



Original Research Paper

# Emulsion templating of poly (acrylic acid) by ammonium hydroxide/sodium hydroxide aqueous mixture for high-dispersed hollow silica nanoparticles



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## ABSTRACT

A water-in-oil (W/O) emulsion, in which the water phase including poly (acrylic acid) (PAA), ammonium hydroxide ( $\text{NH}_3$  aq.), and sodium hydroxide aqueous solutions (NaOH aq.) dispersed in ethanol (EtOH), was proposed for producing hollow silica nanoparticles. The PAA molecules with the  $\text{NH}_3$ -NaOH mixture are insoluble in EtOH and can be a template. When tetraethoxysilane (TEOS) is added as a silica source, a silica shell is formed on the PAA- $\text{NH}_3$ -NaOH template to form a core-shell particle and the addition of water removes the template to form hollow silica nanoparticles. The optimum volume ratio of 25%  $\text{NH}_3$ :1.0 M NaOH was 2:1 to obtain high-dispersed hollow silica nanoparticles. A thermogravimetric analysis indicated that the condensation force of the PAA molecules in the PAA- $\text{NH}_3$ -NaOH template is similar to that in the PAA- $\text{NH}_3$  template. The small angle X-ray scattering (SAXS) analysis also showed that the electron densities in the PAA- $\text{NH}_3$ -NaOH and PAA- $\text{NH}_3$  templates are similar. In the proposed PAA- $\text{NH}_3$ -NaOH system,  $\text{NH}_3$  aq. mainly contributes to form PAA condensation by an ionic interaction and NaOH aq. preferentially work as a sol-gel catalyst for the fast silica coating on the template surface.

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## 1. Introduction

Hollow silica nanoparticles have a nano-sized hollow interior surrounded by a solid shell. Such a structure exhibits a thermal insulation [1], visible transparency [1], light diffusivity [2–4], as well as drug loading/releasing [5], catalyst support [6], etc. The presence of the nano-sized hollow interior reduces the thermal conductivity of a film in which the hollow silica nanoparticles are dispersed by keeping the visible transparency high. The difference in the reflective index between the air and silica shell increases the light diffusivity of the hollow silica nanoparticles. These properties are dominated by the size, shape, and shell microstructure of the hollow silica nanoparticles.

There are many methods for the synthesis of hollow silica nanoparticles, which are mainly categorized as a hard template [7] or soft template [8]. As the former, polystyrene (PS) beads are often utilized as a template, because it is easy to the control particle size and its distribution. A silica source (e.g., tetraethoxysilane, TEOS) is a coating on the PS template surface to prepare the core-shell structure, then the template is removal by a chemical [9] or

thermal etching [7]. During the template removal, any organic waste solutions and harmful gases are eliminated. To overcome these problems, Fuji et al. proposed an inorganic template technique using calcium carbonate and hydroxyapatite nanoparticles in which a dilute acid solution is only required for dissolution of the templates [10,11]. Wu's group developed a synthetic method to procedure a silica coating on the polymer template surface and simultaneous dissolution of the template by adjustment of the  $\text{NH}_3$  aq. quantity [12,13]. Shi Yan used poly (sodium methacrylate) (PMA) as the emulsion template which is insoluble in EtOH, but soluble in water to prepare the hollow silica nanoparticles [14]. Yu et al. utilized poly acrylic acid (PAA) with an ammonium hydroxide solution ( $\text{NH}_3$  aq.) as the emulsion template in EtOH [15]. After TEOS was added to the emulsion, the silica coating was formed on the PAA- $\text{NH}_3$  template to form a core-shell particle. The addition of water in the core-shell particle suspension is only required to remove the template. It is possible that the solute PAA molecules can be re-used to synthesize the template. However, 14 h are required for the silica shell formation on the template surface [15], because the active molecular motion of PAA in the template could disturb the stable silica shell formation. In general, silica formation via the sol-gel route is dominated by the type and amount of the catalyst, pH and temperature of the reaction

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system, reaction time, etc.  $\text{NH}_3$  aq. is known as a weak base ( $\text{p}K_a = 9.25$  [16]) and does not fully dissociate in water. For hydrolysis of the TEOS, the dissociated  $\text{NH}_4^+$  ions gather around the tetrahedral TEOS where the center Si connects four ethoxy ( $-\text{CH}_2\text{CH}_3$ ) groups. When enough  $\text{NH}_4^+$  ions gather, the  $\text{OH}^-$  ion directly attacks the Si atom as a nucleophilic agent. Once one ethoxy group is hydrolyzed, hydrolysis of the other three progressed at an accelerated pace due to the  $\text{NH}_4^+$ 's steric hindrance effect. To promote the silica shell formation on the PAA-inorganic base template without inducing any further PAA molecular motion, a change in the catalyst seems to be one effective solution.

Previously, the addition of multi-functional aliphatic amines was performed except for  $\text{NH}_3$  aq. with the aim of suppressing the PAA's molecular motion by ionic cross-linking using the affinities between  $-\text{NH}_3^+/-\text{NH}_2^+$  in the side/main chains of the amines and  $-\text{COO}^-$  of PAA. An increase in the number of primary- and secondary- amines was effective to promote the silica shell formation [17]. 3,3-Diaminodipropylamine (DDA) with two primary and one secondary amines easily worked to suppress the PAA molecular motion and also act as a catalyst for the silica shell formation, however, a large quantity of the amine solution was required due to their steric hindrance.

