# FACILE ONE POT SYNTHESIS OF HIGHLY MONODISPERSE SILICA NANOPARTICLES IN WATER BASED MEDIUM

## Oka Pradipta Arjasa and Jarot Raharjo

*Pusat Teknologi Material (PTM) - BPPT*
*Jl. MH. Thamrin 8, Jakarta 10340*
*e-mail: oka.pradipta@bppt.go.id*

## ABSTRACT

**FACILE ONE POT SYNTHESIS OF HIGHLY MONODISPERSE SILICA NANOPARTICLES IN WATER BASED MEDIUM.** Highly monodisperse silica nanoparticles (SNs) were successfully prepared using water based synthesis. The right catalyst and controllable release of silanol compounds into water phase was the two mostimportant parameters in the SNs water based synthesis. The particle size of the SNs produced by this method was easily controlled by changing TetraEthyl OrthoSilicate (TEOS) concentration. The particle size ranging from 60 nm to 200 nm can be prepared in one pot synthesis. The SNs were analyzed by using dynamic light scattering.

*Keywords*: Silica nanoparticles, Highly monodisperse, Water based synthesis, One pot synthesis

## ABSTRAK

**SINTESIS SATU LANGKAH BERBASIS AIR YANG MUDAH UNTUK MEMPEROLEH NANO PARTIKEL SILIKA YANG SANGAT MONODISPERSE.** Nanopartikel silika(SNs)yang sangat monodisperse berhasil disintesa dengan menggunakan sintesis berbasis air. Katalis yang tepat dan pelepasan terkendali senyawa silanol ke fasa air adalah dua parameter yang paling penting dalam sintesis SNs berbasis air.Ukuran partikel dari SNs yang dihasilkan oleh metode ini dengan mudah dikontrol dengan mengubah konsentrasi Tetra Etil OrtoSilikat (TEOS).Ukuran partikel mulai dari 60 nm hingga 200 nm dapat disiapkan dengan satu langkah sintesis. SNs dianalisis dengan menggunakan hamburan cahaya dinamis.

*Kata kunci*: Nanopartikel silika, Sangat monodisperse, Sintesis berbasis air, Satu langkah sintesis

## INTRODUCTION

Colloidal silica spheres uniform in size and shape have been widely used and applied as optical filters, pharmaceutical binders, photographic emulsions, chromatographic agents, sensing elements, catalysts, chemical and mechanical polishing materials, stabilizers and coating layers [1-5].
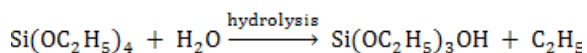
The Stçber process [6] is a well known process to prepare SNs. A lot of nowadays methods used to prepare SNs were inspired by Stçber's work. Stçber use alcohol/water mixture to control the hydrolysis and the condensation of TetraEthyl OrthoSilicate (TEOS). The hydrolysis and condensation reaction of TEOS were catalyzed by ammonia. The technique is proved to have a relatively good control over the particle size and size distribution for low solid contents.

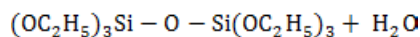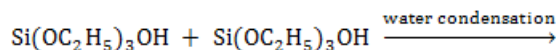However, the Particle Size Distribution (PSD) broadens and the particles become less spherical, for solid contents higher than typically 5 wt% [7]. Therefore there have been numerous method proposed with the main goals were to increase both particle size and solid content while maintaining narrow particle size distributions [8-15].
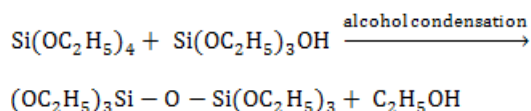
The formation of SNs was often simplified into two main reactions which are the hydrolysis reaction and the condensation reaction.

