Effects of Primary- and Secondary-Amines on the Formation Hollow Silica Nanoparticles by Using Emulsion Template Method

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Abstract

This paper describes the amine effect on sol-gel synthesis which is useful to rapidly form the shell structure of the hollow silica nanoparticles (HSNPs). Poly acrylic acid (PAA)/amine **emulsion templates** for silica coating performed in ethanol, and the **emulsion templates** was removed by water to obtain the HSNPs. To investigate of the ionic cross-linker and catalyst abilities of amine, four types of amines; ethylamine (EA), ethylenediamine (EDA), diethylenetriamine (DETA), and triethylenetetramine (TETA) were used. As a result, HSNPs could be successfully synthesized with a high TEOS conversion ratio (95%) and a shorter reaction time (2h) by using EDA, DETA, and TETA. In this procedure, amine worked as the catalyst for sol-gel reaction and the ionic cross-linkers for PAA. In catalyst ability, EDA worked as the most effective catalyst for sol-gel reaction that was measured by the zeta-potential. In cross-link ability, TETA worked as the most effective cross-linker for PAA condensation that was measured by the viscosity measurement. It showed that both cross-link ability and catalyst ability were important factor on this procedure. It was clarified that HSNPs can be synthesized at short time with high conversion ratio by considering the PAA/amine solution viscosity and interaction of amine with alcohol.

Keywords

Hollow silica nanoparticles

Emulsion template

Ionic cross-linker

Poly acrylic acid

Introduction

Hollow silica nanoparticles (HSNPs) with inner air cavity and outer silica shell exhibit unique properties, for instance a high specific surface area [1], low density, thermal conductivity [2], and optical property [3-5]. They also can be used as a nano-container of solubility materials [6-8]. According to their interesting properties, HSNPs have been synthesized by numerous methods such as, template method, electrostatic atomization method [9], and spray pyrolysis method [10]. Among these methods, the template method attracts much attention because the process can easily control the particles morphology. In the template method, silica source is firstly coated on the template surface by electrostatic interaction to form core-shell particles, then, the template is removed by thermal or chemical treatment.

There are two types of the template methods, which are soft and hard template. In hard template, polystyrene is used as template because of easily control of particle size and distribution [11-13]. Unfortunately, during template removal process, carbon dioxide gas or organic solutions are generated as waste byproducts. To overcome these problems, Fuji et al. developed an inorganic template method using calcium carbonate [14-16] and hydroxyapatite (HAp) [17] for HSNPs. The calcium carbonate can be removed by diluted acid and the generated calcium chloride can be re-used to form calcium carbonate. In soft template, the emulsion is used as template, and the emulsion is stabilized by the surfactant. With surfactant, it is required thermal treatment during removing surfactant [18-20]. Without surfactant, HSNPs are synthesized by using emulsion template in which, poly acrylic acid/ammonia aqueous (PAA/NH₃) and poly methacrylic acid/NH₃ emulsion templates are used as template using dissolution properties that templates are insoluble in ethanol but soluble in water [21-27]. This method is simple without harmful influence on environment.

The PAA powder is dissolved in NH₃ and the PAA/NH₃ solution is dropped in ethanol to form the emulsion. During stirring, tetraethoxysilane (TEOS) is slowly added in the emulsion to form silica shell on the PAA/NH₃ template surface. When water is added, the PAA/NH₃ templates are removed, and then HSNPs are obtained. However, 14h long reaction time is required for silica coating on the PAA/NH₃ templates [21]. It seems that silica shell hardly forms on the unstable template surface due to active molecular motion of PAA in the templates.

To shorten silica coating time on the templates, it is necessary to suppress molecular motion of PAA in the templates. Fuji proposed shorten reaction time technique using aliphatic diamines instead of NH₃ as the ionic cross-linker for PAA molecules [27]. Four kinds of amines with/without primary-, secondary-, and tertiary-amine were used. When 3,3'-diaminodipropylamine was used, HSNPs were successfully prepared for the shortest reaction time as 4h, because primary and secondary amines could work as not only the cross-linker for PAA but also the catalyst for sol-gel reaction.

However, it is still not clear the mechanism that how these amines work as the cross-linker for PAA and the catalyst for sol-gel reaction. In this study, investigate the mechanism that how these amines

work as the catalyst and the ionic cross-linker. For investigating them, four types of aliphatic amines; ethylamine (EA), ethylenediamine (EDA), diethylenetriamine (DETA), and triethylenetetramine (TETA), which have different number of primary- and secondary-amines and different length of hydrocarbon chain were used. It can be expected that number of amines affects ability as the ionic cross-linker and length of hydrocarbon chain affects ability as sol-gel reacting catalyst.