On the other hand, sodium hydroxide (NaOH) is known as a strong base ( $\text{p}K_a = 15.74$  [18]) and non-volatile base. It is expected to be effective as a sol-gel reaction catalyst. PAA becomes insoluble in water along with a strong base like NaOH, which is called counter ion condensation [19]. In this study, the effect of NaOH aq. concentration on the hollow silica particle formation in the PAA-NaOH/EtOH system was investigated and the results were compared to that of the PAA- $\text{NH}_3$ /EtOH system. In addition, the  $\text{NH}_3$ -NaOH mixture was utilized. The structures of the PAA- $\text{NH}_3$ -NaOH templates were characterized by a thermogravimetric analysis and small angle X-ray scattering (SAXS). Based on these results, the role of  $\text{NH}_3$  and NaOH on the hollow silica nanoparticle formation was investigated.

## 2. Materials and methods

A 0.09 g sample of polyacrylic acid (PAA, Mw; 5000) was mixed with inorganic bases, such as a 25% ammonium hydroxide solution ( $\text{NH}_3$  aq.), sodium hydroxide (NaOH aq.) solution, and these mixtures prepared clear solutions, which were represented as PAA- $\text{NH}_3$ , PAA-NaOH, and PAA- $\text{NH}_3$ -NaOH, respectively. These solutions were dropped into 30 ml of EtOH (99.5%) with 500 rpm stirring. The PAA-inorganic base solutions become emulsion templates in EtOH because of the low solubility of PAA in EtOH. These emulsions were denoted as PAA- $\text{NH}_3$ /EtOH, PAA-NaOH/EtOH, and PAA- $\text{NH}_3$ -NaOH/EtOH, respectively. Tetraethoxysilane (TEOS) was slowly added to the emulsion at a fixed rate and stirred for a specific time. The rate of the TEOS addition and the stirring time were adjusted so that the total TEOS volume was 0.75 ml. After the entire TEOS was added, the suspensions were stirred for another 2 h to induce the silica coating on the template surface. During these processes, core-shell particles were formed. The suspensions were then separated using centrifugation at 8000 rpm for 10 min. Distilled water was added twice to the precipitates to remove the template. The precipitates were then washed and dried at 60 °C under vacuum for 24 h. All of the chemicals were purchased from Wako Pure Chemical Industries, Ltd., and used without further purification.

The morphology of the samples were observed by a scanning electron microscope (SEM, STEM, JSM-7600F, JEOL Ltd.). Viscosity of the PAA-inorganic base solutions were measured by a rheometer (Rheo Stress 6000, DC60/1, Thermo Electron Corporation). The particle sizes of the templates in EtOH were measured by dynamic light scattering (Zetasizer Nano, Malvern Instruments, Ltd.). The

pyrolytic behaviors of the templates were characterized by a thermogravimetric analysis (TG/DTA, TG8120, Rigaku Corporation). The degrees of the PAA condensation in the templates were estimated by small angle X-ray scattering (SAXS, SAXSpace, Anton Paar GmbH). A linear X-ray source of  $\text{CuK}\alpha$  was employed (40 kV, 50 mA), and the collection time was from 5 to 60 min to obtain a strong scattering signal at 25 °C. Data processing and Guinier fitting were carried out using SAXSquant software, which is also a program by Anton Paar.

## 3. Results and discussion

### 3.1. Effect of amount of $\text{NH}_3$ aq. on hollow particle formation [17]

Fig. 1 summarizes the results of the viscosity of the template solutions (i.e., PAA and  $\text{NH}_3$  aq. mixture which is denoted by PAA- $\text{NH}_3$ ), mean diameters of the templates (i.e., PAA- $\text{NH}_3$  templates dispersed in EtOH, denoted by PAA- $\text{NH}_3$ /EtOH), and STEM images of the obtained samples, prepared with the additions of (a) 1.5, (b) 2.0, (c) 2.5, (d) 3.0, and (f) 6.0 ml  $\text{NH}_3$  aq. to 0.09 g of PAA. With the addition of less than 1.5 ml, the PAA did not completely dissolve. These details were previously reported [17]. As shown in Fig. 1, the viscosity and mean diameter showed a similar tendency that they decreased with the  $\text{NH}_3$  aq. up to 3.0 ml, then gradually decreased up to 6.0 ml. The STEM images showed that the hollow silica nanoparticles were successfully formed with 1.5 ml of  $\text{NH}_3$  aq. With an increase in the  $\text{NH}_3$  aq., the number of formed hollow particles decreased (2.0 ml, Fig. 1(b)), dense particles were also formed with hollow particles (2.5 ml, Fig. 1(c)), porous particles were only formed (3.0 ml, Fig. 1(d)), and dense particles were only formed (6.0 ml, Fig. 1(e)).

An increase in the  $\text{NH}_3$  aq. decreased the viscosity of the PAA- $\text{NH}_3$  template solutions because of the increase in the  $\text{H}_2\text{O}$  amount. At the interface between the PAA- $\text{NH}_3$  template and EtOH, a high amount of the  $\text{H}_2\text{O}$  moves from the inside and outside the template which results in difficulty for the smooth silica shell formation at the PAA- $\text{NH}_3$ /EtOH interface. Once  $\text{H}_2\text{O}$  leaked to the outside of the template, it freely mixes with EtOH and the  $\text{H}_2\text{O}$  ratio in EtOH increases with the  $\text{NH}_3$  aq. The  $\text{NH}_4^+$  ion also moved toward outside the template along with  $\text{H}_2\text{O}$  leakage, and the ion ratio in EtOH increased with the  $\text{NH}_3$  aq. With an increase in the  $\text{NH}_3$  aq., TEOS in EtOH starts to hydrolyze before it reaches the template surface. This is the mechanism for the dense or porous silica particle formation when the  $\text{NH}_3$  aq. amount increased (Fig. 1(c)–(e)). Based on these results, 1.5 ml of  $\text{NH}_3$  aq. is the optimized amount for the hollow silica nanoparticles.

