

Effect of Tetraethoxysilane Pretreatment on Synthesis of Colloidal Particles of Amorphous Silicon Dioxide

E. Yu. Trofimova, A. E. Aleksenskii, S. A. Grudinkin, I. V. Korokin, D. A. Kurdyukov, and V. G. Golubev

Ioffe Physicotechnical Institute, Russian Academy of Sciences, Politekhnicheskaya ul. 26, St. Petersburg, 194021 Russia

Received November 9, 2010

Abstract—The effect of the time passed after tetraethoxysilane treatment with ammonia on the diameter of particles produced by tetraethoxysilane hydrolysis in alcohol–water–ammonia media is studied. The regulation the time passed after of tetraethoxysilane treatment results in the synthesis of submicron monodisperse spherical silica particles with diameters differing by a factor of two. The difference is explained by the formation of SiO₂ particles with sizes of 10–100 nm in tetraethoxysilane during 10–30 h after treatment with ammonia. These particles enhance the concentration of nucleation centers in a reaction mixture, thus decreasing the final size of monodisperse silica spheres. Opal films with a high structural perfection and pronounced photonic crystal properties are grown based on the obtained monodisperse SiO₂ particles.

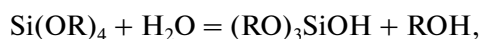
DOI: 10.1134/S1061933X11040156

INTRODUCTION

Artificial opals represent the basis for the production of functional composites, in particular three-dimensional photonic crystals (3D-PCs), i.e., materials that contain a photonic band gap, which suppresses the propagation of light in a certain frequency range [1]. Opals are porous media composed of densely packed monodisperse spherical silica particles (MSSPs) with submicron sizes [2–4]. Opal films are most promising to be used in optics and optoelectronics [5, 6]. One of the procedures for opal film production is the meniscus method proposed in [5]. MSSPs are ordered under the effect of the surface tension and capillary forces acting in a meniscus, which results from the contact of a suspension with a vertically installed substrate. In this situation, spherical SiO₂ particles are packed into a face-centered cubic lattice with plane (111) parallel to the substrate. High-quality opal films may be prepared, provided that the dispersion of MSSP sizes is less than 6% [7].

There are several methods to produce MSSPs, in particular their formation from aqueous SiO₂ sols (the Gaskin–Darragh method) [8], the preparation of slightly aggregated MSSPs from a mixture of a gelation agent (a formate, acetate, or propionate) with an aqueous sodium silicate solution (the Asker–Winyall method) [9], and the hydrolysis of orthosilicic acid esters (the Stöber–Fink–Bohn method) [10]. The Stöber–Fink–Bohn method [10] is most frequently applied because the synthesis takes rather a short time (2–3 h) and does not require the use of expensive reagents; however, the properties of the synthesized particles (the final sizes and their dispersion) strongly depend on the properties of initial tetraethoxysilane (TEOS) [2].

TEOS is known to be readily hydrolyzable with water [11], including that contained in air. The initial stage of TEOS hydrolysis proceeds as follows:



where R is an alkyl C₂H₅ group. Further, hydrolysis products undergo condensation with the formation of disiloxane and hydroxydisiloxane followed by their polycondensation. It was revealed [2] that the presence of polysiloxanes with different degrees of polymerization in TEOS causes the nucleation of primary SiO₂ particles with different sizes and enhances the size dispersion during their growth. It was proposed to remove polysiloxanes by the fractional distillation of TEOS followed by a treatment with ammonia of a fraction having boiling temperature $T_b = 166\text{--}168^\circ\text{C}$ [2, 12, 13]. The treatment of TEOS with an aqueous ammonia solution decreases the size dispersion of silica particles [2].

