



## Investigating the Effect of Ultrasonication Time on Transition from Monolithic Porous Network to Size-Tunable Monodispersed Silica Nanosphere in Stöber Method

M. Nangir, A. Massoudi\*, S.A. Tayebifard

Semiconductors department, Materials and Energy Research Center, P.O. Box 14155/4777, Tehran, Iran.

### PAPER INFO

#### Paper history:

Received 04 January 2019

Accepted in revised form 08 April 2019

#### Keywords:

Stöber method  
Ultrasound  
Porous Network  
Ammonia  
Silica  
Nanosphere

### ABSTRACT

Uniform colloidal monodispersion of silica nanospheres were synthesized via Stöber method using ammonia as a basic catalyst. The effect of TEOS, EtOH, and H<sub>2</sub>O concentrations on the particle size and morphology were investigated. On the results, increasing in ultrasonication time as a new parameter from 12 to 45 min led to transition from monolithic porous network to homogenous nanospheres due to possessing enough time for micelle growth. Decreasing in TEOS concentration from 0.067 to 0.012 mol L<sup>-1</sup> and increasing in H<sub>2</sub>O concentration from 3 to 14 mol L<sup>-1</sup> at NH<sub>4</sub>OH concentration of 14 mol L<sup>-1</sup> accelerated the rate of hydrolysis and condensation of [Si (OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub>-X(OH)X]. Also, EtOH solvent prevented micelle aggregation and formed the spheres with the smallest variance in the size distribution.

## 1. INTRODUCTION

Silica nanostructures have been occupied a prominent position in various scientific and industrial applications due to their various properties such as biocompatibility, hydrophilicity, chemical-mechanical stability, short-time production, and other unique known properties. Using as catalyst (1), humidity sensors (2), corrosion resistance substance (3) drug delivery system (4) and also using in food industry (5), are some important applications of silica nanostructures.

Among the different nanostructures, colloidal silica or monodispersed silica nanoparticle is particularly a popular structure due to the monodispersity and controllability in particle size distribution. The narrow and uniform size distribution of silica nanoparticles, that is the main reason for their various applications, can be tuned by changing the synthesis conditions such as precursor concentration, basic or acidic catalysts, hydrolysis environment, temperature, and processing time (6).

Previously, Chemical route or bottom-up approach such as sol-gel was introduced as a conventional method to produce silica nanoparticle from atomic or molecular scale (7). There are also other methods such as reverse

microemulsion (8) and sonochemical (9) which have been reported for synthesis of spherical and monodispersed silica nanoparticles from an aqueous alcoholic solution.

In the sol-gel process, an inorganic amorphous network is prepared in aqueous solution (sol) by hydrolysis/condensation reactions at low temperatures in the presence of ammonia, potassium hydroxide, sodium hydroxide, hydrofluoric acid or sulfuric acid as a basic or acidic catalyst (10). Transition from colloidal sol to integrated network (gel) is carried out by casting into a mold. Finally, the wet gel is converted into dense particles through heat-treatment and drying (11). Nucleation and growth, the two main steps in the formation and homogeneity of particles, are controlled by hydrolysis and condensation rate (12). In sonochemical method, nucleation of silanol micelles is taken using organic solvent in an acoustic bath. While, in the microemulsion route, using a high concentration of surfactants caused a decrease in particle size distribution (the limiting factor for scaling-up) (8, 9).

Stöber route was firstly developed by Stöber et. al. as a superior process based on NH<sub>4</sub>OH as a basic catalyst for micelles nucleation and monodispersed silica particles growth (13, 14). In this method, uniformity of particle

\* Corresponding Author Email: [massoudi.a@gmail.com](mailto:massoudi.a@gmail.com) (A. Massoudi)

shape is controlled by the concentrations of Tetraethyl orthosilicate (TEOS), Ethanol (EtOH), ammonia (NH<sub>4</sub>OH), and water, followed by Bogush (15). High concentrations of ammonia and water provide OH<sup>-</sup> ions to exchange with four -OC<sub>2</sub>H<sub>5</sub> functional groups in Tetraethyl orthosilicate, causing formation of the homogeneous siloxane polymeric gel; thus it plays a crucial role in formation of homogenous spheres. Using ultrasonic bath in whole of particle formation process causes cavitation phenomenon and subsequently nanobubble formation in the solution. These nanobubbles react with surface of particles, and lead to create pores on the surface (9, 16). Recently, Salavati-Niasari et. al. have shown that increasing the ultrasonication time leads to growth of micelles (17). To best of our knowledge, there is not any report about finding critical time for nuclei growth.