Hydrolysis reaction:

$$Si(OC_2H_5)_4 + H_2O \xrightarrow{hydrolysis} Si(OC_2H_5)_3OH + C_2H_5$$

Condensation reaction:

$$Si(OC_2H_5)_3OH + Si(OC_2H_5)_3OH \xrightarrow{water\ condensation}$$

$$(OC_2H_5)_3Si - O - Si(OC_2H_5)_3 + H_2O$$

$$Si(OC_2H_5)_4 + Si(OC_2H_5)_3OH \xrightarrow{\text{alcohol condensation}}$$

$$(OC_2H_5)_3Si - O - Si(OC_2H_5)_3 + C_2H_5OH$$

The condensation reaction is fast, difficult to control and it is the reaction that responsible for the formation of three dimensional network or single monodisperse particle [16]. The water condensation is a lot more faster than the alcohol condensation [17]. The pH applied during the reaction is also affecting the SNs produced. Too high pH will make the SNs dissolve and low pH will make SNs unstable [8].

Hartlen et al. (2008) [9] and Yokoi et al. (2006)[12] had been working to produce highly monodisperse SNs by using basic amino acids as catalyst in water medium [9,12]. Yokoi et al. were using lysine while Hartlen et al. were using arginine. Yokoi et al. were using D-, L-forms and their mixture of lysine to control the silica particle sizewhich allowed size variation in a fairly limited range [12]. Hartlen et al. were using regrowth method to get size variation in more wider range [9].

In this paper we report a one stage process to produce highly monodisperse size (low poly dispersity index (PDI)) of SNs ranging from 60 nm to 200 nm. The basic principle in this synthesis method is to maintain the oil phase relatively undistributed. The aim is to control the hydrolysis reaction/the release of silanol into the water phase. Since the condensation reaction is faster than the hydrolysis then it would be easier to control hydrolysis reaction. By doing so, it can control the nuclei population at the early stage of reaction.

## EXPERIMENTAL METHOD

### Chemicals

Diethylenetriamine (DETA, reagent grade) from Acros; tetraethyl orthosilicate (TEOS, 98%) from TCI; Toluene (reagent grade) from Sigma Aldrich, were used as received. Deionized water with pH around 6 was used.

### Instruments

Zetasizer Nano (Malvern Co.) and Goniometer with light scattering system BI-200SM (Brookhaven Instrument Co.) from National Taiwan University of Science and Technology was used to determine the size of the SNs and their uniformity. The samples were diluted 100 times using deionised water. The measurements were conducted at standard room temperature (25 ºC). The temperature was automatically controlled by the instruments.

### Synthesis

The synthesis was performed in 20 mL of closed vial by adding a reagent grade of DETA into deionized

**Table 1.** Experimental setup to study the effect of difference Toluene concentration.

| Experiment | DETA (g) | $H_2O$ (g) | Toluene (g) | TEOS (g) | Reaction time (h) |
|---|---|---|---|---|---|
| T0-D3 | 0.03 | 7 | 0 | 0.62 | 24 |
| T0.5-D3 | 0.03 | 7 | 0.31 | 0.62 | 24 |
| T1-D3 | 0.03 | 7 | 0.62 | 0.62 | 24 |
| T1.5-D3 | 0.03 | 7 | 0.93 | 0.62 | 24 |
| T2-D3 | 0.03 | 7 | 1.24 | 0.62 | 24 |

**Table 2.** Experimental setup to study the effect of difference DETA concentration.

| Experiment | DETA (g) | $H_2O$ (g) | Toluene (g) | TEOS (g) | Reaction time (h) |
|---|---|---|---|---|---|
| D1-T1 | 0.01 | 7 | 0.62 | 0.62 | 48 |
| D3-T1 | 0.03 | 7 | 0.62 | 0.62 | 24 |
| D6-T1 | 0.06 | 7 | 0.62 | 0.62 | 24 |
| D10-T1 | 0.1 | 7 | 0.62 | 0.62 | 24 |

**Table 3.** Experimental setup to study the effect of difference TEOS concentration.

| Experiment | DETA (g) | $H_2O$ (g) | Toluene (g) | TEOS (g) | Reaction time (h) |
|---|---|---|---|---|---|
| T0-D3-HT | 0.03 | 7 | 0 | 3.72 | 48 |
| T0.5-D3-HT | 0.03 | 7 | 1.86 | 3.72 | 72 |
| T1.5-D3-HT | 0.03 | 7 | 1.86 | 1.24 | 48 |
| T0-D3 | 0.03 | 7 | 0 | 0.62 | 24 |
| T0.5-D3 | 0.03 | 7 | 0.31 | 0.62 | 24 |
| T1.5-D3 | 0.03 | 7 | 0.93 | 0.62 | 24 |

