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Colloidal Particles of Silicon Dioxide for the Formation of Opal-Like Structures

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Abstract—The conditions of synthesis of silicon dioxide particles with a high degree of monodispersity have been investigated. The particles have been synthesized using both the hydrolysis of tetraethoxysilane in the presence of *L*-arginine and a combination of this technique with the traditional Stöber method. It has been shown that the use of SiO_2 particles synthesized by the heterogeneous hydrolysis of tetraethoxysilane in the presence of the amino acid for their further growth according to the Stöber method makes it possible to obtain particles 100 nm and more in size with a narrow size distribution (the deviation of the diameter is less than 3%), a nearly perfect spherical shape, and a smooth surface.

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1. INTRODUCTION

The formation of opal-like structures (in the form of films and bulk samples) requires structural units in the form of regular spheres with a narrow distribution over their diameters (<5%). The most commonly encountered structural units for the formation of opal-like structures are spherical microparticles of polymers and silicon dioxide.

At present, monodisperse colloidal silicon dioxide microparticles have been frequently synthesized using the Stöber method [1]. This method is based on hydrolysis of silicon alkoxides in a water–alcohol medium in the presence of ammonium hydroxide as a catalyst. The preparation of spherical silicon dioxide particles by means of hydrolysis of tetraethoxysilane (TEOS) in the presence of ammonium was first described by Kolbe [2]. Stöber and co-authors [1] improved this method for synthesizing SiO_2 particles with a nearly ideal spherical shape over a wide range of diameters from several tens of nanometers to several micrometers. The preparation of particles with different specified sizes is provided by varying the concentration and temperature parameters of the system.

The Stöber method makes it possible to perform synthesis of particles with specified sizes by using their multi-stage growth. In this case, the particles obtained in the preceding cycle of their growth are used as seeds in the subsequent cycle. The monodispersity of the seeds determines the final homogeneity of the grown particles. The main disadvantage of the Stöber method is that the synthesis of particles with sizes of smaller than 200 nm and with a narrow size distribution is very complex problem. The smallest particles with diameters of 15–20 nm, which have already actually been synthesized, exhibit a very high polydispersity (above 20%) [4]. Thus, the preparation of particles with a monodispersity of better than 4–5% is a very difficult task in the case of particles with sizes of smaller than 300 nm for both the single-stage and multi-stage variants of the Stöber method.

Yokoi et al. [5] demonstrated the possibility of synthesizing 12- to 23-nm spherical SiO_2 particles that were packed in ordered structures, which characterizes their high monodispersity. Up to now, it has remained impossible to create structures with a high degree of ordering for particles with sizes ranging from 100 to 120 nm, which would be synthesized by the Stöber method. The method described in [5, 6] is based on hydrolysis of tetraethoxysilane in the presence of amino acids. This method makes it possible to obtain particles with a diameter of smaller than 50 nm and with a high degree of monodispersity (the deviation of the diameter is ~3–5%). The disadvantages of the method are the duration of the synthesis process (5–7 days) and the "roughness" of the surface of the synthesized particles. However, the latter disadvantage can be eliminated when these particles are used as seeds in their further growth by the Stöber method. Thus, there has appeared a possibility to combine both methods for preparing particles from 200 to 300 nm in size with a high degree of monodispersity (the deviation of the diameter is less than 3%). In this combined method, at the first stage, monodisperse seeds are obtained by hydrolysis in the presence of amino acids, which, subsequently, are further grown to a specified size with the use of the multi-stage variant of the

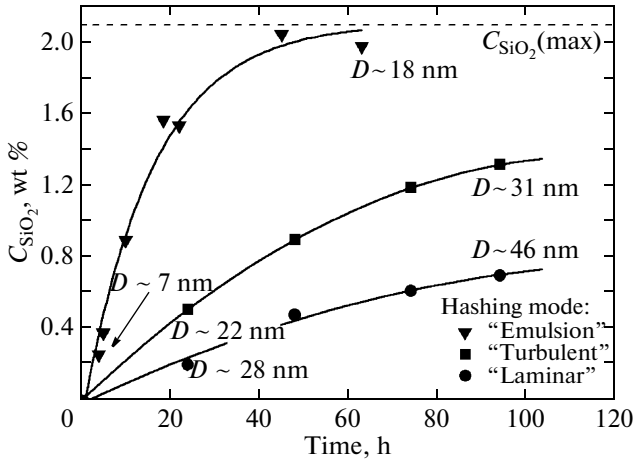

Fig. 1. Illustration of the increase in the weight concentration of silicon dioxide nanoparticles during their synthesis using different regimes of stirring the reaction mixture. Conditions: $V_{Ch}/V_{TEOS} = 0.8$, $T = 60.0 \pm 0.1$°C, and the concentration of *L*-arginine is 7.5 mM. Shown near the curves are the current diameters of particles in the initial and final periods of their growth.

