

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

4

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

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

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

9

10 **Abstract:** SiO₂ shells have been evenly constructed on the surface of negatively charged polymer
11 beads (n-PBs) in a stöber-like process. The reaction system for SiO₂ coating was surfactant-free,
12 which only contained TEOS as the precursor, ethanol as the solvent, NH₃ as the catalyst, and water.
13 Besides, monodisperse hollow SiO₂ particles (HSPs) with the size of around 400nm and the shell
14 thickness of 15~25nm have been fabricated after burning polymer cores away from the SiO₂-coated
15 n-PBs. The as-fabricated HSPs are aggregation-free and fairly robust. Moreover, the following two
16 prerequisites for successful coating of SiO₂ on n-PBs have been revealed: (1) the surface charge
17 density of n-PBs is high; (2) the concentration of water in reaction system is on a low level. We
18 have proposed a reasonable mechanism for the un-expected coating of SiO₂ on n-PBs. NH₃ (NH₄⁺)
19 is believed to play multiple rules in the process of coating, as it not only catalyzed the generation of
20 SiO₂, reduced the energetic barrier for SiO₂ coating n-PBs, but also had the hydrolysis of TEOS and
21 related condensation process occurring on the surface of n-PBs.

22 **Keywords:** SiO₂ coating; Hollow SiO₂ particles; Negatively charged; Polymer beads

1

2 **1. Introduction**

3 In the past several years, because of their potential applications in optical ^[1, 2], loading-
4 releasing ability ^[3], heat insulation ^[4], low k-dielectrics ^[5], etc., hollow SiO₂ particles (HSPs)
5 composed of solid SiO₂ shells and hollow interiors have attracted considerable research attention.
6 Templating method is the general synthetic strategy for HSPs, although recently template-free
7 approaches have also been developed ^[6]. In a typical process of templating method, SiO₂ was firstly
8 coated on templates to form core-shell particles, and then templates were removed away from the
9 core-shell particles to obtain HSPs ^[7]. More specifically, Stöber process ^[8] is commonly adopted for
10 SiO₂ coating in the templating method, where the generation rate of SiO₂ can be well controlled. On
11 the other hand, there are a variety of chemicals can be used as the template, such as CNTs ^[9],
12 polymer ^[10, 11], micelles ^[12], gas bubbles ^[13], etc. In particular, it's possible to fabricate HSPs with
13 narrow size distribution by using monodisperse polymer beads (PBs) as the template. Since
14 monodisperse HSPs can be further applied in the areas of photonic crystals ^[14] and plasmonics
15 derives ^[15], the using of monodisperse PBs in the fabrication of HSPs has been paid close attention.
16 To our knowledge, monodisperse SiO₂-coated PBs, as well as monodisperse HSPs, with tunable
17 size, shell thickness, and porosity have been successfully fabricated ^[16, 17].

18 Normally, PBs used for the fabrication of HSPs have positive surface, since SiO₂ generated in
19 the Stöber process carries negative charges, oppositely ^[18, 19]. In this case, SiO₂ coating could be
20 attributed to the electrostatic attraction between SiO₂ and positively charged polymer beads (p-PBs).
21 However, with respect to negatively charged polymer beads (n-PBs), p-PBs are much harder to
22 obtain, as expensive cationic initiators (e. g., AIBA) and/or surface modification steps are necessary

1 [20]. Even worse, the use of p-PBs will probably result in aggregated HSPs [21]. The reason is, at the
2 initial stage of SiO₂ coating, the apparent surface charge of p-PBs is reduced by immobilized SiO₂
3 particles, so that electrostatic repulsive force between p-PBs is too small to prevent the generation
4 of aggregates. Although the use of surfactants in the process of SiO₂ coating can improve the
5 dispersibility of SiO₂-coated p-PBs and related HSPs, it also increases the complexity of reaction
6 system and post treatment [22].

7 Obviously, replacing p-PBs by n-PBs in the fabrication of monodisperse HSPs is expected to
8 eliminate the above two drawbacks. However, few attempts have been done on the fabrication of
9 HSPs with using n-PBs as the template. It was even believed that n-PBs carrying negative charges
10 are not advantageous for SiO₂ particles (also negatively charged) to coating on [23]. It may be true
11 that electrostatic repulsive force is unfavorable of SiO₂ coating, nonetheless, much more factors,
12 such as the surface charge density of n-PBs, the reaction parameters, etc., need to be taken into
13 consideration before making an appropriate conclusion on whether SiO₂ coating can achieve on the
14 surface of n-PBs or not. In fact, there have been some observations indirectly suggested the
15 possibility of SiO₂ coating on n-PBs. Graf et. al. [13] reported a versatile approach to construct SiO₂
16 shells on various kinds of particles including n-PBs. Although in that work, SiO₂-coated n-PBs
17 could only be obtained by the assistance of surfactant, the negative property of the surface of n-PBs
18 had not been changed, since the surfactant (PVP) used was nonionic. Deng et. al. [14] most recently
19 obtained n-PB@Vinyl-SiO₂ core-Shell particles with using a special precursor of SiO₂ (VTMS).
20 They have also proved the high yield of SiO₂ coating on n-PBs. Unfortunately, both of the above
21 two works have not discussed on the process of SiO₂ coating on n-PBs, as well as its corresponding
22 mechanism in detail.

1 In this work, monodisperse HSPs have been successfully obtained with using n-PBs as the
2 template. The fabrication process is simple and surfactant-free, although there are some additional
3 requirements need to meet, either for the employed n-PBs or for the reaction parameters in SiO₂
4 coating. In this work, n-PBs were obtained by the emulsifier-free polymerization with using anionic
5 initiator KPS, the cost of which is much lower than that for p-PBs. Besides, the merit brought by the
6 use of n-PBs to the dispersibility of obtained HSPs has also been proved by experimental results. In
7 addition, we have proposed a reasonable mechanism for the process of SiO₂ coating on n-PBs,
8 which is different with that for SiO₂ coating on p-PBs.

