

Effect of Alcohol Chain Length on Particle Growth in a Mixed Solvent System

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The preparation of micro-sized uniform silica particles by the hydrolysis and condensation of concentrated tetraethylorthosilicate (TEOS) solutions has been studied in various solvent systems (methanol and ethanol with various long-chain alcohols). Ammonium hydroxide was used not only to initiate hydrolysis and condensation of TEOS, but also to provide the particles with a negative, stabilizing surface charge. Long-chain alcohol was introduced to control the hydrolysis/condensation rate and to reduce the polarity of the system (modified seed growth), as well as to stabilize large particles. To prepare large particles with good uniformity, the solvent composition is important because it determines the stability of both small oligomers and grown particles. The concentration of small seed particles suspended in a solvent and the amount of monomer are also found to be important process parameters in controlling the size and morphology of microspheres. No salt was added to change the surface potential of silica particles. Monodispersed spherical silica particles over 2 μm could be obtained. Moreover, a turbidity experiment showed that the silica growth and nucleation proceeded mainly through the reaction of small oligomers rather than monomeric species.

Key words: sol-gel, silica, particle growth, cosolvent.

Introduction

Monodispersed silica particles uniform in size, shape, and composition, have wide applications not only in the field of physical chemistry dealing with the dynamic behavior and stability of particulate systems, but also in industries such as catalyst, chromatography, ceramic, pigment, pharmacy, photographic emulsion, *etc.* These particles have been prepared by the hydrolysis and condensation of silicon alkoxides leading to the formation of a stable suspension.

Stöber et al. developed a system of chemical reactions to produce uniform silica particles by hydrolysis, condensation and subsequent growth of particles in alcoholic solutions with a morphological catalyst such as ammonia [1]. Since his study, a large number of researches have been carried out to elucidate the hydrolysis and condensation mechanisms and find the optimal conditions for the preparation of uniform particles [2-4]. Bogush et al. extended the work of Stöber to establish the ranges of reagent concentrations (silane monomer, ammonia and water) for the preparation of uniform silica particles of a controlled size [5]. The average particle size increased as the concentrations of NH_3 and H_2O increased up to 2 M and 7 M, respectively.

For the preparation of silica particles of uniform sizes using TEOS, various methods have been tried including salt addition process, surfactant addition process [4], and gel-emulsion process [2, 3]. Among these methods, a seed growth technique and a low temperature synthesis showed the most remarkable results. Tan et al. prepared mm-size powders by lowering the reaction temperature to -20°C and using ammonia-saturated alcohol as a solvent [6]. Monodispersed silica particles of 1.9 μm were prepared with good reproducibility, although the process itself was difficult to apply to industrial application. Bogush and Zukoski [7] prepared monodispersed silica particles of up to 1 μm in size by a seed growth technique, but the process needed long reaction time and multi-addition steps. Furthermore, formation of new particles took place when the final particle size exceeded 900 nm. Nishimori et al. prepared 1.2 μm -sized particles with SDS (sodium dodecyl sulfate) as a surfactant [4].

In this paper, we report a more extensive study on the preparation of large monodispersed silica particles that are important for model studies and industrial applications. A modified seed growth technique was introduced to reduce the long reaction steps and to overcome the final particle size limitation. Long-chain alcohols were introduced as cosolvents, which were expected to decrease the overall polarity of the system and to provide a repulsive force between particles. As mentioned by Bogush et al. [5], in the preparation of large particles without coagulation/flocculation, colloidal

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stability is needed. Long-chain alcohols are expected to overcome the Van der Waals attraction between particles. The particle growth proceeds through a condensation process of siloxane substructures that is influenced strongly by the surface potential of the silica particles and the ionic strength of the reaction medium. This paper describes the preparation of uniform silica particles over a wide range of diameters using this simplifying process.

Experimental Procedure

Tetraethyl orthosilicate (TEOS, 98%) was purchased from Aldrich. All reactions and manipulations were carried out under dry inert gas using a standard Schlenk line technique. Alcohols used in experiments are as follows: methanol (Mallinckrodt, 99.9%), ethanol (J. T. Baker, 99.9%), 1-propanol (Hayman Limited, 99.9%), 2-propanol (Junsei, 99%), 1-butanol (Junsei, 99%), 1-hexanol (Junsei, 98.5%), 1-octanol (Junsei, 98%), 1-decanol (Across, 99%), and 1-dodecanol (Across, 99%). Ammonium hydroxide (Mallinckrodt, 29.2%) was used as a catalyst for the hydrolysis and condensation of TEOS. All chemicals were used as received. Distilled and deionized water was used for the preparation of aqueous solutions.