Stöber method [6]. By adding new portions of tetraethoxysilane at each growth stage for the further growth of particles to a specified size, it is necessary to fulfill the following condition: the concentration of primary particles must not exceed the critical value, because, otherwise, this can lead to a bimodal size distribution of the particles. New portions of tetraethoxysilane must be added only after the completion of the particle growth at the preceding stage. The time required to complete the cycle of particle growth depends on the concentration and temperature parameters of the process.

The purpose of this work was to investigate the conditions of synthesis of monodisperse silicon dioxide particles in the presence of amino acids, the conditions of their further growth using the Stöber method, and the preparation of opal-like structures from these particles.

2. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

2.1. Heterogeneous Synthesis in the Presence of Amino Acids

In our experiments, we used the following chemical reagents: 98% tetraethoxysilane, which was preliminarily purified by distillation in a rectifying column; 99.9% cyclohexane; 99% *L*-arginine (Panreac); and deionized water (~18 MΩ/cm).

The synthesis of SiO_2 particles was carried out in conical flasks. The total volume of the reaction mixture was equal to 250 ml. A portion of *L*-arginine (1.5–7.5 mM) was added to deionized water, and the obtained solution was carefully stirred with an Elmi MS-01 magnetic stirrer equipped with an Elmi TW-2.02 water bath thermostat, which was used to increase the solution temperature to 30–60°C. After the complete dissolution of *L*-arginine, a solution of cyclohexane (Ch) and tetraethoxysilane with a volume ratio $V_{Ch}/V_{TEOS} = 0$–1.6 was added to the reaction mixture. The synthesis was performed in a closed flask at a constant temperature and with a continuous rotation of the stirrer with the speeds ensuring three stirring modes, namely, the "laminar," "turbulent," and "emulsion" modes. During the synthesis, suspensions were sampled in order to determine the weight concentration in water.

2.2. Synthesis of Silicon Dioxide Particles by the Stöber Method

The experiments were carried out with aqueous solutions of ethyl alcohol. The solutions contained from 16 to 25 M water, 1–5 M ammonia, and 0.14 M TEOS. The hydrolysis reaction of TEOS was performed at temperatures ranging from 1.5 to 45.0°C. At the first stage, an aqueous solution of ethyl alcohol was prepared. Then, the obtained solution was saturated with ammonia. A typical volume of the solution used in the experiments was equal to 200 ml. The homogenization of the reaction mixture was provided with the use of the magnetic stirrer. After the specified temperature was reached, tetraethoxysilane was added to the reaction mixture and, at regular time intervals, a sample of the suspension (about 0.1 ml) was taken out of the mixture and applied to a hot metal plate. The solution on the plate almost instantaneously evaporated, and the growth of particles was interrupted. The particle diameter was measured with a Carl Zeiss Supra 50 VP scanning electron microscope.

3. EXPERIMENTAL RESULTS AND DISCUSSION

3.1. Growth of Seeds by the Heterogeneous Synthesis Method

Figure 1 shows the dependences of the increase in the weight concentration of silicon dioxide nanoparticles in the aqueous part of the system, which were obtained during the hydrolysis reaction of tetraethoxysilane, on the duration of the process at different rates of stirring of the reaction mixture. In this case, the following stirring modes of the reaction mixture can be distinguished: (i) the "laminar" mode, when the interface between the aqueous solution of the amino acid and the cyclohexane–tetraethoxysilane solution remains almost horizontal; (ii) the "turbulent" mode, when the liquid forms a "depression cone"; and (iii) the "emulsion" mode, when an emulsion is formed from two immiscible liquid phases.