9

10 **2. Experimental**

11

12 **2.1. Materials.**

13 Styrene (St) was from Kanto Chemical Co., Inc. Japan. Before using, St was first washed with
14 5.0 wt. % NaOH (Wako Pure Chemical Industries, Ltd. Japan) solution for 4 times and DI water for
15 4 times respectively, followed by distilling under reduced pressure. All the following chemicals
16 were used as received without further purification: Acrylic acid (AA, 98.5%), K₂S₂O₈ (KPS, 98.0%)
17 from Kanto Chemical Co., Inc. Japan; Tetraethyl orthosilicate (TEOS, 95.0%), Ethanol (99.5%),
18 Ammonia solution (25.0 %) from Wako Pure Chemical Industries, Ltd. Japan. DI water was
19 produced by RFD250NB distilled water system (Toyo Roshi Kaisha, Ltd. Japan).

20

21 **2.2. Synthesis of n-PBs**

22 Three kinds of negatively charged polymer beads (n-PBs), PS, P(St-co-2.5%AA) and

1 P(St-co-5.0%AA) beads, have been synthesized by a reported emulsifier-free polymerization ^[15]
2 with using an anionic initiator KPS (see **Table 1**). For the as-synthesized P(St-co-AA) beads, the
3 percentage in name denotes the volume ratio of AA to St before polymerization. For the
4 emulsifier-free polymerization, briefly, 170mL DI water, 15mL St and a certain volume of AA were
5 first poured into a 4-neck flask which equipped with a condenser, a thermometer, a gas inlet pipe
6 and a PTFE stirrer. Then N₂ was bubbled into the monomer-water mixture for 20min. Afterward,
7 the system was closed and placed in an oil bath to heat to 70°C. During the heating, stirring was
8 started and controlled at 340rpm. Polymerization was started by pouring 10mL 1.5 wt. % KPS
9 aqueous solution (pre-heated to 70°C) in. The emulsifier-free polymerization lasted for 24h at 70°C
10 with continuous stirring. After the reaction, n-PBs were collected by centrifugation at 6000rpm and
11 washed with DI water for several times. Finally, the well cleaned n-PBs were dried in vacuum at 40
12 °C for 24h.

14 **2.3. Synthesis of SiO₂-coated n-PBs**

15 SiO₂-coated n-PBs were synthesized in a reported stöber process ^[9] with some modifications.
16 In a typical synthesis, 0.414g n-PBs were added into a mixture of 30ml ethanol, 0.5ml water and
17 1mL 25.0 wt. % ammonia solution, followed by a 30min ultrasonic treatment. Then the above
18 suspension was stirred by a magnetic stirrer (600rpm). Meanwhile, 18.5mL TEOS solution (5.4
19 vol. % in ethanol) was poured in. The reaction was allowed to proceed for 12h at room temperature
20 with the same magnetic stirring. The resulting particles were collected by centrifugation at 6000rpm,
21 and followed by washing with ethanol and DI water for several times. Finally, the particles were
22 dried in vacuum at 40 °C for 24h.

1 A supporting experiment was carried out only for the purpose of illustrating the mechanism of
2 SiO_2 coating on n-PBs. In this experiment, n-PBs (P(St-co-5.0%AA)) were preparatory immersed in
3 KCl solution (5.0 wt.%) to absorb a number of K^+ ions on their surface, and then used as the
4 templates for SiO_2 coating. The reaction parameters for SiO_2 coating in this experiment were
5 exactly same with the typical experiment described before. The production was named as “S-KCl”.

6

7 **2.4. Fabrication of HSPs from SiO_2 -coated n-PBs**

8 HSPs were obtained by burning n-PBs away from SiO_2 -coated n-PBs. Briefly, in an electric
9 oven, SiO_2 -coated n-PBs were heated to $600^\circ C$ at a rate of $5^\circ C/min$. The calcination lasted for 5h in
10 air.

11

12 **2.5. Characterizations**

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

20

21 **3. Result and Discussion**

22

1 3.1. SiO₂ coating on n-PBs with different surface charge density

2 Three kinds of n-PBs have been successfully synthesized by emulsifier-free polymerizations.

3 **Table 1** lists the zeta potential (in water) and size of the as-synthesized PS, P(St-co-2.5%AA) and

4 P(St-co-5.0%AA) beads. As seen, all kinds of PBs are negatively charged, while their zeta

5 potentials vary with the change of the addition amount of AA. The negative surface of PS beads is

6 attributed to the SO₃⁻ end-groups, since anionic radical initiator KPS was used for the

7 polymerization. However, because of the low ratio of initiator-to-monomer (0.011 w/w) in the

8 polymerization, the density of SO₃⁻ groups on the surface of PS beads was low, as what the low zeta

9 potential (-1.1mV) revealed. **Table 1** also indicates the low surface charge density can be improved

10 by copolymerizing St with AA, since the negative charges on the surface of P(St-co-AA) beads

11 were not only from the SO₃⁻ end-groups but also from the COO⁻ groups brought by AA. Moreover,

12 **Figure 1a** clearly shows the negative shift of the zeta potential distribution histograms of n-PBs

13 caused by the addition of AA. In addition, the existence of COO⁻ groups in P(St-co-AA) beads has

14 been proved by IR spectra (**supplementary information**). On the other hand, the addition of AA

15 reduced the size of PBs (**Table 1**). In fact, because of the additional electrostatic repulsive force

16 supplied by COO⁻ groups, P(St-co-AA) beads were much easier to reach a steady state, at which

17 they could no longer merge to larger beads, than PS beads in emulsifier-free polymerization.

18 However, the addition of AA has not affected the shape and dispersibility of PBs, as all the three

19 kinds of n-PBs are spherical and aggregation-free (**supplementary information**).

