

Synthesis and Characterization of Colloidal Nanosilica via an Ultrasound Assisted Route Based on Alkali Leaching of Silica Fume

V. Jafari¹, A. Allahverdi^{1*}

1- Cement Research Center, School of Chemical Engineering, Iran University of Science and Technology, Tehran, I. R. Iran

(*) Corresponding author: ali.allahverdi@iust.ac.ir
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Abstract:

Colloidal nanosilica is currently being produced by various methods which are mainly high energy intensive and/or not environmentally friendly. It is therefore essential to develop new energy-efficient and environmentally friendly technologies. This paper introduces a new ultrasound assisted route based on alkali leaching of silica fume for synthesis of colloidal silica nanoparticles. The effects of sonication time on the particle size distribution of the colloidal nanosilica are studied via dynamic light scattering (DLS). The results show that the shape and size of nanoparticles are strongly depended on the ultrasonic time. DLS results show that average diameter of the produced colloidal nanosilica decreases sharply from 337.10 nm to 93.27 nm during the first 5 minutes of sonication. Continued sonication up to 30 minutes, however, shows relatively slight decrease in average diameter of the colloidal nanosilica. Further, the produced colloidal nanosilica is characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffractometry (XRD) and Fourier transform infrared (FTIR) spectroscopy.

Keywords: Nanoparticles, Nanosilica, Colloid, Silica fume, Ultrasound

1. INTRODUCTION

Despite several years of research and many studies, the interest has been focused on materials with nanoscale size because they represent new physicochemical properties which do not appear in the corresponding bulk materials [1]. Silica (SiO₂) is a practical raw material which has been widely used in the field of ceramic, electronic, polymer, cement and concrete industries. Silica nanoparticles have many applications due to high porosity and surface area such as reinforcing and thixotropic agents, thermal insulators, fillers, etc [2,3]. A stable dispersion of silica nanoparticles in a liquid

medium such as water is called colloidal nanosilica. Colloidal nanosilica is used in different industries in which it acts as a binder, polishing agent, coating agent, etc. [4]. Various processes have been proposed for preparing colloidal nanosilica including ion exchange [5-10], dialysis, electro dialysis and neutralizing with acid from sodium silicate solution [11], hydrolysis and condensation from silicon compounds like tetraethoxyorthosilicate (TEOS) [12-16], peptization from silica gel [17], dispersion of pyrogenic silica [11] and dissolution of silicon [18-20]. However, application of these methods for producing colloidal nanosilica has been limited

for a number of reasons such as expensive source materials, relatively high energy consumption and environmental costs due to solvent and resin recycling [21]. Therefore, it is important to develop energy-efficient and environmentally friendly methods based on new technologies.

Generally, there are three types of stability for colloidal systems including phase stability, stability of disperse composition and aggregative stability. The main characteristic of stabilization of the sols is aggregative stability that means the solid particles are suspended in the solution and do not precipitate or agglomerate at an important rate. Stability is influenced by various parameters, among which pH is the most important. The stability of the colloidal silica system is minimum at pH between 2 and 3, it increases at pH between 3 and 8 and reaches the maximum value at pH higher than 8. When pH of colloidal suspension increases from 10.5 to 14, silica particles can be dissolved [3,11].

Ultrasound waves have potential applications for many industrial processes including emulsification, drying, filtration, crystallization, extraction and etc. Y. Iida *et al.* [22] showed that viscosity of the starch solutions can be effectively reduced by the ultrasonic irradiation after gelatinization.

Recently, ultrasound assisted synthesis has been considered in the production of many kinds of materials [23-25]. Ultrasound waves cause important chemical changes owing to cavitation phenomena which can result in many unique properties in the irradiated solution [26]. Furthermore, using other source materials with low cost can significantly reduce the production expenses. One of such materials is silica fume which is rich in silica content and is being used in different industries like cement and concrete [27].

This work is devoted to the synthesis and characterization of colloidal nanosilica via an ultrasound assisted route and using silica fume as a silica-containing source material. The effects of sonication time on the particle size distribution are also investigated. The work, however, does not cover all the effective parameters such as power and frequency of the ultrasound irradiation on the particle size distribution, morphology and other properties of the produced colloidal nanosilica

and further investigations should be done to complete the research in the future.

