A novel method for synthesis of silica nanoparticles

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Abstract

A sequential method has been used, for the first time, to prepare monodisperse and uniform-size silica nanoparticles using ultrasonication by sol–gel process. The silica particles were obtained by hydrolysis of tetraethyl orthosilicate (TEOS) in ethanol medium and a detailed study was carried out on the effect of different reagents on particle sizes. Various-sized particles in the range 20–460 nm were synthesized. The reagents ammonia (2.8–28 mol L\textsuperscript{−1}), ethanol (1–8 mol L\textsuperscript{−1}), water (3–14 mol L\textsuperscript{−1}), and TEOS (0.012–0.12 mol L\textsuperscript{−1}) were used and particle size was examined under scanning electron microscopy and transmission electron microscopy. In addition to the above observations, the effect of temperature on particle size was studied. The results obtained in the present study are in agreement with the results observed for the electronic absorption behavior of silica particles, which was measured by UV–vis spectrophotometry.

Keywords: Silica nanoparticles; Scanning electron microscopy; UV–vis spectrophotometry

1. Introduction

Silica nanoparticles occupy a prominent position in scientific research, because of their easy preparation and their wide uses in various industrial applications, such as catalysis, pigments, pharmacy, electronic and thin film substrates, electronic and thermal insulators, and humidity sensors [1]. The quality of some of these products is highly dependent on the size and size distribution of these particles.

Stober et al. [2], in 1968, reported a pioneering method for the synthesis of spherical and monodisperse silica nanoparticles from aqueous alcohol solutions of silicon alkoxides in the presence of ammonia as a catalyst, and different sizes of silica nanoparticles were prepared ranging from 50 nm to 1 µm with a narrow size distribution. The size of particles depends on the type of silicon alkoxide and alcohol. Particles prepared in methanol solutions are the smallest, while the particle size increases with increasing chain length of the alcohol. The particle size distribution also becomes broader when longer-chain alcohols are used as solvents. After this, a large number of studies were conducted in this area [3–11]. In the present study, two main types of reactions are involved: (i) silanol groups are formed by hydrolysis and (ii) siloxane bridges are formed by a condensation polymerization reaction:

\begin{align*}
\text{Hydrolysis:} & \quad \text{Si}(\text{OR})\text{₄} + \text{H}_2\text{O} \rightleftharpoons \text{Si}(\text{OH})\text{₄} + 4\text{R–OH}, \\
\text{Condensation:} & \quad 2\text{Si}–(\text{OH})\text{₄} \rightarrow 2(\text{Si}–\text{O}–\text{Si}) + 4\text{H}_2\text{O}.
\end{align*}

The condensation rate depends on reaction conditions which might result in the formation either of a three-dimensional network or in formation of single monodisperse particles [12]. A seeded growth technique has described by Bogush et al. [3] for the preparation of larger particles. In this technique a seed suspension is precipitated utilizing a Stober reaction. When the reaction is completed, TEOS and...
water are added to the seed suspension in a 1:2 mole ratio. The drawback of this technique is that, if the amount of TEOS exceeds a critical value, a second population of particles will appear. Using this technique, it is possible to prepare more monodisperse particles and increase their mass fraction in the sol, but with this method, it is not possible to increase the size of the monodisperse particles beyond 1 µm. The effect of electrolyte on size of silica nanoparticles was described by Bogush and Zukoski [5], and in their study, they reported that when the electrolyte (NaCl) concentration was increased from 0 to 10^{-4} M, the particle size increased from 340 to 710 nm.

Huang and co-workers have reported that sonication during a reaction could significantly increase the yield of carbodiimide-mediated amidations [13]. In view of this, in the present study, we have determined the effect of each reagent on particle size in addition to the effect of temperature on ultrasonication. To our knowledge, this is the first report on a sequential addition method for preparation of silica particles by a sol–gel process.

2. Materials and methods

2.1. Reagents

Tetraethyl orthosilicate (TEOS) (99.99%, Aldrich), ethanol (99.99%, Aldrich), and ammonium hydroxide (28%, Wako) were used without any further purification. Milli-Q water (18.2 Ω) was used throughout the experiment.