Variations in the properties of TEOS treated with an aqueous ammonia solution were studied by the IR spectroscopy method in [2]. It was shown that the treatment results in the formation of an intermediate hydrous complex without the saponification of ethoxy groups, which is evident from the appearance of two new absorption bands at 3590 and 3650 cm⁻¹ in the spectral region of the stretching vibrations of OH groups in the IR spectrum of TEOS. The band at 3590 cm⁻¹ is assigned to the stretching vibrations of OH groups of water molecules hydrogen-bonded to oxygen atoms of TEOS ethoxy groups. The band at 3650 cm⁻¹ arises due to the vibrations of OH groups of water molecules bonded to Si atoms of the ether. In other words, TEOS treated with NH₃ contains a large amount of water that is not involved in the chemical interactions with the ether.

The final size of MSSPs synthesized through the Stöber–Fink–Bohn method depends on the concentrations of TEOS [14, 15], H₂O [10], and, to the greatest extent, NH₃ [10] in the initial mixture, as well as on temperature. A twofold increase in TEOS, NH₃, and H₂O concentrations in a reaction mixture leads to a drastic rise in the average MSSP diameter by factors 1.5, 2.5, and 2, respectively [10, 14], while the elevation of the reaction temperature from 20 to 60°C causes a twofold decrease in the size of SiO₂ particles [16]. Because of the strong dependence of the particle size on the concentrations of initial reagents and temperature, it is rather difficult to precisely synthesize monodisperse SiO₂ spheres with strictly preset diameters [17]. More reliable results can be obtained when MSSPs are synthesized by applying the so-called “successive growth” of particle [2, 18, 19]. In this case, particles are grown in two stages. The standard synthesis procedure is performed at the first stage, during which particles with diameter on the order of 100 nm and a low dispersity grow. At the second stage, the precisely preset amount of TEOS is added to synthesize spheres with a desired diameter.

In our work, MSSPs with diameters of 250–700 nm were synthesized from TEOS treated with ammonia during 2–30 h after treatment. At the same ratios between the initial reagents, particles that were produced 30 h after the treatment of TEOS with ammonia had a diameter twofold smaller than MSSPs synthesized from freshly treated TEOS. The developed procedure enables one to gradually regulate the final size of MSSPs in a range of 250–350 nm. Opal films were grown from the MSSPs, and their optical properties were investigated.

EXPERIMENTAL

Spherical silica particles were synthesized by hydrolyzing TEOS in a C₂H₅OH–NH₃–H₂O system [10]. The main substance concentration in the aqueous ammonia solution was 24 wt %. Initial ethanol had a concentration of 95.7 wt %. Ethanol and the ammonia solution were used as received. Deionized water with a resistance of 10 MΩ was applied for the synthesis.

Tetraethoxysilane was subjected to fractional distillation collecting a fraction with boiling temperature $T_b = 166–168^\circ\text{C}$. Then, TEOS was treated with an aqueous 0.5 wt % ammonia solution for 20 min at a TEOS-to-aqueous ammonia solution ratio of 5 : 1, mass/mass (the procedure is described in [12]).

The TEOS : NH₃ : H₂O concentration ratio in the reaction mixtures used to synthesize MSSPs was 0.18 : (1–6) : 9 mol/l, respectively. The first series of the experiments was implemented with TEOS freshly treated with ammonia; in the second series, the experiments were carried out 30 h after the treatment. In all experiments, the temperature of the reaction mixtures was 20°C. The duration of the synthesis was 4 h.

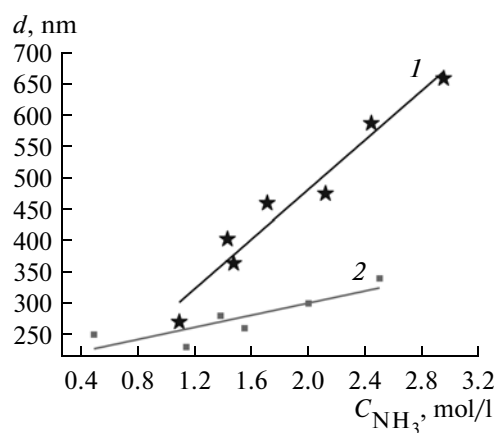


Fig. 1. Average diameters determined by DLS for synthesized particles as functions of ammonia concentration in reaction mixtures containing TEOS, 0.18 mol/l, and H₂O, 9 mol/l. Synthesis was performed using (1) freshly treated TEOS and (2) TEOS aged for 30 h after treatment with ammonia.