Seed particles were prepared by the Stöber process [1]. The final particle size depended mainly on the initial water and ammonia concentration. Ammonium hydroxide and ethanol were mixed in the reaction vessel, and placed in a constant temperature bath. After the temperature of the reaction solution reached a certain point, TEOS solution was added quickly. Based on the experimental data of Bogush et al. [5], SiO_2 powders from 50 nm to 800 nm were produced.

For the growth experiments, seed particles were suspended in an alcoholic cosolvent, and then the suspension was sonicated for an hour for dispersion. Ammonium hydroxide was added to the reaction vessel that was specially designed to prevent NH_3 evaporation. The suspension was stirred for 1 hr again to activate the surfaces of seed particles. TEOS was added dropwise to the mixture solution (Fig. 1). All the growth experiments were carried out in 2.52 M of NH_3 , 6.12 M of water, and 0.15–1.0 M of TEOS. Monomer concentration, seed content, solvent, and temperature were changed separately while other conditions were fixed.

The size and morphology of the resulting particles were determined with a field emission scanning electron microscope (FE-SEM, JEOL JEM-6340F). A zeta sizer (MALVERN ZETA SIZER 1000) was used to measure the average particle diameter and size distribution of seed particles ($< 1 \mu\text{m}$). For the particles over $1 \mu\text{m}$ in size, a particle sizer (SHIMADZU SALD 2001) was used. All powders were dried under vacuum for 3 hrs at 100°C before the characterization.

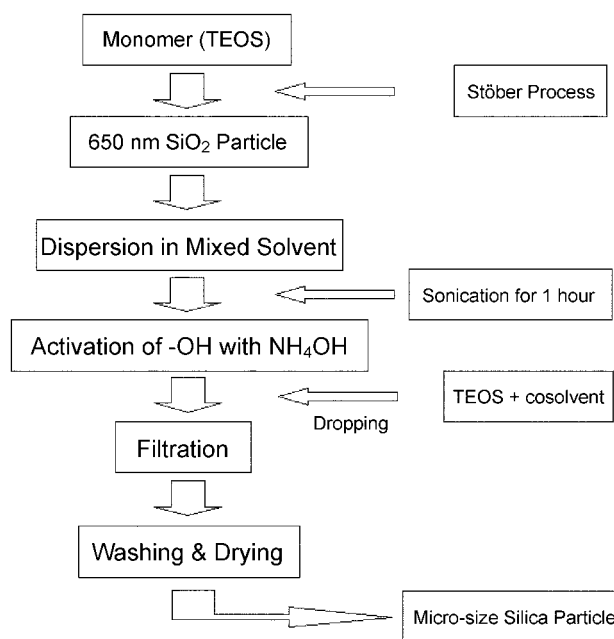


Fig. 1. Schematic flowchart of the modified seed growth.

Results and Discussion

Effect of long-chain alcohol in Stöber process

In a pure alcohol solvent (usually ethanol), the final particle size mainly depended on the initial water and ammonia concentration. Bogush et al. [5] studied the relationships of the final particle size and the concentrations of NH_3 and H_2O . In addition, the properties of alcohol had an important effect on the hydrolysis, condensation rates and the final particle size. Sadasivan et al. [8] and Harris et al. [9] reported that the final particle size increased as the molecular weight of alcohol increased, and assumed that this might be due to the change of viscosity or the polarity of the solvent.

In our experiments, various long-chain alcohols (1-butanol, 1-hexanol, 1-octanol, 1-decanol, and 1-dodecanol) were introduced to investigate the effect of viscosity and dielectric constant of the solvent system on the particle formation mechanism and the final particle size. Long-chain alcohols are expected to have less polarity and viscosity compared with short-chain alcohols.

The effect of long-chain alcohols was examined in the Stöber process at a ratio of methanol to long-chain alcohol of 10. Experimental conditions and dielectric constants of various alcoholic solvents are listed in Table 1 and Table 2.