Experimental section

2.1 Materials

PAA (molecular weight: 5000) used as the emulsion templates. TEOS used as the precursor of silica shell. Ammonia aqueous solution (NH_3 , 25%), EA (70%), EDA, DETA, and TETA used as the catalyst for sol-gel reaction and the ionic cross-linker for PAA. Ethanol (99.5%) used as solvent for sol-gel reaction. All reagents were purchased from Wako Pure Chemical Industries and all chemicals were used as received without further purification.

2.2 Evaluation of catalyst works of each catalysts

A 2.0 mL amine aqueous solution was added into 35.0 mL ethanol by vigorous continuous stirring for 10 min. Following that, 2.0 mL TEOS was dropped into the solution. At target reaction time (0, 10, 30, 60, 90, 120 min), the suspension was evaluated. **Table 1** shows amine and water ratios in which that was adjusted same quantity of amine group. **Figure 1** shows molecular structure of used amines.

2.3 Synthesis of HSNPs via emulsion template method with different amines

A 0.12 g PAA was dissolved in 2.0 mL of amine aqueous solution (**Table 1**) by vigorous continuous stirring for 24h. The 2.0 mL PAA/amine was dropped into 35.0 mL ethanol, followed by injection of 2.0 mL TEOS aliquots totaling 1.2 mL at 1 hour time intervals under vigorous magnetic stirring at room temperature. At target reaction time (0, 2, 4, 6, 8, 10h) after injection of 2.0 mL TEOS, the products were centrifuged and washed by distilled water to remove the PAA/amine template. Finally, products were dried at 180°C under vacuum atmosphere. As a reference, the same procedure was conducted with NH_3 instead of addition of aliphatic amines.

2.4 Characterizations

The cloudiness of the prepared silica nanoparticle suspension against 500 nm light was measured by a UV-vis-NIR spectrophotometer (UV3150, Shimadzu Corp.). The viscosity of the PAA/amine solution was measured by a HAAKE Rheo Stress 6000 (Thermo Fisher Scientific K.K.). The template size distribution of PAA/amine in ethanol and the zeta potential of the template were measured by a

zetasizer (Zetasizer Nano, **Malvern** Instruments Ltd.). For observation, the obtained HSNPs dispersed in ethanol. The suspensions were dropped on a microgrid and observed by a scanning transmission electron microscope (STEM, JSM-7000F, JEOL Ltd.). The TEOS conversion ratio was estimated by inductively coupled plasma atomic emission spectrophotometry (ICP-AES, SPS7800, Seiko Instrument Inc.). The measurement samples were prepared following process. Firstly, supernatant solution after the first centrifuging was collected. Secondly, 0.1 ml supernatant solution was mixed with 20.0 ml 5M NaOH aqueous solution. Finally, the solution was stirred for three days and the obtained samples were measured by ICP. The TEOS conversion ratio was calculated by using following equation (1).

$$A_{\text{TEOS}} = (C_{\text{TEOS}} - C_{\text{ICP}}) / (C_{\text{TEOS}}) \times 100 \dots (1)$$

Where A_{TEOS} is the mean TEOS conversion ratio in %, C_{TEOS} is the mean initial TEOS concentration in ppm, and C_{ICP} is the mean ICP result in ppm. The calibration curves were made by using 0, 1, 10, 100 ppm Si solution.

3. Results and Discussion

3.1 Evaluation of catalyst works of each catalysts

Figure 2 shows the time-dependent changes of transmittance against 500 nm light of prepared silica nanoparticle suspension, which were prepared using EA, EDA, DETA, and TETA as the catalyst for the sol-gel reaction. When TEOS was reacted to silica nanoparticles, the transmittance decreased. In Fig. 2, the transmittance decreased with increasing reaction time in all condition, and the degree of transmittance was different at type of amines. It shows the used amine worked as the catalyst for the sol-gel reaction. The transmittances were 84.1, 1.0, 18.1, and 32.2 % at 30 min with EA, EDA, DETA, and TETA, respectively. In this result, EDA worked as the most efficient catalyst for the sol-gel reaction in the used amines, and the catalyst ability decreased with increasing quantity of secondary-amines in the molecular. As the result, the primary-amine worked as the more efficient catalyst for sol-gel reaction than the secondary-amine. However, EA was not the efficient catalyst for the sol-gel reaction in Fig. 2, because EA had the low solubility in water.

