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Effect of anion electrolytes on the formation of silica nanoparticles via the sol–gel process

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Abstract

Anion electrolyte additives (ammonium salts) have been used for the first time to study the effect on the morphology development of nanometer, monodispersed silica particles by the sol–gel process. The phenomena can be explained by conductivity profile during the process as alternative to normally use zeta potential. Under experimental conditions where TEOS, water, EtOH and feed rate were fixed and without additives, unstable silica particles of ~30 nm were formed at a ratio of $TEOS/NH_3 \geq 0.6$, below that particles from 90 to 250 nm were obtained. However, upon the addition of small amount of anion electrolytes, monodispersed nanosilica powders with particles ranging from ~20 to ~34 nm were obtained depending on the type and concentration of anions added. It was found that all anions were able to reduce the particle size by 73–78%, among them, Br^- and I^- have the highest effect while Cl^- has the least effect. The synthesized silica powder was free from cation impurities.

Keywords: Monodispersed; Nanosilica; Anion electrolytes; Conductivity

1. Introduction

Recently, many research efforts have been made in developing polymer-silica hybrid nanocomposites [1–3]. The combination of superior properties of polymers such as flexibility, dielectric, toughness and process ability, and that of oxides which have high thermal stability, good mechanical and optical properties, can lead to production of highly functionalized materials with desired properties to meet the demands of many industrial and high technology applications [4]. The resulting materials exhibit some excellent properties of its inorganic counterpart to be utilized in electrical, optical, structural, photoelectrical, and non-linear optical applications [5,6].

Highly dispersed nanometer silica particles are essential in the synthesis of nanocomposites in order to ensure homogeneity, which is associated to the quality of the final products. The most interesting and popular process in obtaining nanometer silica is through hydrolysis and condensation of silicon alkoxide at low temperature [7–10]. During hydrolysis and condensation process, the silicate monomer nucleates in a supersaturated solution and grows to form dimeric, cyclic, spherical particles or gel network [11]. Thus, different particles size and morphology of silica particles can be produced by sol–gel process through controlling parameters such as concentration of alkoxide, amount of water, concentration of ammonia or acid (pH), and solvent, aging time and admixture [12–17].

Kim et al. [17] have reported that mono-valent electrolyte additives such as NaI can reduce the size of nanosized silica particles up to 17.5 nm. Based on our literature search, so far no studies have been reported on investigating the effect of

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ammonium salts in enhancing surface charge and thus reducing the size of silica particles through sol–gel process. When ammonium salts, NH_4X dissolved in ammonia (act as catalyst in sol–gel process), the solution will contain ionic species of NH_4^+ and X^-. We believe that any changes in the morphology of the synthesized silica are caused solely by the anion presence. For the first time we use the conductivity profile to explain the effect of anion on the silica particle growth as alternative to the normally used zeta potential technique.

2. Experimental

The procedure for the preparation of nanosize silica was modified from Stöber et al. [7] and summarized in Fig. 1. The alkoxide used was tetraethylorthosilicate (TEOS, 99.0%, Fluka). Ethanol (EtOH, 99.5% Systerm) was used as solvent. Ammonia solution (NH_3, 25%, Merck) was used as received while all the analytical grade ammonium salts were purchased from Fluka. For experiment without the addition of additives (electrolytes), the amount of TEOS, water, feed rate and EtOH were fixed, while the TEOS/NH_3 mol ratios were varied from 1 to 0.01.

For electrolyte studies, the ammonium salts were dissolved in ammonia solution 25% which gives final concentrations of 10^{-4}, 10^{-5}, 10^{-6}, 10^{-8} and 10^{-10} M in the final mixture. Reaction temperature is ~45 °C. The pH of the reaction mixture is 11 ± 1. For preparation of 1×10^{-4} M NH_4Cl solution, 6 ml of 7.12×10^{-4} M NH_4Cl solution was added to a mixture of 30 ml EtOH + 0.7 ml H_2O + 6 ml TEOS. The final volume of the mixture was now 42.7 ml. The 6 ml of the electrolyte solution carries 4.27×10^{-6} mol of NH^{4+} and the same amount of Cl^- ions to the reaction mixture. Thus, the concentration of Cl^- ion would be 1×10^{-4} M in the mixture.

Morphologies of the samples were examined by using TEM (Philips CM12), while the particle size distributions (PSD) was measured using analySIS software. Conductivity measurements were conducted with Cyberscan 500, automated conductivity meter. FTIR analysis was carried out by using a Perkin-Elmer 2000.

3. Results and discussion

3.1. The formation of silica nanoparticles

Generally, it is agreed that the morphology development of silica particle via sol–gel based on the Ströber method is controlled by parameters such as amount of water, concentration of ammonia or acid, solvent, aging time, temperature and admixture [12–17]. Park et al. [13] have reported the detail studies on the morphology development parameters and successfully prepared nanosilica particles with minimum particles size of 30 ± 5 nm at the optimal experimental conditions.