As shown in Fig. 2, the particle size showed a gradual increase with an increase in the molecular weight and the amount of long-chain alcohol used with methanol. As the dielectric constant of the solvent became lower, the larger particles became stable. Sadasivan et al. showed a close relationship between the average particle size and dielectric constant ϵ [8]. Under a given

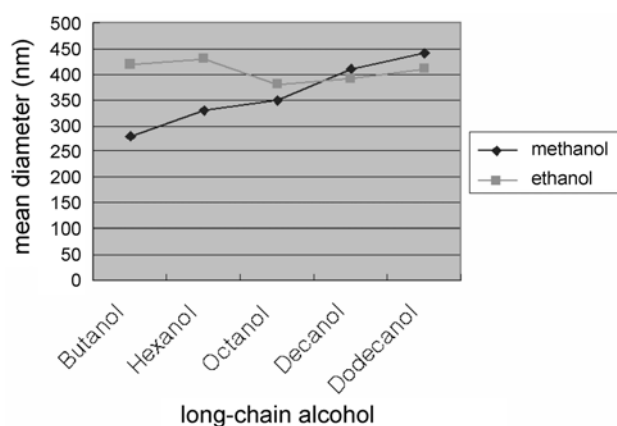
Table 1. The final particle size and turbidity time for five different cosolvents and different cosolvent ratio ($[\text{NH}_3] = 0.50$, $[\text{H}_2\text{O}] = 1.25$, $[\text{TEOS}] = 0.01$, $T = 25^\circ\text{C}$)

Solvent composition		Final particle size (nm)
A0	Methanol	225
A1	Methanol / Butanol (10:1)	280
A2	Methanol / Hexanol (10:1)	330
A3	Methanol / Octanol (10:1)	350
A4	Methanol / Decanol (10:1)	410
A5	Methanol / Dodecanol (10:1)	440
B1	Ethanol / Butanol (10:1)	420
B2	Ethanol / Hexanol (10:1)	440
B3	Ethanol / Octanol (10:1)	380
B4	Ethanol / Decanol (10:1)	390
B5	Ethanol / Dodecanol (10:1)	410

set of conditions, the final particle size was inversely proportional to the value of $(\varepsilon - 1.0)/(\varepsilon + 2.0)$. Using this method, the dielectric constant of the mixed solvent system could be easily estimated.

The particle formation rates in various cosolvent systems were investigated by monitoring the turbidity time when the solution became opalescent. Turbidity time follows an order of $A5 > A4 > A3 > A2 > A1$ and $B4 > B3 > B2 > B1$. As can be seen in Table 1, when the polarity of the solution decreased, the turbidity showed up earlier and larger particles were formed. This resulted from the decreased solubility of soluble silica species with the addition of long-chain alcohols. In the sol-gel process, it has been known that TEOS undergoes hydrolysis to produce soluble silicas. When the concentration of soluble silica particles reaches a critical value, self-nucleation occurs to release the supersaturation. In other words, soluble silica particles condense when they become insoluble in the system. At this stage, the solution becomes turbid. From this experiment, it was concluded that the lowered polarity of the system with the addition of a long-chain alcohol made small silica species (small oligomers) insoluble, entailing the early burst of nucleation. Lowered polarity also made the particles aggregate to each other in order to obtain the colloidal stability. Sadasivan et al. also observed similar result [8].

The turbidity variation (time to get turbid) in this experiment indicated that the particle formation and growth are mainly caused by the reaction of small oligomers. A number of researches have been carried out to elucidate which species (monomers or clusters) are important for the formation of new nuclei and the

**Fig. 2.** Average particle size under different solvent composition.

subsequent condensation to the surface of existing nuclei. Bailey and Mecartney showed that TEOS underwent hydrolysis to form low-density polymers [10]. These low-density polymers grew in size until they became insoluble in alcohol and phase separated to form high-density clusters or seed particles. These seed particles further grew by the aggregation to form smooth spheres. Matsoukas and Gulari proposed a “monomer-addition growth model” to describe the nucleation and growth process. In this model, nucleation was the result of condensation of two hydrolyzed monomers. Once nucleated, the particles grew by the addition of hydrolyzed monomer [11-13]. Bogush and co-workers proposed a “controlled aggregation model”, in which particle formation resulted from the aggregation of subparticles that were slowly produced during the entire reaction period [5, 7]. Van Blaaderen et al. [14] proposed a model in which particle formation was controlled by the aggregation of soluble species. The particle growth involved the “surface-reaction controlled addition of the soluble species” to the particle surface. According to this model, the partially hydrolyzed TEOS monomers underwent polymerization to form clusters of different sizes and degrees of cross-linking until the clusters became insoluble and collapsed.