20 All kinds of the obtained n-PBs have been used as the templates for SiO₂-coating to observe

21 the influence of surface charge density. **Figure 1b~d** show the morphology of PS, P(St-co-2.5%AA)

22 and P(St-co-5.0%AA) beads after SiO₂ coating, respectively. As seen, although immobilized SiO₂

1 particles can be found in all samples, SiO_2 achieved complete coating only on the n-PBs that have
 2 high surface charge density: there are numerous free SiO_2 particles can be found in the SiO_2 -coated
 3 PS beads, while only a small proportion of SiO_2 particles have been immobilized on the surface of
 4 templates; free SiO_2 particles can still be found in SiO_2 -coated P(St-co-2.5%AA), but the number of
 5 immobilized SiO_2 particles has significantly increased; there are no free SiO_2 particles in the sample
 6 of SiO_2 -coated P(St-co-5.0%AA) beads, and the surface of cores has been fully occupied by
 7 immobilized SiO_2 . In addition, the high dispersibility of SiO_2 -coated P(St-co-5.0%AA) beads can
 8 also be seen in the SEM image. Furthermore, EDS mapping has proved the core-shell structure of
 9 SiO_2 -coated P(St-co-5.0%AA) beads (**Figure 2**). As seen, carbon element only distributes inside
 10 composite particles while both of the silicon and oxygen content are maximal at the edge.
 11 Meanwhile, the TEM image indicates SiO_2 shells formed on P(St-co-5.0%AA) beads are uniform
 12 and complete, and their thickness is around 15nm.

13

Table 1. As-synthesized n-PBs and their zeta potential and size

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

14

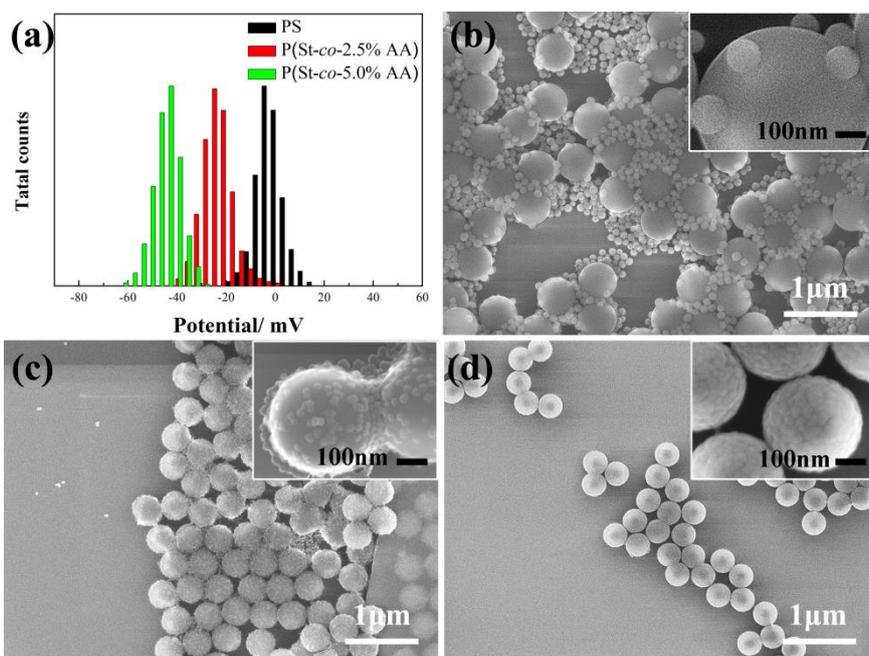


Figure 1. (a) zeta potential (in water) distribution histograms of the as-synthesized n-PBs; SEM images of PS (b), P(St-co-2.5% AA) (c) and P(St-co-5.0% AA) (d) beads after SiO₂ coating; inserts in (b)~(c) are high-magnification SEM images.

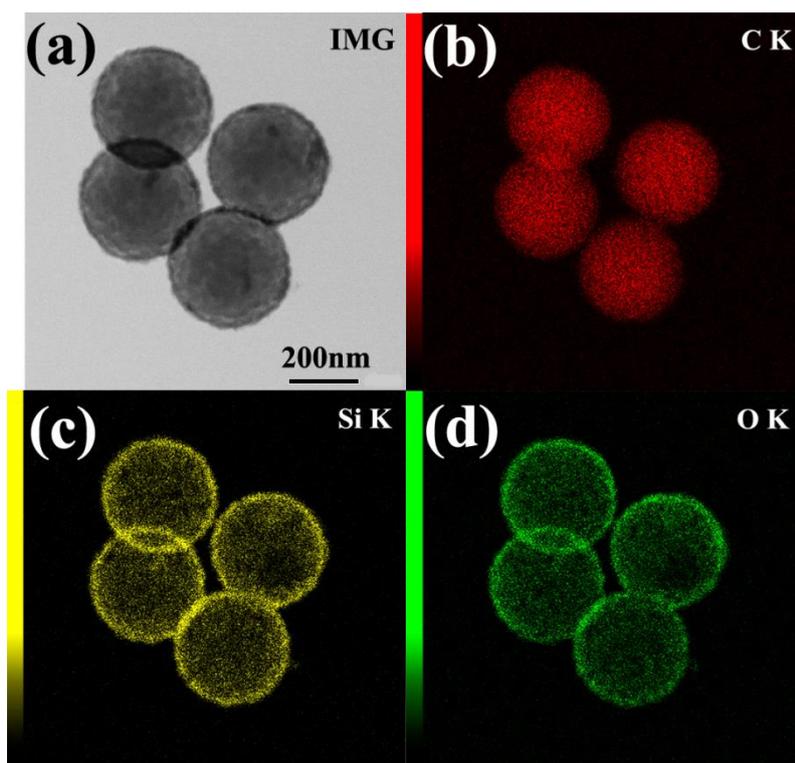


Figure 2. TEM image of SiO₂-coated P(St-co-5.0% AA) beads (a); corresponding EDS mapping of Carbon (b), Silicon (c) and Oxygen (d) respectively.

1
2
3
4

1 3.2. The Mechanism of SiO_2 Coating on n-PBs

2 In order to have a better understanding of the SiO_2 coating on n-PBs, intermediate productions
3 at different coating times were collected sequentially for SEM observations and zeta potential
4 measurements. **Figure 3** shows the SEM images of un-coated P(St-co-5.0%AA) beads and the
5 intermediate productions collected at 10min, 90min, 3h, 6h, and 9h after the SiO_2 coating. It's found
6 SiO_2 particles started to form on the surface of n-PBs at the beginning of reaction (within 10min),
7 and their amount increased with the time elapsing. Moreover, after 3h of the reaction, the surface of
8 n-PBs had been totally occupied by SiO_2 particles (**Figure 3d**). From then on, immobilized SiO_2
9 particles merged with each other, and the size of SiO_2 -coated n-PBs started to increase. It's
10 noteworthy that there was no freestanding SiO_2 particle could be found in the whole process of SiO_2
11 coating on n-PBs, implying the immobilized SiO_2 particles formed on the surface of n-PBs directly.
12 On the other hand, as seen in **Figure 4**, "surface charge reversal" phenomenon, which always
13 occurred in the process of SiO_2 coating on p-PBs, was absent in the process of SiO_2 coating on
14 n-PBs. The above observations suggest the mechanism of SiO_2 coating on n-PBs is different with
15 that on p-PBs, and it's important to find out the driving force of SiO_2 coating on n-PBs. Apparently,
16 electrostatic attraction force can't be use to explain the coating of SiO_2 on n-PBs, since both of
17 them are negatively charged, and even n-PBs with high surface charge density are advantageous for
18 SiO_2 coating.