### 3.2. Optimization of NaOH concentration for hollow silica nanoparticles

Fig. 2 shows the STEM ((a)–(d)) and SEM ((e)(f)) images of the samples prepared with the additions of (a) 0.1, (b) 0.5, (c) 0.75, (d) 1.0, (e) 3.0, and (f) 5.0 M NaOH aq., respectively. Table 1 shows the pH and viscosity of the template solutions (PAA-NaOH aq.), and mean diameter of the template in EtOH (PAA-NaOH/EtOH emulsion). The concentration range between (c) 0.5 and (d) 1.0 M NaOH aq. seems to undergo a major change to determine whether or not the hollow structure formed. With the addition of a low concentration (0.1 M, Fig. 2(a)), most of the hollow particles with a thin shell were broken in the small amount of formed precipitates. With an increase to 0.5 M (Fig. 2(b)), the formed hollow particles were not broken. The formed particles were non-spherical and have a thin shell, and they strongly aggregated with each other. With an increase to 0.75 M (Fig. 2(c)), the morphology of the obtained particles were similar to that of the 0.5 M ones and the yield of the

25 % NH <sub>3</sub> aq. [ml]	(a) 1.5	(b) 2.0	(c) 2.5	(d) 3.0	(e) 6.0
Viscosity of PAA-NH <sub>3</sub> aq. [mPas]	2.9	2.5	1.6	1.4	1.0
Mean diameter of PAA-NH <sub>3</sub> template in ethanol [nm]	220.2	165.3	101.6	61.78	47.21
STEM images	Hollow	Hollow	Hollow + dense	Porous	Dense

Fig. 1. Effect of NH<sub>3</sub> aq. amount on viscosity of PAA-NH<sub>3</sub> aq., mean diameter of PAA-NH<sub>3</sub> in EtOH, and STEM images of the obtained particles [17].

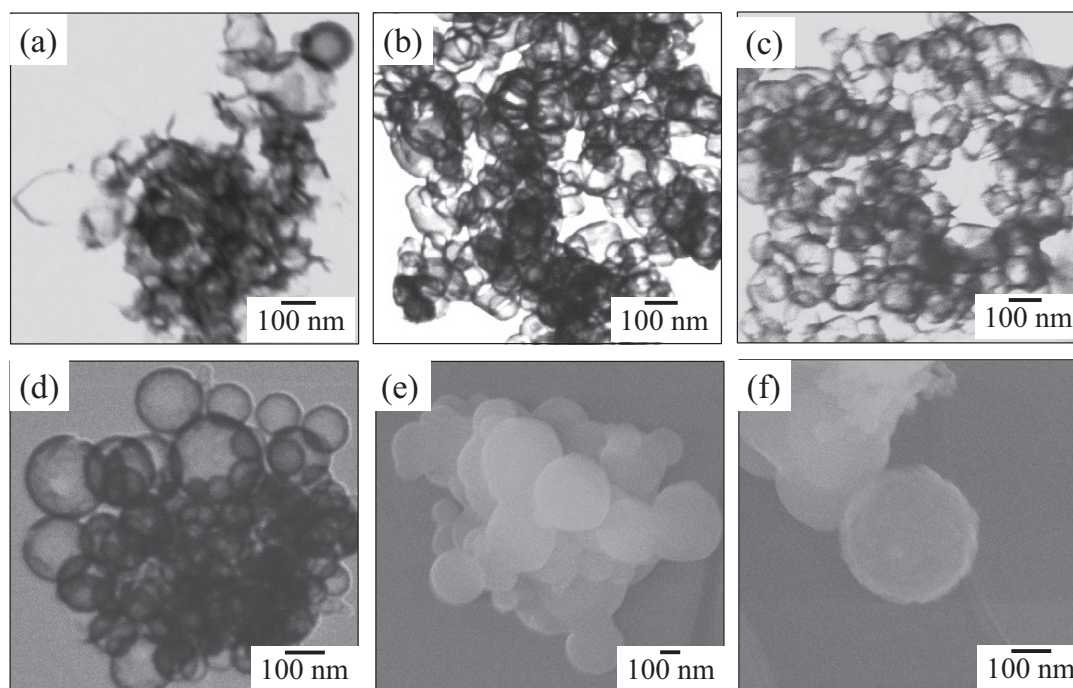


Fig. 2. STEM and SEM images of samples prepared with the addition of 1.5 ml of (a) 0.1, (b) 0.5, (c) 0.75, (d) 1.0, (e) 3.0, and (f) 5.0 M NaOH aq.

Table 1

Effect of NaOH concentration on pH and viscosity of PAA-NaOH aq., mean diameter of PAA-NaOH droplet, and STEM results.