3.2 Synthesis of HSNPs by using the PAA/amine template

Figure 3 shows time-dependent changes of HSNPs between 0 and 6 h by STEM, which were prepared using (a) PAA/EA, (b) PAA/EDA, (c) PAA/DETA, and (d) PAA/TETA, respectively. As a reference, results of samples prepared using (e) PAA/NH₃ were also shown.

With PAA/NH₃, after 0 and 2h just after TEOS addition completed ((e)-0, 2h), HSNPs with the size between 20 and 150 nm were observed, and a part of HSNPs were broken. It might be due to that silica shells were unstable and very thin (5 nm). At 4 and 6h ((e)-4, 6h), there was no broken shell and the shell thickness was 10 nm at 6 h. The size of HSNPs was not changed with increase reaction time.

With PAA/EA, after 0h just after TEOS addition completed ((a)-0h), large HSNPs with between 150 and 200nm were observed, and obtained HSNPs were broken and a lot of small dense silica nanoparticles were observed around the HSNPs. After 2h ((a)-2, 4, 6h), the HSNPs covered by small dense silica nanoparticles were observed. The TEOS reacted not only on the template surface but also in ethanol due that a part of EA might exist in ethanol. The size of HSNPs was not changed with increase reaction time.

With PAA/EDA, after 0h just after TEOS addition completed ((b)-0h), HSNPs were not observed, and the broken shell was observed. After 2h ((b)-2, 4, 6h), there was no broken shell and the shell thickness was 10 nm at 6 h. The obtained particle size was from 20 nm to 150 nm.

With PAA/DETA, after 0h just after TEOS addition completed ((c)-0h), HSNPs were observed, the shell was broken. After 2h ((c)-2, 4, 6h), HSNPs were observed and the shell thickness was 10 nm at 6 h. The obtained particles sizes were from 20 nm to 150 nm.

With PAA/TETA, after 0h just after TEOS addition completed ((d)-0h), HSNPs were observed, the shell was broken. After 2h ((d)-2, 4, 6h), there was no broken shell and the shell thickness was 10 nm at 6 h. The obtained particles sizes were from 20 nm to 150 nm.

From these results, HSNPs using EDA, DETA, and TETA formed faster (2h) than that using NH_3 (4 h). With EA, silica shell was quickly formed at 2 h. However, obtained HSNPs were covered with small dense silica nanoparticles and obtained HSNPs were bigger than the other conditions. It seems that formation mechanism is different between EA and other amines.

Figure 4 shows the template size distribution curves of (a) PAA/EA, (b) PAA/EDA, (c) PAA/DETA, and (d) PAA/TETA, respectively. As a reference, results of samples prepared using (e) PAA/ NH_3 were also shown. The average **template** sizes were 265, 192, 170, 170, and 210 nm at PAA/EA, PAA/EDA, PAA/DETA, PAA/TETA, and PAA/ NH_3 , respectively. These **template** sizes were almost same as obtained HSNP sizes in Fig. 3 with each PAA/amine. It shows that the PAA/amine were used as **the templates**. Compared with PAA/ NH_3 , the **templates** became smaller with PAA/EDA, PAA/DETA, and PAA/TETA. On the other hand, with EA, the **templates** became bigger than with PAA/ NH_3 **templates**.

3.3 Evaluate of PAA solution with different amines

In this procedure, it is thought that amines worked as catalyst for sol-gel reaction and the ionic cross-linker for PAA. The amino group interacted with carboxyl group of PAA, and PAA/amines solution mobility decreased. With decreasing PAA/amines solution mobility, the solution viscosity increased. For evaluating the cross-linker ability, the PAA/amines solution viscosity was measured.

Figure 5 shows viscosities of PAA/EA, PAA/EDA, PAA/DETA, and PAA/TETA solution, respectively. As a reference, viscosities of samples prepared using 6 wt% PAA/water and PAA/ NH_3 were also shown. The viscosity of PAA/water was 0.6 mPa·s, and PAA/ NH_3 was 2.1 mPa·s. The

PAA solution viscosity increased by adding NH_3 , therefore NH_3 worked as the ionic cross-linkers for PAA. The viscosities of PAA/amine were 23.1, 8.7, 18.3, and 32.2 $\text{mPa}\cdot\text{s}$ with EA, EDA, DETA, and TETA, respectively. All of the PAA/amine viscosity increased more than PAA/water. It indicates that all of the used amines have interaction with PAA molecules in aqueous media. Although, EA has only one amino group at one end group, EA exhibited high viscosity. It seems that interaction between EA and PAA is not high compared to the other three amines. There was a report that EA formed micelle and it formed stable emulsion solution [28]. In general, the solution viscosity increases with increasing particle concentration. In PAA/EA solution, EA might form emulsion that consisted of EA and PAA solution, and it might increase viscosity of PAA/EA. Focusing on amines excluding EA (EDA, DETA, TETA), the viscosity increased with increasing in the number of amino group. It can be thought that these amino groups contribute to PAA condensation by the cross-link. In used amines, TETA worked as the most effective ionic cross-linker.

