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Control over the Stöber silica particles size within two orders of magnitude by tailoring the nucleation

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Abstract. A panoscopic approach for governing the size of Stöber silica particles over a wide length scale, from tens of nanometers to several microns has been suggested. Low-size particles (10–400 nm) are obtained by changing the silica precursor, mid-size particles (0.4–0.7 mm) are synthesized with variation of ammonia concentration, large particles (up to 4 mm) are made by successive growth method.

Keywords: amorphous silica, Stöber particles, successive growth, tetraethoxysilane, 3-methacryloxypropyltrimethoxysilane

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Синтез по методу Штобера частиц кремнезема контролируемого размера, варьируемого в пределах двух порядков

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Аннотация. Предложен универсальный подход для управления размером частиц кремнезема, синтезируемых по методу Штобера, в широком диапазоне размеров – от десятков нанометров до нескольких микрон. Частицы малого размера (10–400 нм) получены путем замены кремниевого прекурсора, частицы среднего размера (0.4–0.7 мкм) синтезированы за счет варьирования концентрации аммиака, крупные частицы (до 4 мкм) получены методом послойного доращивания.

Ключевые слова: аморфный кремнезем, штоберовские частицы, послойное доращивание, тетраэтоксисилан, метакрилоксипропилтриметоксисилан

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Introduction

Spherical silica particles (SSPs) are one of the most important and widely used materials in many advanced applications, such as catalysis, chromatography, sensor technology, photonics, and biomedicine [1–5]. Monodisperse SSPs are used, in particular, for the fabrication of opal-like photonic crystals [6], whose pores are filled with various semiconductor materials for optical contrast enhancement [6, 7]. Traditionally SSPs are synthesized by hydrolysis of orthosilicic acid ethers, such as tetraethoxysilane (TEOS), in the C_2H_5OH-H_2O-NH_3 media (the Stöber–Fink–Bohn (SFB) method [8]). The diameter of spherical particles prepared by the SFB method depends on together with temperature, the concentrations of TEOS [9, 10], H_2O [8] and NH_3 [8] in a reaction mixture. A doubling in the concentration of each reagent leads to an approximately twofold enlargement of the SSP diameter [8, 10, 11]. To obtain the particles with the sizes over 1 μm the successive growth method is applied [12]. To vary the size of SSP in a wide range (up to an order of magnitude), it is often necessary to substantially modify the synthesis procedure. As a result, the conditions for obtaining the particles with the sizes of tens and hundreds of nanometers vary significantly, which raises technological problems [10, 11]. The goal of this work was to develop an approach to the synthesis of SSPs that would allow varying their sizes in a wide range (from tens of nanometers to several microns) through minimal changes of the synthesis parameters.

Materials and Methods

Materials. TEOS, $Si(OC_2H_5)_4$, 99+% (Acros), 3-methacryloxypropyltrimethoxysilane (MPTMOS), $C_{10}H_{20}O_5Si$, 98+% (Aldrich); aqueous ammonia (NH_3), 24% wt., ≥ 99.99%; ethanol (C_2H_5OH), 95% wt.; deionized water (H_2O) 10 MΩ. TEOS was subjected to fractional distillation collecting a fraction with boiling temperature T_b = 166–168 °C.

Methods. SSPs were synthesized via basic hydrolysis of TEOS (or TEOS+MPTMOS) in a H_2O-NH_3-C_2H_5OH mixture (1 L) at 30 °C. We performed three sets of syntheses. The ratio of the reagent concentrations (TEOS:NH_3:H_2O) in the first set was 0.18 : 1.8 : 9 mol L^{-1}, respectively. A part (0–12.5 % mol.) of the silica precursor TEOS was replaced by MPTMOS. In the second set only ammonia concentration was varied in the range 1.8–3.5 mol L^{-1}. A successive growth method was used to obtain the particles with the sizes over 700 nm. For this purpose, 5-g portions of TEOS were added every 10 min to 1 L of NH_3 : H_2O : C_2H_5OH (3.4 : 9 : 14 mol L^{-1}, respectively) mixture containing 1 g of 720 nm SSPs. The obtained particles were centrifuged, dried, and annealed in air for 2 h at 500 °C.