NaOH conc. [M]	(a) 0.1	(b) 0.5	(c) 0.75	(d) 1.0	(e) 3.0	(f) 5.0
pH of PAA-NaOH aq.	–	6.09	11.25	12.91	13.95	>14
Viscosity of PAA-NaOH aq. [mPa·s]	–	1.5	1.7	4.3	6.3	8.3
Mean diameter of PAA-NaOH droplet in EtOH [nm]	57.9	144.5	198.3	968.5	–	–
STEM results	Deformed hollow	Deformed hollow	Hollow	Hollow	Dense	Dense

hollow particles increased. From 0.5 M to 0.75 M, the pH of PAA-NaOH aq. significantly increased from 6.09 to 11.25 as shown in Table 1. With the subsequent increase to 1.0 M (Fig. 2(d)), the STEM image showed spherical hollow silica particles with around a 100 to 200 nm size. Though they showed aggregation, there were no broken or deformed shells observed. From 0.75 to 1.0 M, the

mean diameter of the PAA-NaOH templates caused a large increase from 198.26 to 968.53 nm as shown in Table 1. The viscosity of the PAA-NaOH aq. also significantly increased from 1.72 to 4.25 mPa·s. With the increase in the NaOH to 3.0 M (Fig. 2(d)), no hollow particles were formed. Particulates of around 100–200 nm were only observed, which appear to be dense silica particles. With a further

increase to 5.0 M (Fig. 2(f)), the size of the dense silica particles increased. The pH of the template solutions did not change significantly and the viscosity of the template solutions continuously increased as shown in Table 1.

When the PAA and NaOH aq. were mixed, ion exchange between the  $H^+$  of PAA and  $Na^+$  of NaOH occurred and  $H_2O$  was generated [19]. The PAA-Na polymer is known as a water absorptive polymer and its polymer network holds much  $H_2O$  at the optimum  $Na^+$  concentration. The PAA-Na polymer with  $H_2O$  dispersed in EtOH can be a template for hollow silica nanoparticles. The rapid increase in pH of the PAA-NaOH aq. (from 0.5 to 0.75 M, Table 1) seems to be derived from the increase in the free NaOH which does not interact with the  $-COO^-$  of PAA. The free NaOH can be a sol-gel reacting catalyst for the TEOS.

At 1.0 M NaOH aq., hollow particles were only formed without any dense or bulk silica (Fig. 2(d)). The PAA-Na network tightly held a lot of  $H_2O$  and a large PAA-NaOH template formed in the EtOH (968.53 nm, Table 1). At the stable surface of the swollen PAA-NaOH template, the silica coating was promoted using the free NaOH which stays near the template surface due to its good affinity with  $H_2O$ .

With a decrease in the  $Na^+$  ions (0.5 and 0.75 M, Fig. 2(b) and (c)), excess  $H_2O$ , which the sparse PAA-Na network cannot hold, leaked from the PAA-NaOH template. The size of the PAA-NaOH template decreased and the unstable template surface could only provide small and deformed hollow silica particles. The high increase in the pH of the PAA-NaOH aq. from 0.5 to 0.75 M increased the excess NaOH which increased the yield of hollow particles. With a further decrease in the  $Na^+$  ion (0.1 M, Fig. 2(a)), the unstable droplet surface provided a small amount of hollow particles and broken silica shells. However, with the increase in the  $Na^+$  concentration (3.0 and 5.0 M, Figs. 2(e) and (f) and S1 (a) and (b)), the added TEOS in EtOH starts to be hydrolyzed before it reaches the PAA-NaOH template surface. Once the silica cluster forms in EtOH, it continuously grows as large dense silica particles.

According to Yu's report, the PAA-NH<sub>3</sub> system needs 12 h for the TEOS addition and a further 2 h for promotion of the hydrolysis and condensation [15]. In the PAA-NaOH system, reduction of the reaction time was attempted. Fig. 3 shows STEM images of the samples prepared for 2 h and 14 h in the PAA-NH<sub>3</sub> and PAA-NaOH systems, respectively. In the PAA-NH<sub>3</sub> system, a 2-h reaction time was not enough to form the hollow silica nanoparticles. At 14 h, spherical hollow nanoparticles with a high dispersibility were formed with an approximate 100 nm size. However, in the PAA-NaOH system, even for 2 h, hollow silica nanoparticles were formed although aggregation occurred. The surfaces of the hollow silica nanoparticles were odd-shaped and the shell thickness was thin. With an increase in the time to 14 h, the odd-shaped particle surface disappeared. Spherical hollow particles with a thick shell and smooth surface were obtained. The particle aggregation still occurred.

Although the PAA-NH<sub>3</sub> system slows the silica coating rate, particle dispersibility of the obtained hollow silica nanoparticles was not inhibited. On the other hand, the PAA-NaOH system indeed promoted the silica coating on the emulsion template surface, inducing an unfavorable particle aggregation. The two inorganic bases seem to play different roles in the emulsion system. By combining the advantages of these two inorganic bases, it is expected that a high dispersion and reduction in the reaction time can be simultaneously achieved.

### 3.3. Effect of NH<sub>3</sub>-NaOH mixture on hollow particle formation

Based on the above results, 1.5 ml of the 25% NH<sub>3</sub> aq. or 1.5 ml of the 1.0 M NaOH aq. seem to be optimum to synthesize the hollow silica nanoparticles. With the total volume of the inorganic base mixture of 1.5 ml, the effect of the ratios of the 25% NH<sub>3</sub> aq.

