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FTIR, TEM and NMR Iinvestigations of Stöber Silica Nanoparticles

Aldona BEGANSKIENĖ [1], Valdas SIRUTKAITIS [2], Marytė KURTINAITIENĖ [3], Remigijus JUŠKĖNAS [3], Aivaras KAREIVA [1]

[1] *Department of General and Inorganic Chemistry, Vilnius University, Naugarduko 24, LT-03011 Vilnius, Lithuania*
[2] *Laser Research Center, Vilnius University, Saulėtekio al. 10, LT-10223 Vilnius, Lithuania*
[3] *Department of Materials Structure, Institute of Chemistry, A. Goštauto 9, LT-01108 Vilnius, Lithuania*

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In this work, the sol-gel process in non-aqueous system of tetraethylorthosilicate (TEOS) has been investigated. The formation of spherical silica nanoparticles was studied using ^{1}H and ^{13}C NMR, FTIR spectroscopies and TEM. It was demonstrated that FTIR, TEM and ^{1}H NMR can be employed to monitor effectively the conversion of TEOS into insoluble SiO_2 from the supersaturation of hydrolyzed monomers. This leads to the formation of colloidal silica primary particles. The optimized sol-gel parameters allow to produce the monodisperse spherical silica particles suitable for the development of technology for antireflection coatings.

Keywords: Stöber silica nanoparticles, sol-gel synthesis, antireflection coatings.

INTRODUCTION

Light reflections from computer monitors, car dashboards and TV screens impair the legibility of the displays by degrading the transmission of optical components. The decrease in transmission of a transparent optical medium is caused by the abrupt change in the refractive index at the interface between a medium and its environment. Antireflection (AR) coatings reduce the reflection considerably improving the quality of optical lens systems [1 – 4]. The refractive indices of glass and transparent plastic substrates are typically $n_s \approx 1.5$. The optimal refractive index for a single–layer broad–band antireflection coating is $n_f = \sqrt{n_s} \approx 1.22$. The lowest refractive indices for dielectrics are on the order of 1.35 (CaF_2, MgF_2). A value of $n_f = 1.22$ is therefore unreachable for conventional single layer AR coatings. Despite of intensive research work, the availability of broadband antireflection coatings is still limited by lack of materials with low refractive indices.

Recently Thomas [5] suggested to use a porous silica films. When the pore size is much smaller than the visible wavelengths, the effective refractive index of the nanoporous medium is dependent on film porosity. To lower the refractive index to ~1.23 using a material with a refractive index of ~1.5, a porosity of ~60 % has to be introduced. The coatings of layers of colloidal silica nanoparticles, which packed in a manner that results in an overall porosity of ~50 %, have refractive index about 1.22 [6 – 8]. Besides, such silica AR coatings are distinguished for large threshold of the laser damage, that it is very important for the optics used in high-peak-power laser systems.

At the end of seventies Stöber [9] has reported sol-gel synthesis method for the preparation of monodispersed spherical silica particles with sizes covering almost the whole colloidal range. This was done by hydrolysis of tetraethylorthosilicate (TEOS) in ethanolic medium and in the presence of ammonia. The need for well-defined silica nanoparticles has increased dramatically, as high-technological industries (computer science, biotechnology, pharmaceuticals and other) provide an elevated demand for such materials. Stöber silica particles have been used as model colloids in a large number of experimental investigations. Recently, several investigators [10 – 14] have shifted their attention to the study of the mechanisms of formation and growth of these particles. For this purpose various techniques, such as nuclear magnetic resonance, conductometry, Raman scattering, dynamic light scattering, transmission electron microscopy, small angle X-ray scattering ant others were applied to investigate and characterize both the chemistry and the physical properties of the particles, more noticeably the dynamics of growth [15 – 17]. Despite these intensive investigations, a clear and complete picture for the formation of uniform silica particles has not yet emerged.

In this work the sol-gel process in non-aqueous system of tetraethylorthosilicate was investigated using ^{1}H and ^{13}C nuclear magnetic resonance spectroscopy (NMR), Fourier transform infrared spectroscopy (FTIR) and transmission electron microscopy (TEM). The optimized parameters of the sol-gel process could allow to produce the monodisperse spherical silica particles 20 nm in size and suitable for the development of the technology for antireflection coatings.