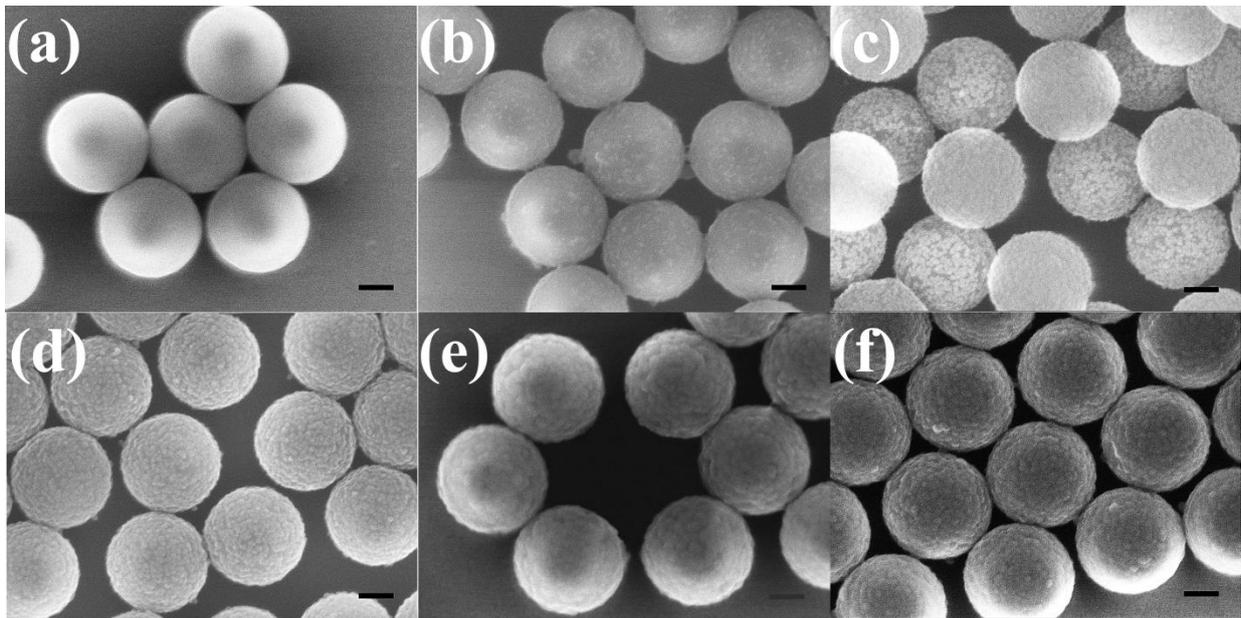


Figure 3. SEM images of P(St-co-5.0%AA) beads without SiO₂ coating (a), and intermediate productions collected at 10min (b), 90min (c), 3h (d), 6h (e) and 9h (f); each scale bar represents 100nm.

1

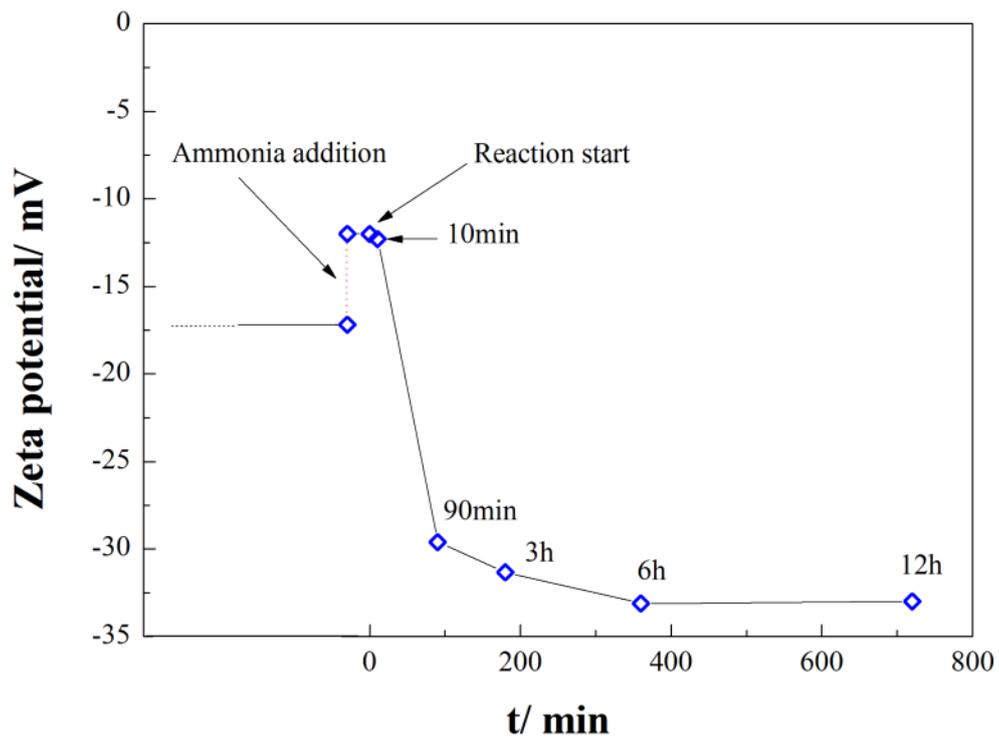


Figure 4. The change of zeta potential (in ethanol) before and in the course of SiO₂-coating; P(St-co-5.0%AA) beads were used.

2

Table 2. pH measured in supporting experiment (I) and the calculated concentration of NH₄⁺.