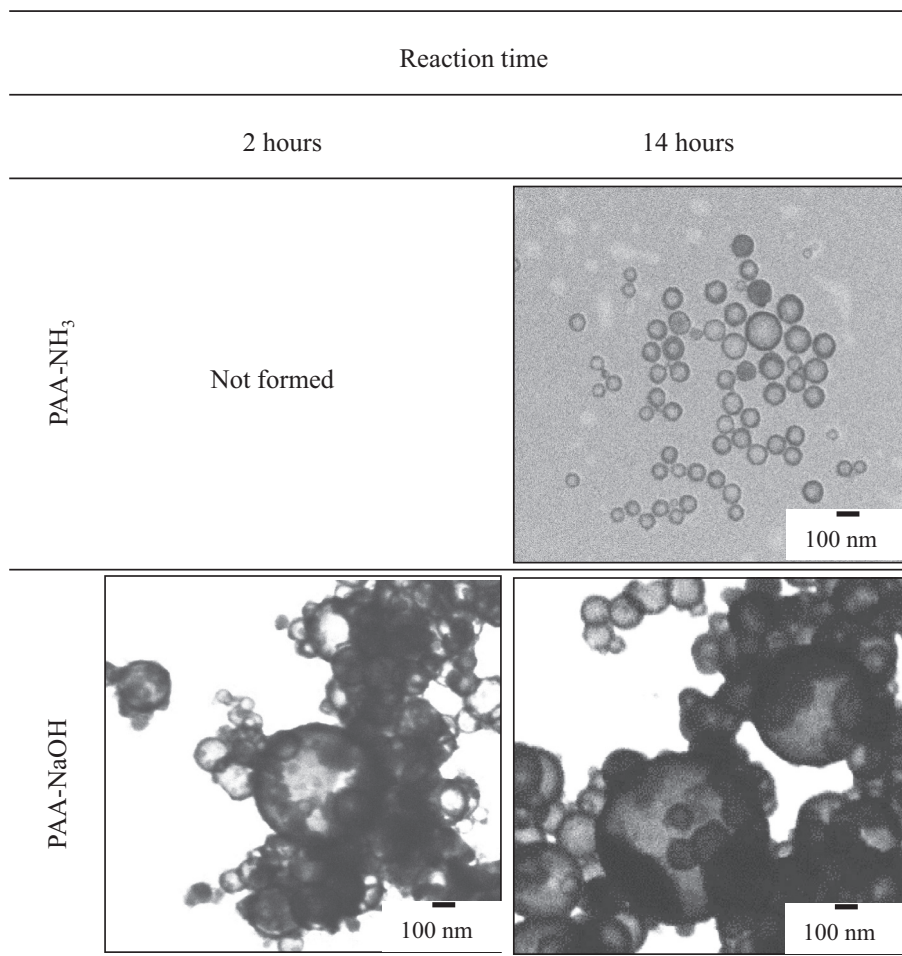
and 1.0 M NaOH aq. on the formation of the hollow silica nanoparticles was investigated. Fig. 4 shows STEM images of the samples prepared with 25% NH<sub>3</sub> aq.:1.0 M NaOH aq. of (a) 4:1, (b) 2:1, (c) 1:1, (d) 1:2, and (e) 1:4 volume ratios. Table 2 shows the pH and viscosity of these PAA-base mixture solutions (PAA-NH<sub>3</sub>-NaOH aq.) and mean diameters of the emulsion templates (PAA-NH<sub>3</sub>-NaOH/EtOH emulsion). The total reaction time was fixed for 14 h.

Interestingly, highly-dispersed hollow silica nanoparticles were formed at the ratio of 2:1, as shown in Fig. 4(b). Although they showed a bimodal distribution of less than 100 nm and 100–200 nm, the particles did not aggregate. With an increase in the NH<sub>3</sub> aq. to 4:1, hollow particles with a thin shell were formed, but some of the shells were broken (Fig. 4(a)). With an increase in the NaOH aq. to 1:1 (Fig. 4(c)), the shell thickness increased and aggregation occurred compared to that prepared at 2:1. With an increase in the NaOH aq. to 1:2 (Fig. 4(d)), the size of the hollow particles increased and aggregation still existed. With a further increase in the NaOH aq. to 1:4 (Fig. 4(e)), most of the particles were broken.

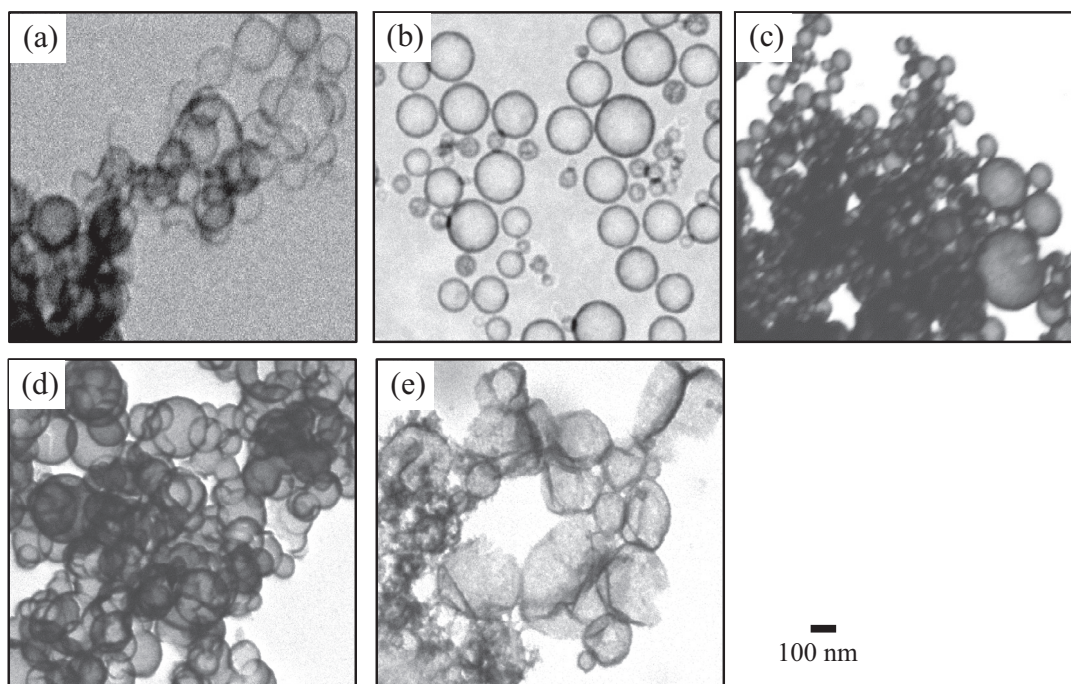
As shown in Table 2, the pH of the PAA-based mixture solutions did not significantly change with the NH<sub>3</sub>:NaOH ratio changed. The viscosity of the PAA-based mixture also did not show a large change, whose values were between 4 and 5 mPa·s. Given that the viscosity of PAA aq. before the inorganic base addition was 0.58 mPa·s, it seems that the PAA and  $NH_4^+$  and/or  $Na^+$  have some interaction. As indicated in Fig. 1 and Table 1, the viscosity of the PAA-NH<sub>3</sub> aq. (25%, 1.5 ml) was 2.90 mPa·s and that of the PAA-NaOH aq. was 4.25 mPa·s (1.0 M, 1.5 ml). Each inorganic base has an individual interaction with the PAA. Despite the fact that the number of  $Na^+$  ions in 1.5 ml of 1.0 M NaOH was much lower than that of the  $NH_4^+$  ions in 1.5 ml of 25% NH<sub>3</sub> aq., the increase in the viscosity of the PAA-NaOH was more apparent than that of PAA-NH<sub>3</sub>. The viscosity of the PAA-NH<sub>3</sub>-NaOH (NH<sub>3</sub>:NaOH = 2:1) further increased to 5.22 mPa·s. When both ions were mixed, an obvious interaction with the PAA existed. However, changes in the ratios of NH<sub>3</sub> and NaOH did not significantly affect the interaction.