In this work, nanospherical silica particles were synthesized via Stöber method through variation of TEOS, water, and EtOH concentrations. Effect of ultrasonication time on formation of nanospheres and nucleation growth were investigated. Furthermore, the mechanism of hydrolysis of silicon alkoxide, micelle nucleation and condensation of silicic acid has been explained.

## 2. EXPERIMENT

### 2.1. Synthesis of Silica Nanoparticles

Silica nanoparticles were synthesized by hydrolysis of TEOS (99.98% purity, Merck, Germany) in an aqueous alcoholic solution in the presence of ammonium hydroxide (NH<sub>4</sub>OH, 28%, Merck, Germany). First, Ethanol (EtOH, 96%, Hamoonteb, Iran) and deionized water were mixed, and then after 10 min, TEOS was added to the solution, and then, Twenty minutes later, NH<sub>4</sub>OH (14M) was added and the mixture was sonicated for several minutes. This process was done in an ultrasonic bath. SiO<sub>2</sub> nanoparticles were subsequently obtained after heat treatment at 100 °C for 3 hours. The molar ratio of reaction components and process time are tabulated in table 1.

### 2.2. Materials Characterization

Phase structure of the prepared samples was investigated by X-ray diffractometer (Phillips pw 3710, German) with Cu K<sub>α</sub> radiation (λ=1.54 Å) at 0.02 °/min in the 2θ the ranges of 5° to 85°. The morphology of nanoparticles was characterized by Field-Emission Scanning Electron Microscope (MIRA3 TESCAN). Elemental characterization of samples was identified by Energy dispersive X-ray spectroscopy (EDS) (MIRA3 TESCAN).

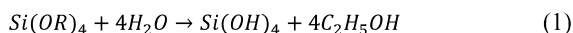
## 3. RESULTS AND DISCUSSION

### 3.1. The formation mechanism of Spherical silica particles

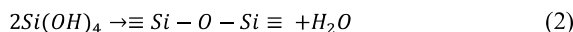
In the present synthetic system, variation of TEOS, EtOH and water concentrations as well as ultrasonication time played important roles in tuning particle size of SiO<sub>2</sub> as previously introduced by Bogush et. al. (15). As well perceive from table 1, SiO<sub>2</sub> particles with 330 nm size were synthesized by 0.067M TEOS, 3M water and 8M EtOH during 75 minutes (sample 7). An increase in TEOS concentration from 0.067M to 0.012M at the same condition, caused a decrease in the particle size of colloidal monodispersed SiO<sub>2</sub> from 330 to 65 nm (sample 6). Note that NH<sub>4</sub>OH concentration was constant throughout the experiment (14M). Additionally, it was observed that increasing water and TEOS concentrations to 14M and 0.045M, respectively, at constant EtOH concentration of 4M enabled to form smaller particles with size of 10±1 nm. The high dielectric constant of EtOH (24.3) increases the static repulsive force between nuclei and hence prevents aggregation of nuclei which leads to formation of smaller particles. The effect of EtOH polarity on prepared particle aggregation was also reported by Wang et. al. (16).

In the sol-gel method, there are two main processes including hydrolysis and condensation of a precursor that cause to micelle nucleation and formation of colloidal particles. The existence of acid and base as a catalyst accelerates the chemical reaction rate. As mentioned by Rahman, in Stöber method, NH<sub>4</sub>OH as a base catalyst provides OH<sup>-</sup> ions that leads to accelerating TEOS hydrolysis (12). The steps of SiO<sub>2</sub> synthesis are summarized in two below reactions and also schematically were illustrated in Figure 1.