EXPERIMENTAL

The pH values of the solutions were determined with Mettler Toledo MP 200 pH-meter. IR spectra of the materials were recorded in KBr powders using Perkin-Elmer Spectrum BX FT-IR spectrometer. Transmission electron microscopy was performed on the PEM-100 electron microscope. A copper grid with a holey carbon film was dipped in the sol, dried at room temperature and analyzed in TEM. The ^{1}H and ^{13}C NMR spectra were recorded using 300 MHz Varian Unity Inova apparatus. All NMR experiments were performed at 25 °C in CD_3OD. The resulting spectra were internally referenced to tetramethylsilane (TMS) standard.

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[*] Corresponding author. Tel.: +370-5-2366073; fax: +370-5-2366081.
E-mail address: *aldona.beganskiene@chf.vu.lt* (A. Beganskienė)

Sol-gel synthesis of colloidal SiO_2 nanoparticles was performed in non-aqueous system of TEOS. The precursor sol (3.0, 6.0 wt. percentage equivalent SiO_2) was prepared by the base catalyzed hydrolysis of tetraethylorthosilicate (Fluka, 99 %) following the method of preparation of Stöber et al.'s silica [8]. Required amount of ammonium hydroxide (33 %, Riedel-de Haen) was added to half of the required volume of anhydrous ethanol. The alkaline solution was added to the solution of TEOS in ethanol with continuous stirring at room temperature (20 ±2 °C). The molar ratio of ammonium hydroxide to alkoxide was varied from 0.06 to 1.10 mol, water – from 0.3 to 6 mol, solvents – from 9 to 37.71 mol. The obtained reaction mixture was stored for appropriate time at room temperature to allow hydrolysis as much as possible. The final product consisted of colloidal suspension of SiO_2 nanoparticles in anhydrous solvent. Particle size was determined from the micrographs obtained from TEM measurements. These results summarized from over hundred particles were used for the calculation of the average particle size and standard deviations of each sample.

RESULTS

The ammonia-catalyzed reactions of TEOS with water in alcohols (Stöber synthesis) were used for the preparation of monodisperse, spherical silica nanoparticles that range in the size from 20 up to 1000 nm. In general, the hydrolysis reaction of TEOS could be expressed by the following simple equation:

$$Si(OR)_4 + 2H_2O \rightarrow SiO_2 + 4ROH. \quad (1)$$

In fact, the controlled hydrolysis process produces the singly-hydrolyzed monomer $[(OR)_3Si(OH)]$:

$$Si(OR)_4 + xH_2O + NH_3 \rightarrow (^{-}O)_xSi(OR)_{4-x} + xROH + NH_4^+. \quad (2)$$

These intermediate reaction products participate in the condensation reactions (Eqs. (3) and (4)), and finally silica nanoparticles are forming.

$$Si(OR)_4 + (OH)Si(OR)_3 \rightarrow (OR)_3Si\text{-}O\text{-}Si(OR)_3 + ROH\ ; \quad (3)$$

$$(OR)_3Si(OH) + (OH)Si(OR)_3 \rightarrow (OR)_3Si\text{-}O\text{-}Si(OR)_3 + H_2O. \quad (4)$$

In this work our attempts were focused to establish in a more quantitative fashion the concentration ranges over which monodispersity could be achieved. Also, to develop a correlation which can be used to predict final particle sizes for given set of concentrations of starting materials (solvent, ammonia, water and TEOS) is only possible by studying a wide range of initial reaction conditions (see Table 1).

The hydrolysis rate of TEOS depends on the concentrations of H_2O and NH_3. With increasing concentration of NH_3 in the system, H_2O dissociates according to Eq. (1) producing higher amount of OH^- ions, which attack the Si atoms and increase rate of the hydrolysis. While it has been well observed that the equilibrium between the hydrolysis of TEOS and condensation is controlled by amounts of NH_3 and H_2O, the question how these reactants affect the particle size still has to be answered.