**Table 4.** Experimental setup to synthesize high solids content of SNs.

| Experiment | DETA (g) | $H_2O$ (g) | Toluene (g) | TEOS (g) | Reaction time (h) |
|---|---|---|---|---|---|
| T0-D3-HT | 0.03 | 7 | 0 | 3.72 | 48 |
| T0-D6-HT | 0.06 | 7 | 0 | 3.72 | 48 |
| T0-D8-HT | 0.08 | 7 | 0 | 3.72 | 48 |
| T0-D10-HT | 0.1 | 7 | 0 | 3.72 | 48 |

water at the beginning. Then the co-solvent (Toluene) slowly added, followed by the TEOS. Toluene was used as the co-solvent in these experiments because it's poor solubility in water. The term "co-solvent" was used rather than "solvent" is because, beside of its little amount,it act to preserve the TEOS from being distributed in the water (by magnetic stirrer) and at the end of the synthesis process those hydrocarbon liquid will be auto removed or vaporized, leaving only a mixture of nanoparticles, water and probably some ethanol in the form of sol. The solutions were stirred but keep the oil phase relatively undistributed and continued by heating at 60 ºC until the reaction reach completion. The colloidal SNs were filtered without cooling to remove any scrap formed during the synthesis. Finally the colloidal SNs were cooled to room temperature for further analysis. The experimental setups are presented  Table 1 to Table 4.

## RESULTS AND DISCUSSIONS

### The Effect of Co-Solvent

The studies start with synthesizing SNs in aqueous phase with an addition of co-solvent. The aims was to investigate the effect of co-solvent in the
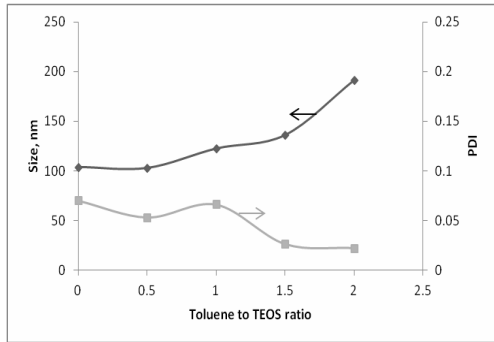
**Figure 1.** The effect of cosolvent concentration on SNs produced. DETA = 0.04 M; TEOS = 0.425 M; reaction time = 24 hours; solid content = 2 wt%.



**Figure 3.** The SNs produced at different DETA concentration. Toluene to TEOS ratio = 1:1; TEOS = 0.425 M; reaction time = 24 hours (48 hours for 0.014 M of DETA); Solid content = 2 wt%.

synthesize process. In order to have stable nuclei growth condition, co-solvent was used. The co-solvent was able to slow down the release of hydrolyzed TEOS in water phase through hydrophobic interaction [9]. The TEOS was aggregated with co-solvent, and the hydrolysis reaction took place at the oil-water interface, while the condensation reactions happened in the water phase because the catalyst used was miscible in the water. Thus condition would slow down the population of nuclei in the water phase and ensured its stability.

As co-solvent concentration increase, the SNs size also increase as shown by Figure 1. The result indicates that the co-solvent works more effectively at higher concentration to slow down the silanol release into the water phase. Hence the water phase was not populated with new silica nuclei. The number of silica nuclei was able to be kept constant and the addition of silanol into the water phase made the existed nuclei to grow. Nevertheless, without the existence of co-solvent the SNs produced still has high uniformity in size at 0.04 M of DETA.