Artificial opal films were grown from the synthesized dispersions by the meniscus method [5] on quartz substrates with sizes of 25 × 25 × 1 mm. The concentration of MSSPs in the aqueous suspension was 1 wt %.

Variations occurring in TEOS after the treatment with ammonia and final sizes of MSSPs were determined by the dynamic light scattering (DLS) method with a Zetasizer Nano instrument (Malvern, Great Britain) at 25°C. Reflectance and transmission spectra of the grown opal films were recorded at a normal incidence of light with Ocean Optics USB4000 and Ocean Optics NIR512 spectrometers in wavelength ranges of 500–900 and 900–1600 nm, respectively. Microscopic studies were performed applying a SMENA (NT-MDT, Russia) atomic force microscope (AFM) in the tapping mode.

RESULTS AND DISCUSSION

Diameters d of the synthesized silica particles, as measured by the DLS method, are presented in Fig. 1 as functions of ammonia concentration in reaction mixtures. Increasing ammonia concentration leads to a rise in the average particle diameter. At constant ratios between other reagents, spheres prepared from freshly treated TEOS have larger diameters than those obtained from TEOS aged for 10–30 h after the treatment with ammonia. Note that the dependence of particle diameter on NH₃ concentration plotted for freshly treated TEOS (Fig. 1, curve 1) coincides with the dependence that Stöber established in [10].

The plotted curves may be described by the following linear function:

$$D_{\text{sphere}} = k C_{\text{NH}_3} + b, \quad (1)$$

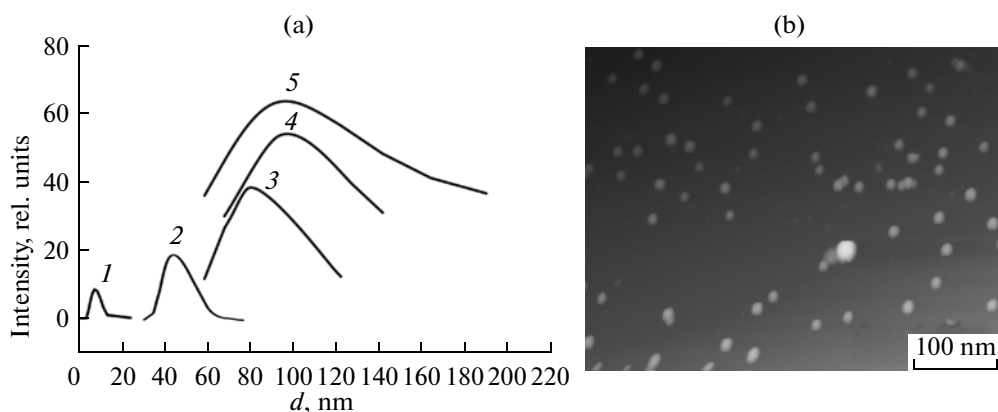


Fig. 2. Panel (a) DLS spectra measured for TEOS in (1) 10, (2) 15, (3) 22, (4) 30, and (5) 40 h after its treatment with ammonia; spectra 3–5 are shifted along the ordinate axis for convenience and panel (b): AFM image of TEOS dried on a silicon substrate 10 h after treatment with aqueous ammonia solution.

where D_{sphere} is the diameter of MSSPs being synthesized, nm; C_{NH_3} is the concentration of ammonia, mol/l; k is the proportionality coefficient, nm l/mol; and b is a constant, nm.