The effect of concentration of initial materials on the final particle size was investigated at room temperature by selecting appropriate aging times of 5 and 13 days. The chemical composition of starting materials, ageing time and average size of silica nanoparticles obtained are presented in Table 1.

Table 1. Chemical composition of starting materials, aging time and average particle size of silica

No	Reaction mixture Solvent: $NH_3 : H_2O$: TEOS (molar ratio)	Ageing (days)	Size (nm)
1	37.71 : 1.10 : 2.78 : 1.0	13	55 – 65
2	16.00 : 0.56 : 2.40 : 1.0	13	35 – 40
3	15.40 : 0.11 : 4.60 : 1.0	13	50 – 60
4	15.40 : 0.11 : 2.40 : 1.0	5	25 – 35
4a	15.40 : 0.11 : 2.40 : 1.0	13	35 – 40
5	9.00 : 0.06 : 2.40 : 1.0	5	<10
6^1	23.00 : 0.11: 2.40 : 1.0	5	<10
7^2	16.70 : 0.11 : 2.40 : 1.0	5	35 – 45
8^3	17.20 : 0.11 : 2.40 : 1.0	5	75 – 100

Solvent – ethanol, ^{1} methanol, ^{2} 2-propanol, ^{3} acetone.

The TEOS concentration was fixed (1 M) changing the concentrations of ammonia and water in a systematic manner. From the results presented in Table 1 we can conclude that the particle size of the synthesis product decreases with decreasing concentrations of water and ammonia. The doubling of H_2O concentration from 2.40 to 4.60 at constant concentration of NH_3 (0.11 M) has negligible effect on the particle size in comparison with the same influence of doubling of NH_3 concentration from 0.06 to 0.11 at the constant amount of water (2.40 M).

The pH measurements of reaction mixtures showed, that pH values of all reaction mixtures decreased from 11.4 – 10.8 to 10.3 – 9.6 in due to consuming of the NH_3 during ageing time. The pH value remained constant just after the initial period is finished.

The influence of solvent on the formation of colloidal silica particles was also examinated. The smallest particles were formed in methanol (mixture 6), and largest – in acetone (mixture 8). It was also demonstrated that the solvent shows a strong infuence on the formation of primary particles. This size dependence has been largely correlated to the decrease in the polarity of the solvents. Also the decreasing twise the concentration of NH_3 from 0.11 to 0.06 in an ethanol (mixture 5) leads to the formation of the same size particles as in the methanol (mixture 6).

The extraordinary influence of synthesis conditions on the textural properties and morphology of colloidal silica prepared by the sol-gel technique is well exhibited by TEM measurements. Fig. 1 shows the TEM micrographs of silica particles obtained from different syntheses.

IR spectroscopy has been also widely applied to investigate of sol-gel silica films [18]. Analysis of IR spectra provides an important indication of the influence of processing parameters on films microstructure. The typical FTIR spectra of the colloidal silica particles obtained at different ageing times are shown in Fig. 2.

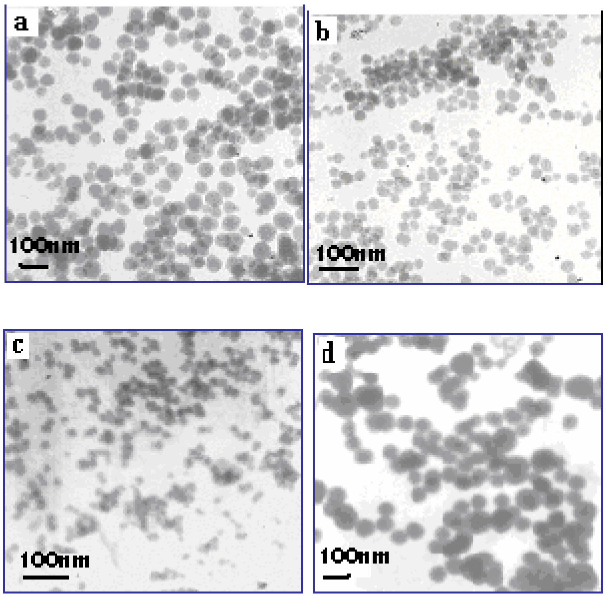

Fig. 1. TEM images (×80 000) of silica particles obtained from reaction mixtures of solvent : NH_3:H_2O:TEOS (mol): a – ethanol: 1.10 : 2.78 : 1.0; b – ethanol: 0.11 : 2.40 : 1.0; c – ethanol: 0.06 : 2.40 : 1.0 and d – acetone: 0.11 : 2.40 : 1.0