It can be seen from the dependences presented in Fig. 1 that the weight of silicon dioxide formed per unit

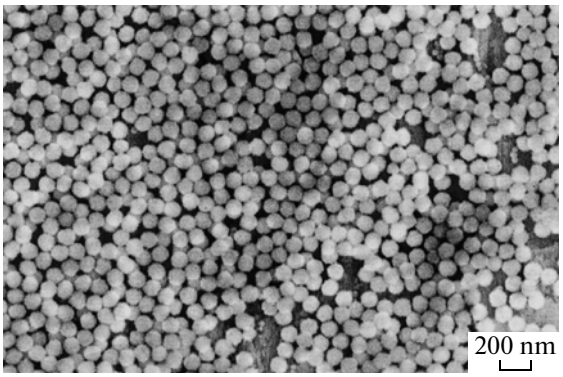

Fig. 2. Micrograph of silicon dioxide particles (diameter $D = 103 \pm 2$ nm) synthesized by heterogeneous hydrolysis of TEOS.

time increases with an increase in the stirring rate of the reaction mixture. This is associated with the fact that an increase in the stirring rate of the reaction mixture leads to an increase in the interfacial area of two interacting liquid phases, which, in turn, results in an increase in the production rate of the process with respect to silicon dioxide.

A decrease in the reaction rate of tetraethoxysilane hydrolysis with time (gently sloping portions of the curves shown in Fig. 1) is caused by the decrease in the concentration of tetraethoxysilane in the reaction mixture with cyclohexane due to its consumption in the course of the reaction and the formation of ethyl alcohol (the product of the hydrolysis reaction) in the cyclohexane–tetraethoxysilane solution. Ethyl alcohol has an unlimited solubility in all the liquids involved in the reaction zone (i.e., in water, cyclohexane, and tetraethoxysilane). Consequently, ethyl alcohol is distributed between two immiscible liquid phases in proportion to their volumes. Apart from the production rate of the process with respect to silicon dioxide, the stirring rate of the reaction mixture also determines the size and homogeneity of the synthesized nanoparticles. An increase in the stirring rate of the reaction mixture leads to a decrease in the average size of the particles, whereas their homogeneity is enhanced. A change in the temperature exerts a weaker influence on the production rate of the synthesis with respect to silicon dioxide, because the limiting stage of the synthesis process is the mass transfer through the interface between two liquid phases.

The performed investigations of the influence of hydrodynamics of the reaction mixture, as well as the temperature and concentration parameters of the hydrolysis reaction, on the size and homogeneity of the synthesized nanoparticles allowed us to choose the following optimum conditions of the process: the stirring of the reaction mixture was performed in the turbulent mode, the cyclohexane/tetraethoxysilane volume ratio was 0.8, the concentration of *L*-arginine was

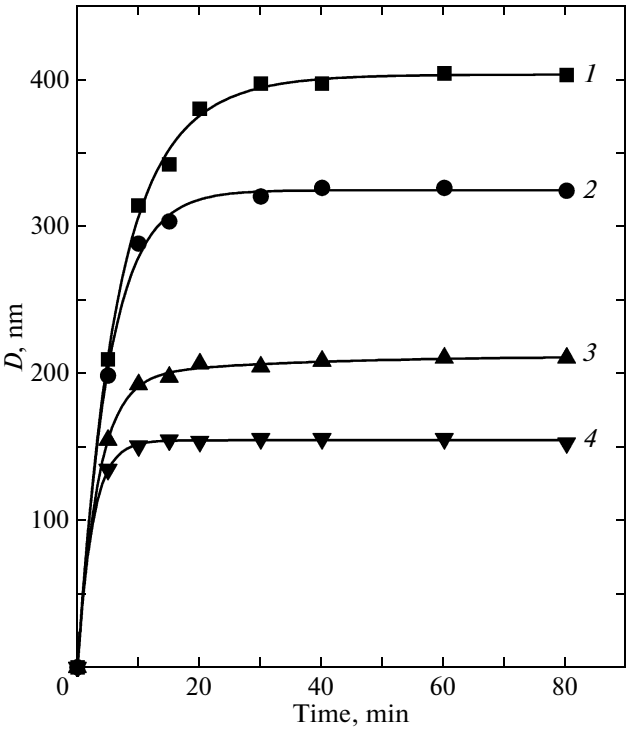

Fig. 3. Dependences of the diameter of SiO_2 particles on the synthesis time at the TEOS, H_2O, and NH_3 concentrations equal to 0.14, 25, and 1 M, respectively, and at reaction temperatures $T =$ (*1*) 1.5, (*2*) 11.0, (*3*) 23.0, and (*4*) 32.5°C.

7.0–7.5 mM, the concentration of tetraethoxysilane was 0.3–0.4 M, and the synthesis temperature was 50–60°C. The prepared SiO_2 particles had a developed surface (Fig. 2) and a nonideal spherical shape. Typical deviations of the particle diameters from the average value were equal to ~5%.