Hydrolysis and formation of silicic acid:



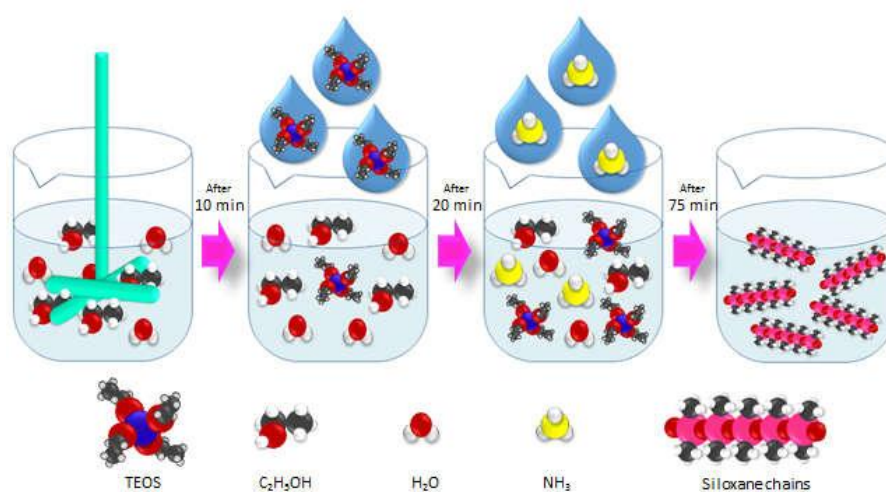
Condensation and formation of siloxane bridges:



Hydrolysis of silicon alkoxide (Si(OR)<sub>4</sub>) with one molecule of water causes to replacement of one OR<sup>-</sup> group with one OH<sup>-</sup> group, which will result in formation of silanol with a chemical formula of (Si(OR)<sub>3</sub>OH) and one molecule of EtOH as a byproduct. A complete hydrolysis and formation of a silicic acid monomer require four OH<sup>-</sup> agents. Adding ammonia catalyst accelerates hydrolysis reaction by providing four OH<sup>-</sup> ions to form the symmetric silicic acid monomer (Si(OH)<sub>4</sub>). Formation of Si(OH)<sub>4</sub> is the main reason for the preparation of spherical particles. In low concentrations of NH<sub>4</sub>OH, hydrolysis reaction

accomplishes slowly. Therefore, there will be the facility to form the non-symmetric molecular form of  $\text{Si}(\text{OR})_{4-x}(\text{OH})_x$ , which is the main reason of aggregation and formation of non-spherical particles. Furthermore, condensation of  $\text{Si}(\text{OH})_4$  monomer in the presence of ammonia causes to form siloxane polymeric gel, and thereby  $\text{SiO}_2$  nanosphere (16). Figure 2a shows the X-ray

diffraction patterns of silica particle synthesized with TEOS at 0.067M concentration. The broad peak at about  $26^\circ$  was adopted with PDF #47-0715 reference card number. An amorphous lattice structure was mentioned for the synthesized silica owing to the large width of the peak at the half height.



**Figure 1.** The process of silica particles formation synthesized by Stober method

Figure 3 shows the energy dispersive X-ray spectroscopy of sample 4. It can be clearly observed that there is no additional peak corresponded to impurity. Moreover, the weight percentages of the Si and O elements confirm formation of the  $\text{SiO}_{2.5}$  composition.