The result apparently would be different for higher concentration of DETA as shown in the next discussion topic. The used of water medium to synthesize monodispersed SNs was considered as a breakthrough and recently only few references available such as Hartlen et al., Yokoi et al., Davis et al. and Snyder et al. which were using basic amino acids as
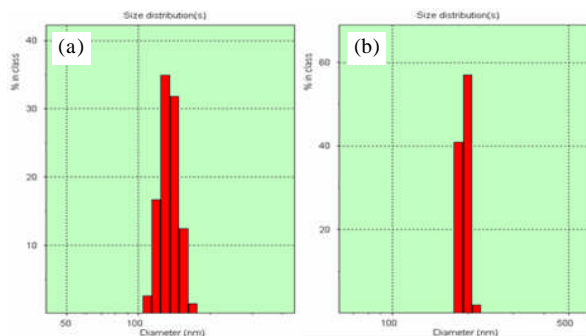
the catalyst [9, 10, 12, 18, 19] and Donatti et al. which were using hydrogen chloride acid as the catalyst [20].

Nevertheless only Hartlen et al. used solvent to guide the hydrolysis reaction of TEOS in water medium. Though they used cyclohexane to slow down the hydrolysis reaction, but the effect given by tolune in these experiments was similar because both are miscible in water. Hartlen et al. also tried to use small amount of ethanol instead of cyclohexane but resulted in rather polydisperse of SNs [9].

## The Effect of DETA Concentration

Higher concentration of DETA increases the hydrolysis rate of reaction, hence the TEOS was consumed faster to form new nuclei and thus population of nuclei in the early stage would also increase. The final SNs will be smaller because more of TEOS was used to form new nuclei (Figure 3). Dense population of nuclei increased the probability of collision between them.

DLS measurement shows that the SNs produced at 0.14 M of DETA was similar like it was found when ammonia was used as the base. The SNs produced had bimodal size distribution (Figure 4).

Observation on the reactor condition reveals that, the big silica particles that existed in the final product



**Figure 2.** (a). Average particle size of 136 nm obtained at 1.5:1 toluene to TEOS ratio, (b). Average particle size of 191 nm obtained at 2:1 toluene to TEOS ratio.
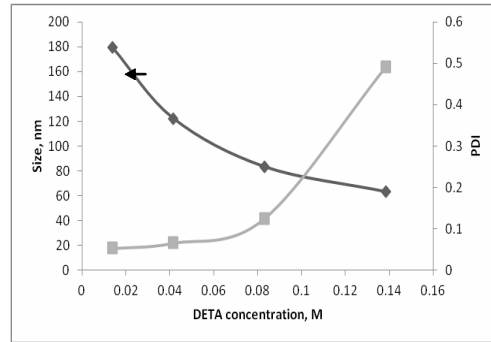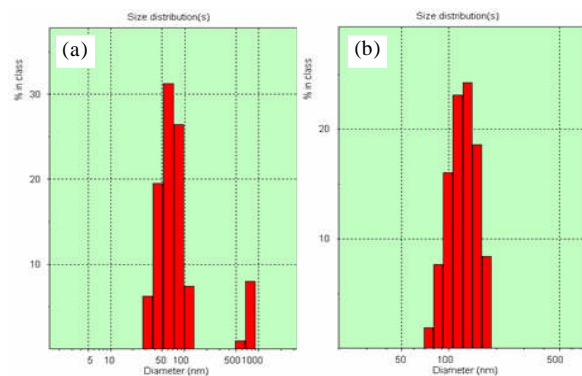


**Figure 4.** PSD of SNs produced at DETA concentration of (a) 0.14 M and (b) 0.04 M. Average Particle size = (a) 71.7 nm; (b) 122.3 nm. Toluene to TEOS ratio = 1:1; TEOS = 0.425 M; Solid content 2 wt%.
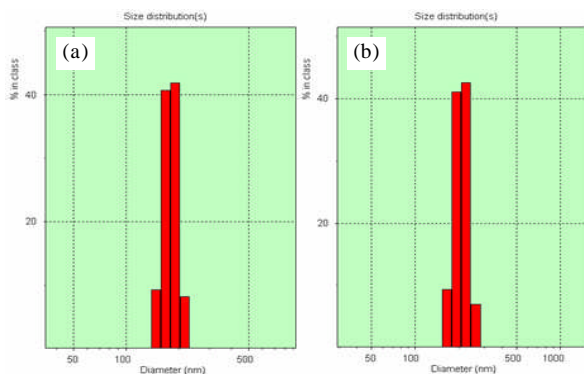
**Figure 5.** PSD of SNs obtained using 0.014 M DETA. (a) 179.4 nm. (b) 209.1 nm. Toluene to TEOS ratio = 1:1; TEOS = 0.425 M; Solid content 2 wt%.