In our studies, we have fixed reaction conditions for TEOS, feed rate and vary the mol ratio of TEOS/NH_3 from 0.1 to 1. The small quantity of water was used to initiate hydrolysis process and more water would be generated through the condensation reaction. Fig. 2 shows the graphs of mean particles sizes and the yield against TEOS/NH_3 mol ratios. The results showed that the particle sizes remained almost constant at TEOS/NH_3 ranged from 1 to 0.6 and exponentially increased on further decreased in TEOS/NH_3 ratios. The trend of the results can be explained as follows. At higher TEOS/NH_3 ratio, we found that the pH of the mixture in the ranged of 9–10, and at this stage the silicate monomer starts to nucleate in a supersaturated solution and grows to form dimeric, cyclic and spherical particles through aggregation process [10,18,19]. When the pH of the mixture increases above 10, i.e at lower TEOS/NH_3, further growth occurs by Ostwald ripening mechanism whereby particles grows in size and decrease in number as highly soluble particles dissolve and reprecipitate on larger particles. The particles grow at a significant rate to form bigger particles, which can be easily separated by centrifugation. Thus, nanometer silica particles can be synthesized at pH below 10 or at lower concentration of NH_3. However, at this condition the silica particles were found to be in the form of cloudy sol, which can not be efficiently centrifuged resulting in lower yield as shown by decreasing yields with increasing TEOS/NH_3 ratio. A stable, relatively larger spherical silica can be easily obtained at pH > 10 or TEOS/NH_3 < 0.6. This is in agreement with the previous works [13,17–19], which

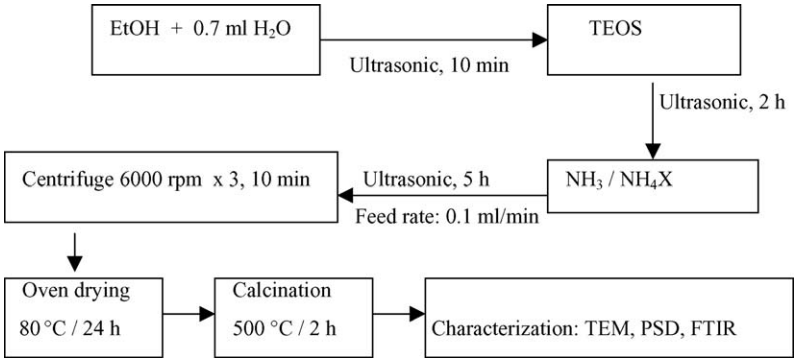

Fig. 1. Flow chart for silica synthesis.

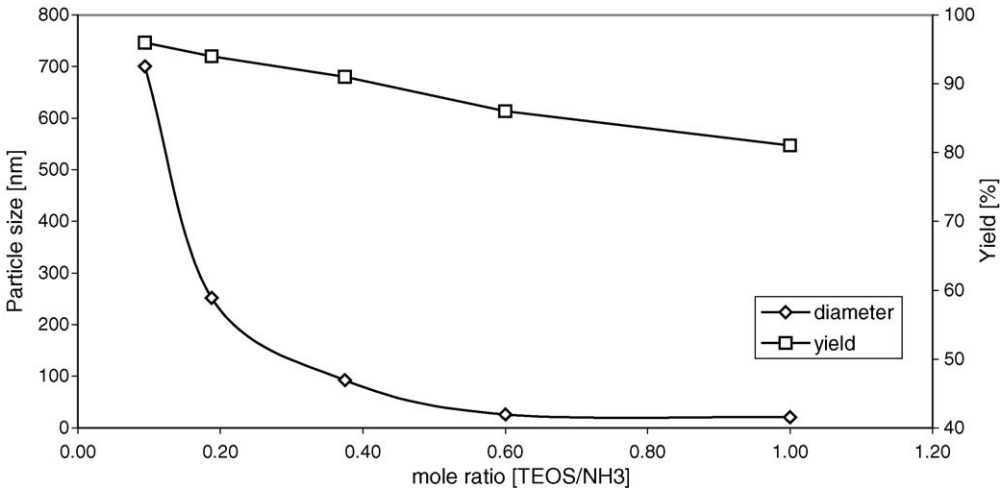

Fig. 2. Effect of TEOS/NH_3 mol ratios on particles size (◇) and experimental yield (□) of silica nanoparticles.

demonstrated that ammonia catalyzed the hydrolysis and condensation reactions leading to a faster kinetic rate and generated larger particles. Fig. 3 shows the TEM of spherical silica particles prepared at different TEOS/NH_3 ratios and particle size distribution of the samples was presented in Fig. 4. It is observed that at TEOS/NH_3 $\geq$ 0.6. the particles size are ~30 nm and uniformly distributed. At TEOS/NH_3 ratio <0.6, a mixture of large and small particles was observed with a wider distribution. Particles ranged from 90 to 250 nm were easily obtained.