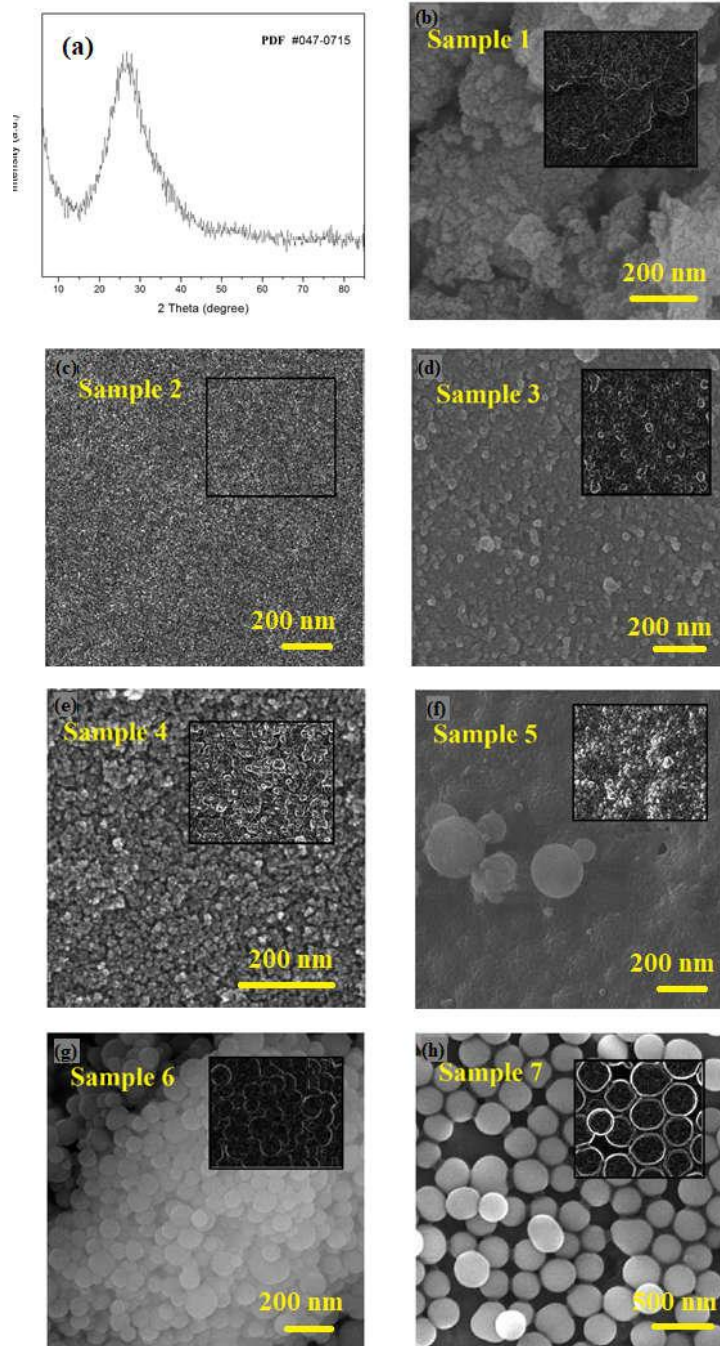
### 3.2. The Effect of Ultrasonication Time

Figure 2b-e show the morphology of spherical silica particles that were treated by ultrasound at 12, 20, 45, and 75 min in the presence of 4M EtOH, 0.045M TEOS,  $[\text{H}_2\text{O}]/[\text{TEOS}]=311$ , and 14M  $\text{NH}_4\text{OH}$ . Figure 2b shows that a monolithic porous network was formed after 12 min of ultrasonication. Porosity of the structure was clearly illustrated in the legended picture. Non-existence of distinctive edge for micelles and forming cohesion structure during 12 min of ultrasonication led to name the structure "monolithic porous network". As the time was increased to 20 min, the transition from porous network to separate particles took place. The narrow size distribution of particles was measured to be  $6.5 \pm 1.5$  nm in 20 min. It seems that 20 min of ultrasonication is the optimum time for preparation of particles and starting micelle growth. After 45 min of sonication, the size distribution of nanoparticles was shifted to  $30 \pm 7.5$  nm because the micelles had enough time for growth. Agglomeration and non-uniformity was also observed in particles after 45 min of ultrasonication. The effect of

ultrasonication time on the trends of average size of spherical silica nanoparticles is listed in Table 1. Increasing the ultrasonication time from 45 to 75 min resulted in the homogeneous and narrow size distribution particles with spherical morphology. After 75 min, most of particles were uniformly synthesized with a size of about 10 nm. Salavati-Niasari et. al. had also concluded that increasing ultrasonication time can affect the morphology and size distribution of the particles (17).