3.2. Growth of Particles by the Stöber Method

Figure 3 shows the experimental dependences of the change in the diameter of SiO_2 particles on the duration of synthesis at the concentrations [TEOS] = 0.14 M, $[H_2O] = 25$ M, and $[NH_3] = 1$ M and at different reaction temperatures. It can be seen from this figure that the time required to complete the process of growth of SiO_2 particles with an increase in the reaction temperature from 1.5 to 32.5°C decreases from 60 to 15 min.

The final average diameter of the particles in this case decreases from 400 to 150 nm. This means that, at different reaction temperatures, the same amount of tetraethoxysilane is required to obtain different amounts of SiO_2 particles (at a temperature of 32.5°C, the amount of SiO_2 particles is ~20 times larger than that at a temperature of 1.5°C). This is associated with the fact that the first step in the multi-stage growth of particles includes two stages, namely, the induction

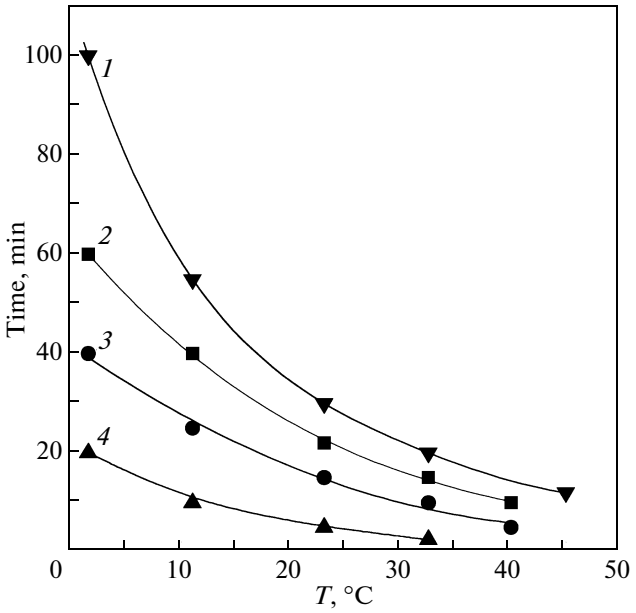

Fig. 4. Dependences of the time required to complete the growth of SiO_2 particles on the reaction temperature at a TEOS concentration of 0.14 M and different concentrations of H_2O and NH_3 (M): (*1*) 16 and 1, (*2*) 25 and 1, (*3*) 25 and 3, and (*4*) 25 and 5.

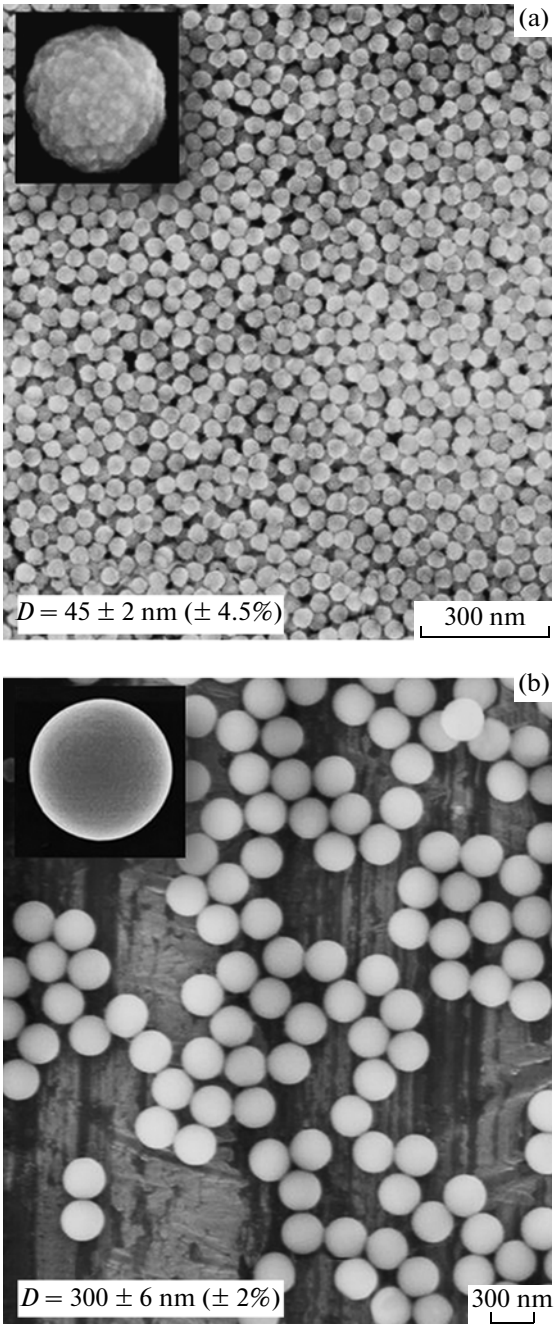

Fig. 5. Micrographs of (a) seeds and (b) final particles synthesized by the heterogeneous hydrolysis of TEOS and the Stöber method, respectively. The insets show the morphology of the seeds and final particles.