Larger particles continue to grow on the consumption of smaller particles on further decrease in TEOS/NH_3 ratio until a uniformly distributed particles is again obtained.

3.2. The efficiency of anion electrolytes in reducing the size of silica nanoparticles

The lower yield and difficulties faced in obtaining nanometer particles as discussed above, prompt us further investigation. Kim et al. [17] have successfully prepared monodispersed nanosilica particles by using monovalent metal salts as additives. The reducing effect might be due to the presence of cations and anions in the mixture. In addition, the powder might be contaminated with unnecessary cation impurities. Thus, we chose ammonium salts as additives in order to study only the effect of anions on particles growth and to produce powder free from cation

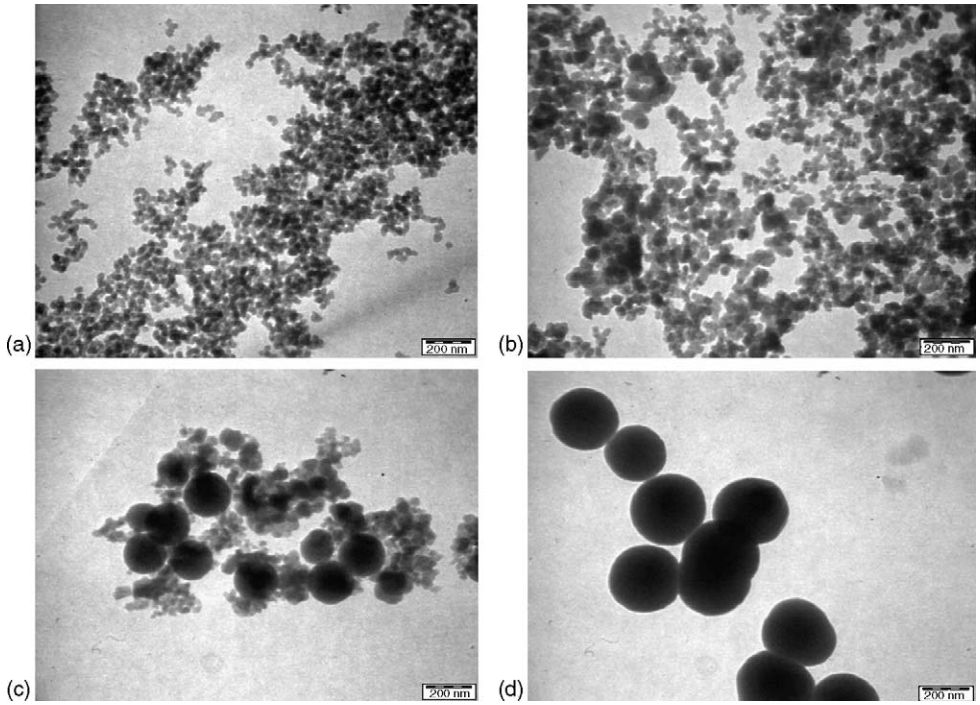

Fig. 3. TEM images of silica particles produced at different TEOS/NH_3 ratio: (a) 1.00; (b) 0.60; (c) 0.38; and (d) 0.19.

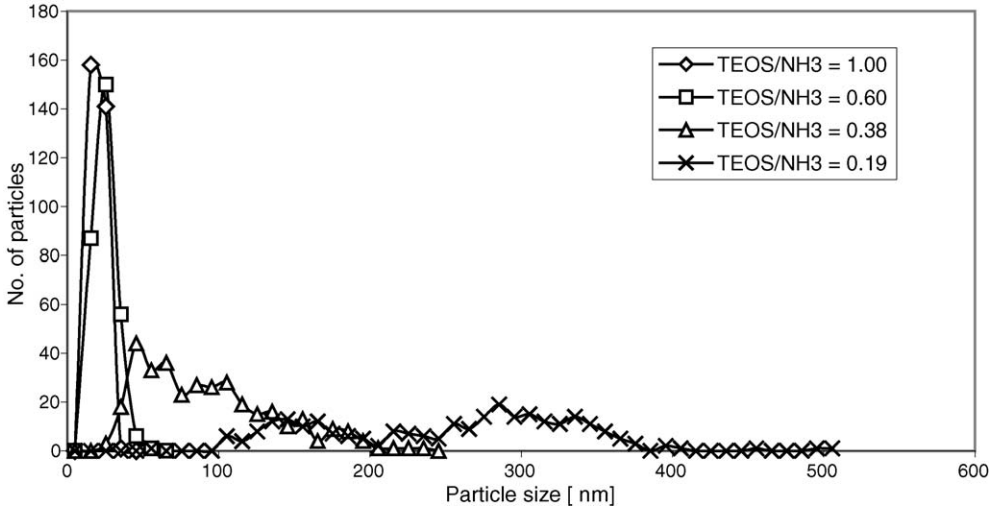

Fig. 4. Size distribution of silica particles at different TEOS/NH_3 ratios.