### 3.3. The Effect of EtOH Concentration

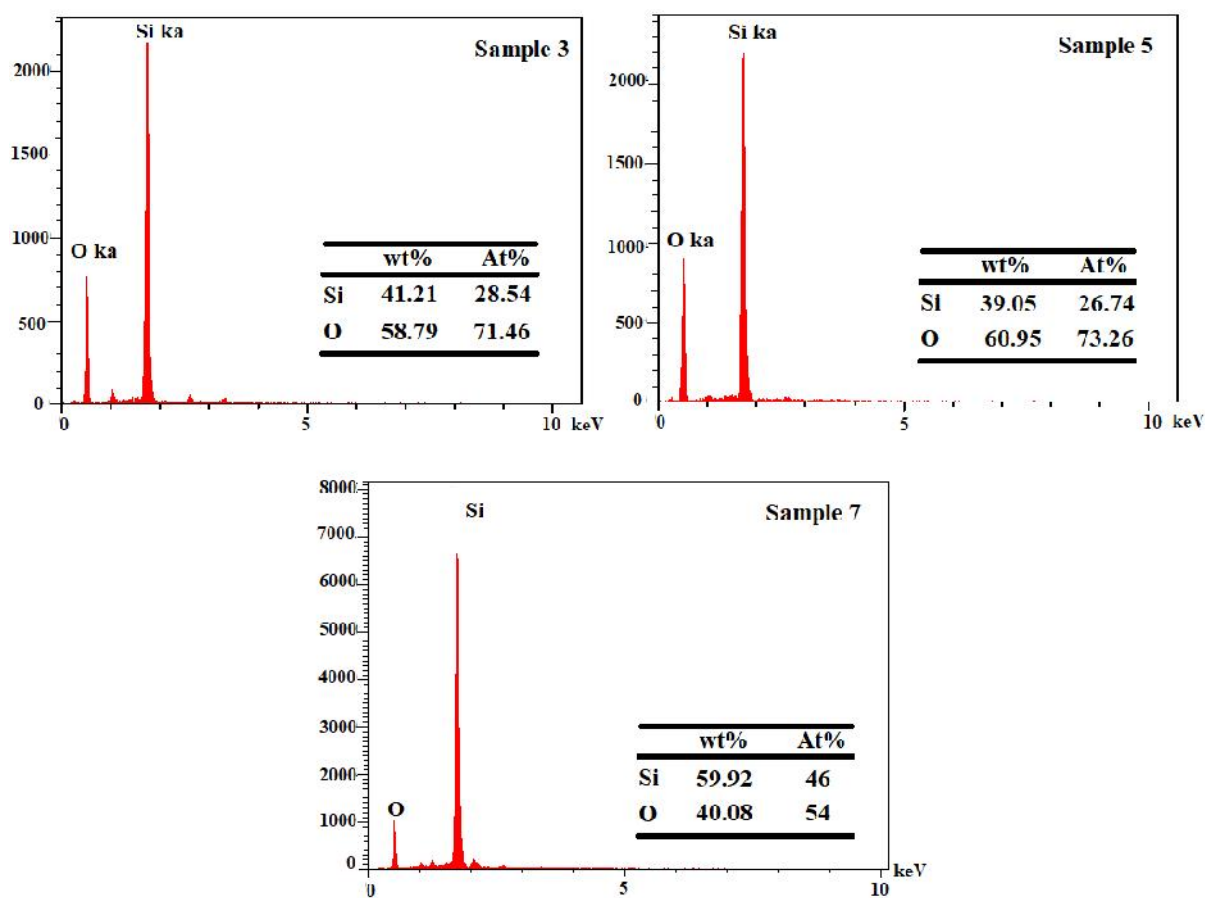
The effect of solvent concentration was investigated between sample 4 and sample 5 under experimental conditions of 0.045M TEOS, 14M  $\text{NH}_4\text{OH}$ , and 14 M  $\text{H}_2\text{O}$ . The results are shown in Figure 2e-f and Table 1. Increasing EtOH concentration from 4M to 8M caused an increment in particle size of colloidal monodispersed silica from  $10 \pm 1$  nm to  $20 \pm 6.5$  nm. High dielectric constant of EtOH (24.3) increases the static repulsive force between nuclei and hence, it prevents the aggregation of nuclei. Production of additional EtOH as a byproduct during hydrolysis helped to further hydrolysis of seeds and formation of the more monomers. Thereby, larger particles were synthesized after condensation and drying at higher concentrations. Wang et. al. also reported the effect of EtOH polarity on aggregation of prepared particle (16).