2.2. Characterization

Silica particles were prepared using a sol–gel process with a sequential addition technique in an ultrasonication bath. Various types of experiments were conducted in which the concentration of one reagent was fixed and the concentration of other reagents were changed one by one.

Particle sizes were measured using field emission scanning electron microscopy (FE-SEM, JEOL, F 6500, Japan). Clean glass capillaries were used to transfer a droplet of each sample of suspension to highly oriented pyrolitic graphite (HOPG). The samples were allowed to dry and then micrographs were taken at a number of random locations on the grid. The size of the particles was calculated from the SEM pictures using an average of 100 to 200 particles in almost all cases. The electronic absorption behavior was analyzed using a UV PC spectrophotometer (Shimadzu 3100).

2.3. Synthesis of silica nanoparticles

The monodisperse uniform-sized silica nanoparticles were prepared by hydrolysis of TEOS in ethanol medium in the presence of ammonium hydroxide. Fig. 1 is a schematic diagram of the synthesis of silica particles and homogeneous samples were prepared by the following procedure.

First, ethanol was taken and kept in a sonication bath. After 10 min, a known volume of TEOS was added while sonication, and after 20 min, 28% ammonium hydroxide was added as a catalyst to promote the condensation reaction. Sonication was continued for a further 60 min to get a white turbid suspension. All the above experiments were conducted at room temperature.

3. Results and discussion

According to Bogush and Zukoski [5], five parameters play an important role in the size and size distribution of silica nanoparticles: (i) concentration of TEOS, (ii) concentration of ammonia, (iii) concentration of water, (iv) effect of alcohol, and (v) reaction temperature. In the present study, a systematic study was carried out by a sol–gel process using a sequential addition method and the results are discussed. The main parameters and their effects on particle size are summarized in Table 1.

Fig. 2 illustrates the preparation of different sizes of silica nanoparticles mentioned in Table 3. Nineteen experiments were conducted and took three levels for each to get uniformity in the results. Fig. 2 (samples 1, 3, and 4) represents the effect of TEOS on particle size. Fig. 2 (sample 2) shows that small and uniform-sized particles, size 20.5 nm (SD < 1.0), were obtained under experimental conditions at ethanol 4 M, 0.045 M TEOS, and 14 M of NH3. Fig. 2 (samples 1 and 2) represents the effect of ethanol concentration on size of the silica nanoparticles. Also notice from Fig. 2

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Property</th>
<th>Size (nm): d = diameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Effect of ethanol</td>
<td>Size (nm)</td>
<td>20.5 &lt; d &lt; 224.2</td>
</tr>
<tr>
<td>Effect of TEOS</td>
<td>Size (nm)</td>
<td>60.1 &lt; d &lt; 417</td>
</tr>
<tr>
<td>Effect of ammonia</td>
<td>Size (nm)</td>
<td>242.8 &lt; d &lt; 30.6</td>
</tr>
<tr>
<td>Effect of water</td>
<td>Size (nm)</td>
<td>224.2 &lt; d &lt; 20.5</td>
</tr>
<tr>
<td>Effect of temperature</td>
<td>Size (nm)</td>
<td>116.0 &lt; d &lt; 462.03</td>
</tr>
</tbody>
</table>

Note. The average size and other reaction conditions are presented in Table 2.
Fig. 2. SEM images of SiO$_2$ particles synthesized by sequential addition method: (sample 1) Exp. No. 1, (sample 2) Exp. No. 3, (sample 3) Exp. No. 4, (sample 4) Exp. No. 5, (sample 5) Exp. No. 7, (sample 6) Exp. No. 8, (sample 7) Exp. No. 9, (sample 8) Exp. No. 10.

