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Synthesis of High-Purity Silica Nanoparticles by Sol-Gel Method

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Abstract

Colloidal silica (silica sol) nanoparticles were synthesized by ammonia- and hydrochloric acid-catalyzed hydrolysis of tetraethoxysilane with subsequent condensation and polymerization. Silica particles with the size of 12–160 nm were obtained at different temperatures and ratios of the initial reactants and studied by means of TEM, AFM, IR spectroscopy and zeta-potential measurements. The reaction conditions providing the minimum particle size in the final product of the most complete hydrolysis were determined. At pH above 8.5, an increase in the SiO_2 content of the sol to 23 wt.% did not change the particle size. At a low (~ 1.8 wt.%) SiO_2 content of the sol, a wide variation in pH also did not exert a significant effect on the particle size. Stability of the silica sols synthesized in an alkaline medium was enhanced by the replacement of alcohol with water during evaporation at pH 8.5–9.5. The possibility to produce silica sols with the required characteristics (particle size, pH, stability, purity, and SiO_2 content in an aqueous or alcohol medium) makes them applicable in various industries.

1. Introduction

Colloidal silica (silica sol) is a system consisting of amorphous silica particles that are distributed in a liquid medium. Nanostructural monodisperse colloidal silica is widely applied in various fields due to the polymeric nature of its particles, the highly developed surface area, and the presence of functional (silanol) groups [1–6]. Silica sols are used to produce adsorbents, catalysts, supports [7, 8], fillers of workpieces for radio and quantum electronics, high-precision casting moulds, to polish semiconductor materials [9, 10], and to obtain carriers for the delivery of therapeutic agents [11, 12]. The addition of silica nanoparticles improves thermal, mechanical, physical and chemical properties of functional materials [13]. High purity silica is a precursor for the synthesis of silicon carbide, which is widely used in industry [14]. The ability of colloidal SiO_2 to form films as well as its thermal stability, strength, adhesion and electric properties make it possible to use silica sols for the development of anticorrosive, insulating and high-temperature composite coatings [15, 16]. Homogeneous silica particles are employed also as model systems for studying the adsorption, film formation, and self-organization of the particles [17, 18].

Depending on the application field, silica sols should possess the specified particle size, SiO_2 content, pH, concentration of the impurities, and stability. In semiconductor, electronic and pharmaceutical industries, a mandatory requirement to silica sols is a high purity of the product [19–21]. The admissible content of inorganic impurities cannot exceed 10^{-4} wt.%; and organic ones – 10^{-3} wt.%. This determines the choice of the synthesis method of SiO_2 sols and conditions of the process implementation and instrumentation, which should prevent contamination of the product with micro-impurities. The stability of silica sols implies the absence of coagulation of their particles or gelation for a certain time.

Silica sols are commonly synthesized by the ionic exchange of alkali metal silicates or the hydrolysis of alkoxysilanes. The ionic exchange of sodium silicate has many advantages: low cost,

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availability of the feedstock, simple technology, and high SiO_2 content in the final product. Nevertheless, this product contains a great amount of sodium impurity and its removal requires additional processes, thus complicating the overall technology. The sol-gel process using alkoxysilanes yields a highly pure product and ensures particle size control in the synthesis step. Taking into account availability of the feedstock and non-toxicity of the process reactants and by-products, in our study silica sols were synthesized by the hydrolysis of tetraethoxysilane (TEOS) in the presence of various catalysts in an ethanol solvent medium, which was followed by condensation and polymerization. Physicochemical properties of the sols synthesized by the chosen method depend on various factors affecting the rate of hydrolysis and condensation reactions: pH, temperature, the initial reactants ratio, the order of reactant addition, reactant supply rate, catalyst type and concentration, molar ratio H_2O/alkoxysilane, duration and temperature of the aging step [22–25]. The deliberate control of the listed parameters makes it possible to vary properties of the final product in a wide range. The hydrolysis is performed most often in the presence of mineral acids (HCl) or bases (NaOH, NH_4OH) as the catalysts [26]. The widely known Stöber process [27] was chosen as a basis for the synthesis of silica nanoparticles via the hydrolysis of TEOS in the presence of ammonia. The effect exerted by the process temperature, the ratio of initial reactants and the catalyst type on the properties of synthesized silica sols was studied. The dependence of the particle size and stability of colloidal systems on pH and SiO_2 content was examined. Depending on the catalyst type, different approaches to the synthesis of silica sols were employed. The obtained results and techniques can be useful in the production of colloidal silica on an industrial scale.

