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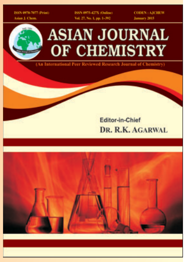

Size Evolution of Silica Nanoparticles in Different Solvents

Fengguo Liu[1,2,3,4], Wangjin Yang[1], Ying Wang[1], Xiangxin Xue[1,2,3,4,*] and He Yang[1,2,3,4]

[1]School of Materials and Metallurgy, Northeastern University, Shenyang, P.R. China
[2]Liaoning Key Laboratory of Metallurgical Resource Recycling Science, Northeastern University, Shenyang, P.R. China
[3]Liaoning Engineering and Technology Research Center of Boron Resources Comprehensive Utilization, Northeastern University, Shenyang, P.R. China
[4]Liaoning Provincial Universities Key Laboratory of Boron Resources Ecological Utilization Technology and Boron Materials, Northeastern University, Shenyang, P.R. China

*Corresponding author: Tel/Fax: +86 24 83681735; E-mail: xuexx@mail.neu.edu.cn

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Monodisperse silica nanoparticles were prepared by a sol-gel method with ultrasonication using tetraethoxy silane (TEOS) as silicon source and ammonia as catalyst in methanol, ethanol and acetone as different solvents. The morphologies of growing silica nanoparticles were observed by transmission electron microscopy (TEM) at different reaction times. The diameter distribution was analyzed statistically by Image J software. The results indicated that the diameter of silica in methanol as solvent was smallest and the uniformity of silica particle size in ethanol as solvent was optimal. The formation mechanisms of the resultant silica nanoparticles in different solvents related to the size evolution were discussed.

Keywords: Morphology, Polydispersity, Silica Nanoparticles, Statistical Calculation.

INTRODUCTION

Silica is an inorganic non-metallic material, which plays an important role in industry because of its excellent chemical stability, distinct biocompatibility, high strength and toughness[1]. The silica particles in nano-scale with ultrahigh specific surface area exhibit unique surface effect and quantum size effect. Generally, there are many oxhydryl groups on the surface of silica nanoparticles, they can be as a bridge for silica modification. Thereby, silica with various functionalization was developed to greatly improve the compatibility with the polymers[2]. The application scope of silica was enlarged. Up to now, silica nanoparticles have been extensively applied in many industrial fields, such as catalysis[3], coating filler[4], polymeric composites[5], biolabeling[6], chromatographic agents[7], drug delivery[8], *etc*.

The properties of silica nanoparticles are extremely dependent on the morphology and size distribution. Thus, the researches on the reaction control of monodispersed silica nanoparticles formation were quite fundamental. So far, several preparation methods of silica nanoparticles have been developed by researchers including vapor-phase synthesis[9], seeded growth technique[10], chemical precipitation[11] and microemulsion method[12]. The most successful method called Stöber method was reported by Stöber *et al.*[13]. The spherical and monodisperse silica nanoparticles were prepared ranging from 50 nm to 1 μm with a narrow size distribution, starting from aqueous alcohol solutions of silicon alkoxides in the presence of ammonia as a catalyst. Subsequently, the extensive studies were conducted on the formation mechanism and improved method was also studied[14-17]. Rao *et al.*[18] reported a sequential addition method for preparing silica particles by a sol-gel process. They determined the effect of each reagent on particle size in addition to the effect of temperature on ultrasonication. Sakka *et al.*[19] proved that the hydrolysis and condensation of tetraethoxysilane was a quite complex reaction process. The potential fundamental reactions were as follows.

$$Si(OR)_4 + 4H_2O \rightarrow Si(OH)_4 + 4ROH \qquad (1)$$

$$Si(OH)_4 \rightarrow SiO_2 + 2H_2O \qquad (2)$$

$$Si(OR)_4 + nH_2O \rightarrow Si(OH)_n(OR)_{4-n} + nROH \qquad (3)$$

$$Si(OH)_n(OR)_{4-n} + Si(OR)_4 \rightarrow (OR)_{4-n}(OH)_{n-1}SiOSi(OR)_3 + ROH \qquad (4)$$

$$2Si(OH)_n(OR)_{4-n} + H_2O \rightarrow (OR)_{3-n}(OH)_n SiOSi(OH)_n(OR)_{3-n} + 2\,ROH \qquad (5)$$

$$2Si(OH)_n(OR)_{4-n} \rightarrow (OR)_{4-n}(OH)_{n-1} SiOSi(OH)_{n-1}(OR)_{4-n} + H_2O \qquad (6)$$

where R is C_2H_5. All the chemical reactions above were in process simultaneously. It was difficult to describe the hydrolysis or condensation independently[20].