(Sample 3) that monodisperse uniform-sized silica nanoparticles obtained at low concentrations of TEOS at 0.012 M have size 60.1 nm with SD (<3 nm) and maximum size of particles was obtained at 0.12 M of TEOS, which was observed under TEM. The TEOS concentration was varied between 0.012 and 0.12 M under the experimental conditions 8 M ethanol and 14 M NH$_3$. The particle sizes increased with increasing TEOS. A decrease of particle size with increasing TEOS was also noticed at 4 M of ethanol and 14 M of ammonia. This may be due to high concentration of water under the present experimental conditions, as seen from Fig. 2 (samples 5 and 6). Fig. 2 (samples 1, 7, and 8) represents the effect of ammonia on the size of silica particles. A decrease in particle size was observed with increasing ammonia concentration, whereas the effect was reversed in both batch and semibatch methods.

3.1. Effect of TEOS concentration

Stober et al. [2] reported that there was no effect of TEOS on final particle size. In contrast to Bogush et al. [4] who reported larger particles due to increasing TEOS concentrations, van Helden et al. [3] found that the particle size decreased. The size of the silica nanoparticles was found to increase with TEOS and with increasing concentration of water and ammonia up to 7 and 2 M, respectively, after which the effect was reversed [1,3,11]. In the present study, increased size of the silica nanoparticles was observed with increasing the TEOS concentration in the range 0.012–0.12 M at 8 M ethanol, 3 M water, and 14 M ammonia concentration (Exps. No. 4–6). In contrast, a decrease in size was noticed with increasing TEOS in the range 0.012–0.12 M at 4 M ethanol, 14 M water, and 14 M ammonia.
Table 2
Average particle sizes under different reaction conditions

<table>
<thead>
<tr>
<th>Experiment no.</th>
<th>Name of the sample</th>
<th>Experimental conditions</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Alcohol (mol L⁻¹)</td>
<td>TEOS (mol L⁻¹)</td>
<td>[H₂O]/[TEOS]</td>
</tr>
<tr>
<td>1</td>
<td>Sample-1</td>
<td>8</td>
<td>0.045</td>
</tr>
<tr>
<td>2</td>
<td>Sample-TEM1</td>
<td>6</td>
<td>0.045</td>
</tr>
<tr>
<td>3</td>
<td>Sample-2</td>
<td>4</td>
<td>0.045</td>
</tr>
<tr>
<td>4</td>
<td>Sample-3</td>
<td>8</td>
<td>0.012</td>
</tr>
<tr>
<td>5</td>
<td>Sample-4</td>
<td>8</td>
<td>0.067</td>
</tr>
<tr>
<td>6</td>
<td>Sample-TEM2</td>
<td>8</td>
<td>0.11</td>
</tr>
<tr>
<td>7</td>
<td>Sample-5</td>
<td>4</td>
<td>0.012</td>
</tr>
<tr>
<td>8</td>
<td>Sample-6</td>
<td>4</td>
<td>0.067</td>
</tr>
<tr>
<td>9</td>
<td>Sample-7</td>
<td>8</td>
<td>0.045</td>
</tr>
<tr>
<td>10</td>
<td>Sample-8</td>
<td>8</td>
<td>0.045</td>
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Temperature effect

<table>
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<tr>
<th>Temperature</th>
<th>T1</th>
<th>T2</th>
<th>T3</th>
<th>T4</th>
<th>T5</th>
<th>T6</th>
<th>T7</th>
<th>T8</th>
<th>T9</th>
<th>T10</th>
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<tbody>
<tr>
<td>Ethanol</td>
<td>8</td>
<td>8</td>
<td>8</td>
<td>6</td>
<td>6</td>
<td>6</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>8</td>
</tr>
<tr>
<td>TEOS</td>
<td>0.045</td>
<td>0.045</td>
<td>0.045</td>
<td>0.045</td>
<td>0.045</td>
<td>0.045</td>
<td>0.045</td>
<td>0.045</td>
<td>0.045</td>
<td>0.045</td>
</tr>
<tr>
<td>[H₂O]/[TEOS]</td>
<td>66.7</td>
<td>66.7</td>
<td>66.7</td>
<td>184</td>
<td>184</td>
<td>184</td>
<td>311</td>
<td>311</td>
<td>311</td>
<td>311</td>
</tr>
<tr>
<td>NH₄OH</td>
<td>14</td>
<td>14</td>
<td>14</td>
<td>14</td>
<td>14</td>
<td>14</td>
<td>14</td>
<td>14</td>
<td>14</td>
<td>14</td>
</tr>
<tr>
<td>Average particle size (nm)</td>
<td>372</td>
<td>345</td>
<td>324.1</td>
<td>228.13</td>
<td>347.96</td>
<td>462.03</td>
<td>116</td>
<td>128.5</td>
<td>150.5</td>
<td>23.33</td>
</tr>
</tbody>
</table>

Note. T1, T4, and T7 are at 30°C; T2, T5, and T8 are at 50°C; T3, T6, and T9 are at 70°C.