2. Materials and methods

All of the reactants used in our experiment were of high-purity. To synthesize high-purity silica sols, a special space was equipped, the so-called ‘clean room’ (Fig. 1). Conditions created in this room prevent the ingress of impurities into the product above the admissible amount.

The synthesis of silica sols in the presence of ammonia was carried out by the following procedure. A hydrolyzing solution of water, ethanol and ammonia was placed in a thermostatically controlled flask. At a temperature of 30–70 °C, a silicon solution containing TEOS and ethanol was poured into the hydrolyzing solution at a rate of 1–4 ml/min under continuous stirring. After that, the resulting silica sol was held under the indicated conditions for at least 2 h to bring the reaction to completion. The synthesized silica sols with the SiO_2 content below 3 wt.% had pH 10–11.

Fig. 1. A specially equipped room for the synthesis of high-purity products.

SiO_2 content of the sol was increased by the concentration process using evaporation with the replacement of ethyl alcohol by water (Fig. 2). The process was carried out under continuous stirring at a temperature of 80–90 °C. The pH was maintained within 8.5–9.5 by adding an aqueous solution of ammonia during evaporation.

For the synthesis of silica sol in the presence of acid catalyst TEOS, ethanol and water acidified with HCl to pH 1.5–2 were placed in a thermostatically controlled flask and mixed in a molar ratio 1:5:6 [18]. Aging of silica sol was performed for 2 h at a temperature of 50 °C under constant stirring. The pH value of the reaction mixture and aged silica sol did not exceed 2. The aged silica sol was diluted with water to bring pH to ~ 4.

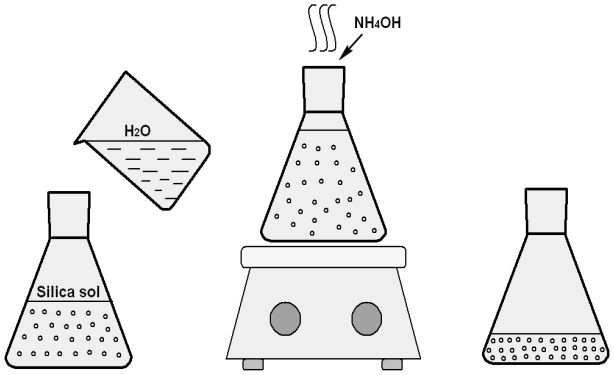

Fig. 2. Evaporation of silica sol with the replacement of ethyl alcohol by water.

Silica sols were dialyzed using a ZelluTrans/ Roth polymer membrane with a pore size of 10 Å. The prepared solution (20 ml) with the measured pH was transferred to the membrane soaked in distilled water. Depending on the purpose, the membrane was then placed in a beaker with distilled water or a buffer solution. The volume of dialysis solution was varied within 0.5–1 L. The dialysis was carried out for 24–52 h.

A high resolution transmission electron microscopy (HRTEM) study of silica sols was performed on a JEM-2010 (JEOL, Japan) electron microscope (accelerating voltage 200 kV and lattice resolution 1.4 Å). Samples were deposited by an ultrasonic disperser on standard carbon-coated copper grids that were placed in special holders.

Silica sol samples were studied by IR spectroscopy in the region of natural vibrations. The spectra were recorded on a BOMEM MB102 Fourier transform IR spectrometer in the region of 200–2000 cm^{-1}. The samples were dried at 100 °C, powdered, and mixed with KBr in a ratio of 1:100. After that, the mixture was pressed to obtain 65–75 mg/cm^2 thick pellets.

To examine silica sols on a SolverP47Bio atomic-force microscope (AFM) in the tapping mode, they were diluted in distilled water to a concentration of 0.1 mg/ml. After that, a 20 μl drop of the sample was deposited on a fresh mica chip with an area of ~25–30 mm^2. The adsorption was carried out at room temperature for 1 h, and then the residual liquid was removed with filter paper.