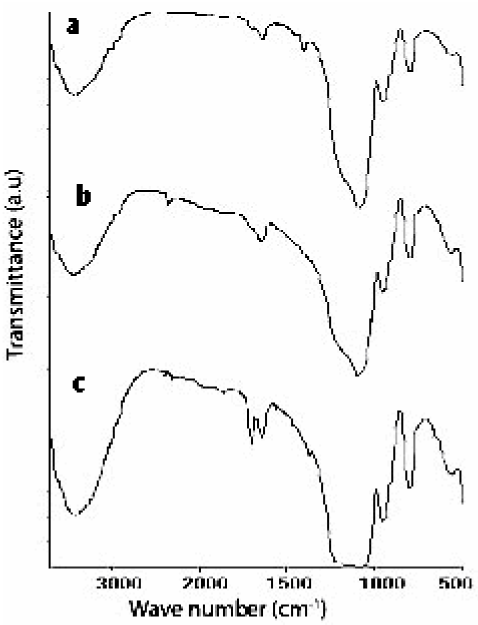

Fig. 2. IR spectra of silica particles obtained from reaction mixture C_2H_5OH: NH_3 : H_2O : TEOS 15.40 : 2.40 : 1.0 (mol) at different ageing times: a – 1 day, b – 5 days, c – 13 days

The FTIR spectra of the colloidal particles show absorption bands arising from asymmetric vibration of Si–O (1090 cm^{-1}), asymmetric vibration of Si–OH (950 cm^{-1}), and symmetric vibration of Si–O (795 cm^{-1}). The absorption bands between 800 and 1260 cm^{-1} have been described as a superimposition of various SiO_2 peaks, Si–OH bonding and peaks due to residual organic groups. Water shows an intense characteristic absorption band between 3300 cm^{-1} and 3500 cm^{-1} assigned to O–H stretching in H-bonded water. Also this band can be cross checked through the 1635 cm^{-1} band due to scissor bending vibration of molecular water. The absorbtion band 2980 cm^{-1} (CH_3) and 2930 cm^{-1} (CH_2) can be used to identify the presence of unreacted TEOS in the silica particles. The intensity of C–H absorbance group decreases with increasing ageing time, while the intensity of brod absorbance band in the O–H stretching 3300 – 3600 cm^{-1} region (H-bonded H_2O, hydroxyl terminals, H-bonded OH vibrations of alcohol and H-bonded Si–OH in chain) increases respectively with ageing time. Also, it can be observed that intensity of the 1635 cm^{-1} band due to vibration of molecular water decreasing, while intensity of absorbtion band at 1695 cm^{-1} (the origin of which is not clear) increases with ageing time.

The kinetic experiments of TEOS hydrolysis were performed on the system of 1.1 M NH_3, 2.4 M H_2O and 1 M TEOS in CD_3OD using ^{1}H- and ^{13}C–NMR spectroscopies. The ^{1}H-NMR spectra (Fig. 3) show the presence of ethoxy groups: CH_3 peaks at 1.1 ppm, and CH_2 of TEOS at 3.9 ppm and CH_2 of ethanol and silanols at 3.7 ppm, and water at 4.7 ppm. The CH_3 and CH_2 intensities of TEOS decrease, while intensities of ethanol and silanols ethoxy groups increase due to TEOS hydrolysis during the ageing time.