Particle size distribution (PSD) of synthesized SSPs was determined by dynamic light scattering (DLS) at 25 °C with the use of a Malvern Zetasizer Nano analyzer. The PSD was calculated using the built-in analyzer software. Transmission electron microscopic measurements (TEM) were performed using a Jeol JEM-2100F microscope (accelerating voltage 200 kV, point-to-point resolution 0.19 nm). Large particles were additionally studied using an optical microscope.

Results and Discussion

The mechanism of SSPs formation is based on the aggregative model of the particle growth and lies in the fact that TEOS hydrolysis is occurred in the reaction mixture of H_2O-NH_3-C_2H_5OH under intensive stirring with the formation of the initial SiO_2 particles of several nanometers in size, which then coagulate into submicron spherical aggregates. The formation, growth rate and the final size of SSPs directly depends on the conditions chosen. Fig. 1 shows the values of the synthesized particles diameters depending on the synthesis parameters. The size of the particles was determined by TEM, DLS (for D < 1.5 μm) and optical microscopy (for D > 2 μm).

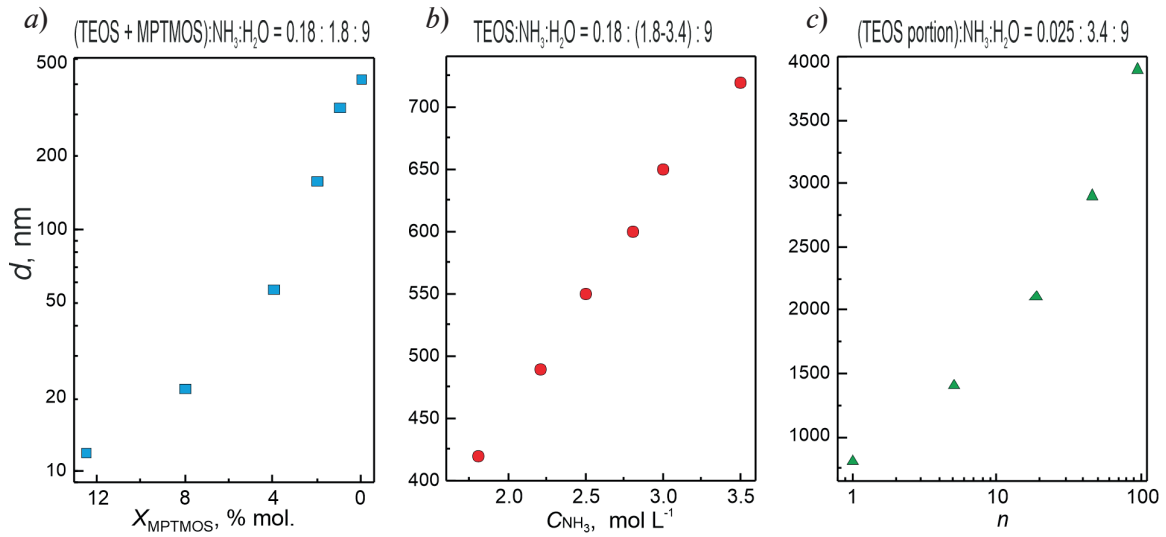

Fig.1 Dependence of particle diameter on: MPTMOS content in organosilane precursor (*a*); ammonia content in the reaction mixture (*b*); number of successive growth runs (*c*). The main synthesis parameters are shown above the panels

It can be seen (Fig.1, *a*) that an increase of the final size of the particles obtained by at least an order of magnitude can be achieved by reducing MPTMOS content (X_{MPTMOS}) in the mixture of organosilanes. In Ref. [11], the mechanism by which MPTMOS affects the particle nucleation process was considered. The MPTMOS molecule has, compared with TEOS one, only three, rather than four, alkoxy groups subject to hydrolysis, the methacryloyloxypropyl group is not hydrolyzed. In the TEOS molecule, the electron density is uniformly distributed among the silicon atom and oxygen atoms. In turn, silicon is bonded in the MPTMOS molecule to a carbon atom, instead of the fourth oxygen atom, which leads to a shift of the electron density (the electronegativities of C and O are 5.2 and 8.1, respectively) and to a larger effective negative charge on three oxygen atoms of methoxy groups. This increased charge on oxygen atoms hinders the deprotonation of hydrolyzed monomers. As a result, the joint hydrolysis of TEOS + MPTMOS leads to a larger content of electroneutral (with respect to those ionized) orthosilicic acid monomers that can form siloxane bonds and, accordingly, nucleate as compared with a reagent mixture containing only TEOS. As X_{MPTMOS} is reduced from 12.5 to 0 % mol., the number of nucleation centers becomes