In the present work, we used transmission electron microscopy (TEM) to observe the morphologies of growing silica nanoparticles at different reaction times and analyzed the size evolution of silica nanoparticles in methanol, ethanol and acetone as solvents, respectively. The growth mechanisms of silica nanoparticles in different solvents were also discussed.

EXPERIMENTAL

In this experiment, tetraethoxysilane (TEOS), ammonium hydroxide (25 %), methanol, ethanol and acetone were purchased from Sinopharm Chemical Reagent Co., Ltd. All the reagents were used without any purification.

Preparation of silica nanoparticles: The silica nanoparticles were prepared as following procedures. Firstly, 5 mL of tetraethoxysilane was mixed in 22 mL of methanol and 12 mL of distilled water mixture. The mixture was kept in an ultrasoni-cation bath for 10 min. Subsequently, a mixture containing 8 mL of methanol and 3 mL of ammonium hydroxide was added as a catalyst to promote the hydrolysis and condensation reaction. Ultrasonication was continued for a further 240 min to obtain a white turbid suspension. During the reaction, a small portion of the colloid was sampled for TEM observation. The sampling times were 30, 120 and 240 min, respectively. All the above experiments were conducted at room temperature (24 ± 2 °C). Ethanol and acetone as solvent were also investigated as the same experimental procedure instead of methanol, respectively. The schematic diagram of preparation procedure of silica nanoparticles was shown in Fig. 1.

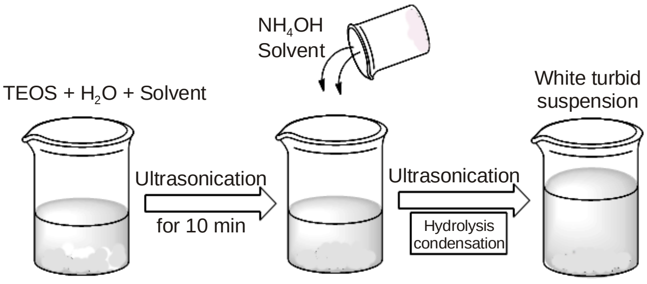


Fig. 1. Schematic of preparation of Silica Nanoparticles

TEM observation: A small portion of the colloid sampled was diluted by adding corresponding solvent of 5 mL. A drop of solution was removed and cast onto TEM grid. And then the TEM grid was dried in vacuum for 3 h. TEM images were obtained using a Tecnai $G^2$20 transmission electron microscope (FEI, USA, performed at 200 KV).

Statistical calculation of particle diameters: The TEM images were analyzed using Image J software (free from http://rsb.info.nih.gov/ij/). A plugin "Measure_Roi" (http://www.optinav.com/Measure-Roi.htm) was also utilized to measure the diameters of nanoparticles automatically. This plugin can measure the maximum distance between any two points in the region of interest as the length. The width is defined as the maximum distance on the edge in the perpendicular direction to the defined length. For sphere particles, the diameter is calculated by mean value of length and width. For each sample, more than 300 particles were calculated statistically.