Electrokinetic potential was measured on a NICOMP 380ZLS instrument. The method is based on measuring the average velocity of particles motion under the action of external electric field with a strength of 6.5 V/cm. To calculate zeta-potential the Doppler displacement of the light beam scattered by the particles was measured with subsequent recalculation using the Smulykhovsky equations.

3. Results and Discussion

3.1. Effect of the synthesis temperature on the particle size of silica sols synthesized in the presence of ammonia

According to the literature data, in the synthesis of silica sols by the Stöber method the particle size of SiO_2 decreases with raising the synthesis temperature [28]. Figure 3 displays TEM images of the silica sols synthesized at 50 °C (Fig. 3a) and 70 °C

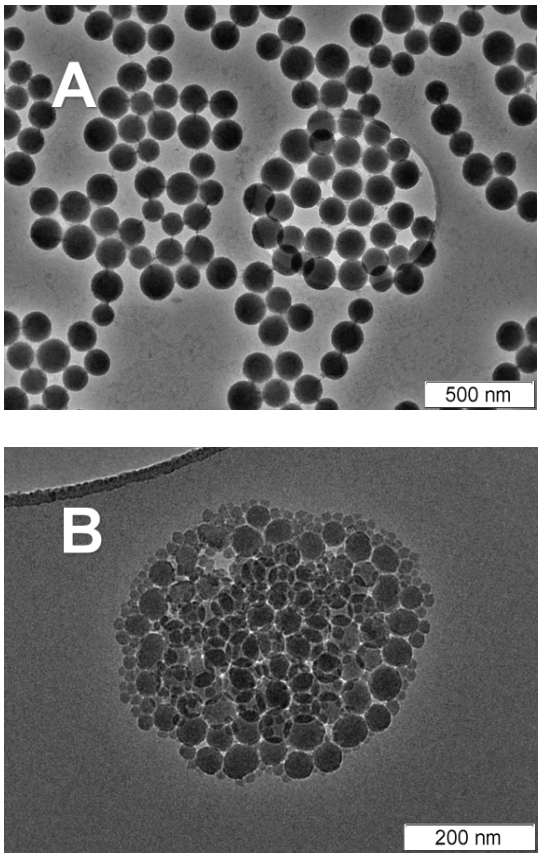

Fig. 3. TEM images of silica sols synthesized at 50 (a) and 70 °C (b).

(Fig. 3b) with molar ratio of the initial reactants TEOS : H_2O : C_2H_5OH : NH_3 = 1 : 21 : 20 : 1.5.

When the synthesis temperature is raised from 50 to 70 °C at constant ratios of the initial reactants, the particle size of SiO_2 decreases approximately by a factor of 3, from 100–150 to 30–50 nm. The non-uniform particle size distribution is clearly seen on Fig. 3b. This may occur because when the temperature is raised at high concentrations of water and catalyst, the hydrolysis and condensation proceed much faster than the consumption of the precursor, thus leading to the formation of secondary particles [29]. It should be noted that silica sols synthesized at the indicated reactant ratio and a temperature below 50 °C have a much greater particle size, which leads to SiO_2 precipitation. The temperature dependence of the particle growth is related to changes in the rate of hydrolysis and nucleation, which significantly decreases with lowering the reaction temperature. According to the LaMer and Dinegar model [30], when the reaction temperature decreases, the concentration of silicic acid becomes insufficient for the formation of new nuclei, so TEOS is consumed for the particle grow.

3.2. The effect of reactant ratio on the particle size of silica sols synthesized in the presence of ammonia

It is known that changes in the concentrations of TEOS, water, ammonia and solvent in the synthesis of silica sols by the Stöber method strongly affect the particle size of SiO_2 [31–33]. The effect exerted by changes in the ratio of reactants on the particle size of silica sols is shown in Table 1 and Fig. 4. An increase in the ethanol amount decreases the concentration of TEOS and hence the calculated SiO_2 content in the sol. Therewith, the particle size of SiO_2 is 25–30 nm (sample no. 1). A simultaneous decrease in the amount of water and ammonia in the reaction mixture allowed obtaining particles with the size smaller than 20 nm (samples nos. 2 and 3).