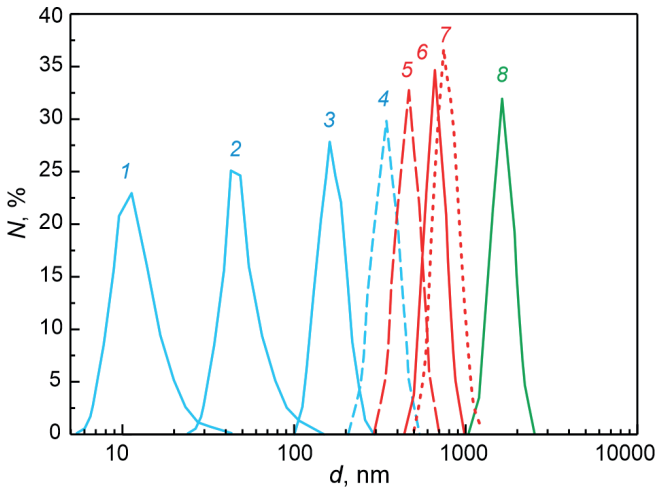

Fig.2 Particle size distribution (by number) measured by DLS method. (*1*–*4*) SSPs synthesized at NH_3 concentration of 1.8M and variable MPTMOS content in organosilane precursor: (*1*) – 12.5 % mol., (*2*) 4 % mol., (*3*) 2% mol., (*4*) 1% mol.; (*5*–*7*) SSPs synthesized using TEOS as silica precursor and variable NH_3 concentration: (*5*) 1.8M, (*6*) 2.5M, (*7*) 3.4M. (*8*) SSPs obtained by successive growth of 720 nm nuclei at NH_3 concentration of 3.4M (5 TEOS portions were added)

four to five orders of magnitude lower [11], which leads, at a constant precursor concentration, to a larger particle size. As a result, at the same total content of precursor and as amount of MPTMOS in the TEOS + MPTMOS mixture is reduced from 12.5 % to 0 mol., the final size of the resulting SiO_2 particles increases from ~10 nm to ~400 nm (Fig. 1, 2). SSPs, synthesized at low MPTMOS content, have low size deviation (Fig. 2 curves *3*–*4*) and remain spherical (Fig. 3, *b*, *c*). The results of DLS measurements (Fig. 2) correlate with TEM data (Fig. 3).