Thus, we find that the growth of particle sizes is described by the following equations $D_{\text{sphere}} = 85 + 200C_{\text{NH}_3}$ and $D_{\text{sphere}} = 200 + 50C_{\text{NH}_3}$ for systems comprising TEOS freshly treated with ammonia and that aged for 30 h after treatment, respectively. In order to explain the differences that arose in the D_{sphere} vs. C_{NH_3} dependence, the changes occurring in TEOS after its purification with ammonia were investigated. During initial 10 h, no changes in TEOS were observed. Then, the appearance of particles with an average hydrodynamic radius of approximately 10 nm was recorded in it (Fig. 2a). Figure 2b illustrates the AFM image of TEOS aged for 10 h after the purification with ammonia, applied onto a silicon substrate, and dried at 200°C. The micrograph demonstrates spherical particles, the majority of which have a size of ~10 nm, which coincides with the results of DLS measurements. Over 25–30 h, the size of particles in TEOS reaches ~100 nm; then, it remains almost unchanged (Fig. 2a). Most likely, these particles consist of $\text{SiO}_2 \cdot x\text{H}_2\text{O}$ and result from the chemical reaction between TEOS and complexed H_2O . The product of the hydrolysis is hydrated amorphous SiO_2 (polysiloxane). SiO_2 particles have a spherical shape (Fig. 2b), which minimizes their surface free energy.

The formation process of SiO_2 particles in TEOS essentially influences the growth of MSSPs and their sizes. When freshly distilled and ammonia-treated TEOS is used, the nucleation and subsequent growth of particles to a final size obviously proceeds during the synthesis [13, 15]. Thirty hours after the treatment with NH_3 , nucleation centers ($\text{SiO}_2 \cdot x\text{H}_2\text{O}$ particles) are already present in TEOS; therefore, the successive

growth process, i.e., an increase in the particle sizes similar to that described in [2, 18, 19], takes place.

The difference in the average diameters of MSSPs formed from freshly treated and aged TEOS at the same reagent concentration ratios (Fig. 1) may be explained as follows. The same total volume of SiO_2 particles is formed from the same amount of TEOS. Seemingly, the number of nuclei present in aged TEOS is several times larger than the amount of nuclei formed immediately during the hydrolysis of freshly treated TEOS in a reaction mixture. Therefore, a smaller number of particles with a larger diameter are obtained from freshly treated TEOS, while the application of aged TEOS results in the formation of a larger number of suspensions of particles with smaller sizes.

In order to prove the feasibility of PC production from the synthesized MSSPs, opal films were grown from SiO_2 dispersions obtained from freshly treated and aged TEOS and their optical properties were studied.

The AFM image of the external surface of artificial opal is depicted in Fig. 3a. Freshly treated TEOS was applied for the synthesis. The fcc packing of the spheres seen in the AFM image suggests that plane (111) is oriented parallel to the substrate surface. According to the statistical processing of the data on the particle sizes (Fig. 3a), their average diameter is 605 ± 25 nm. Dispersion of the sizes of MSSPs obtained from aged TEOS was no higher than 4%.

The reflectance and transmission spectra of opal films grown from suspensions of SiO_2 particles resulting from different series of the experiments on synthesis implemented at an ammonia concentration in the reaction mixtures of 2.6 mol/l are illustrated in Fig. 3b. The maxima in the reflectance spectra and the minima in the transmission spectra result from the Bragg light diffraction on planes (111) of the opal films. Their

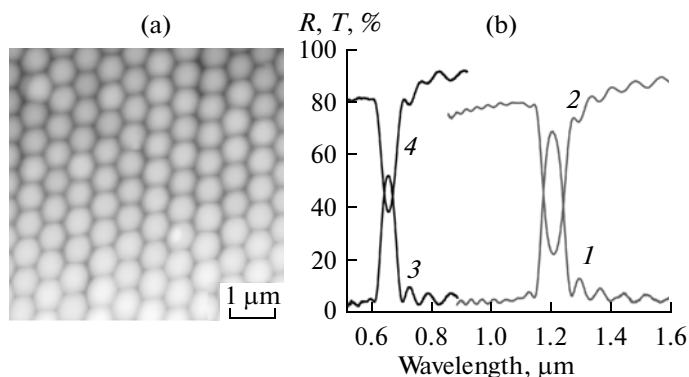


Fig. 3. Panel (a) AFM image of opal film synthesized from TEOS freshly treated with ammonia and panel (b): (1, 3) reflectance and (2, 4) transmission spectra measured at normal incidence of light for synthetic opal films grown from (1, 2) freshly treated and (3, 4) aged TEOS.