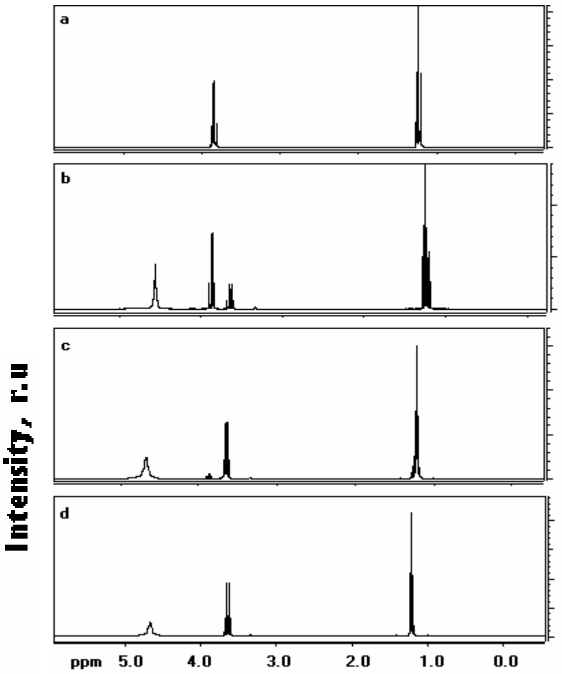

Fig. 3. ^{1}H-NMR spectra of kinetic experiment of: a – TEOS; b – mixture TEOS and NH_3 (1 : 1.1), after 2 h; c – TEOS and NH_3 (1 : 1.1), after 6 h; d – TEOS and NH_3 (1 : 1.1), after 24 h

The ^{13}C-NMR signals of TEOS were observed at 18.4 and 60.2 ppm for the equivalent carbons of the –CH_3 and OCH_2-, respectively. The residual solvent (MeOH–D_4) peaks were centered at 49.0 ppm. Fig. 4 shows the results of the ^{13}C-NMR kinetic study of the reaction mixture having different molar ratio of constituents.

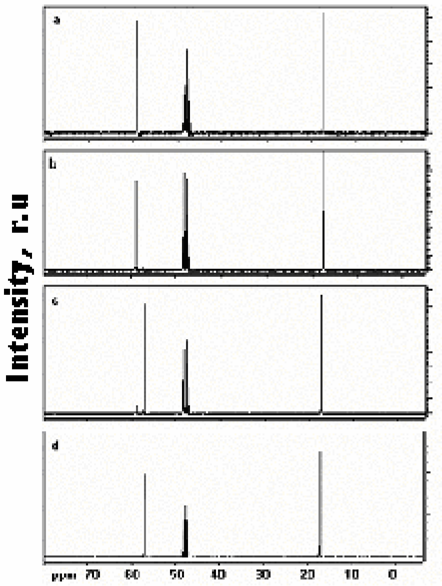

Fig. 4. ^{13}C-NMR spectra of kinetic experiment of : a – TEOS; b – mixture TEOS and NH_3 (1 : 1.1), after 2 h; c – TEOS and NH_3 (1 : 1.1), after 6 h; d – TEOS and NH_3 (1 : 1.1), after 24 h

The reducing peak intensities at 18.4 and 60.2 ppm correspond to the TEOS. The release of the ethanol due to the hydrolysis and condensation of TEOS (Eqs. 1, 2 and 3) was observed from the increasing peak intensities at 18.3 ppm (CH_3) and 58.3 ppm (CH_2). The NMR spectral information were used to determine the effect of the concentration of NH_3, H_2O and solvent on the hydrolysis of TEOS and resolve witch soluble silica species are present before primary particle formation.

CONCLUSIONS

We have shown that FTIR, TEM and NMR techniques can be easily employed to monitor the conversion of TEOS into insoluble SiO_2 from the supersaturation of hydrolysed monomers. This leads to the formation of colloidal silica primary particles, their continuous nucleation, and structural development. The successful use of these techniques suggests the following: the solution (TEOS, NH_3, H_2O and solvent) chemistry controls the reaction rate and particle size; the NH_3 and H_2O concentrations control the equilibrium between the hydrolysis and the condensation processes of hydrolyzed monomers. The smallest particles were formed in ethanol solution at 1 M TEOS, 0.06 M NH_3 and 2.40 M H_2O. The optimized sol-gel parameters allow to produce the monodisperse spherical silica particles suitable for the development of technology for antireflection coatings.

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