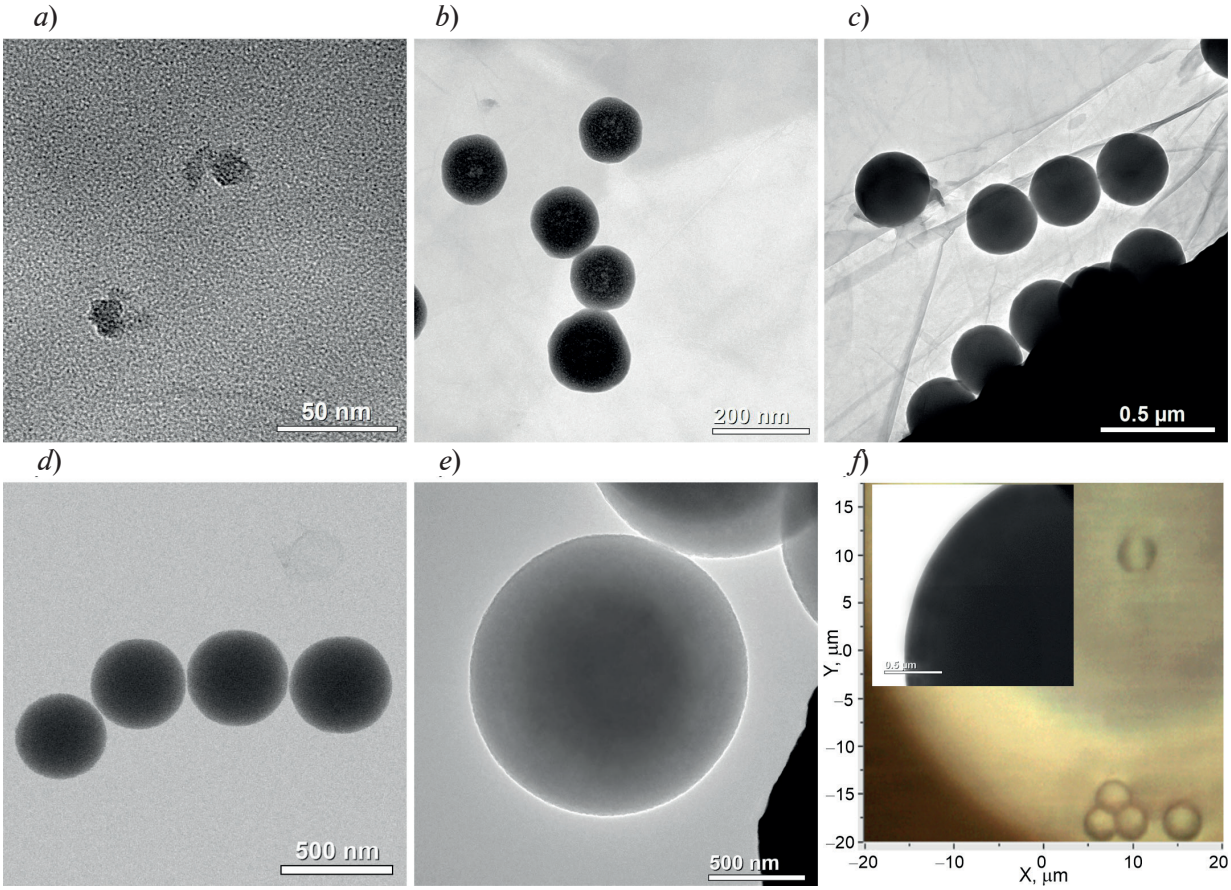

Fig.3 TEM (*a*–*e*, *f* (*inset*)) and optical microscopy (*f*) images of the particles obtained. (*a*–*d*) SSPs synthesized at NH_3 concentration of 1.8M and variable MPTMOS content in organosilane precursor: (*a*) – 12.5 % mol., (*b*) 2 % mol., (*c*) 1% mol., (*d*) 0 % mol. (*e*–*f*) SSPs obtained by successive growth of 720 nm nuclei at NH_3 concentration of 3.4M: (*e*) 5 growth runs; (*f*) 95 growth runs were done

Ammonia in the reaction mixture act as a catalyst of the TEOS hydrolysis reaction. As the ammonia concentration increases the rate of TEOS hydrolysis and condensation of its products increase as well, which leads to a fast formation and growth of SSP. In this case new nucleation centers are not formed – they appear and dissolve [13]. When the ammonia concentration is increased in our reaction mixture from 1.8 to 3.5 mol L^{-1} the diameter of particles increases from ~400 to ~700 nm (Fig. 1, *b*, Fig. 2, Fig. 3). Note, at higher ammonia concentration the particles obtained possess the lowest root-mean-square deviation of the sizes (< 4 %), spherical shape and low surface roughness of a few nanometers (Fig. 3, *d*).

We used a successive growth method to obtain particles with the sizes over 700 nm. Portions of TEOS (5 g) were added every 10 min to 1 L of ammonia-water-alcoholic mixture containing 1 g of 720 nm SSPs. TEOS hydrolysis products were concentrated in the vicinity of the submicron particle surface and coated the particles with a layer of hydrated a-SiO_2 and, hence, providing their further growth. Ammonia concentration was 3.4 mol L^{-1} in the reaction mixture in order, first, to reduce the duration of the TEOS hydrolysis process to 10 min and, second, to prevent the formation of new nucleation centers [9, 12]. It can be seen (Fig. 1, *c*), that after addition of 5 TEOS portions the particle diameter doubled, 20 portions – tripled, and after addition of

95 portions the diameter increases up to ~4 μm. Fig. 3, *e*, *f* demonstrates that the particles are covered with a uniform SiO_2 layer as a result of TEOS portions addition, they have smooth surface and the root-mean-square deviation of the sizes does not exceed 10%.