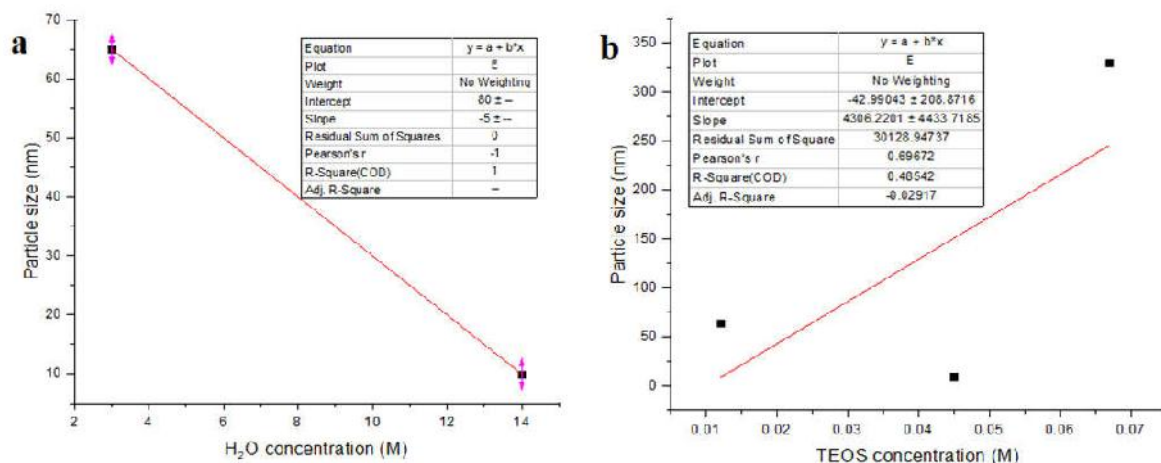


**Figure 2.** (a) The X-ray diffraction patterns of silica synthesized with TEOS at 0.067M concentration; and FESEM images of synthesized silica particles at 0.045M TEOS, 4M EtOH, and 14M H<sub>2</sub>O during (b) 12 min, (c) 20 min, (d) 45 min, and (e) 75 min ultrasonication; (f) the synthesized particles at 0.045M TEOS, 8M EtOH, and 14M H<sub>2</sub>O during 75 min; (g) the synthesized particles at 0.012M TEOS and (h) 0.067M TEOS at 8M EtOH and 3M H<sub>2</sub>O. The legended pictures on every micrograph illustrate the particles edge.

**TABLE 1.** Experimental conditions of monodispersed SiO<sub>2</sub> particles synthesis

Exp.	Name	Exp. Conditions					Results	
		Time (min)	EtOH (M)	TEOS (M)	[H <sub>2</sub> O]/[TEOS]	NH <sub>4</sub> OH (M)	Particle size (nm)	SD (± nm)
1	Sample 1	12	4	0.045	311	14	Porous network	-
2	Sample 2	20	4	0.045	311	14	6.5	1.5
3	Sample 3	45	4	0.045	311	14	30	7.5
4	Sample 4	75	4	0.045	311	14	10	1
5	Sample 5	75	8	0.045	311	14	20	6.5
6	Sample 6	75	8	0.012	250	14	65	30
7	Sample 7	75	8	0.067	45	14	330	120

**Figure 3.** The EDS patterns of three arbitrary samples of synthesized silica nanoparticle



**Figure 4.** Effect of concentration of (a) TEOS and (b) H<sub>2</sub>O on the particle size

### 3.4. The Effect of Water Concentration

Figure 2f-g compares the average particle size of colloidal monodispersed silica particles at 3M and 14M concentrations of water.