With an increase in the NaOH ratios (NH<sub>3</sub>:NaOH = 1:1, 1:2, 1:4), the viscosity of the PAA-inorganic based mixtures slightly decreased (4.38, 4.32, 4.03 mPa·s). This indicated that the interaction between the PAA and inorganic base decreased by degrees with an increase in the NaOH ratio and decrease in the NH<sub>3</sub> ratio. It seems that the increase in the viscosity of the PAA-base preferentially occurred by the  $NH_4^+$  ions. That is, the  $-COO^-$  of PAA preferentially interacts with the  $NH_4^+$  ions to form the emulsion template and the  $Na^+$  ions preferentially work as a sol-gel catalyst near the droplet surface to promote the silica coating. The ratio of NH<sub>3</sub>:NaOH = 2:1 is the best for the highly-dispersed hollow silica nanoparticles so that both ions play their proper roles. With an increase in the NaOH (1:1 and 1:2, Fig. 4(c) and (d)), the silica coating was indeed promoted, and particle aggregation was also induced. The free NaOH, which does not interact with the PAA, seems to induce the particle aggregation. With a further increase to 1:4 (Fig. 4(e)), the lack of  $NH_4^+$  ions makes the PAA's molecular motion more active, therefore, the silica coating on the unstable template did not progress. On the other hand, with an increase in the NH<sub>3</sub> aq. (NH<sub>3</sub>:NaOH = 4:1), the viscosity of the template solution slightly decreased to 4.61 mPa·s. A reduction in the reaction time for the hollow silica nanoparticles was attempted using the PAA-NH<sub>3</sub>-NaOH system (NH<sub>3</sub>:NaOH = 2:1). Fig. 5 shows an STEM image of the samples prepared at the NH<sub>3</sub>:NaOH ratio of 2:1 for 2 h. Hollow silica nanoparticles of around 100 nm were successfully formed. It can be clarified that such a fast silica formation is achieved by the free NaOH as a catalyst which remains near the droplet surface.

How the emulsion droplet formed in the PAA-NH<sub>3</sub>, PAA-NaOH, and PAA-NH<sub>3</sub>-NaOH systems was next investigated. Fig. 6 shows



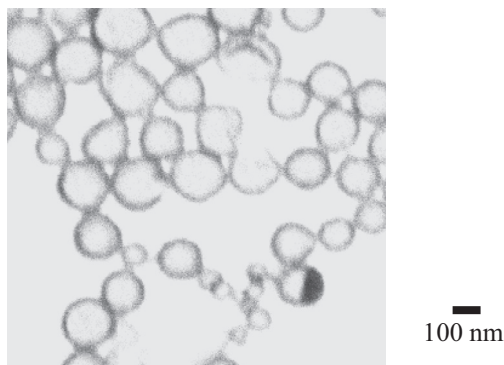
**Fig. 3.** STEM images of samples prepared for 2 and 14 h in PAA-NH<sub>3</sub> and PAA-NaOH templates.



**Fig. 4.** STEM images of samples prepared with NH<sub>3</sub>:NaOH of (a) 4:1, (b) 2:1, (c) 1:1, (d) 1:2, and (e) 1:4 for 14 h.

**Table 2**Effect of  $\text{NH}_3$  and NaOH ratio on pH, viscosity of PAA-inorganic base mixture, and mean diameter of template in EtOH.