and causing the bimodal size distribution may also cause by the scraps on the reactor wall or the breaking of oil phase in the beginning of reaction. The scrap formation is caused by the SNs, in which attracted and stick to reactor's glass wall. The scrap is found on all of condition used in this study. Nevertheless, several careful run at 0.14 M of DETA cannot diminish the formation of bimodal size distribution. Some of the samples obtained from 0.14 M of DETA were able to form gel. The gel formation should be avoided.

The result indicates that the reaction is more stable at DETA concentration region equal/below 0.08 M. Nevertheless, lower the DETA concentration with constant TEOS concentration means slower reaction rate and thus would increase the size of SNs produced. The reaction at 0.014 M of DETA was extended to 48 h to ensure the completion of reaction and showed bigger particle size than the others in which they had much higher of DETA concentration (Figure 5). This situation have to be consider for synthesizing higher solid content of colloidal SNs.

The result shows in these experiments are reasonable and in good agreement with the previous results [9, 18].Arginine and Lysine had been proved to be good catalyst to synthesize monodisperse SNs in water medium because of their ability to functionalized SNs surface and stabilize them at the water [21]. Their structures are somewhat similar with DETA, having secondary amine groups which enable them to functionalize the SNs surface. In other cases when ammonia was used as the catalyst, the SNs surface were only stabilized by the –OH groups [22] which less effective compare to long chains of amine groups like lysine, arginine and DETA.

## The Effect of TEOS Concentration

Form previous result of experiments, the factors affecting the rate of reaction can be defined. Factors such as DETA concentration and co-solvent concentration play a major role in SNs synthesis. Another factors that did not observed but believed to

**Table 5.** SNs particles obtained from different TEOS concentration at 0.04 M DETA.

| Toluene : TEOS | TEOS (M) | Size (nm) | PDI | SC (wt%) | Reaction time (h) |
|---|---|---|---|---|---|
| 1.5 : 1 | 0.425 | 136 | 0.026 | 2.84 | 24 |
| 1.5 : 1 | 0.85 | 205 | 0.018 | 3.75 | 48 |
| 0.5 : 1 | 0.425 | 103 | 0.053 | 2.86 | 24 |
| 0.5 : 1 | 2.55 | 154 | 0.016 | 7.4 | 72 |
| 0 : 1 | 0.425 | 115 | 0.054 | 2.86 | 24 |
| 0 : 1 | 2.55 | 152 | 0.055 | 8.22 | 48 |

have impact on reaction rate are the mixing rate and the interfacial area between water and oil phase.

Here the TEOS concentration was increase to get higher solid concentration of SNs. The first study was to observe the stability of the reaction at high concentration of TEOS. High reactant concentration surely would increase the rate of reaction.

The experiment was conducted at different TEOS concentration and different co-solvent to TEOS ratio. The results shown at Table 5 suggest that as the TEOS concentration increase, the uniformity of SNs produced do not change. Nevertheless, the trend is showing that the SNs produced are more uniform since it having narrow size distribution. In general, as the oil phase concentration increase (with or without co-solvent) the particle size increase as well and the SNs produced have more narrow size distribution. The result is strengthening the suspected reaction mechanism that at high oil phase concentration, the TEOS is getting strongly held in oil phase. Hence, the hydrolysis reaction is slow and the release of silanol to water phase is also slow. Thus the population of nuclei in water phase is remained at stable population, preventing them to have collision with each other. The stable nuclei are then growing into stable SNs.
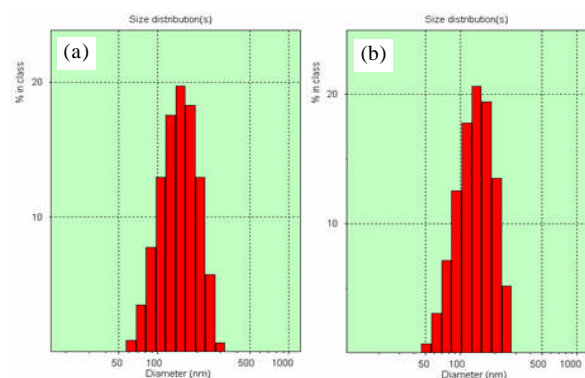


**Figure 6.** PSD of high solid content SNs synthesized at different DETA concentration. (a) 0.11 M DETA, 137 nm; (b) 0.14 M DETA, 125 nm.