3.4 Effect of amines as catalyst for sol-gel reaction

In this procedure, the amines were added excess quantity against PAA as the ionic cross-linker. A certain amount of amines works as the cross-linker for PAA, and residue amines work as the catalyst for sol-gel reaction. The residue amines existed in the **template** or between the **template** and ethanol (on the **template** surface), or in ethanol. The residue amines existing on PAA/amine **template** surface can work as the catalyst for sol-gel reaction. The amines near the PAA/amine **template** surface were evaluated by zeta potential, using that PAA has carboxyl groups with negative charge, and while amine has positive charge. When amines exist rather on the PAA/amine **template** surface than in PAA/amine **template**, the zeta potential increases.

Table 2 shows zeta potential of PAA/EA, PAA/EDA, PAA/DETA, and PAA/TETA **template** in ethanol, respectively. As a reference, zeta potential of PAA/ NH_3 **template** was also shown. In Table 2, the zeta potentials of each **template** were -31.3, -2.8, -24.1, -36.5, and -58.6 mV with PAA/EA, PAA/EDA, PAA/DETA, PAA/TETA, and PAA/ NH_3 , respectively. Used all of amines, PAA/amine **template** had the higher zeta potential than PAA/ NH_3 **template**. It indicates that used amines were present in larger amounts on the PAA/amine **template** surface than on the PAA/ NH_3 **template** surface.

The used amines have carbon chain in these structures, and the hydrophobicities are different. The hydrophobicity is very important factor in this procedure. When the used amines have the higher hydrophobicity, the amine exists rather on the PAA/amine **template** surface than in the **template**. The amines near the PAA/amine **template** surface could work as catalyst for sol-gel reaction. The hydrophobicity can be evaluated by octanol/water partition coefficients ($\log \text{Pow}$). With this parameter, higher $\log \text{Pow}$ shows that the reagent has the higher hydrophobicity, and lower $\log \text{Pow}$ shows that the reagent has the higher hydrophilicity. **Table 3** shows $\log \text{Pow}$ of (a) EA, (b) EDA, (c)

DETA, and (d) TETA. In Table 3, log Pow of EA, EDA, DETA, and TETA were -0.27, -1.2, -1.3, and -1.4, respectively. EA had the highest value in the used amines and the log Pow value was nearly zero, which indicates that EA easily dissolves in both water and ethanol. EA dissolved in ethanol works as the catalyst for sol-gel reaction and small dense silica nanoparticles were formed in ethanol in Fig. 2 (a). With EDA, DETA, and TETA, the log Pow values were not excessively high hydrophobicity, and it shows that these amines easily dissolve in water, and hardly dissolve in ethanol. In these amines, EDA has the highest log Pow value, and PAA/EDA had the highest zeta potential. It seems that EDA was present in larger amounts on the PAA/amine **template** surface than other amines. It is thought that EDA worked as the most effective catalyst for sol-gel reaction.

3.5 Effect of amines on the formation silica shell

As discussed above, number of primary and secondary amines and length of hydrocarbon chain of amines affected the **template** size and silica forming speed on the **template** surface. In this procedure, amines worked as the catalyst for sol-gel reaction and the ionic cross-linker for PAA.

With EDA, DETA, and TETA, a part of amines worked as the ionic cross-linker for PAA in the **template** and the **templates** were stabilized. The amine worked as the more effective ionic cross-linker in the PAA/amine **template** than NH_3 than in PAA/ NH_3 **template**, and stabilized PAA/amine solution formed smaller template in ethanol than PAA/ NH_3 **template**. TETA was the most effective cross-linker, because it has four amino groups in the molecular. EDA was the least effective cross-linker in these amines, because it has only two amino groups in the molecular. The residue amines which didn't work as the cross-linker existed in or on the PAA/amine **template**, and the PAA/amine **template** surface amines worked as catalyst for forming silica shell. EDA was present in larger amounts on the PAA/amine **template** surface than other amines, because EDA prefer to exist on the PAA/amine template. TETA was present in fewer amounts on the PAA/amine **template** surface than other amines, because TETA prefers to exist in the PAA/amine **template**. In Fig.2, the primary-amine worked as the more effective catalyst than the secondary-amine. As a result, in catalyst ability, EDA was the most effective catalyst for sol-gel reaction. In cross-link ability, TETA was the most effective cross-linker for PAA condensation.