The experiments demonstrated that variation in the temperature and concentration of the initial reactants and catalyst affects the rates of hydrolysis and condensation and makes it possible to produce SiO_2 particles with different sizes.

The effect of SiO_2 concentration in the reaction mixture on the particle size of the final sols was studied with silica sol samples nos. 2 and 3. The concentration of silica was controlled by varying the TEOS : C_2H_5 ratio. An increase in the initial SiO_2 content from 3 to 4.8 wt.% exerted no effect on the properties of the final product. A further increase in the SiO_2 content to 7 wt.% increased the particle size and resulted in precipitation of SiO_2.

Table 1
Particle size of silica sols synthesized in the presence of ammonia vs. the ratio of initial reactants.

Sample	Reaction temperature, °C	Amount, mol				Particle size, nm
		TEOS	Water	Ethanol	Ammonia	
1	70	1	21.6	57	2	25-30
2	70	1	4.8	33	0.6	16-20
3	70	1	15	33	0.2	12-14

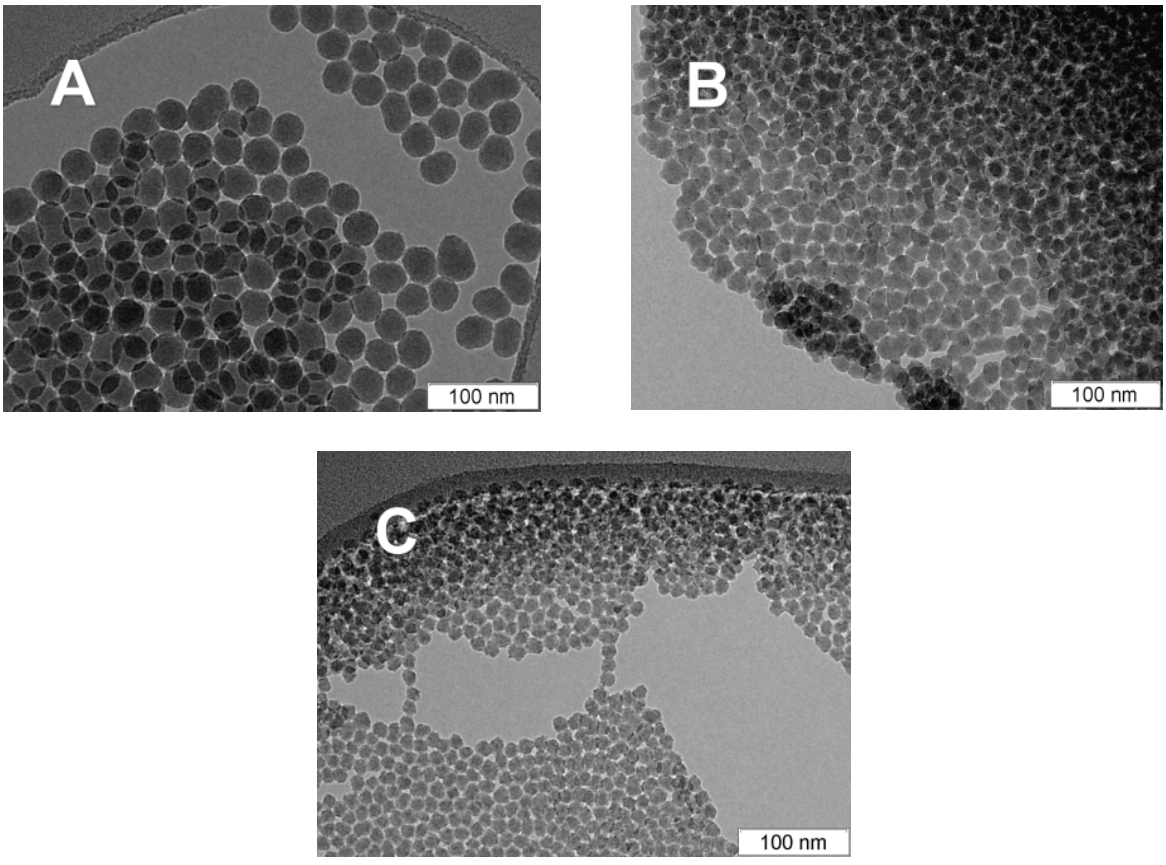

Fig. 4. TEM images of silica sol samples nos. 1 (a), 2 (b) and 3 (c) synthesized at different ratios of the initial reactants and catalyst.