2. MATERIALS AND METHOD

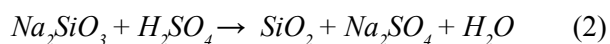
2.1. Materials

Silica fume, taken from Iran Ferroalloy Industries Company, was used as silica source material for synthesis of colloidal silica nanoparticles. The chemical composition of the silica fume (in wt.%) was as follows: SiO₂—96.12, Al₂O₃—0.82, K₂O—0.40 and LOI—0.63. Other chemical reagents such as sodium hydroxide pellets (NaOH, 97%) and sulphuric acid (H₂SO₄, Analytical grade, 95-97%) were purchased from Merck Chemical Company.

2.2. Procedure

2.2.1. Preparation of silica gel

Silica gel was prepared by a well-known method as a dissolution-precipitation process. On the basis of reaction conditions as listed in Table 1, silica fume was reacted with sodium hydroxide solution according to Eq. (1) and the suspension was then filtered. Subsequently, sulfuric acid solution was added drop by drop to the obtained sodium silicate solution under stirring. After the reaction completed, a white precipitate as silica gel was formed, as described by Eq. (2). The resulting gel mixture was then washed by distilled water for several times to remove solutions.



2.2.2. Converting silica gel to colloidal silica nanoparticles

The produced wet gel was mixed with diluted sodium hydroxide solution for adjusting pH in the range of stable sols. The alkaline wet gel was then irradiated with a Bandelin ultrasonic probe system, HD 3200 with tapered tip KE 76 made of titanium alloy with the power and frequency of 30 W and 20 kHz, respectively, for converting silica gel to colloidal nanosilica.

Table 1: Experimental procedure for preparation of colloidal nanosilica by ultrasound assisted synthesis

Steps	Conditions		
	Temperature (°C)	pH	Time (min)
Preparation of sodium silicate solution with reaction between 100 ml 2.5 M NaOH and 1 g silica fume	80	>13	30
Preparation of wet silica gel by adding 2.5 M H ₂ SO ₄ solution	25	Changing from 13.5 to 8.5	-
Stabilization by pH adjustment using diluted NaOH	25	Adjusting in the range of 8.5 to 10.5	-
Application of ultrasound waves with power and frequency of 30 W and 20 kHz, respectively	25	In the range of 8.5 to 10.5	5, 10, 15 and 30

2.3. Characterization

Dynamic light scattering (DLS) measurements were performed to determine the particle size distribution of colloidal nanosilica samples using a zetasizer Nano ZS (red badge) ZEN 3600 from Malvern Instruments. A 633 nm He-Ne laser source and a detection angle of 90° were used for analysis. Polydispersity index (PDI) derived from DLS analysis is a dimensionless number between 0 and 1 showing the homogeneity and quality of the sample in terms of light scattering. The sample with a very broad size and shape distribution has a higher value of PDI [28,29].

The morphology of the produced colloidal nanosilica was investigated using both scanning and transmission electron microscopes (SEM and TEM). SEM studies were performed on Vega II TESCAN scanning electron microscope at 30 kV in

the secondary electron mode. For SEM analysis, one droplet of the sample was placed on a glass slide and allowing it to dry completely at room temperature (25°C). After sputtering the sample with a thin gold layer, SEM image was created. TEM studies were performed on a Zeiss EM900 transmission electron microscope at an acceleration voltage of 80 kV. For TEM analysis, a drop of the sample was deposited on a carbon coated copper grid. The solvent was evaporated at room temperature (25°C (and then TEM image was created.

X-ray diffractometry (XRD) analysis was done with a JEOL JDX-8030 X-ray diffractometer with Cu-K α radiation for phase identification of the produced colloidal nanosilica. The operating voltage and current were 30 kV and 20 mA, respectively.

Fourier transform infrared (FTIR) spectroscopy was obtained on a Perkin Elmer Spectrum RX 1 in the range of 400 cm⁻¹ to 4000 cm⁻¹ with the KBr pellet method in which silica powder was mixed with potassium bromide (KBr) and then the mixture was pressed into a thin tablet.

3. RESULTS AND DISCUSSION

3.1. Particle size distribution

Particle size distribution in terms of light scattering intensity is the first order result from DLS experiment which can be converted into a volume distribution of particles using Mie theory [28,29]. Figure 1 illustrates the particle size distribution of the silica gel and prepared colloidal nanosilica at different sonication times of 5, 10, 15 and 30 minutes in terms of intensity and volume of particles.