$\text{NH}_3$ aq.: NaOH aq.	(a) 4:1	(b) 2:1	(c) 1:1	(d) 1:2	(e) 1:4
25% $\text{NH}_3$ aq. [ml]	1.2	1.0	0.75	0.5	0.3
1 M NaOH aq. [ml]	0.3	0.5	0.75	1.0	1.2
pH of PAA-inorganic salts aq.	11.8	11.9	11.9	12.1	12.3
Viscosity of PAA-inorganic salts aq. [mPa·s]	4.61	5.22	4.38	4.32	4.03
Mean diameter of PAA-inorganic salts template in ethanol [nm]	167.7	131.2	208.0	145.5	223.5

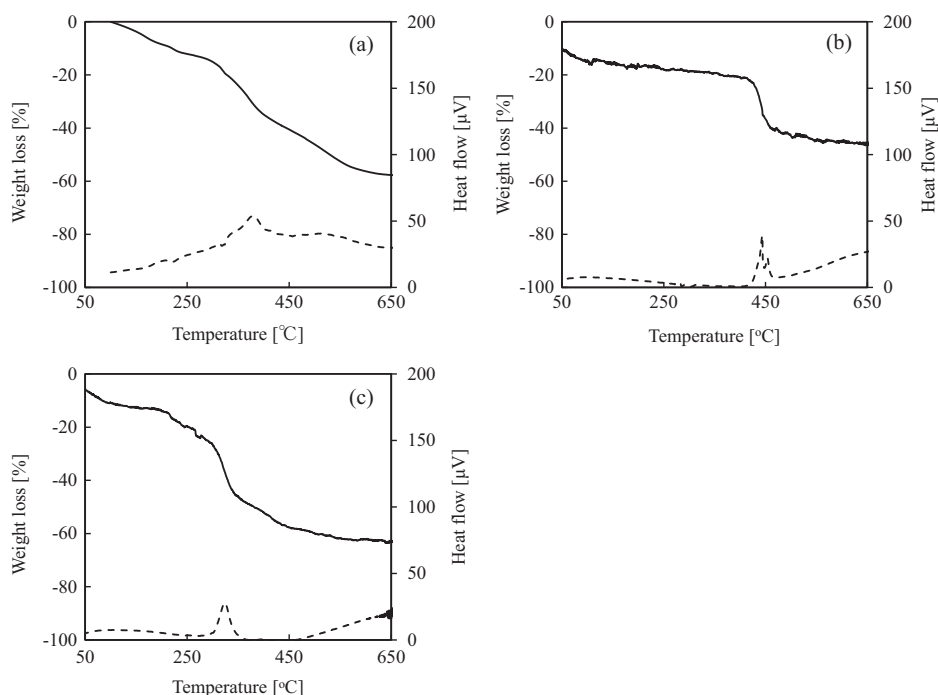
**Fig. 5.** STEM image of samples prepared for 2 h in PAA- $\text{NH}_3$ -NaOH system.

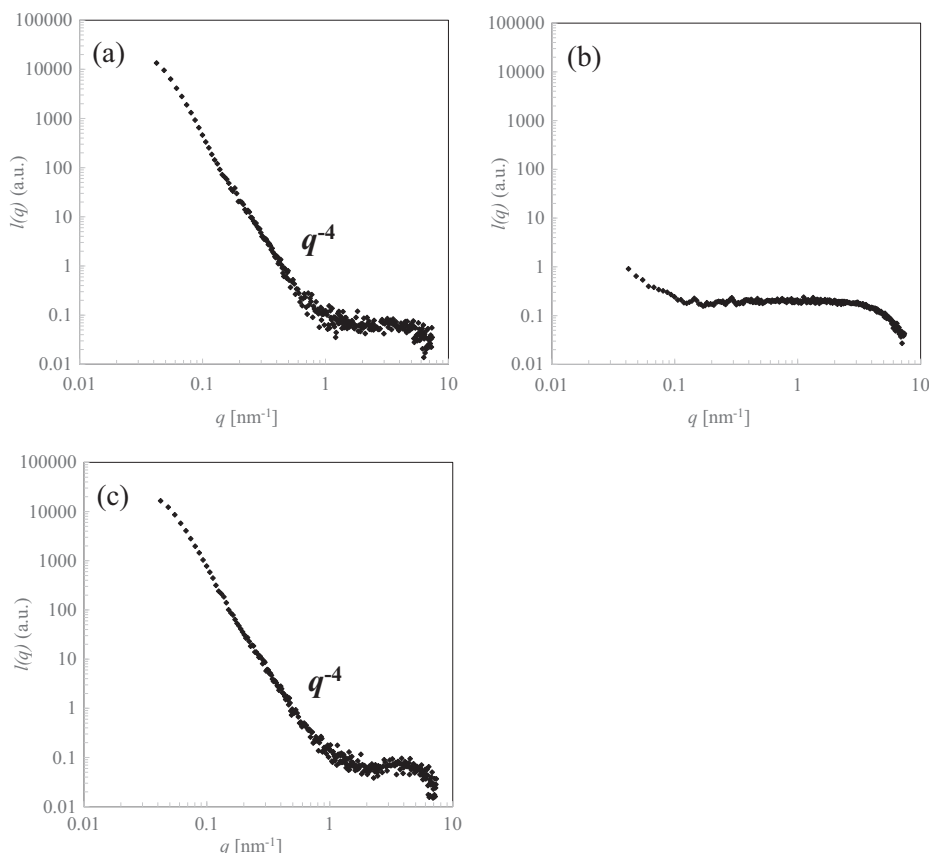
the TG/DTA of the core-shell particles (before core removal) prepared using the (a) PAA- $\text{NH}_3$ , (b) PAA-NaOH, and (c) PAA- $\text{NH}_3$ -NaOH ( $\text{NH}_3$ :NaOH ratio of 2:1) templates. Using the PAA- $\text{NH}_3$  template (Fig. 6(a)), the weight loss of the core-shell particles mainly appeared in three steps. The first gradual weight loss at around 200 °C is thought to be derived from vaporization of the free ammonia and  $\text{H}_2\text{O}$ . The second weight loss of 27 mass% is composed of three gentle peaks between 200 and 410 °C, and the third weight loss of 22 mass% is from 410 to 570 °C. These second and third weight losses could be derived from free the PAA and PAA that interacted with the  $\text{NH}_4^+$  ions. The residual substance is the sil-