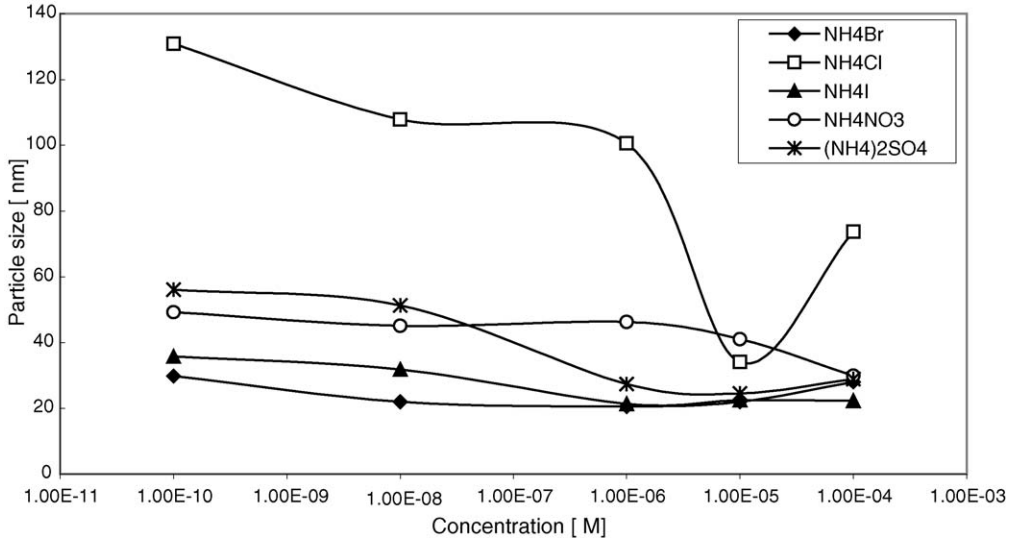

Fig. 5. Particle size verses concentration of different ammonium salts.

impurities for our further uses. We again use similar experimental conditions with fixed amount of TEOS, feed rate, water, TEOS/NH_3 = 0.38 (final pH ~11, multi-modal distributed conditions) and vary the concentration of ammonium additives. The results show that all ammonium salts are able to reduce the particle size with optimum concentration except for NH_4NO_3, which show the trend to the higher concentration (Fig. 5). The optimum concentration and mean particle sizes are summarized in Table 1. Particle size distributions of silica powders prepared in the presence of different concentrations of electrolytes are given in Fig. 6. The results showed that PSD was moving from a wide distribution to a narrow distribution at smaller size range (optimal concentration) for all additives.

The phenomena observed can be explained as follows. Below optimal concentration of electrolytes, there is no significant reduction in the particle size due to very dilute concentrations. Above that, the particle size was enhanced due to particle aggregation because of the depression of particle charge due to absorption of electrolyte onto the particles [17]. The anions were fed into the reaction mixture together with the NH_3 solution which act as catalyst. So, each drop of ammonia will carry certain dilute amount of anion (Cl^-, Br^-, I^-, NO_3^-, SO_4^{2-}), which is believed to give repulsion effect that can inhibit silica particle growth. Thus, the reducing effect of the anions on particles can be arranged in the order of:

$$Cl^- < Br^- \approx I^- < NO_3^- \approx SO_4^{2-}$$

The trend is closely related to the increasing order of the size of anions:

Cl^- (1.81 Å) < Br^- (1.95 Å) < I^- (2.16 Å) < NO_3^- (4.50 Å)[1] < SO_4^{2-} (4.64 Å)[1]

[1] Estimated values from ionic radius.