From the experimental results shown in Table 1, we can conclude that TEOS hydrolyzed into $\text{Si}(\text{OH})_x(\text{OR})_{4-x}$, and condensed into $\text{Si}_x\text{O}_y(\text{OH})_z$ which eventually deposited onto the surface of silica as a growth intermediate. These intermediate molecules grew until they became insoluble in the system. The oligomers, which are not large enough to collapse (when they are stable), can be called soluble species. The solubility of oligomers should depend on their size and the polarity of solvent. The addition of long-chain alcohol reduced the

Table 2. Dielectric constants of alcoholic solvents

	Methanol	Butanol	Hexanol	Octanol	Decanol	Dodecanol
Dielectric constant	33	17.84	13.03	10.3	7.93	5.82

polarity of the solvent causing a short turbidity time and the formation of large particles. This is good evidence that silica growth and nucleation proceed through the condensation reaction of small oligomers. However, the size of the smallest insoluble silica species could not be estimated.

Effect of long-chain alcohol in modified seed growth

For the preparation of uniform, spherical and large particles over 1 μm , a seed growth technique is recommended. However this technique also requires careful control of experimental conditions to avoid nucleation and aggregation. In the growth process, the formation of new particles has to be suppressed. As has been widely studied [15], growth and nucleation are competitive reactions during the monomer addition process. When the concentration of soluble species reaches a critical value, the nucleation occurs to relieve the supersaturation, and if the production rate of the soluble silica species is slow compared to that of the condensation reaction on the existing seed particles, the concentration of soluble silica species remains below the critical value for nucleation and no new particle is formed. Bogush and Zukoski [7] showed from conductivity measurements that the hydrolyzed alkoxide solutions remained highly concentrated until the final stage in the particle growth process. For the preparation of uniform particles, a balance must be maintained between the production rate of reactive species and the condensation rate of these species onto the particle surfaces, so that the concentration of soluble silica species does not exceed the critical nucleation concentration.

In order to optimize the reaction conditions described above, a modified seed growth technique was introduced, through the slow release of monomer by dropping and the use of long-chain alcohol (octanol). The dropp-

Table 3. Conditions for reactant and solvent composition ($[\text{NH}_3] = 2.50$, $[\text{H}_2\text{O}] = 6.25$, $T = 34^\circ\text{C}$)

	Solvent	R ratio	TEOS concentration
C1	Methanol / octanol	1	0.15 M
C2	Methanol / octanol	2	0.15 M
C3	Methanol / octanol	5	0.15 M
C4	Methanol / octanol	12	0.15 M
D1	Ethanol / octanol	1	0.25 M
D2	Ethanol / octanol	2	0.25 M
D3	Ethanol / octanol	5	0.25 M
D4	Ethanol / octanol	12	0.25 M

ing process is expected to maintain the concentration of soluble silica species below the critical nucleation concentration. In contrast with other researches requiring continual addition of monomers at several hours' interval during the growth process, the modified seed growth technique requires only a simple dropping process.

The preparation of large particles without the formation of new particles was achieved by controlling the reaction parameters such as solvent composition, amount of seed, dropping rate, and amount of added monomer. Firstly, the optimal cosolvent composition was investigated at an R ratio in the range of 1-12 (R ratio = $[\text{methanol}]/[\text{octanol}]$ or $[\text{ethanol}]/[\text{octanol}]$). Experimental conditions and SEM images of resulting particles are presented in Table 3 and Fig. 3.

We already demonstrated the effect of solvent polarity on the final particle size. The ionic strength of the reaction medium affects the morphology and the size of particles. Therefore, the amount of octanol added ($\epsilon = 10.30$) should be more than that for a solvent with a high dielectric constant (methanol $\epsilon = 33.0$) compared to a solvent with a low dielectric constant (ethanol $\epsilon =$