positions in the spectra are described by the Bragg law as follows:

$$\lambda_{111} = 2d_{(111)}\sqrt{n_{\text{eff}}^2 - \sin^2 \theta}, \quad (2)$$

where λ_{111} is the spectral position of an extreme, $d_{(111)} = D_{\text{sphere}}\sqrt{2/3}$ is the interplanar spacing along the (111) direction, n_{eff} is the effective refractive index of opal, and θ is the light incidence angle relative to the normal to the sample surface. The effective refractive index of opal can be presented in the following form:

$$n_{\text{eff}} = \sqrt{n_{\text{sphere}}^2 f_{\text{sphere}} + n_{\text{air}}^2 (1 - f_{\text{sphere}})}, \quad (3)$$

where $n_{\text{sphere}} \approx 1.4$ is the refractive index of SiO_2 particles [20], $n_{\text{air}} \approx 1$ is the refractive index of air, and $f_{\text{sphere}} = 0.74$ is the volume fraction occupied by the particles.

The diameters of SiO_2 particles calculated from the Bragg equation (2) are 590 and 305 nm for dispersions synthesized from freshly treated TEOS and that aged for 30 h after the treatment with the ammonia solution. The spectra demonstrate oscillations resulting from the Fabry–Perot interference on the opal film. The observed interference testifies that the film is plane-parallel. The positions of the interference peaks were used to determine the thicknesses of the prepared films [5], which amounted to 14 and 22 layers for SiO_2 particles with diameters of 305 and 590 nm, respectively. Bragg reflection coefficients R_B of opal films depend on their thickness. According to [21, 22], R_B of opal films composed of 14 and 22 layers must be on the order of 50 and 65%, respectively. The measured R_B coefficients correspond to the aforementioned values, which indicates the high structural perfection of our films.

CONCLUSIONS

Spherical silica particles with a dispersion of sizes of less than 4% were synthesized from tetraethoxysilane aged for 2–30 h after its treatment with ammonia. The application of TEOS freshly treated with ammonia resulted in the formation MSSPs with sizes in the range of 250–700 nm. Using TEOS aged for 30 h after the treatment, MSSPs were obtained with sizes of 250–350 nm. At the same reagent ratio in the initial mixtures, the difference in the final diameters of synthesized MSSPs was only governed by the time elapsed after the TEOS treatment with ammonia. In 10–30 h after the treatment, SiO_2 particles with sizes on the order of 10–100 nm were formed in TEOS. These particles were the products of TEOS hydrolysis with water that was introduced into it with the ammonia solution. Seemingly, reaction mixtures based on freshly treated and aged TEOS contained different amounts of nucleation centers, and this circumstance affected the final size of SiO_2 particles.

At a constant concentration of TEOS, the final diameters of MSSPs were related to the ammonia concentrations in the initial mixtures as $D_{\text{sphere}} = 85 + 200C_{\text{NH}_3}$ for TEOS freshly treated with ammonia and $D_{\text{sphere}} = 200 + 50C_{\text{NH}_3}$ for aged TEOS. Therefore, the application of aged TEOS results in the more gradual regulation of final MSSP diameters within a range of 250–350 nm by varying NH_3 concentration. The reflectance and transmission spectra of opal films grown from the synthesized MSSPs contain intense Bragg and interference bands characteristic of film opal-like photonic crystals with a high structural perfection.