Table 3
Reagent Concentration range (mol L⁻¹)

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Concentration range (mol L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alcohol</td>
<td>1–8</td>
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<tr>
<td>TEOS</td>
<td>0.012–0.12</td>
</tr>
<tr>
<td>NH₃</td>
<td>2.8–28</td>
</tr>
<tr>
<td>H₂O</td>
<td>3–14</td>
</tr>
</tbody>
</table>

Fig. 3. Comparative study of temperature and [H₂O]/[TEOS] effect on particle size.

(Exps. No. 7–8). This may be due to high concentration of water, at which the rate of hydrolysis is first-order in the orthosilicate and the pseudo-first-order rate constant is a function of the water concentration. Thus, the rate constant must increase with increasing water concentration and this should lead to faster kinetics and result in producing smaller particles [14]. In addition to this, the effect of \( R = [\text{H}_2\text{O}]/[\text{TEOS}] \) on size of particles at different temperatures was studied. Fig. 3 explains the particle size increase with increased temperature at higher \( R' \) values, whereas at lower values the particle size decreases with increasing temperature.

3.2. Effect of water and ammonia concentration

Generally hydrolysis is a very slow reaction, though acids or bases are used as catalysts. Ammonium hydroxide is used as a catalyst for hydrolysis and condensation of TEOS in ethanol. According to Matsoukas and Gulari [14], the larger particles were obtained by increasing the concentrations of ammonia and water. The ammonia acted as a catalyst, which increased the rate of hydrolysis and also condensation, resulting in faster kinetics. As a result, increased water concentration leads to smaller particles. Surprisingly, in the present method, a reverse effect was observed. With increasing the concentration of ammonia, a decrease in the size of silica nanoparticles was noticed. As seen in Fig. 4A, a decrease in the size of silica particles from 242 to 30.6 nm with increasing ammonia concentration in the range 2.8–28 M was noticed under experimental conditions 8 M ethanol, 3 M water, 0.045 M TEOS. Matsoukas and Gulari [14] also mentioned that the increase in water concentration yields smaller particles. On the other hand, Park et al. [15] obtained larger particles at higher water concentrations. According to Park et al. [15], in the presence of high water concentration, a high nucleation rate occurs and a lot of subparticles are produced.
during a short period. But the hydrogen bond of SiO\textsubscript{2} sub-particles is stronger at higher water concentration compared to lower water concentration, because of excess water. As a result, the agglomeration causes the formation of large particles. In the present study, from Fig. 4B, it can be seen that the size was increased up to 10 M of water and after that a decrease in size was noticed with increasing water concentration under experimental conditions at 0.045 M TEOS, 14 M ammonia.

3.3. Effect of ethanol

Different studies were conducted to know the effect of ethanol concentration on particle size. The studies were conducted between 4 and 10 M of ethanol. Ethanol plays a major role in affecting monodispersity and size of the silica nanoparticles. In the present study, the particle size was decreased with decreasing ethanol concentration in the range 8–4 M. It can be seen from Fig. 5 that the particle size increases with increasing ethanol up to 6 M, and after that a decrease in particle size was observed with decreasing ethanol up to 4 M at 0.045 M TEOS and 14 M ammonia. The monodisperse and uniform size particles were obtained bearing the size 20 nm at 4 M ethanol, 0.045 M TEOS, and 14 M of ammonia concentration (Fig. 2, sample 2).