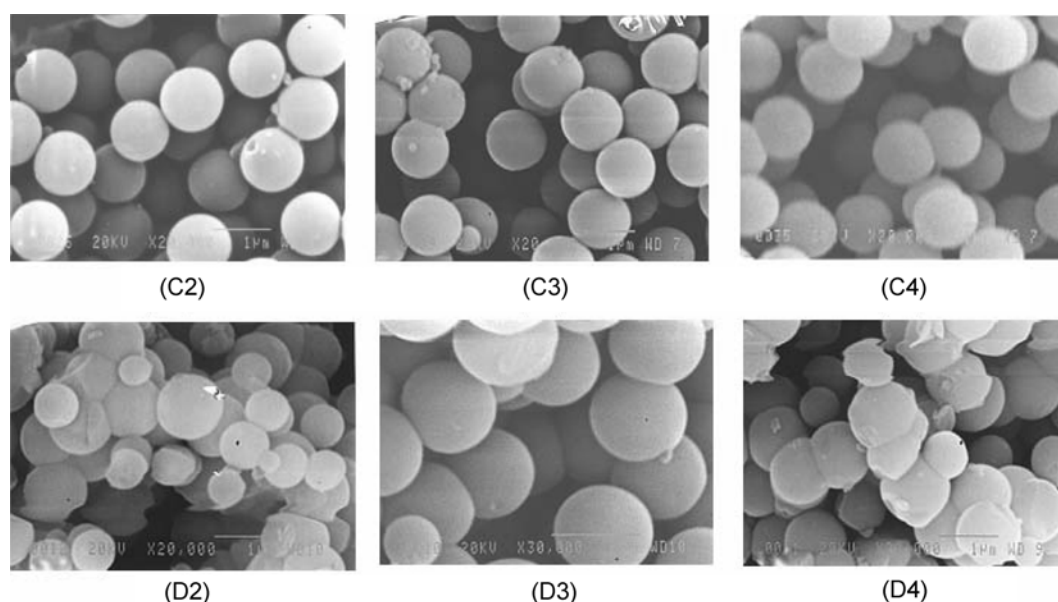


Fig. 3. SEM images of particles grown by the modified seed growth in different solvent system.

Table 4-1. The number density and total surface area in the modified seed growth ($[\text{NH}_3] = 2.52 \text{ M}$, $[\text{H}_2\text{O}] = 6.12 \text{ M}$, $[\text{TEOS}] = 0.76 \text{ M}$, $T = 34^\circ\text{C}$)

Seed	Number density of seeds ($\times 10^{10}/\text{mL}$)	Total external surface of seeds (cm^2/mL)	Final diameter (μm)	Relative standard deviation
0.8 μm	9.325	1875	1.58	1.8

Table 4-2. The number density and total surface area in Chen's method ($[\text{NH}_3] = 2 \text{ M}$, $[\text{H}_2\text{O}] = 6 \text{ M}$, $[\text{TEOS}] = 0.22 \text{ M}$, $T = 25^\circ\text{C}$)

Seed	Number density of seeds ($\times 10^{10}/\text{mL}$)	Total external surface of seeds (cm^2/mL)	Final diameter (μm)	Relative standard deviation
0.9 μm	0.362	93.2	1.56	2.6

25.3), in order for both systems to have identical solvent polarity. The effect of octanol on the morphology and the size of grown particles is shown in Fig. 3. A methanol cosolvent system containing 33% of octanol ($R = 2$), and an ethanol cosolvent system containing 16.7% of octanol ($R = 5$) were optimal conditions for the preparation of stable discrete large particles. In addition, octanol seemed to provide the steric barrier between large particles so that the suspension could be stably dispersed in the solution. The excess amount of octanol, however, caused aggregated particles.

The total surface area of seeds for both systems (C2 and D3) was examined. When the total surface area of seeds is not large enough for the heterocondensation, new particles will be formed. Chen et al. [16] showed that the number density and the surface area were important factors to determine the homo/hetero condensation during the growth of silica particles. They concluded that the larger the total surface area of the seeds, the fewer the newly formed particles during the growth.