Table 1
Optimal concentrations of each ammonium salts in reducing the size of the silica nanoparticles (mean particle size blank sample: 92.3 ± 44.3 nm)

Electrolyte	Optimal concentration (M)	Mean size (nm)	S.D. (±nm)	Size reduction (%)
NH_4Cl	1×10^{-5}	34.1	29.3	63
NH_4Br	1×10^{-6}	20.5	3.5	78
NH_4I	1×10^{-6}	21.4	3.7	77
NH_4NO_3	1×10^{-4}	29.9	6.0	68
$(NH_4)_2SO_4$	1×10^{-5}	24.5	4.2	73

3.3. Conductivity studies

The conductivity measurement was used as alternative to zeta potential in an attempt to explain the effect of anions on the silica particle growth. At the initial state, the reaction mixture contains EtOH, H_2O and TEOS. It is expected that each mixture solution should give a very low conductivity reading (i.e. below 1.0 μS) since this is a non-aqueous

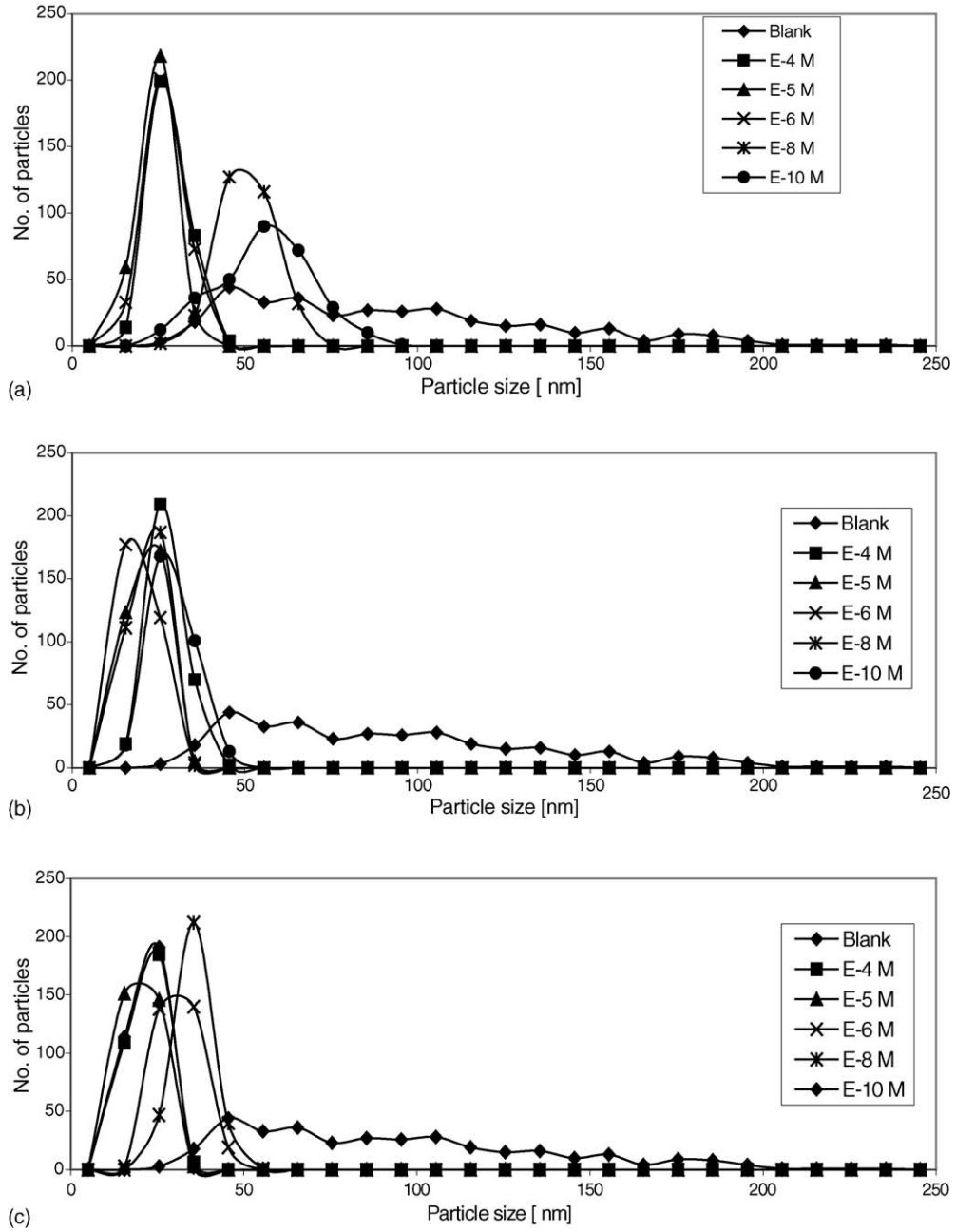

Fig. 6. Particle size distribution at different concentration of: (a) NH_4Cl; (b) NH_4Br; (c) NH_4I; (d) NH_4NO_3; and (e) $(NH_4)_2SO_4$.