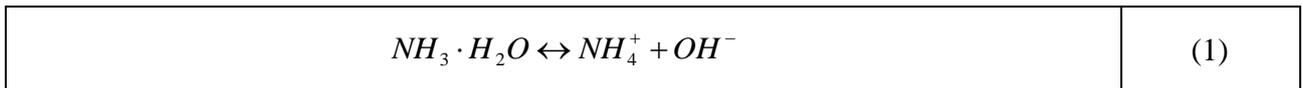
	pH ²	C(NH ₄ ⁺) / mM ³	ΔC(NH ₄ ⁺) / mM
Original solution ¹	11.7	5.01	--

Supernatant of P(St-co-5.0% AA)	10.2	0.16	-4.85
Supernatant of P(St-co-2.5% AA)	11.3	2.00	-3.01
Supernatant of PS	11.6	3.99	-1.02

¹ The solution is a mixture of 30ml ethanol, 0.5ml water and 1mL 25.0 wt. % ammonia solution; ² measured after 30min ultrasonication; ³ $\log_{10}C(\text{NH}_4^+) = \log_{10}C(\text{OH}^-) = \text{pH} - 14$.

1

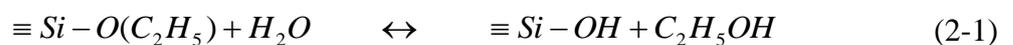
2 In fact, it shouldn't ignore the adsorption of NH_4^+ on the surface of n-PBs. As seen in **Figure**
3 **4**, the surface charge of n-PBs was partly screened after the addition of ammonia solution, implying
4 the adsorption of cationic NH_4^+ on them. The adsorption of NH_4^+ on n-PBs has been further proved
5 by investigating the concentration of NH_4^+ in solution. Because of the existence of the following
6 equilibrium (eq. 1) in the solution containing ammonia, the concentration of NH_4^+ in solution can
7 be obtained by the pH measurement.



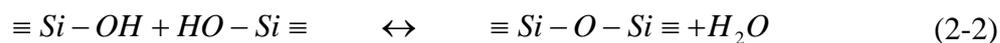
8 As seen in **Table 2**, the concentration of NH_4^+ in the solution sharply decreases from 5.01 to
9 0.16mM after n-PBs (P(St-co-5.0%AA)) were added in, indicating there have been a considerable
10 amount of NH_4^+ adsorbed on the surface of n-PBs. Besides, the adsorption of NH_4^+ shows a close
11 relation with the surface charge of n-PBs, as P(St-co-2.5% AA) and PS can hardly make the NH_4^+
12 accumulate on them efficiently. Moreover, it seems the adsorption of NH_4^+ ions further caused the
13 transferring of OH^- ions to the surface of n-PBs, as the pH also decreased after the dispersion of
14 n-PBs. In fact, we believe an electric double layer containing NH_4^+ and OH^- ions formed on the
15 surface of n-PBs.

16 As we know, the generation of SiO_2 in the *stober* process can be described by the following
17 two reactions ^[16]:

TEOS hydrolysis:



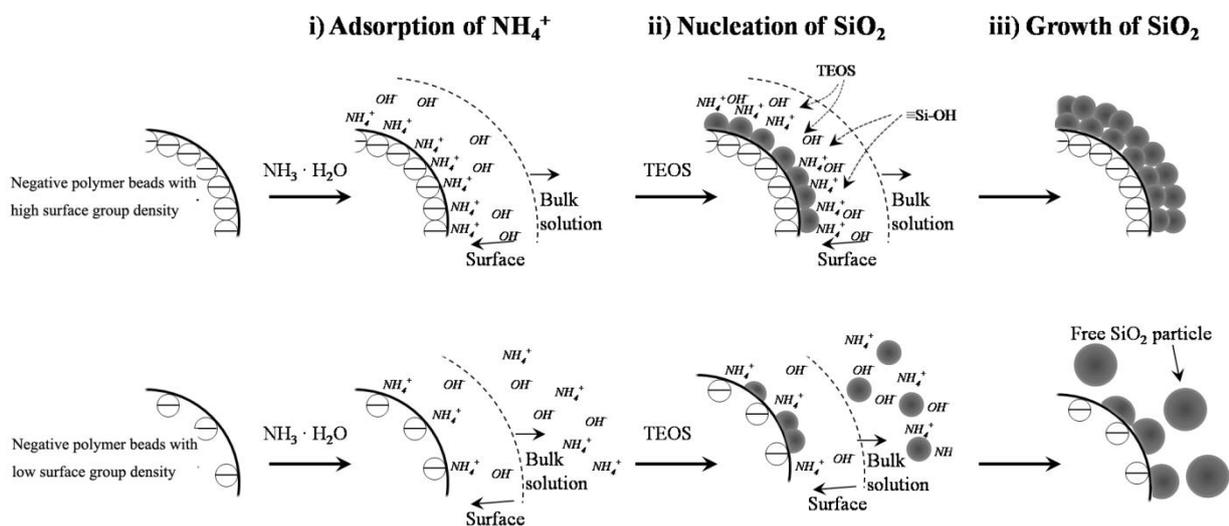
Condensation:



1 Since both of these two reactions are nucleophilic, in which silicon atom is attacked by OH⁻, the
2 generation of SiO₂ can be catalyzed by ammonia solution, from which the OH⁻ ions derived. In
3 other words, the generation of SiO₂ mainly occurs in where OH⁻ and NH₄⁺ accumulated. Therefore,
4 in the process of SiO₂ coating on n-PBs, adsorbed NH₄⁺ ions made the hydrolysis of TEOS and
5 condensation of silanol directly on the surface of polymer beads, and followed by the
6 immobilization of the generated SiO₂. Especially in the case of P(St-co-5.0%AA) beads used, the
7 high surface charge density made the distribution of NH₄⁺ and OH⁻ so concentrated on the surface
8 of n-PBs that SiO₂ can hardly generate in bulk solution but on the surface of n-PBs. Therefore, all
9 the generated SiO₂ particles were immobilized on the surface of n-PBs, and followed by the
10 formation of SiO₂ shells. On contrary, when P(St-co-2.5%AA) beads or PS beads was used for
11 SiO₂-coating, there were still a considerable amount of NH₄⁺ and OH⁻ in bulk solution for
12 catalyzing the generation of SiO₂. Therefore, both immobilized and freestanding SiO₂ can be found
13 in productions. In addition, it's found in the supporting experiment that if the adsorption of NH₄⁺
14 and OH⁻ was suppressed by other ions (i. e. K⁺, Cl⁻), freestanding SiO₂ particles generated even
15 P(St-co-5.0%AA) beads was used (**Supplementary information**).