The uniform size distribution of silica particles at 0.045M TEOS, 8M EtOH and 14M water was measured to be 20 nm. When water concentration was decreased to 3M in the presence of 8M EtOH and 0.012M TEOS, the particle size of monodispersed silica was significantly increased to 65 nm. Decreasing water concentration caused the hydrolysis rate of TEOS to slow down and decreased nucleation of silicic acid micelles. The latter (decrease in nucleation) occurred because silicon alkoxide molecules were not quickly surrounded by numerous water molecules and thereby, particle size was increased (Figure 4a). The effect of water concentration increment on decreasing particle size was also reported by Matsoukas (18).

### 3.5. The Effect of TEOS Concentration

In term of the tuning size distribution, the effect of TEOS concentration was investigated [14]. TEOS concentration plays a crucial role on the nucleation rate of silicic acid micelles. As can be seen in Figure 2h, 330 nm-monodispersed particles could be prepared at 0.067M TEOS. Decreasing TEOS concentration from 0.067M to 0.012M in the presence of 8M EtOH, 3M water and 14M NH<sub>4</sub>OH caused the particle size to decrease from 330 nm to 65 nm (Figure 2g); because the number of silicon alkoxide molecules for hydrolysis and micelle nucleation was dramatically decreased from  $0.403 \times 10^{23}$  molecules at 0.067M TEOS to  $0.072 \times 10^{23}$  molecules at 0.012M TEOS in the presence of  $18 \times 10^{23}$  molecules of water at 3M concentration. Subsequently, the intermediate (product) (Si(OR)<sub>3</sub>OH) would be increased rapidly, and consumed quickly by condensation reaction; Thus, the

total number of nuclei would be less and particle size would be relatively larger (19). The particles edge recognized in the legend of each FESEM picture shows the smooth or rough surface of particles, agglomeration and better characterization of size measurement. Figure 4b shows the particle size variation versus TEOS concentration. It can be observed that particle diameter was increased as the TEOS concentration increased. The positive effect of increment in TEOS concentration on increasing particles size have been confirmed by Wang et al. (16).

## 4. CONCLUSION

Silica nanospheres were synthesized via Stöber method at a constant NH<sub>4</sub>OH concentration of 14M. The particle size was in the range of 6.5-330 nm. The XRD and EDS results clearly confirmed an amorphous lattice structure with SiO<sub>2-δ</sub> composition. The effect of different concentrations of TEOS, EtOH, H<sub>2</sub>O, and also ultrasonication time on the particle size and morphology were investigated. Increasing of ultrasonication time as a new parameter led to transition from monolithic porous network to homogenous nanospheres. Increment in TEOS and H<sub>2</sub>O concentrations caused the particle size to increase due to fast consumption of silicic acid micelles through condensation reaction. Moreover, increasing in EtOH concentration caused to increase particle size because of further micelles hydrolysis.

## ACKNOWLEDGEMENT

The authors acknowledge the Institute of Materials and Energy (MERC) in Tehran, Iran for funding of this research.