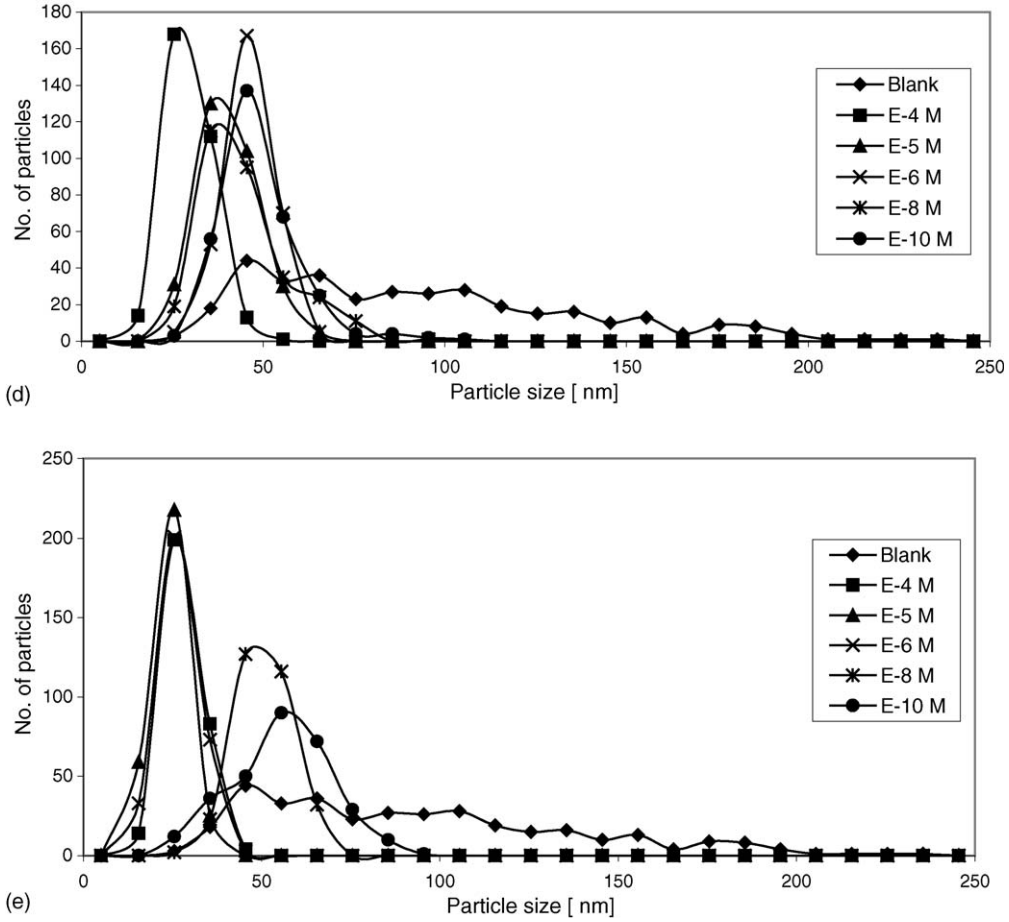

Fig. 6. (*Continued*).

system. At the final state, the solution consists of extra amount of water (compare to the initial state), produced from the condensation reaction of hydrolyzed species of TEOS in the sol–gel process, i.e. change in conductivity is due to the chemical species present and processes occurring in solution. It is found that, conductivity is high when concentrations of ions (electrolytes) are high. The final solution contains: H^+, OH^-, NH_4^+, $Cl^-/Br^-/I^-/NO_3^-/SO_4^{2-}$, monomeric silicic acid ionic species ($\equiv SiO^-$) and EtOH. The trends also shows that the conductivity decreases when the size of the ionic species increases due to reduce mobility of the ions (Fig. 7). Thus, it is possible to use

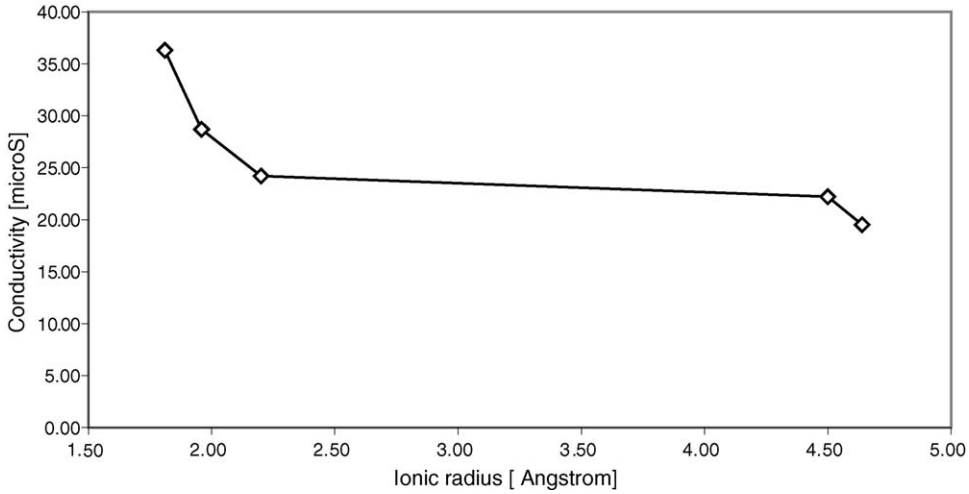

Fig. 7. Conductivity verses ionic radius of anions present in the reaction medium at the concentration of 10^{-6} M.