RESULTS AND DISCUSSION

Fig. 2 showed the TEM images of silica nanoparticles prepared in different solvents at different times and corresponding size distribution histograms obtained by statistical analysis of over 300 particles. The morphology and size distribution of silica nanoparticles can be observed intuitively from TEM images. It was shown that the silica nanoparticles prepared under different conditions were spherical and monodisperse. The size distribution was basically approximate normal distribution as shown in histograms. The average diameters and polydispersity were summarized in Table-1, which revealed the size evolution process of silica particles in different solvents. In methanol, the average diameter of silica particles increased from 148 nm at 30 min to 171 nm at 240 min. In addition, the frequency of silica with the diameter between 80 and 100 nm decreased conspicuously. It indicated the silica particles with such size were in growth process in this duration. In ethanol, the average diameter of silica particles increased from 592 nm at 30 min to 627 nm at 240 min as in acetone it increased from 698 nm at 30 min to 938 nm at 240 min. The polydispersity of silica particles in ethanol is the smallest comparing with that in methanol and acetone. This means the uniformity of silica particle size was optimal among three investigated solvents. The formation of silica nanoparticles in solvent consist of a complex competition among the hydrolysis, nucleation and particle growth. The nucleation process occurs in the former period in a fast speed. Hydrolysis is a rate-limiting step of the whole reaction. Therefore, the factors, which can accelerate the hydrolysis process, can also promote the nucleation and particle growth.

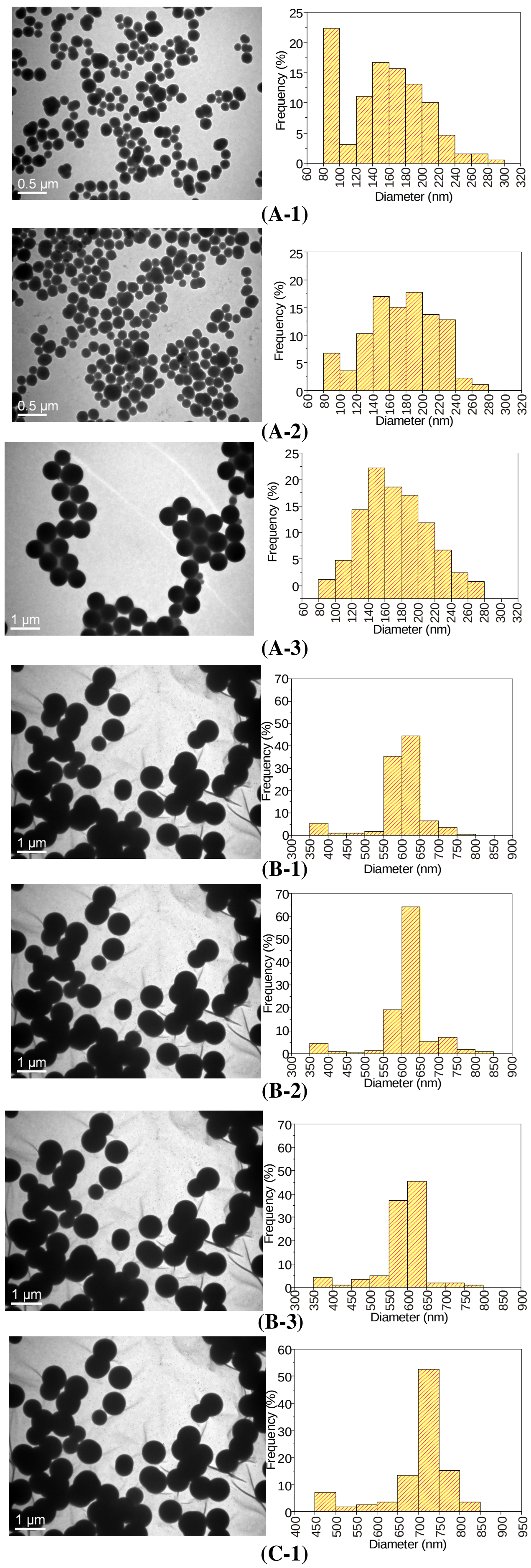
According to the classic DLVO (Derjguin-Landau-Verwey-Overbeek) theory on the colloid stability[21], there are two forces among the colloid particles, one is electrostatic repulsion produced by the overlap of electric double layer and another is long-range van der Waals forces among particles. The colloid stability is dependent on the interaction of such two forces. Therefore, the total potential energy among particles can be described as following equation:

$$V_b = -\frac{Ak\alpha}{12} + 2\pi\varepsilon_0\varepsilon_r\alpha\psi^2$$

TABLE-1
DIAMETER DISTRIBUTION OF SILICA PARTICLES IN DIFFERENT SOLVENTS

Reaction time (min)	Silica in methanol			Silica in ethanol			Silica in acetone		
	D_{avg} (nm)	σ (nm)	Polydispersity (%)	D_{avg} (nm)	σ (nm)	Polydispersity (%)	D_{avg} (nm)	σ (nm)	Polydispersity (%)
30	148	79	53.4	592	89	15.0	698	90	12.9
120	166	43	25.9	607	69	11.4	732	110	15.0
240	171	52	30.4	627	46	7.3	738	140	19.0