**Table 6.** High solid content of SNs synthesized at different DETA concentration.

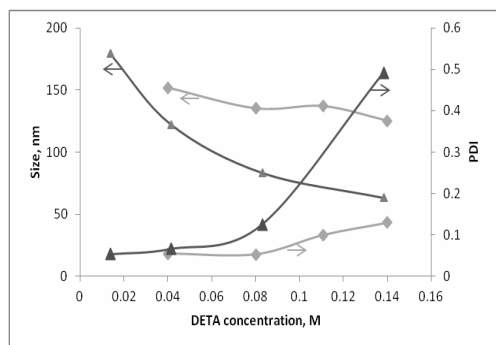| DETA (M) | Size (nm) | PDI | SC (%) | Reaction time (h) |
|---|---|---|---|---|
| 0.04 | 152 | 0.055 | 8.22 | 48 |
| 0.08 | 135 | 0.053 | 11.42 | 48 |
| 0.11 | 137 | 0.100 | 11.40 | 48 |
| 0.14 | 125 | 0.130 | 11.51 | 48 |

***Figure 7.*** SNs synthesized with varying DETA concentration at (▲) 0.425 M and (■) 2.55 M of TEOS. Toluene:TEOS = (▲) 1; Toluene:TEOS = (■) 0.

The experiment was expanded to observe the result of the synthesis without co-solvent at high DETA concentration. The DETA concentration was increase up to 0.14 M where the bimodal size distribution was found. The result is presented in the Table 6. Examples of particle size distribution (PSD) from DLS measurement are presented in Figure 6.

The data from Figure 6 can be joined with the data presented in Table 6 and it strengthen the hypothetical mechanism that an increase in the oil phase have an impact in increasing particle size as well as the stability of the SNs produced (low PDI).

At 2.55 M of TEOS concentration, the inclination of the particle size curvedue to the reduction of DETA concentration was not so steep. The synthesis of 2.55 M of TEOS was performedwithout co-solvent while the synthesis of 0.425 M of TEOS was performed with toluene:TEOS equal to 1. The TEOS at 0.425 M was having difficulties to reach the oil-water interface because of the TEOS molecules had to diffuse through the mass transfer boundary layer resistance in oil phase. Thus would slow down the reaction and made the final size of the SNs produced bigger (Figure 7).Though this method was using water medium but the principle of the reaction control is similar with Stçber method. Stçber method was using ethanol medium with small amount of water [6, 13, 15, 23, 24]. By controlling the amount of water, it was able to limit the hydrolysis reaction and therefore able to control nuclei population .

## CONCLUSION

The method to produce colloidal SNs had been improved based on Stçber method. Using similar method to control the reaction but with different medium than Stçber, and by using miscible co-solvent with the right catalyst, the highly monodisperse SNs can be produced.The Stçber technique is proved to have a relatively good control over the particle size and size distribution for low solid contents. However, the particle size distribution (PSD) broadens and the particles become less spherical, for solid contents higher than typically 5 wt%. The method presented in this paper is able to produce high solid content of colloidal SNs while maintaining their uniformity (low PDI) through one stage synthesis process. The SNs with size variationranging from 60 nm to 200 nm can be prepared in single stage process. Further experiments need to be conducted to know the effect of other parameters such as the temperature and the interfacial area between the oil phase and water phase.