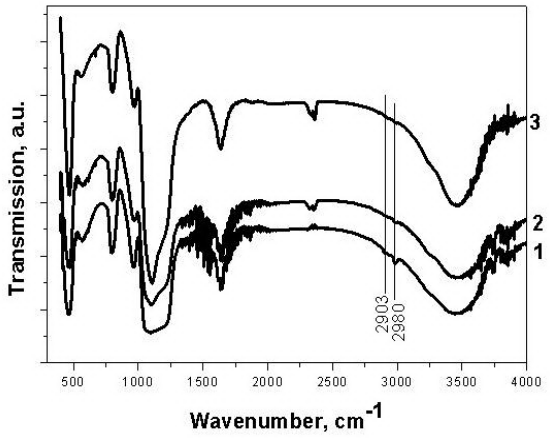

Fig. 5. IR spectra of silica sols synthesized at different [TEOS] : [H_2O] ratios: (1) – 1:4.8; (2) – 1:10; (3) – 1:15.

Among problems in the synthesis of silica sols with tetraethoxysilane as the precursor is incomplete hydrolysis [34]. Thus, it is necessary to select the optimal conditions for attaining the greatest possible depth of the reaction. The completeness of the hydrolysis depends on the reaction temperature, aging duration of silica sol, and amount of water. The effect of the water to TEOS ratio in the reaction mixture was studied by means of IR spectroscopy. Figure 5 displays IR spectra of the silica sol samples with the [TEOS] : [H_2O] molar ratio equal to 1:4.8, 1:10 and 1:15. One can see that the intensity of the bands at 2903–2980 cm^{-1} corresponding to C-H stretching vibrations [35] decreases with increasing the water amount, which may testify to a decrease in the amount of unreacted TEOS in the silica sol samples.

Thus, when choosing the optimal ratio of the initial reactants for silica sol synthesis, it is necessary to maintain a balance that allows obtaining silica sol particles of a desired size and ensures the most complete hydrolysis, thus controlling the quality of the final product.

3.3. The effect of SiO_2 content on the particle size and stability of silica sols

Depending on the application field, silica sols should have a specified content of SiO_2. When producing composite materials and coatings, the catalysts and other materials, the use of highly concentrated sols is economically and technologically advantageous. However, the concentrated sols are less stable: the process of their concentration and storage may be accompanied by undesirable coagulation; so they should be concentrated under special conditions. Silica sols synthesized by the hydrolysis of alkoxysilanes can be concentrated by two methods: evaporation and vacuum concentration. Our study was performed using a simpler technology – evaporation with the replacement of ethyl alcohol by water. Zeta-potential measurements of silica sols containing 1.9 wt.% SiO_2 were used to estimate the effect of such a replacement, which was introduced as the final step of the synthesis, on stability of colloidal systems. Zeta-potential of the sol with a water medium was -6.5 mV; and with a water-alcohol medium, -14 mV. The introduction of the replacement step was shown to increase stability of the sol. Further, we used this step when increasing the silica concentration in the sols.

Earlier, monodisperse silica nanoparticles with a diameter less than 20 nm and SiO_2 concentration up to 15 wt.% were prepared [36]. We successfully synthesized a stable silica sol with the particles 12–14 nm in size and concentration 23 wt.%. For sample no. 3 (Table 1 and Fig. 4c), an increase in SiO_2 content after evaporation from 3 to 15 wt.% (Fig. 6a) and 23 wt.% (Fig. 6b) did not change its particle size. The formation of the aggregate structure was not observed [37]. The absence of coagulation in the concentrated samples was observed during a 6-month storage.