16 Based on the above discussion, we propose a mechanism for the SiO₂ coating on n-PBs, as given in
17 **Scheme 1**. This mechanism is reasonable, since it not only illustrate the SiO₂ coating can be
18 achieved on the surface of n-PBs, but also explains why the n-PBs with high surface charge density
19 are advantageous for SiO₂ coating. We believe the electrostatic repulsive force still exists between
20 SiO₂ and n-PBs, as it suppressed the transferring of SiO₂ particles generated in bulk solution onto

1 the surface of n-PBs. Nonetheless, when n-PBs with high surface charge density were used, the
 2 influence of electrostatic repulsive force could be neglected according to the mechanism, and it was
 3 even weakened by the adsorption of NH_4^+ to a large extent (i. e., surface charge screening).



Scheme 1 Mechanism of SiO_2 -coating on n-PBs with high (up) or low (down) surface charge density.

4 **3.3. Monodisperse HSPs from SiO_2 -coated n-PBs**

5 Since SiO_2 shell has been successfully constructed on the surface of n-PBs, as proved by above
 6 observations, the obtained SiO_2 -coated n-PBs can be further used for the fabrication of HSPs.
 7 FT-IR spectra in **Figure 5** indicate polymeric templates of SiO_2 -coated n-PBs (P(St-co-5.0%AA)
 8 beads) has been completely removed by calcination (5h at 600°C), as all the characteristic peaks of
 9 P(St-co-AA) beads, including that for aromatic C=C ($1700\text{-}1500\text{ cm}^{-1}$), aromatic C-H ($860\text{-}680$
 10 cm^{-1}), alkyl C-H (2921 cm^{-1}) and carboxylic C=O (1731 cm^{-1}), disappeared after the calcination. On
 11 contrary, characteristic peaks of SiO_2 (at 799 , 942 and 1089 cm^{-1}) maintained after the calcination.
 12 Furthermore, SEM and STEM images in **Figure 5b** and **5c** intuitively indicate the hollow structure
 13 and high monodispersibility of the HSPs obtained by calcining SiO_2 -coated P(St-co-5.0%AA)
 14 beads. Since there are no collapsed hollow particles or fragments of SiO_2 shell can be found in the

1 obtained HSPs, it's believed SiO₂ shells exhibited sufficient mechanical strength for sustaining
 2 their spherical shape while polymer cores was being burning away, though they are ultra-thin.
 3 Moreover, the high dispersibility of obtained HSPs has also been demonstrated by DLS
 4 measurements (**Figure 5d**), as the corresponding poly-dispersity index is only 0.085. In addition, a
 5 visible Mie scattering phenomenon could be observed when place the obtained HSPs on a black
 6 background with illumination (insert of **Figure 5c**), which is possibly attributed by the high
 7 monodispersibility and ultra-thin shells of HSPs [].

8

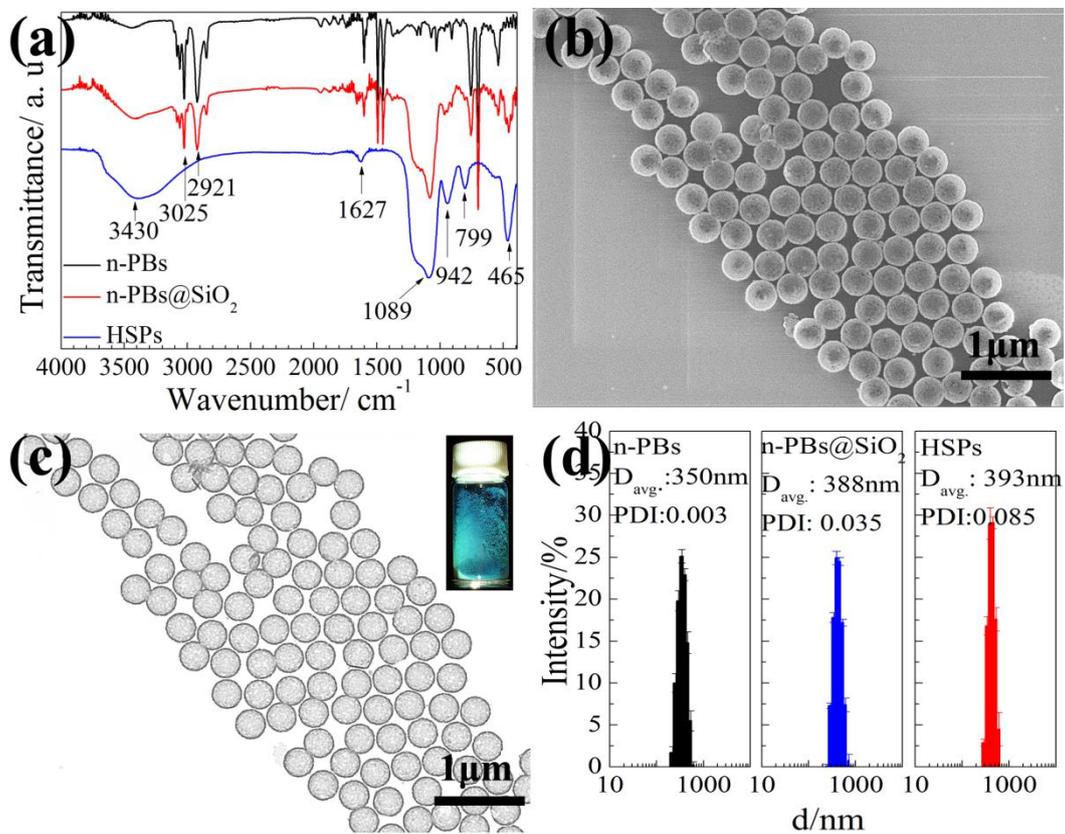


Figure 5 FTIR spectra of P(St-co-5.0%AA) beads, SiO₂-coated P(St-co-5.0%AA) beads and HSPs (a); SEM (a) and STEM (b) images of HSPs obtained by calcining SiO₂-coated P(St-co-5.0%AA) beads; size distribution histograms of P(St-co-5.0%AA) beads, SiO₂-coated P(St-co-5.0%AA) beads and HSPs in water (d);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