## ACKNOWLEDGE

## REFERENCES

[1].  GOSA, K.-L. and V. URICANU, *Colloids and Surfaces A*: *Physicochemical and Engineering Aspects*, . **197** (1-3) (2002) 257-269

[2].  K.K. UNGER, D. KUMAR, M. GRÜN, G. BÜCHEL, S. LÜDTKE, T. ADAM, K. SCHUMACHER, S. RENKER, *Journal of Chromatography A*, **892** (1-2) (2000) 47-55

[3].  G. LEDER, T. LADWIG, V. VALTER, S. FRAHN, J. MEYER, *Progress in Organic Coatings*, **45** (2-3) (2002) 139-144

[4].  H.T. CHUA, K.C. NG, A. CHAKRABORTY, N.M. OO, M.A. OTHMAN, *Journal of Chemical & Engineering Data*, **47** (5) (2002) 1177-1181

[5].  VATTA, L.L., J. KRAMER, and K.R. KOCH, *Separation Science and Technology*, **42** (9) (2007) 1985-2002

[6].  STÖBER, W., A. FINK, and E. BOHN, *Journal of Colloid and Interface Science,* **26** (1) (1968) 62-69

[7].  S. KANG, S.I. HONG, C.R. CHOE, M. PARK, S. RIM, J. KIM, *Polymer*, **42** (3) (2001) 879-887

[8].  BERGNA, H.E. and W.O. ROBERTS, *Colloidal Silica Fundamentals and Applications*, New York: Taylor & Francis Group, LLC (2006)

[9].  HARTEN, K.D., A.P.T. ATHANASOPOULOS, and V. KITAEV, *Langmuir*, **24** (2008) 1714-1720

[10]. YOKOI, T., et al., *Chemistry of Materials,* **21** (2009) 3719-3729

[11]. IBRAHIM, I.A.M., A.F.F. ZIKRY, and M.A. SHARAF, *Journal of American Science*, **6** (11) (2010) 985-989

[12]. T. YOKOI, Y. SAKAMOTO, O. TERASAKI, Y. KUBOTA, T. OKUBO, T. TATSUMI, *Journal of the American Chemical Society*, **128** (42) (2006) 13664-13665

[13]. K.S. RAO, K. EL-HAMI, T. KODAKI, K. MATSUSHIGE, K. MAKINO, *Journal of Colloid and Interface Science*, **289** (1) (2005) 125-131

[14]. L. SINGH, S. BHATTACHARYYA, G. MISHRA, S. AHALAWAT, *Applied Nanoscience*, **1** (3) (2011) 117-122

[15]. X.-D. WANG, Z.-X. SHEN, T. SANG, X.-B. CHENG, M.-F. LI, L.-Y. CHEN, Z.-S. WANG, *Journal of Colloid and Interface Science*, **341** (1) (2010) 23-29

[16]. R. LINDBERG, G.R. SUNDHOLM, B. PETTERSEN, J. SJO¨BLOM, S.E. FRIBERG, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **123-124** (0) (1997) 549-560

[17]. KIM, K.-S., J.-K. KIM, and W.-S. KIM, *Ceramics International*, **28** (2) (2002) 187-194

[18]. M.A. SNYDER, J.A. LEE, T.M. DAVIS, L.E. SCRIVEN, M. TSAPATSIS, *Langmuir*, **23** (20) (2007) 9924-9928

[19]. T.M. DAVIS, M.A. SNYDER, J.E. KROHN, M. TSAPATSIS, *Chemistry of Materials*, **18** (25) (2006) 5814-5816

[20]. DONATTI, D. and D. VOLLET, *Journal of Sol-Gel Science and Technology*, **17** (1) (2000) 19-24

[21]. PATWARDHAN, S.V. and S.J. CLARSON, *Inorg. Organomet Polym.*, **13** (1) (2003) 49-53

[22]. BRAMBILLA, R., F. SILVEIRA, and J.H.Z. DOS SANTOS, *Investigating Morphological Changes on Octadecyl Modifiedsilicas by SEM and AFM*, (2007)

[23]. BOGUSH, G.H., M.A. TRACY, and C.F. ZUKOSKI IV, *Journal of Non Crystalline Solids,* **104** (1) (1988) 95-106

[24]. G. CANTON, R. RICCO, F. MARINELLO, S. CARMIGNATO, F. ENRICHI, *Journal of Nanoparticle Research*, **13** (9) (2011) 4349-4356