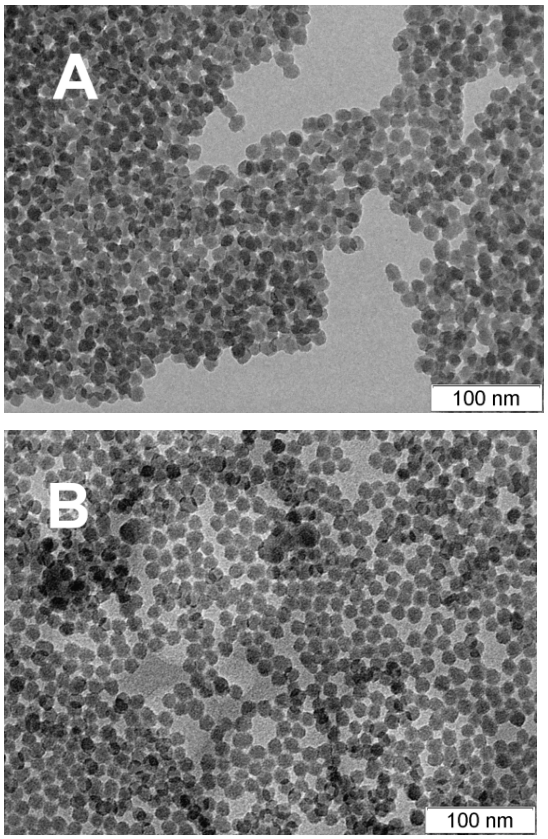

Fig. 6. TEM images of silica sol with different SiO_2 content: (a) 15 wt.% and (b) 23 wt.%.

According to the particle growth mechanism [29], all the particles are formed at the beginning of the reaction and then grow until TEOS is consumed. When using the Stöber method, the particle growth completes within 2 h [38]. Since the particle size did not change during concentration, we can conclude that the introduction of the step in which alcohol is replaced by water leads to complete hydrolysis.

3.4. The effect of pH on the particle size of silica sols synthesized in the presence of ammonia and HCl

It is known that stability of sol particles is ensured by a similar charge of the particle surface in acid or alkaline media. When silica sols are employed in nanobiotechnologies, it is important to control the pH of the preparations and retain stability of the sols at pH close to physiological values, i.e. to 7. The pH of silica sols synthesized in the presence of ammonia (pH > 10) and hydrochloric acid (pH ~ 4) was gradually changed to nearly neutral values by means of dialysis. Such method of changing the pH and purifying the sols with subsequent AFM analysis of the particle size was earlier used in [39, 40]. In the case of silica sol synthesized in the presence of ammonia catalyst, pH was decreased from 10.3 to 7.17. A TEM study revealed that silica sol sample no. 2 (Table 1) before (Fig. 4b) and after dialysis against distilled water (Fig. 7) had the same particle size of SiO_2. The indicated silica sol was stable during a 6-month storage.

The pH of silica sols synthesized in the presence of HCl was increased from 3.98 to 6.65 using dialysis against a buffer solution with pH 6.86 for 24 h. Fig. 8 displays the 3D AFM images of the sol particles' height before (Fig. 8a) and after dialysis

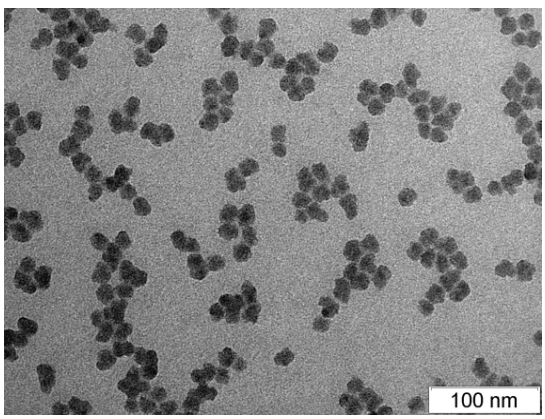

Fig. 7. TEM image of silica sol sample no. 2 after the dialysis.