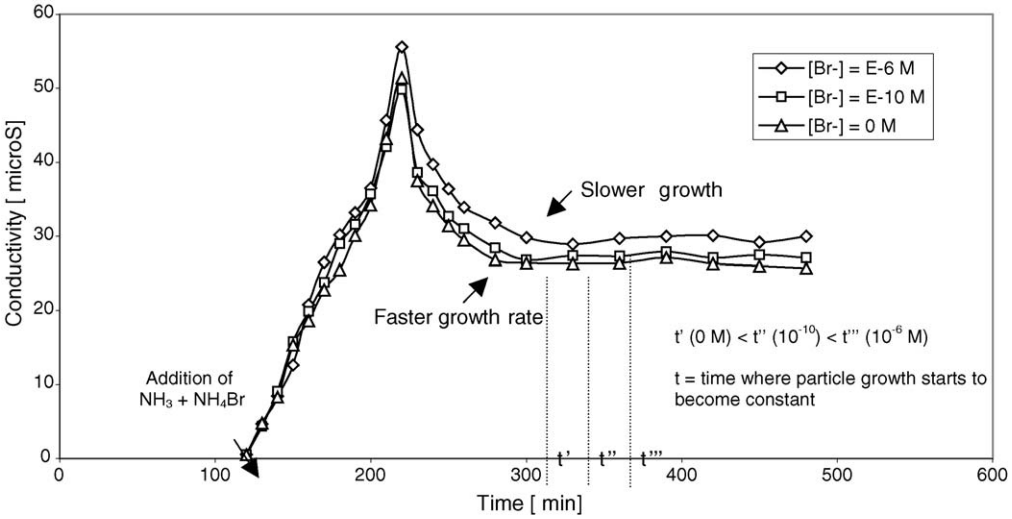

Fig. 8. Conductivity of the reaction medium containing different concentrations of Br^- ion as a function of time as compared to blank sample.

conductivity measurement of the medium to monitor the particles growth.

Fig. 8 shows conductivity profiles of the reaction mixture containing different concentrations of bromide ion (most effective anions) compared to the blank sample. The conductivity increases steadily up to the maximum point at ~220 min at similar rate which may be related to the induction period [13,17]. At this period NH_3 (and bromide

