negatively charged polymer beads in the typical stöber process for SiO₂ coating is a practical and low-cost synthetic strategy for high-quality SiO₂-coated polymer beads and HSPs.

***Corresponding Author**

Tel.: +81 572 24 8110; Fax: +81 572 24 8109.

E-mail address: fuji@nitech.ac.jp

Acknowledgment

This study was supported by the Advanced Low Carbon Technology Research and Development Program (ALCA) of the Japan Science and Technology Agency (JST).

Reference

- [1] Andrés Guerrero-Martínez, Jorge Pérez-Juste, Luis M. Liz-Marzán, Recent Progress on Silica Coating of Nanoparticles and Related Nanomaterials, *Adv. Mat.* 22 (2010) 1182-1195; doi: 10.1002/adma.200901263.
- [2] Hua Zou, Shishan Wu, Jian Shen, Polymer/Silica Nanocomposites: Preparation, Characterization, Properties, and Applications, *Chem. Rev.* 108 (2008) 3893-3957; doi: 10.1021/cr068035q.
- [3] Chika Takai; Hideo Watanabe; Takuya Asai; Masayoshi Fuji. Determine Apparent Shell Density for Evaluation of Hollow Silica Nanoparticle, *Colloids Surf., A* 404 (2012) 101-105; doi: 10.1016/j.colsurfa.2012.04.019.
- [4] Masayoshi Fuji; Takahiro Shirai; Hideo Watanabe; Takashi Takei. Shape-controlled Hollow Silica Nanoparticles Synthesized by An Inorganic Particle Template Method, *Adv. Powder Technol.* 2012, 23, 562-565.
- [5] Markus Retsch; Marcus Schmelzeisen; Hans-Jürgen Butt; Edwin L. Thomas, Visible Mie

- Scattering in Nonabsorbing Hollow Sphere Powders, *Nano Lett.* 11 (2011) 1389-1394; doi: 10.1021/nl2002445.
- [6] Lee A. Fielding; Oleksandr O. Mykhaylyk; Andreas SchmidL, Diego Pontoni, Steven P. Armes, Patrick W. Fowler., Visible Mie Scattering from Hollow Silica Particles with Particulate Shells, *Chem. Mater.* 26 (2014) 1270-1277; doi: 10.1021/cm4039347.
- [7] Jaemoon Yang, Jaewon Lee, Jinyoung Kang, Kwangyeol Lee, Jin-Suck Suh, Ho-Geun Yoon, Yong-Min Huh, Seungjoo Haam. Hollow Silica Nanocontainers as Drug Delivery Vehicles, *Langmuir* 24 (2008) 3417-3421; doi: 10.1021/la701688t.
- [8] Linn Ingunn C. Sandberg, Tao Gao, Bjørn Petter Jelle, Arild Gustavsen, Synthesis of Hollow Silica Nanospheres by Sacrificial PS Templates for Thermal Insulation Applications. *Adv. in Mater. Sci. Eng.* 2013, Article ID 483651; doi: <http://dx.doi.org/10.1155/2013/483651>.
- [9] Werner Stöber, Arthur Fink. Controlled Growth of Monodisperse Silica Spheres in the Micron Size Range, *J. Colloid Interface Sci.* 26 (1968) 62-69; doi: 10.1016/0021-9797(68)90272-5.
- [10] Asep Bayu Dani Nandiyanto, Yui Akane, Takashi Ogi, Kikuo Okuyama, Mesopore-free hollow silica particles with controllable diameter and shell thickness via additive-free synthesis, *Langmuir* 28 (2012) 8616-8624; doi: 10.1021/la301457v.
- [11] Yu Lu, Joe McLellan, Younan Xia, Synthesis and crystallization of Hybrid Spherical Colloids composed of polystyrene cores and silica shells, *Langmuir* 20 (2004) 3464-3470; doi: 10.1021/la036245h.
- [12] Christina Graf; Dirk L. J. Vossen; Arnout Imhof; Alfons van Blaaderen. A General Method to Coat Colloidal Particles with Silica. *Langmuir* 19 (2003) 6693-6700; doi: 10.1021/la0347859.

- [13]Tian-Song Deng, Frank Marlow, Synthesis of monodisperse polystyrene@vinyl-SiO₂ core-shell particles and hollow SiO₂ spheres, Chem. Mater. 24 (2012) 536-542; doi: 10.1021/cm203099m.
- [14]Brian T. Holland , Christopher F. Blanford , Thang Do, Andreas Stein, Synthesis of Highly Ordered, Three-Dimensional, Macroporous Structures of Amorphous or Crystalline Inorganic Oxides, Phosphates, and Hybrid Composites, Chem. Mater., 11 (1999) 795–805; doi: 10.1021/cm980666g
- [15]Naser Sharifi-Sanjani, Morteza Soltan-Dehghan, Nader Naderi, Ali Ranji, Emulsifier-Free Emulsion Polymerization of Styrene, J. Appl. Polymer. Sci. 94 (2004) 1898-1904; doi: 10.1002/app.20893.
- [16]Lijuan Zhang , Maria D’Acunzi , Michael Kappl , Günter K. Auernhammer, Doris Vollmer, Hollow Silica Spheres: Synthesis and Mechanical Properties, Langmuir, 25 (2009) 2711-2717; doi: 10.1021/la803546r
- [17]C.J. Brinker, hydrolysis and condensation of silicates: effects on structure, J. Non-crystalline solids 100 (1988) 31-50; doi: 10.1016/0022-3093(88)90005-1.
- [18]Hua Zou , Shishan Wu , Qianping Ran, Jian Shen, A Simple and Low-Cost Method for the Preparation of Monodisperse Hollow Silica Spheres, J. Phys. Chem. C 112 (2008) 11623-11629; doi: 10.1021/jp800557k.

Graphical Abstract

Accumulation of NH_4^+ and OH^-

Stöber process

TEOS

Low $C_{\text{H}_2\text{O}}$

(No surface charge reversal)

Calcination

HSPs with high dispersibility

SiO_2 -coated polymer beads with high dispersibility