ACKNOWLEDGMENTS

This work was supported by the Physical Sciences Division of the Russian Academy of Sciences, the Scientific and Educational Center of the Federal Agency for Science and Innovations (State Contract 02.740.11.0108), and the Russian Foundation for Basic Research (project no. 11-02-00865).

REFERENCES

1. Bush, K. and John, S., *Phys. Rev. E: Stat. Phys., Plasmas, Fluids, Relat. Interdiscip. Top.*, 1998, vol. 58, p. 3896.
2. Deniskina, N.D., Kalinin, D.V., and Kazantseva, L.K., *Blagorodnye opaly (prirodnye i sinteticheskie)* (Noble Opals (Nature and Synthetic)), Novosibirsk: Nauka, 1987.
3. Miguez, H., Lopez, C., Meseguer, F., et al., *Appl. Phys. Lett.*, 1997, vol. 71, p. 1148.
4. Lopez, C., *Adv. Mater.* (Weinheim, Fed. Repub. Ger.), 2003, vol. 15, p. 1679.
5. Jiang, P., Bertone, J.F., Hwang, K.S., and Colvin, V.L., *Chem. Mater.*, 1999, vol. 11, p. 2132.

6. Wong, S., Kitaev, V., and Ozin, G.A., *J. Am. Chem. Soc.*, 2003, vol. 125, p. 15589.
7. Rengarajan, R., Mittleman, D., Rich, C., and Colvin, V., *Phys. Rev. E: Stat. Phys., Plasmas, Fluids, Relat. Interdiscip. Top.*, 2005, vol. 71, p. 016615.
8. Darragh, P.J., Gaskin, A.J., and Sanders, J.V., *Sci. Am.*, 1976, vol. 234, p. 84.
9. Asker, E.G. and Winyall, M.E., US Patent, 1977, no. 4049, p. 781.
10. Stober, W., Fink, A., and Bohn, E., *J. Colloid Interface Sci.*, 1968, vol. 26, p. 62.
11. Andrianov, K.A., *Kremniorganicheskie soedineniya (Organosilicon Compounds)*, Moscow: Goskhimizdat, 1955.
12. Ryabenko, E.A., Kuznetsov, A.I., Shalunov, B.Z., et al., *Zh. Prikl. Khim. (Leningrad)*, 1977, vol. 50, p. 1625.
13. Potapov, V.V. and Kamashev, D.V., *Fiz. Khim. Stekla*, 2006, vol. 32, p. 124.
14. Masalov, V.M., Aldushin, K.A., Dolganov, P.V., and Emel'chenko, G.A., *Phys. Low-Dimens. Struct.*, 2001, nos. 5/6, p. 93.
15. Santamaria Razo, D.A., Pallavidino, L., Garrone, E., et al., *J. Nanoparticle Res.*, 2008, vol. 10, p. 1225.
16. Lee, Y.G., Park, J.H., Oh, C., et al., *Langmuir*, 2007, vol. 23, p. 10875.
17. Van Blaaderen, A., Van Geest, J., and Vrij, A., *J. Colloid Interface Sci.*, 1992, vol. 154, p. 481.
18. Bogush, G.H., Tracy, M.A., and Zukoski, I.F., *J. Non-Cryst. Solids*, 1988, vol. 104, p. 95.
19. Serdobintseva, V.V., Kalinin, D.V., Danilyuk, A.F., et al., *React. Kinet. Catal. Lett.*, 2005, vol. 84, p. 389.
20. Grudinkin, S.A., Kaplan, S.F., Kartenko, N.F., et al., *J. Phys. Chem. C*, 2008, vol. 112, p. 17855.
21. Galisteo-Lopez, J.F., Palacios-Lidon, E., Castillo-Martinez, E., and Lopez, C., *Phys. Rev. B: Condens. Matter*, 2003, vol. 68, p. 115109.
22. Garcia, P.D., Sapienza, R., Froufe-Perez, L.S., and Lopez, C., *Phys. Rev. B: Condens. Matter*, 2009, vol. 79, p. 241109.