As can be seen, silica gel had a relatively broad size distribution showing that a high portion of it was not located in the nanometer range. The appearance of three peaks in the both intensity and volume distributions confirms intensive agglomeration or presence of particles with large diameter in the gel structure. Significant results have been observed in the particle size distributions by applying ultrasound waves to the silica gel. The average diameter and PDI of the silica gel and colloidal nanosilica samples synthesized at different sonication times are reported in Table 2. As can be seen from the

table, before sonication silica gel had a relatively high average diameter equal to 337.10 nm with only 11% (in terms of volume) of particles demonstrating sizes smaller than 50 nm. The average diameter of particles reduced sharply to 93.27 nm during the first 5 minutes of sonication so that 60% (in terms of volume) of particles represented sizes below 50 nm. Continued sonication, however, resulted in much lower rates of size reduction. After 30 minutes of sonication, the average diameter of the particles reduced to 78.48 nm with only 73% (in terms of volume) of particles demonstrated sizes less than 50 nm.

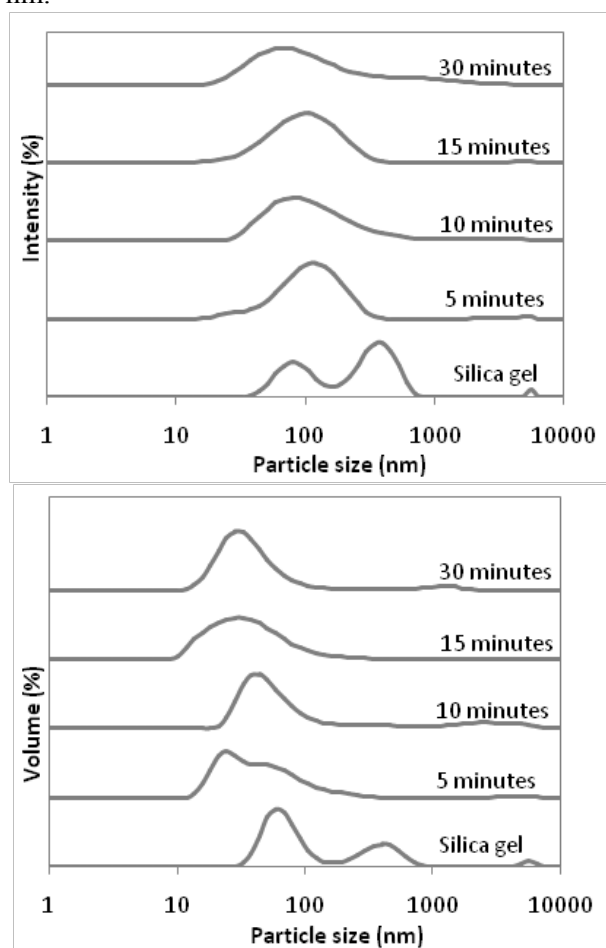


Figure 1: Particle size distribution of the silica gel and colloidal nanosilica samples prepared by ultrasound assisted synthesis in terms of light scattering intensity (up) and volume (down)

As shown in table 2, sonication also significantly alters the size and shape dispersity of the sample.

The silica gel represented a PDI of 0.58 showing the presence of both micro and nanosize particles. PDI is related to both size and shape of the suspended particles in the colloids [28,29]. The results of DLS analyses confirm continuous particle size reduction throughout the whole 30-min course of sonication; whereas PDI values show a sharp decrease at the beginning, after the first 5 minute, followed by limited fluctuations. The increase in PDI after 10 and 30 minutes of sonication can be attributed to an agglomeration phenomenon which affects the shape of the suspended nanoparticles. The colloidal nanosilica sample obtained after 15 minutes sonication demonstrated the minimum PDI value of 0.25. Longer sonication times up to 30 minutes resulted in relatively high PDI equal to 0.41. These variations in PDI confirm that sonication destroys the initial structure of the silica gel and alters the size and shape of the formed clusters with particle re-agglomeration.

Table 2: Effect of sonication time on the average diameter and PDI of colloidal nanosilica samples prepared by ultrasound assisted synthesis

Sonication time (min)	Average diameter (nm)	PDI
silica gel	337.10	0.58
5	93.27	0.26
10	88.90	0.36
15	82.52	0.25
30	78.48	0.41

3.2. SEM and TEM studies

According to DLS results, PDI value of the colloidal nanosilica sample produced after 15 minutes of sonication was the lowest value among others. SEM and TEM studies were therefore performed on the same sample.