To confirm the above assumption, TEOS conversion ratio was measured. **Figure 6** shows TEOS conversion ratio from 0h to 10h after addition of 2.0 ml TEOS with PAA/EDA, PAA/DETA, and PAA/TETA templates. As a reference, TEOS conversion ratio with PAA/ NH_3 **template** was shown. With PAA/ NH_3 **template**, the TEOS conversion ratio was 80% at 0h, and 85% at 6h, and then it became almost constant. With PAA/EDA, PAA/DETA, and PAA/TETA templates, the TEOS conversion ratio shows almost same tendency that was 90% at 0h, and 95% at 6h, and then it became almost constant. When amines were used as catalyst, the sol-gel reaction was promoted than using NH_3 as the catalyst. When amines were used, PAA/amine template was stabilized by the ionic

cross-link for PAA. It was evaluated by viscosity measurement in Fig. 5. In addition, when amine was used, the PAA/amine **template** surface catalyst increased. It was evaluated by zeta-potential in Table. 2. With these works, TEOS could be quickly reacted to silica on the PAA/amine **template** surface. With EDA, DETA, and TETA, the TEOS conversion ratio (95%) and silica shell forming speed (2h) were almost same. It showed that both cross-link ability and catalyst ability were important factor on this procedure.

4. Conclusions

HSNPs were successfully synthesized with using the PAA/amines **template**, accompanying with a high TEOS conversion ratio (95%) and shorten reaction time (2 h). In catalyst ability, EDA was the most effective catalyst for sol-gel reaction, because a larger amount of EDA existed on the **template** surface, **and the primary-amine could work as the more efficient catalyst than the secondary-amine**. In cross-link ability, TETA was the most effective cross-linker for PAA condensation, because it has four amino groups in the molecular. Besides, the TEOS conversion ratio and silica shell forming speed of EDA, DETA, and TETA were showed similar. It was clarified that HSNPs can be synthesized at short time with high TEOS conversion ratio by considering the PAA/amine solution viscosity and interaction of amine with alcohol. It can be expected that number of amines affects ability as the PAA/amines solution viscosity and length of hydrocarbon chain affects ability as interaction of amine with alcohol.

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29. (a) ICSC No. 0153, (b) ICSC No. 0269, (c) ICSC No. 0620, (d) ICSC No. 1123

Table 1. Each amine **aqueous solution concentration**

Description	Amine solution	Amine / mmol	total volume / ml
PAA/NH ₃	25% ammonia aq.	20.4	
PAA/EA	70% ethylamine aq.	20.4	
PAA/EDA	Ethylenediamine	10.2	2.00
PAA/DETA	Diethylenetriamine	6.8	
PAA/TETA	Triethylenetetramine	5.1	

Table 2. The zeta potential of the PAA/amine **templates** in ethanol

Description	Zeta potential / mV
(a) PAA/EA	-31.3
(b) PAA/EDA	-2.8
(c) PAA/DETA	-24.1
(d) PAA/TETA	-36.5
(ref) PAA/NH ₃	-58.6

Table 3. The log Pow values of amines [29]

Amines	log Pow
(a) EA	-0.27
(b) EDA	-1.2
(c) DETA	-1.3
(d) TETA	-1.4~-1.66

Fig. 1. Molecular structure of amines; (a) EA, (b) EDA, (c) DETA, and (d) TETA

Fig. 2. The time-dependent changes of transmittance against 500 nm light of prepared silica nanoparticle suspension, which were prepared using EA, EDA, DETA, and TETA as the catalyst for the sol-gel reaction.

Fig. 3. STEM observations of HSNPs by using (a) PAA/EA, (b) PAA/EDA, (c) PAA/DETA, (c) PAA/TETA, and (e) PAA/NH₃, respectively. All scale bars are 100nm.

Fig. 4. The **template** size distribution curves of PAA/amine in ethanol; (a) EA, (b) EDA, (c) DETA, (d) TETA, and (e) NH₃ in ethanol

Fig. 5. The viscosity of PAA mixture; PAA/Water, PAA/NH₃, PAA/EA, PAA/EDA, PAA/DETA, and PAA/TETA

Fig. 6. TEOS conversion ratio from 0 to 10h after addition of TEOS by using PAA/EDA, PAA/DETA, PAA/TETA, and PAA/NH₃ as templates