ica shell. In the PAA-NaOH system (Fig. 6(b)), a quick weight loss of 20 mass% started from about 430 °C. There is a difference in the weight loss behavior between the PAA- $\text{NH}_3$  and PAA-NaOH systems of a gradual decrease and quick decrease, respectively. The difference in the initiation temperature of the weight loss indicates a difference in the condensation force of the PAA molecules in the PAA-base templates. That is, the PAA's condensation force of the PAA- $\text{NH}_3$ -NaOH template is similar to that of the PAA- $\text{NH}_3$  template. The difference in the weight loss behavior indicates the uniformity of the condensation force of the PAA molecules in the template. In the PAA- $\text{NH}_3$ -NaOH template, PAA molecules uniformly condense which is similar to the PAA-NaOH template.

It is thought that the PAA- $\text{NH}_3$ -NaOH template mainly forms PAA- $\text{NH}_4^+$  and this ionic interaction homogeneously exists in the template. Based on the lower weight loss (20 mass%) seen in the PAA-NaOH system than in the PAA- $\text{NH}_3$  system (49 mass%), it is thought that the PAA-NaOH template consists of a coarse PAA-Na polymer network, and has a high heat resistance.

Fig. 7 shows X-ray scattering curves by SAXS of the (a) PAA- $\text{NH}_3$ /EtOH, (b) PAA-NaOH/EtOH, and (c) PAA- $\text{NH}_3$ -NaOH/EtOH ( $\text{NH}_3$ :NaOH ratio of 2:1) emulsions. Based on the decreased behavior of the scattering curves of PAA- $\text{NH}_3$ -NaOH/EtOH and PAA- $\text{NH}_3$ /EtOH, the shapes of these templates were estimated as spherical. All of the scattering curves were analyzed by the pair distance distribution function (PDDF). The size of the PAA- $\text{NH}_3$ -NaOH and PAA- $\text{NH}_3$  templates were greater than 100 nm. The scattering curve of the PAA- $\text{NH}_3$ /EtOH emulsion was similar in behavior to that of

**Fig. 6.** TG/DTA curves of core-shell particles prepared with (a) PAA- $\text{NH}_3$ , (b) PAA-NaOH, and (c) PAA- $\text{NH}_3$ -NaOH systems.



**Fig. 7.** SAXS curves of emulsions prepared with a) PAA-NH<sub>3</sub>/EtOH, (b) PAA-NaOH/EtOH, and (c) PAA-NH<sub>3</sub>-NaOH/EtOH emulsions.

the PAA-NH<sub>3</sub>-NaOH/EtOH emulsion which means that the electron density distributions in the emulsion templates are similar in these two emulsions. In other words, the PAA's condensation density in the emulsion template is similar in the two. It can be said that the PAA's condensation is mostly made by interaction between the PAA and NH<sub>3</sub>. On the other hand, the intensity of the scattering curve of the emulsion in the PAA-NaOH/EtOH emulsion was significantly lower compared to the other two (Fig. 7(b)) in spite of the increase in NaOH concentration. The PAA-Na polymer network in the emulsion droplet is very coarse compared to the other two.

#### 4. Conclusion

An ammonium hydroxide (NH<sub>3</sub>) and sodium hydroxide (NaOH) mixture (volume ratio of 2:1) with poly (acrylic acid) (PAA) provided highly-dispersed hollow silica nanoparticles within a short time in a water-in-oil (W/O) emulsion. The characteristics of the obtained PAA-NH<sub>3</sub>-NaOH template were similar to those of the PAA-NH<sub>3</sub> template rather than those of the PAA-NaOH template based on a thermogravimetric (TG) and small angle X-ray scattering (SAXS) analysis. However, with an increase in the NaOH ratio, the dispersibility of the hollow silica nanoparticles decreased. It is thought that the PAA template is mainly made by the interaction with NH<sub>4</sub><sup>+</sup> ions and most of the NaOH works as a catalyst at near the template surface.

In the proposed W/O emulsion, by simply mixing NH<sub>3</sub> and NaOH with PAA, a high dispersibility and fast reaction of a uniform silica coating on the emulsion surface were achieved. PAA with an inorganic base mixture can be an emulsion template in EtOH and the addition of water dissolves the PAA-base template after the silica coating. In order to promote a uniform silica coating, the design of the template is required such that the PAA-base template is

“rigid” as well as miscible with water and the catalytic basic ions remain near the template surface.

Although Yu's group developed the PAA-NH<sub>3</sub> template method for uniform hollow silica nanoparticles, it took a long time for the silica coating [15]. To suppress the PAA's molecular motion, we previously used aliphatic amines which interact with the PAA [17]. However, both a high dispersibility and reactivity have not yet been achieved. Besides, the interaction between the PAA and ions, formation mechanism and structure of the emulsion droplet were only discussed in this paper.

Hollow silica nanoparticles have a significant potential such as superior transparent thermal insulation [1] and a light diffusion film [2,3] which were previously reported. The proposed emulsion technique is more effective for obtaining a stable high dispersibility in an eco-friendly process.

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#### Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apt.2016.10.010>.

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