Figure 2 shows the SEM images of the sample prepared at the highest properly possible magnifications available on the equipment.

As can be seen in these images, there exist most of the silica particles in the background with a darker color and some particles with brighter color or even in white. The bright color of particles is because of their position on top of the underlying layer, allowing

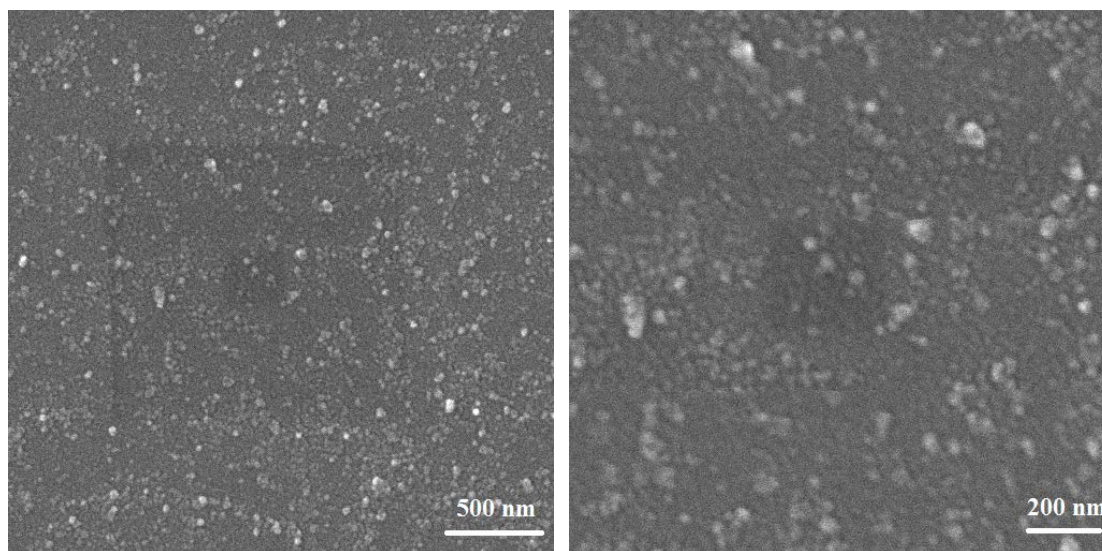


Figure 2: SEM images of colloidal nanosilica prepared after 15 minutes of sonication

them to absorb and reflect more electrons. The silica particles in the background are almost spherical in shape and nano sizes. However, the brighter particles seem to be larger in size and possess different shapes due to agglomeration phenomenon. It must be noted that the agglomeration of these relatively larger silica particles can also be attributed to drying of sample droplet on glass slide for SEM analysis. Figure 3 indicates the TEM images of the sample. Observations by TEM have confirmed similar results obtained by SEM studies. Agglomeration

of the nanoparticles as well as short silica chains made up of few nanosilica particles can be clearly observed. The observations are in good agreement with results obtained by DLS analysis.

3.3. X-ray diffraction analysis

Figure 4 represents X-ray diffractogram of the colloidal nanosilica sample produced after 15 minutes of sonication. The broad diffraction rise centered at 2θ angle of about 22.5° is a known typical