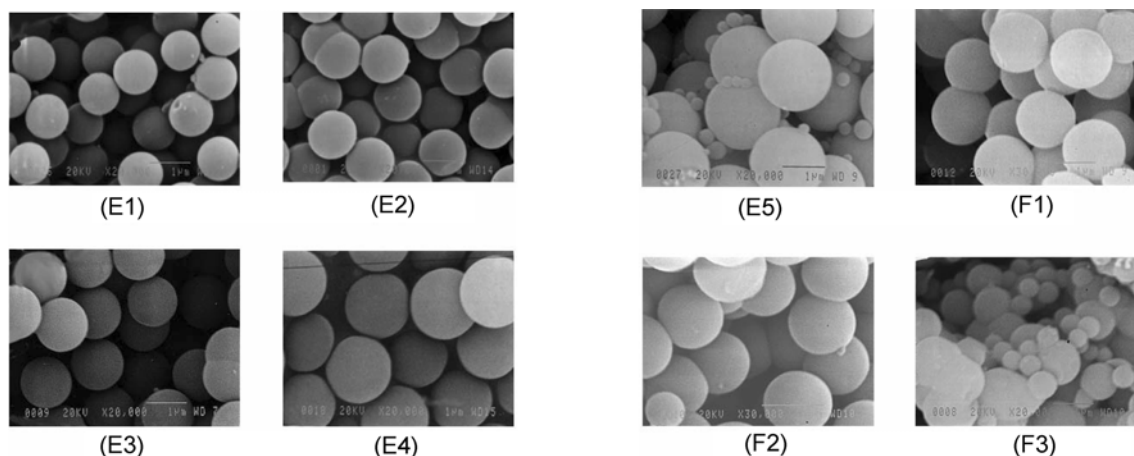
Stable particles were prepared when the total surface area of the seed particles was around $1875 \text{ cm}^2/\text{mL}$, which is the optimum surface area for 800 nm-sized seed particles. When a lower amount of seeds was used, more new particles (nucleation) were observed. On the other hand, the aggregation of particles appeared when the amount of seeds exceeded a critical value.

Table 5. Variation of added monomer concentration and the size of grown particles ($[\text{NH}_3] = 2.50$, $[\text{H}_2\text{O}] = 6.25$, $T = 34^\circ\text{C}$)

	Solvent	R ratio	Monomer concentration (mole/litter)	Uniformity
E1	Methanol / octanol	2	0.15 M	
E2	Methanol / octanol	2	0.25 M	
E3	Methanol / octanol	2	0.4 M	
E4	Methanol / octanol	2	0.75 M	
E5	Methanol / octanol	2	1.0 M	Nucleation
F1	Ethanol / octanol	5	0.15 M	
F2	Ethanol / octanol	5	0.25 M	
F3	Ethanol / octanol	5	0.4 M	Nucleation

Therefore, the large surface area increased the probability of soluble silica reacting with the silica particle surface, while a small surface area caused the particle-particle coagulation. The number density and total surface area of modified seed growth and Chen et al.'s method are listed in Table 4. The total surface area of seeds in our experiment was 20 times larger than that used in Chen et al.'s method.

To maximize particle size without aggregation/nucleation, the monomer concentration was varied. Experimental conditions and SEM images of resulting particles are listed in Table 5 and Fig. 4. In the methanol/octanol system (C2), particles could grow stably up to

**Fig. 4.** SEM images of grown particles with increasing amount of monomer added.

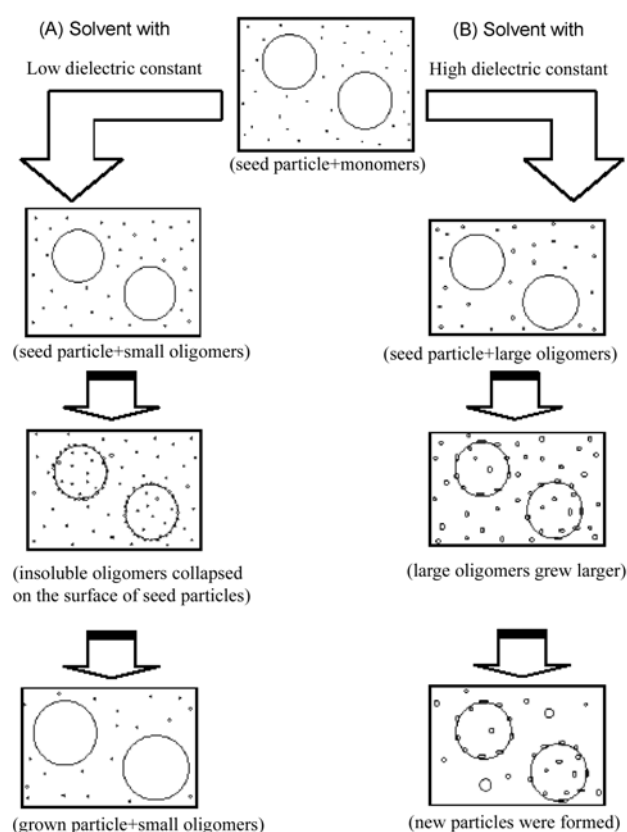


Fig. 5. Scheme of the particle growth in different solvent systems (modified seed growth).