## REFERENCES

- Joo S.H., Park J.Y., Tsung C.-K., Yamada Y., Yang P., Somorjai G.A., "Thermally stable Pt/mesoporous silica core-shell nanocatalysts for high-temperature reactions", *Nature Materials*, Vol. 8, No. 2, (2009), 126-31.
- Wu Y., Chen C., Liu S., "Enzyme-functionalized silica nanoparticles as sensitive labels in biosensing", *Analytical Chemistry*, Vol. 81, No. 4, (2009), 1600-7.
- Vijayalakshmi U., Vaibhav V., Chellappa M., Anjaneyulu U., "Green synthesis of silica nanoparticles and its corrosion resistance behavior on mild steel", *Journal of the Indian Chemical Society*, Vol. 92, No. 5, (2015), 675-8.
- Slowing I.I., Vivero-Escoto J.L., Wu C.-W., Lin V.S.-Y., "Mesoporous silica nanoparticles as controlled release drug delivery and gene transfection carriers", *Advanced Drug Delivery Reviews*, Vol. 60, No. 11, (2008), 1278-88.
- Bernardos A., Kourimska L., "Applications of mesoporous silica materials in food—a review", *Czech Journal of Food Sciences*, Vol. 31, No. 2, (2013), 99-107.
- Zainala N.A., Shukor S.R.A., Wabb H.A.A., Razak K., "Study on the effect of synthesis parameters of silica nanoparticles entrapped with rifampicin", *Chemical Engineering*, Vol. 32, (2013).
- Reverchon E., Adami R., "Nanomaterials and supercritical fluids", *The Journal of Supercritical Fluids*, Vol. 37, No. 1, (2016), 1-22.
- Bagwe R.P., Yang C., Hilliard L.R., Tan W., "Optimization of dyed silica nanoparticles prepared using a reverse microemulsion method", *Langmuir*, Vol. 20, No. 19, (2004), 8336-42.
- Masjedi-Arani M., Ghanbari D., Salavati-Niasari M., Bagheri S., "Sonochemical synthesis of spherical silica nanoparticles and polymeric nanocomposites", *Journal of Cluster Science*, Vol. 27, No. 1, (2016), 39-53.
- Dorcheh A.S., Abbasi M., "Silica aerogel; synthesis, properties and characterization", *Journal of Materials Processing Technology*, Vol. 199, No. 1-3, (2008), 10-26.
- Gurav J.L., Jung I.-K., Park H.-H., Kang E.S., Nadargi D.Y., "Silica aerogel: synthesis and applications", *Journal of Nanomaterials*, (2010), 23.
- Rahman I.A., Padavettan V., "Synthesis of silica nanoparticles by sol-gel: size-dependent properties, surface modification, and applications in silica-polymer nanocomposites—a review", *Journal of Nanomaterials*, Vol. 2012, (2012), 8.
- Stöber W., Fink A., Bohn E., "Controlled growth of monodisperse silica spheres in the micron size range", *Journal of Colloid and Interface Science*, Vol. 26, No. 1, (1968), 62-9.
- Rao K.S., El-Hami K., Kodaki T., Matsushige K., Makino K., "A novel method for synthesis of silica nanoparticles", *Journal of Colloid and Interface Science*, Vol. 289, No. 1, (2005), 125-31.
- Bogush G., Zukoski C., "Studies of the kinetics of the precipitation of uniform silica particles through the hydrolysis and condensation of silicon alkoxides", *Journal of Colloid and Interface Science*, Vol. 142, No. 1, (1991), 1-18.
- Wang X.-D., Shen Z.-X., Sang T., Cheng X.-B., Li M.-F., Chen L.-Y., Wang, Z.S., "Preparation of spherical silica particles by Stöber process with high concentration of tetra-ethyl-orthosilicate", *Journal of Colloid and Interface Science*, Vol. 341, No. 1, (2010), 23-9.
- Gholami T., Salavati-Niasari M., Bazarganipour M., Noori E., "Synthesis and characterization of spherical silica nanoparticles by modified Stöber process assisted by organic ligand", *Superlattices and Microstructures*, Vol. 61, (2013), 33-41.
- Matsoukas T., Gulari E., "Dynamics of growth of silica particles from ammonia-catalyzed hydrolysis of tetra-ethyl-orthosilicate", *Journal of Colloid and Interface Science*, Vol. 124, No. 1, (1988), 252-61.
- Ibrahim I.A., Zikry A., Sharaf M.A., "Preparation of spherical silica nanoparticles: Stober silica", *Journal of American Science*, Vol. 6, No. 11, (2010), 985-9.