9

10 3.4. The influence of C_{NH3} and C_{H2O}

1 In the process of SiO₂ coating on n-PBs, the SiO₂ yield closely associated with the concentration of
 2 NH₃ (C_{NH3}) and the concentration of water (C_{H2O}) in reaction system. **Table 2** lists seven different
 3 experimental conditions for SiO₂ coating, in which C_{NH3} and C_{H2O} are varied independently. The
 4 polymer beads used in all those experiments were P(St-co-5.0%AA). SiO₂ yields (Y_{SiO2}/%) were
 5 calculated with following equations,

$$Y_{SiO_2} (\%) = \frac{W_{SiO_2}}{W_{thero-SiO_2}} * 100\% \quad (3-1)$$

$$W_{thero-SiO_2} = \frac{V_{TEOS} * \rho_{TEOS} * M_{SiO_2} / M_{TEOS}}{m_{n-PBs} + V_{TEOS} * \rho_{TEOS} * M_{SiO_2} / M_{TEOS}} \quad (3-2)$$

6 where W_{SiO2} is the weight percent of SiO₂ in SiO₂-coated n-PBs, which is calculated from the
 7 corresponding TG curve (**Figure 6a, 7a**); W_{thero-SiO2} is the theoretical value of W_{SiO2} with assuming
 8 that the conversion rate of TEOS is 100%; m_{n-PBs} (0.414g) is the weight of n-PBs, V_{TEOS} (1ml) is the
 9 volume of TEOS, ρ_{TEOS} is 0.933g/ml, M_{SiO2} is 60.08g/mol, and M_{TEOS} is 208.33g/mol. The
 10 calculated SiO₂ yields are also listed in **Table 2** for reference. By analyzing the plot of Y_{SiO2} vs.
 11 C_{NH3} (insert of **Figure 6a**), it's clear that the SiO₂ yield increases linearly with the increasing of
 12 C_{NH3}. For instance, the SiO₂ yield was only 60.6% when the C_{NH3} was 0.29M, but it increased to
 13 87.5% when the C_{NH3} reached to 0.49M. Furthermore, the improvement of SiO₂ yield was also
 14 reflected in the shell thickness of HSPs. In **Figure 6b~d**, HSPs with different shell thickness have
 15 been obtained by varying the C_{NH3} from 0.29 to 0.49, and the positive correlation between SiO₂
 16 shell thickness and C_{NH3} is significant. On the other hand, increasing C_{H2O} in the reaction system
 17 has also improved the SiO₂ yield (**Figure 7a**). However, it was found that an excessively high C_{H2O}
 18 would exert negative influence on the SiO₂ coating. Typically, when C_{H2O} was 3.06M in reaction
 19 system, despite the SiO₂ yield reached to 90.4%, SiO₂ shells did not formed on the surface of PBs,

1 as the immobilized SiO_2 particles only connected loosely with each other (**Figure 7b**).
 2 Correspondingly, HSPs fabricated from this kind of SiO_2 -coated n-PBs was so fragile that even
 3 couldn't endure the ultrasonic treatment during SEM sampling. Although it needs, of course, further
 4 experiments (out of the scope of this paper) to address the incomplete coating of SiO_2 on n-PBs
 5 under high C_{H_2O} , we give a probable explanation here: since polymer beads owned hydrophobic
 6 surface, the high concentration of water in reaction system increased the difficulty of the
 7 transferring of SiO_2 precursors from bulk solution to the surface of cores; therefore, SiO_2 precursors
 8 preferred to participate in the growth of already immobilized SiO_2 particles, which oppositely
 9 owned hydrophilic surface, rather than form new nucleation on the surface of polymer beads; as a
 10 result, the SiO_2 -coating under this condition was incomplete but with a high yield of SiO_2 .

11

Table 2. SiO_2 coating with different C_{NH_3} and C_{H_2O} ^{1,2}

Sample	V_{water}/ml	$V_{25.0\ wt.\ \% \ ammonia}/ml$	C_{water}/M	C_{NH_3}/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.