0.75 M TEOS, while in the ethanol/octanol system, particles could grow stably only up to 0.25 M TEOS concentration. In both cases, uniform particles with a diameter of 1.58 μm were produced (Table 5 and Fig.

4). Compared with previous studies (the monomer multi-addition [5] and the excess solvent process [16]), the modified seed growth approach (Fig. 5) was proven to be a simpler and more economical process for the preparation of micro-sized uniform silica particles. SEM images of grown particles by the modified seed growth are shown in Fig. 6.

Conclusions

The proper selection of an alcohol solvent for the preparation of SiO_2 particles was very important with the given $[\text{NH}_3]$, $[\text{H}_2\text{O}]$, and $[\text{TEOS}]$. Particle formation and its growth were influenced strongly by the surface potential of the silica particles and the ionic strength of the reaction medium. A long-chain alcohol hinders hydrogen bonding and provides a repulsive force between particles. The polarity of the solvent is a key factor for the final particle size. The final particle size increased with decreasing solvent polarity. Also, the lowered polarity decreased the solubility of small oligomers in the system, which shortens the turbidity time. From the relationship of dielectric constant and turbidity time, it was concluded that the reaction participating units are small oligomers rather than monomers.

Monodispersed large silica particles were successfully prepared by a modified seed growth method. The reduced polarity induced hetero-condensation reaction, leading to the formation of uniform particles. The process was simple and operated with a high concentration of seeds and added monomer such as to be applicable in industry.

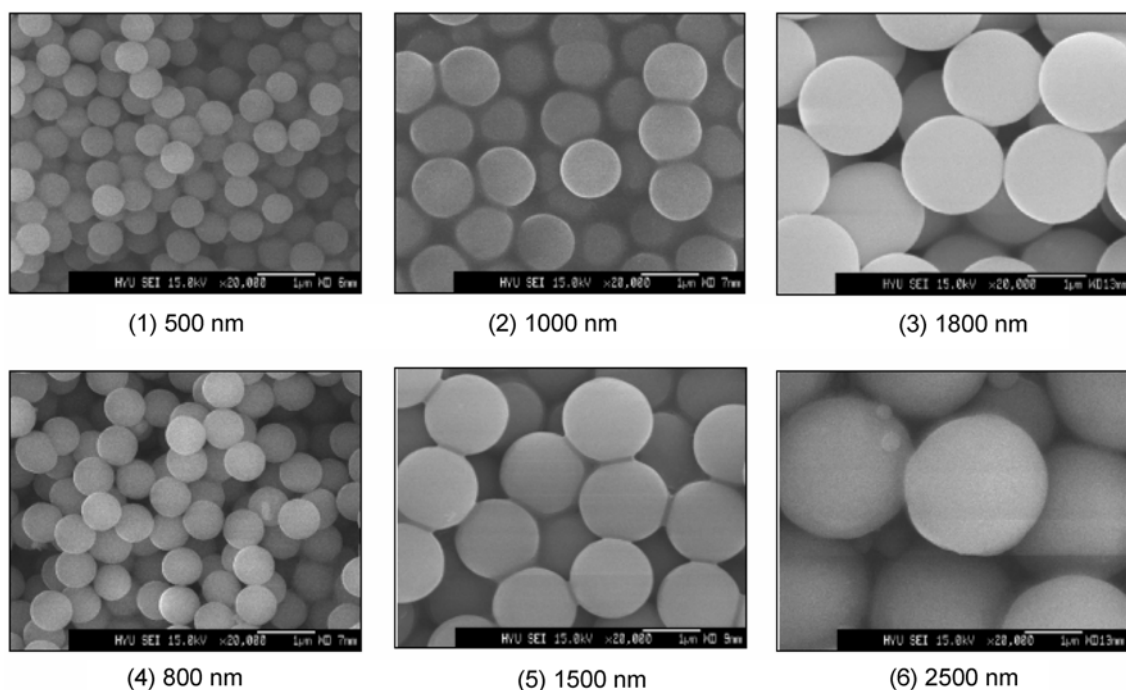


Fig. 6. Monodispersed SiO_2 particles by modified seed growth.

Acknowledgment

Young Sik Lee wishes to acknowledge the support supplied by Kyung Hee University (2003).

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