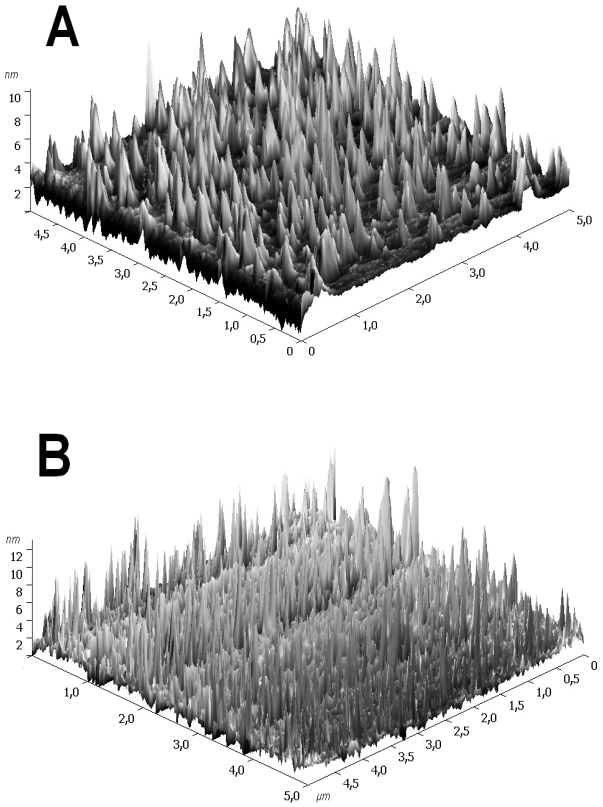

Fig. 8. AFM images of silica sol samples synthesized in the presence of HCl before (a) and after (b) the dialysis (a 3D image of the field).

(Fig. 8b). The increase in pH produced no significant change in the particle size. However, stability of the resulting silica sol was not high: in a month the sol turned into a gel. In addition, due to dialysis against a phosphate buffer solution, the sol may contain phosphorus, sodium and potassium impurities; so this silica sol cannot be considered as a high-purity product.

3.5. The formation mechanism of colloidal silica

Regardless of the solution pH, the hydrolysis proceeds via an nucleophilic attack of the water oxygen on the silicon atom [41]; the mechanism of the process includes a substitution of the –OH group for CH_3CH_2O- in tetraethoxysilane and a restoration of the tetrahedral oxygen environment of the silicon atom. The hydrolysis in an alkaline medium proceeds slower than in an acid one. After aging under the reaction conditions, silica sol synthesized in the presence of ammonia contains minor amounts of unreacted TEOS (Fig. 5). The addition of excess water and an increase in temperature at the step where ethyl alcohol is replaced by water lead to complete hydrolysis of the precursor.

When HCl is used as the catalyst, relatively low H_2O/Si ratios lead to the formation of weakly branched "polymeric" networks [41]. The gel formation rate is affected also by the pH value, the sol concentration and the acid type. In a weakly acidic region, the acceleration of gelling corresponds to the strength of acids (dissociation constants). In this case, despite the low concentration, the sol is in the lowest stability region [42].

4. Conclusions

The possibility to control the properties of silica sols in the synthesis step by varying the process parameters is one of the main advantages of the sol-gel technology. Variation of the synthesis conditions (catalyst type, process temperature, and ratio of the initial reactants) allowed us to synthesize silica sols with the particle size 12–150 nm, SiO_2 content 3–23 wt.%, and high resistance to agglomeration.

The reaction conditions that provide a minimum particle size in the final product at the most complete hydrolysis were determined.

In a weakly alkaline medium (pH 8.5–9.5), the dispersion stability of silica sol is retained in a wide range of concentration (3–23 wt.%).

At low concentrations of SiO_2 (1.8 wt.%), a transition from acid or alkaline medium to neutral one does not change the particle size, thus testifying to stability of the sol.

For silica sols synthesized in the alkaline medium, the replacement of alcohol by water during evaporation with pH maintained in a range of 8.5–9.5 was shown to increase the product stability.

The synthesis of colloidal silica nanoparticles by the hydrolysis of alkoxysilanes complying with chemical purity requirements excludes the presence of metal impurities in the final product. Thus, the synthesized silica sols can be classified as ultra-pure substances that can be used in the fields where high-purity is the mandatory requirement.

The developed synthesis methods and the revealed regularities of the processes make it possible to synthesize colloidal silica particles having a widely variable size and other desired characteristics.

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