σ is the standard deviation, polydispersity calculated is the standard deviation divided by the average particle diameter



(A-1)

(A-2)

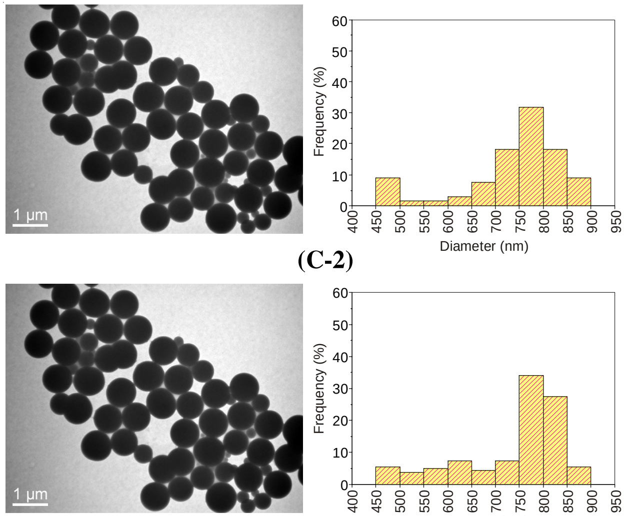
(A-3)

(B-1)

(B-2)

(B-3)

(C-1)



(C-2)

(C-3)

Fig. 2. TEM images of silica nanoparticles prepared in different solvents at different times (left) and corresponding size distribution histograms obtained by statistical analysis of over 300 particles (right). A-1: methanol at 30 min, A-2: methanol at 120 min, A-3: methanol at 240 min, B-1: ethanol at 30 min, B-2: ethanol at 120 min, B-3: ethanol at 240 min, C-1: acetone at 30 min, C-2: acetone at 120 min, C-3: acetone at 240 min

where A is effective Hamaker constant, which is related to the particle dispersed medium; a is the diameter of spherical particle; k is Debye-Huckel constant; ε_0 is dielectric constant in vacuum; ε_r is the dielectric constant of mobile phase; ψ is the surface energy of particle. In the present experiment, A is determined by the water and different solvents as the ammonia acted as catalyzer without adding any other electrolytes. In this system, the ionic strength of the solvent can be regarded as a constant and the potential energy among particles are mainly determined by the surface energy, dielectric constant and particle size. The dielectric constant of methanol, ethanol and acetone are decreased successively, resulting the increase in silica particle size correspondingly.

The hydrolysis process of TEOS catalyzed by ammonia is shown in Fig. 3[22,23].

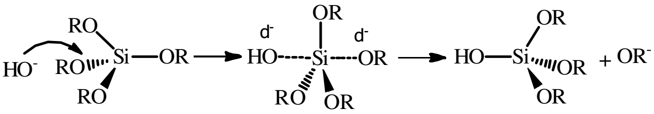


Fig. 3. Hydrolysis process of TEOS under basic condition

When the ammonia participates in reactions as a basic catalyst, the hydroxide ion with small diameter, can directly take nucleophilic attack to silicon atom. This attack makes silicon atom be negatively charged and then the electron clouds move to OR groups on the other side. As a consequence the bond Si-O is weaken until chemical bond rupture and separation from OR group. Eventually the hydrolysis is over. The lower polarity of the solvent is the more benefit to the reaction process described above. Polarity of methanol, ethanol and acetone are lower in proper order, so the diameters of silica particles are increased accordingly.

Conclusion

In this work, the morphologies of growing silica nanoparticles by a sol-gel method were observed by TEM at different reaction times. The diameter distribution was analyzed statistically using Image J software. The different solvents including methanol, ethanol and acetone, influences on the growth process of silica nanoparticles were investigated. The results indicated that the diameter of silica in methanol as solvent was smallest and the uniformity of silica particle size in ethanol as solvent was optimal. The size evolution of silica nanoparticles in different solvents were related to the properties of solvents and the growth mechanisms.

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