3.4. Effect of temperature

The effect of temperature on size of silica particles at different concentrations of ethanol was also explored. The reactions were carried out at 8, 6, and 4 M ethanol under experimental conditions 0.045 M TEOS and 14 M ammonia. Various comparative studies were conducted to know the effect of temperature on particle size between 30 and 70 °C. According to Tan et al. [16], monodisperse particles were obtained from TEOS–water–ethanol solutions with a size of about 2 µm with decreased temperature. The temperature effect related to the saturation concentration of ammonia, which decreased with increasing temperature. In the present method, different types of trends in size of silica nanoparticles and obtained monodisperse and uniform-sized silica particles were noticed. As seen from Fig. 6 (T4, T5, and T6) and Fig. 6 (T7, T8, and T9), the particle sizes increased with increasing temperature at 6 and 4 M ethanol, respectively, under experimental conditions 0.045 M TEOS and 14 M NH\textsubscript{3}, whereas at 8 M ethanol, 0.045 M TEOS, and 14 M ammonia, a decrease in particle size was observed with increasing temperature (Fig. 6 (T1, T2, and T3)). In addition to this, a distorted spherical shape of silica nanoparticles were observed at 70 °C temperature under experimental conditions 8 M ethanol, 0.045 M TEOS, and 14 M NH\textsubscript{3} (Fig. 7). From Fig. 8, SiO\textsubscript{2} particles of maximum average size 462.03 nm with SD 25.51 were obtained at a medium concentration of ethanol 6 M, TEOS 0.045 M, and NH\textsubscript{3} 14 M at temperature 50 °C. In addition to this, heterodisperse particle size distributions were observed at 4 M ethanol, 0.045 M TEOS, and 14 M ammonia. A plausible explanation is that silica particles are stabilized by electrostatic repulsion. The charge originates from silanol groups, which are relatively acid and dissociate in the presence of ammonia [3]. As a consequence, at high temperatures, the ammonia gets evaporated easily and the presence of a high concentration of water in the reaction mixture in turn causes an increase of particle size.
Fig. 6. SEM images of SiO$_2$ nanoparticles prepared by sequential addition method at various temperatures: (T1) Exp. No. 11, (T2) Exp. No. 12, (T3) Exp. No. 13, (T4) Exp. No. 14, (T5) Exp. No. 15, (T6) Exp. No. 16, (T7) Exp. No. 17, (T8) Exp. No. 18, (T9) Exp. No. 19.

Fig. 7. SiO$_2$ particles of average size 324.1 ± 15.7 nm under experimental conditions 8 M ethanol, 0.045 M TEOS, and 14 M NH$_3$ at 70 °C. Average \( d = (a + b)/2 \) (nm).

3.5. Electronic absorption spectra of silica nanoparticles

The electronic absorption spectra of silica nanoparticles was investigated by Shimadzu 3100PC UV–vis absorption spectrophotometer in the range of 400–700 nm and the ethanol is taken as a medium for all substrates. Fig. 9 shows the effect of different concentrations of ethanol, water, TEOS, and ammonia on the absorbance of the silica nanoparticles. All the spectra have been normalized to the sample spectral wavelength of 650 nm. All spectra, except sample 6, have the same shape and are centered at wavelength 525 nm. The absorption peak around 525 nm could be called a van Hove singularity [17]; it appears in the local density states of silica nanoparticles, according to Lieber

Fig. 8. Comparative study of ethanol and temperature effect on particle size.
[18–20], who demonstrated the dependence of band gap energy and van Hove singularity peak. This information permits us to confirm that silica is far from being conducting, and thus was considered as isolate material. However, these samples have different spectrum width around the peak 525 nm, which typically characterizes the interaction between particles and predicts that the silica had large and small diameters of the particles. This prediction was proved by scanning electron microscopy (SEM), as shown in Fig. 2. Therefore, the composition of these samples modified their absorption spectrum.

4. Conclusions

The present method is a simple and convenient method compared to other existing methods such as batch and semi-batch methods. So far, we have studied all the parameters that affect the size of silica particles. Experiments on the effect of ultrasonication power on the size of silica particles are in progress. The influence of multiparametric optimization in sequential manner will be taken up.

References