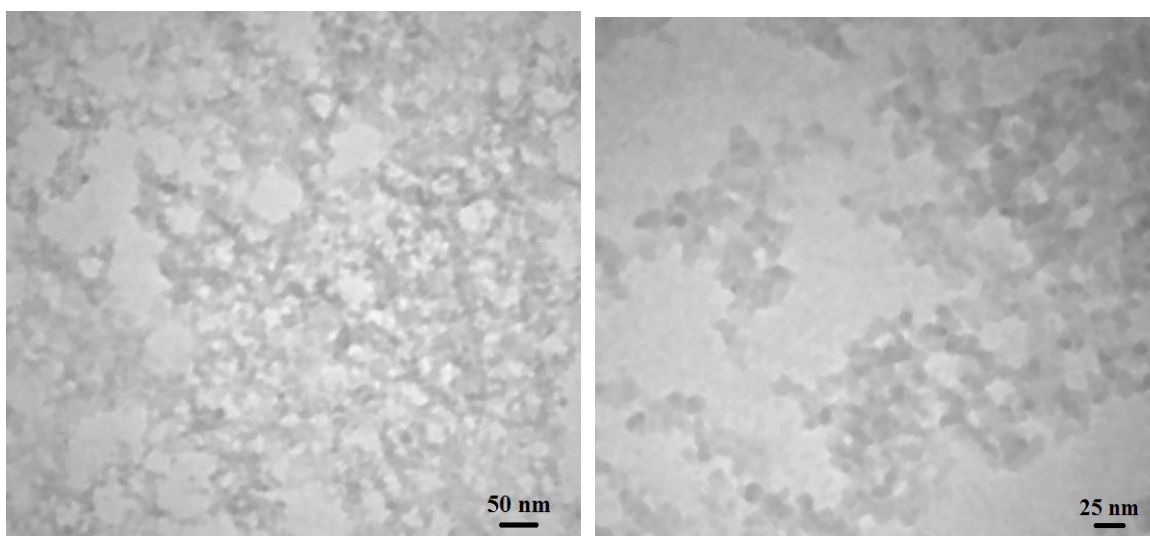


Figure 3: TEM images of colloidal nanosilica prepared after 15 minutes of sonication

characteristic of silica [30]. As seen, the absence of any ordered crystalline structure confirms the amorphous nature of the produced nanosilica [31].

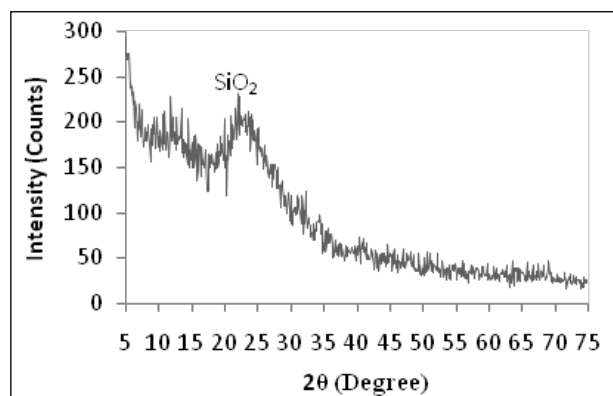


Figure 4: X-ray diffraction pattern of colloidal nanosilica prepared after 15 minutes of sonication

3.4. FTIR spectroscopy analysis

FTIR results of the produced colloidal nanosilica sample after 15 minutes of sonication are reported in Table 3. The peaks appearing in the range of 450 cm^{-1} to 1300 cm^{-1} are typical of silica samples [32]. The FTIR results confirm the three main characteristic peaks of silica at 1093 cm^{-1} , 788 cm^{-1} and 466 cm^{-1} attributed to the asymmetric, symmetric stretching vibration and the bending modes of silica, respectively [30,31].

Table 3: FTIR results of colloidal nanosilica prepared after 15 minutes of sonication

Peak position (cm^{-1})	Transmittance (%)	functional groups
3440	44.71	H–O–H stretching mode of the adsorbed water
1645	53.28	H–O–H bending mode of the adsorbed water
1093	16.25	–Si–O–Si asymmetric bond (Si–O)
788	52.32	–Si–O–Si symmetric bond (Si–OH)
466	29.73	–Si–O–Si bond bending vibration (Si–O–Si, siloxane)

The absorption bands at 3440 cm^{-1} and 1645 cm^{-1} were assigned to the H–O–H stretching and bending modes of the adsorbed water, respectively, related to the silanol –OH groups and water bound to the silica surface [30-32]. The results confirmed that the product consisted of pure nanosilica.

4. CONCLUSION

Colloidal nanosilica can be simply produced via an ultrasound assisted route based on alkali leaching of silica fume. DLS results showed that the average diameter of particles sharply reduced from 337.10 nm to 93.27 nm upon only 5 minutes of sonication with 60% (in terms of volume) of particles representing sizes below 50 nm . Continued sonication, however, resulted in much lower rates of size reduction with evidences of agglomeration. SEM and TEM studies confirmed that most of the silica particles were almost spherical in shape and nano sizes. According to the results of X-ray diffractometry and FTIR spectroscopy, the product consisted of pure amorphous nanosilica.

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