12

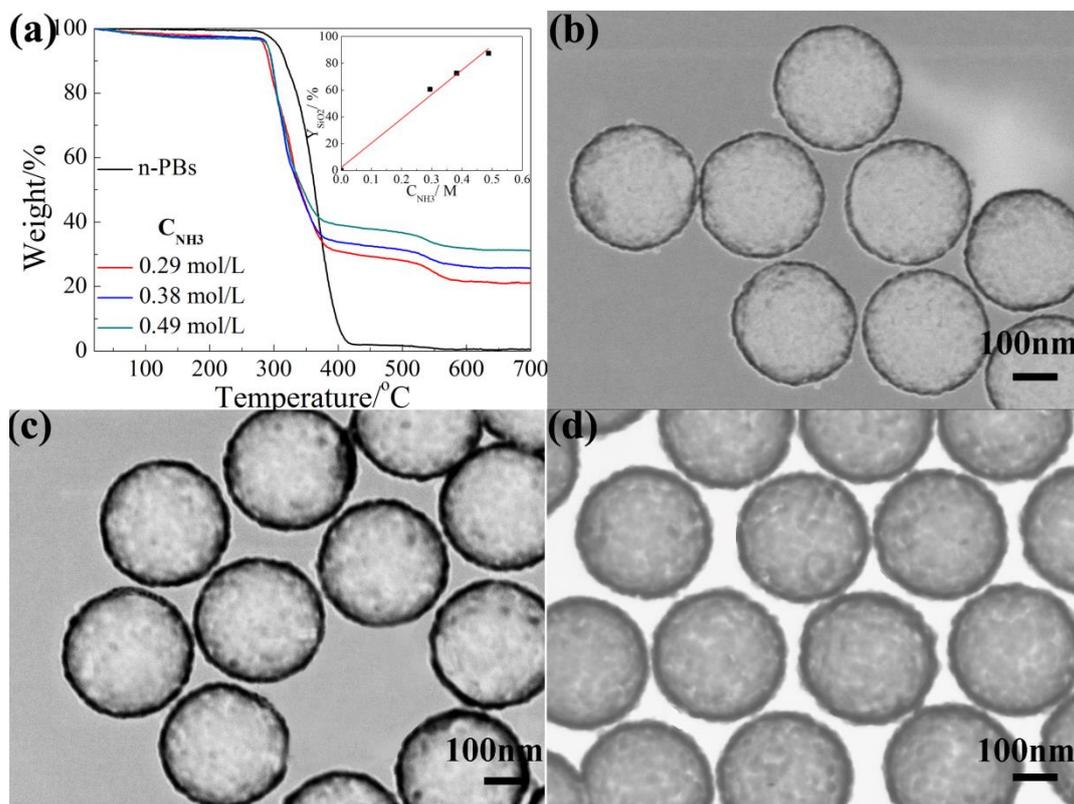


Figure 6 TG curves of SiO_2 -coated n-PBs synthesized with different C_{NH_3} (a); the insert of plots Y_{SiO_2} vs. C_{NH_3} ; STEM images of HSPs obtained from the sample A1 (a), A2 (b) and A3 (c).

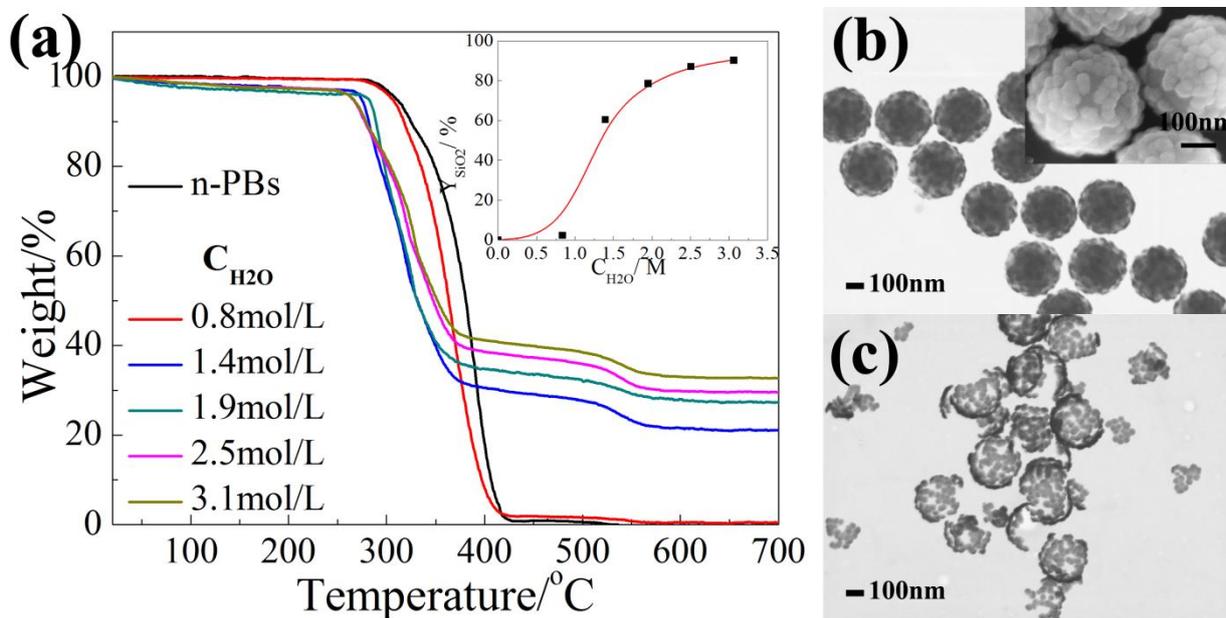


Figure 7 TG curves of SiO_2 -coated n-PBs synthesized with different $C_{\text{H}_2\text{O}}$ (a); the insert of plots Y_{SiO_2} vs. $C_{\text{H}_2\text{O}}$; SEM and STEM images of sample B4 synthesized with $C_{\text{H}_2\text{O}}=3.0$ (b); STEM image of HSPs obtained from sample B4 (c).

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22

4. CONCLUSION

In summary, we have demonstrated n-PBs can be used as the template for the fabrication of HSPs. Quality SiO₂-coated n-PBs and HSPs with high dispersibility and monodisperse size have been obtained in a simple and surfactant free process. With the using of n-PBs instead of p-PBs, the cost for fabricating HSPs has been reduced and the dispersibility of HSPs has been improved. Furthermore, in the process of SiO₂ coating on n-PBs, the influence of the surface charge density of n-PBs, concentrations of NH₃ and water in reaction system have been discussed in detail, and the prerequisites for successful SiO₂ coating has also been point out. The prerequisites are: (1) the surface charge density of n-PBs is high; (2) the concentration of water in reaction system is on a low level. Moreover, we have proposed a reasonable mechanism for explaining the coating of SiO₂ on n-PBs, in which the adsorption of NH₄⁺ is emphasized.

This work suggest PBs that suitable for SiO₂ coating can be extended to a wider range, without considering if their surface is positively charged or negatively charged. Even more importantly, our discussion on the mechanism of SiO₂-coating on negatively charged polymer beads revealed the multi-rule of NH₃ (NH₄⁺) plays and its interaction with target cores, which is helpful for better understanding the coating of SiO₂ in a stöber-like method. In addition, we believe constructing a “no surface charge reversal” process for SiO₂ coating can be seen as a practical synthetic strategy for hollow particles with high dispersibility in future works.

***Corresponding Author**

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

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

2

3 **Acknowledgment**

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

6

7

8

9

10 **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]G.H. Bogush; M.A. Tracy, C.F. Zukoski IV, Preparation of Monodisperse Silica Particles: Control of Size and Mass Fraction. *J. Non-Cryst. Solids* 104 (1988) 95-106; doi: 10.1016/0022-3093(88)90187-1.
- [13]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.
- [14]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.
- [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]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.
- [17]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.
- [18]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.

1

2

3

1
2
3
4
5
6
7
8
9
10
11
12
13
14