Conclusion

An approach has been developed to one-pot synthesis of spherical silica particles which allows controlling over the size of the particles in the wide range 10–4000 nm. The proposed approach is based on the governing the nucleation process within the reaction mixture by either varying the number of nuclei within five orders of magnitude by changing the concentrations of MPTMOS and ammonia or its forced suppression in the case of successive growth of the artificially added nucleation centers. It has been shown that by sequentially varying just one parameter of the reaction mixture – the composition of the silicon precursor, the concentration of ammonia or the number of additional portions of TEOS, it is possible to controllably change the final size of the resulting particles within two orders of magnitude in a single technological cycle.

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REFERENCES

1. **Ghimire P.P., Jaroniec M.,** Renaissance of Stöber method for synthesis of colloidal particles: New developments and opportunities, Journal of Colloid and Interface Science. 584 (2021) 838–865.

2. **Gao W., Rigout M., Owens H.,** Facile control of silica nanoparticles using a novel solvent varying method for the fabrication of artificial opal photonic crystals, Journal of nanoparticles Research. 18 (2016) 387.

3. **Huang Y., Li P., Zhao R., Zhao L., Liu J., Peng S., Fu X., Wang X., Luo R., Wang R., Zhang Z.,** Silica particles: Biomedical applications and toxicity, Biomedicine and Pharmacotherapy. 151 (2022) 112053.

4. **Walcarius A.,** Silica-based electrochemical sensors and biosensors: Recent trends, Current Opinion in Electrochemistry. 10 (2018) 88–97.

5. **Ren X., Cao E., Lin W., Song Y., Liang W., Wang J.,** Recent advances in surface plasmon-driven catalytic reactions, RSC Advanced. 7 (50) (2017) 31189–31203.

6. **Galisteo-Lypez J.F., Ibisate M., Sapienza R., Froufe-Pérez L.S., Blanco Б., Lypez C.,** Self-assembled photonic structures, Advanced Materials. 23 (2011) 30–69.

7. **Bogomolov V.N., Golubev V.G., Kartenko N.F., Kurdyukov D.A., Pevtsov A.B., Prokof'ev A.V., Ratnikov V.V., Feoktistov N.A., Sharenkova N.V.,** Fabrication of regular three-dimensional lattices of submicron silicon clusters in an SiO_2 opal matrix, Technical Physics Letters. 24 (4) (2017) 326–327.

8. **Stöber W., Fink A., Bohn E.,** Controlled growth of monodisperse silica spheres in the micron size range, Journal of Colloid and Interface Science. 26 (1) (1968) 62–69.

9. **Masalov V.M., Aldushin K.A., Dolganov P.V., Emel'chenko G.A.,** SiO_2-microspheres ordering in 2D structure, Physics of Low – Dimensional Structures. 5–6 (2001) 45–54.

10. **Santamaria Razo D.A., Pallavidino L., Garrone E., Geobaldo F., Descrovi E., Chiodoni A., Giorgis F.,** A version of Stöber synthesis enabling the facile prediction of silica nanospheres size for the fabrication of opal photonic crystals, Journal of Nanoparticle Research. 10 (2008) 1225–1229.

11. **Eurov D.A., Kirilenko D.A., Kurdyukov D.A.,** Nucleation of silica Stöber particles in the presence of methacryloxypropyltrimethoxysilane, Colloid Journal. 79 (2017) 56–60.

12. **Grudinkin S.A., Feoktistov N.A., Trofimova E.Yu., Kurdyukov D.A., Bogdanov K.V., Baranov A.V., Fedorov A.V., Golubev V.G.,** Spherical microresonators with luminescent a-Si:C:H coating, Technical Physics Letters. 39 (4) (2013) 341–343.

13. **Matsoukas T., Gulari E.,** Dynamics of growth of silica particles from ammonia-catalyzed hydrolysis of tetra-ethyl-orthosilicate, Journal of Colloid and Interface Science. 124 (1) (1988) 252–261.

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