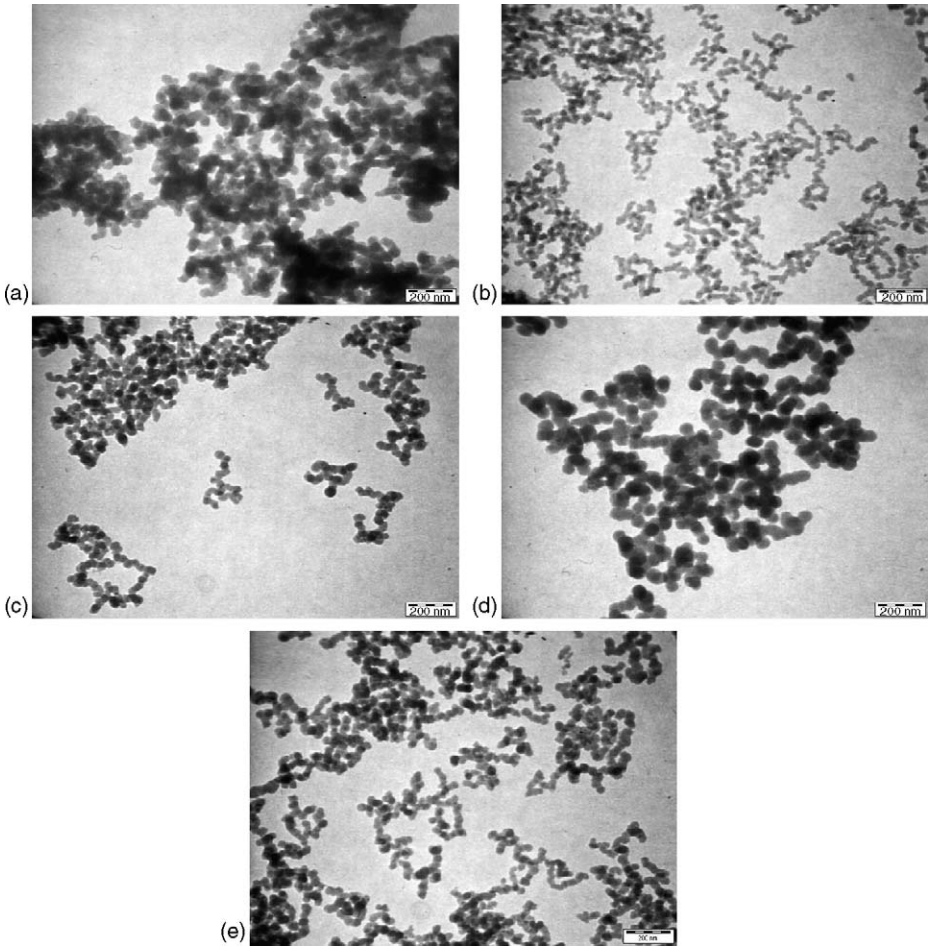

Fig. 9. TEM micrographs of silica nanoparticles synthesized in the presence of ammonium salts: (a) NH_4Cl 10^{-5} M; (b) NH_4Br 10^{-6} M; (c) NH_4I 10^{-6} M; (d) NH_4NO_3 10^{-4} M; and (e) $(NH_4)_2SO_4$ 10^{-5} M.

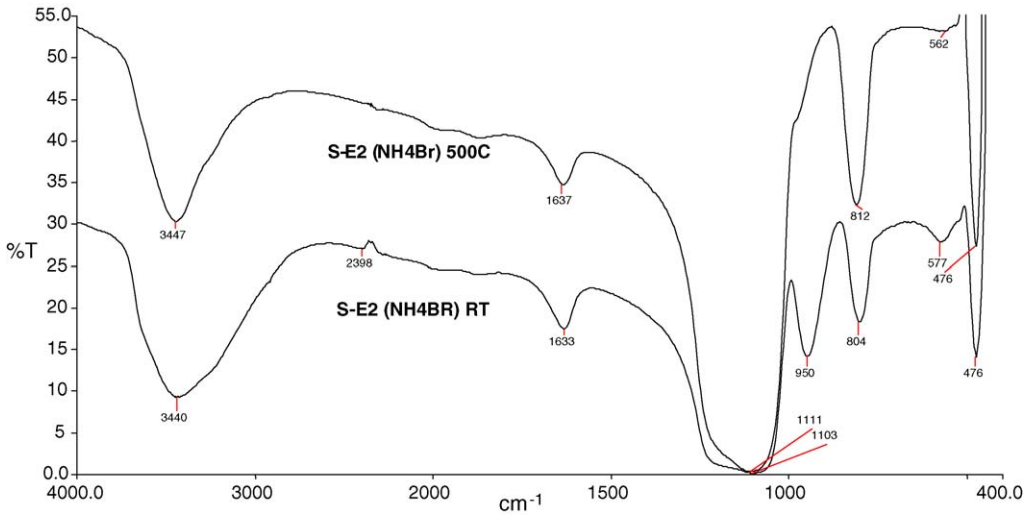

Fig. 10. FTIR spectra of silica powder prepared in the presence of bromide ion before and after calcination.

ions) was added slowly together with gradually increased of pH, and hydrolysis and condensation take place concurrently leading to the nucleation and aggregation process as discussed earlier. After the induction period, the conductivity slowly decreases to a constant value as the ionic monomeric silicic acid species were consumed in the growth process. The conductivity of the system containing 10^{-6} M of Br^- drops at slowest rate and followed by 10^{-10} M after the blank sample (without electrolyte) indicating the presence of anions in the reaction medium actually inhibits the particle growth and produces smaller size particles. A similar trend was also observed for others additives. Fig. 9 shows TEM micrographs of silica nanoparticles produced from different amount of electrolytes.

FTIR analysis of the samples before and after calcinations shows that the synthesized silica nanoparticles are pure and free of contaminants (Fig. 10). The Si–OH of the silica is observed at 916 cm^{-1}. Peak at ~1270 cm^{-1} indicates Si–O–Si bond while peak at ~3480 cm^{-1} indicates –OH group.

4. Conclusions

Thus it was found that, the nucleation and growth of nanometer silica particles by Ostwald ripening mechanism depended on the TEOS/NH_3 mol ratios. The sol particles of ~30 nm were formed at TEOS/NH_3 ratio $\geq$0.6, below that the particles ranging from 90 to 250 nm were easily obtained.

The addition of small amount of anion electrolytes produced monodispersed nanosilica powders with particles size ranging from 20.5 to 34.1 nm depending on the anions used. It was found that the effectiveness in reducing silica particles sizes can be related to the size of anions with Br^- and I^- have the highest effect while Cl^- has the least. The phenomena observed can be explained by conductivity changes during the reaction. The powders prepared are free from contamination.

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