period of the formation of nuclei and their further growth. During the induction period (shorter than 1 min), there occur increase in the concentration and polymerization of molecular SiO_2 into microparticles. The concentration of molecular SiO_2 and the amount of microparticles formed during the induction period depend on the reaction temperature. Since the reaction rate of hydrolysis (and, consequently, the rise in the concentration of molecular SiO_2) increases with an increase in the temperature, the amount of microparticles formed during the induction period also increases. The high concentration of microparticles and the high reaction temperature, which increases the number of active collisions of particles during their aggregation, ensure the formation of a large number of nuclei during the induction period. Molecular silicon dioxide and the microparticles formed from it, which come in the system in the course of the reaction, are consumed for an increase in the size of nuclei formed during the induction period and do not form new nuclei.

Figure 4 shows the dependences of the time it takes for particles to attain their final sizes on the reaction temperature for different concentrations of water and ammonia in the reaction system. An increase in the concentration of water in the reaction system leads to a decrease both in the growth time of particles and in their final sizes. This is explained by the fact that an increase in the concentration of water in the reaction system promotes the hydrolysis reaction and, consequently, increases the number of nuclei formed during the induction period. An increase in the concentration of ammonium hydroxide leads to a decrease in the growth time of particles, on the one hand, and to an increase in their final sizes, on the other hand. This is associated with the double role played by ammonium hydroxide in the processes of formation of SiO_2 particles. As a catalyst, ammonium hydroxide promotes the hydrolysis reaction of tetraethoxysilane, but, at the

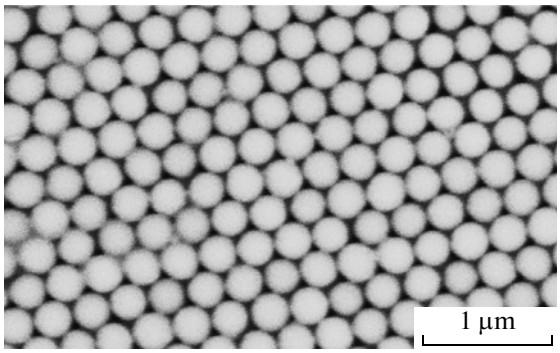

Fig. 6. SEM image of the film consisting of packed SiO_2 particles 290 nm in diameter. The particles were synthesized by heterogeneous hydrolysis of TEOS in combination with the Stöber method.

same time, imparts a negative charge to the microparticles through the adsorption of hydroxyl ions by them, which hinders the aggregation of the microparticles into nuclei.

It has been established experimentally that, in the studied ranges of concentrations (from 16 to 25 M for water and from 1 to 5 M for ammonia at a constant TEOS concentration of 0.14 M) and temperatures (from 1.5 to 45.0°C), the time required to complete the cycle of particle growth lies in the interval from a few minutes to ~2 h. It has also been established that, when the concentration of water in the reaction system increases from 16 to 25 M, the size of particles decreases, whereas an increase in the concentration of ammonia from 1 to 5 M leads to an increase in the size of particles, all other factors being equal. An increase in the temperature of the hydrolysis reaction from 1.5 to 45.0°C results in a decrease in the final size of particles. The particles synthesized by the Stöber method have a nearly perfect spherical shape and a smooth surface.

3.3. Combined Method of Synthesizing Silicon Dioxide Particles

The silicon dioxide particles synthesized by the heterogeneous method can be used as seeds for their further growth by the Stöber method. In this case, we can use the advantages of both techniques. The heterogeneous method of hydrolysis provides the initial narrow distribution of seed particles over their diameters, while the Stöber method ensures a regular spherical shape and a smooth surface of the final particles.

Figure 5a shows the micrograph of seed particles (45 nm in diameter) prepared by the hydrolysis of tetraethoxysilane. Figure 5b shows the micrograph of the final particles (300 nm in diameter) grown from these seeds by the Stöber method. As can be seen from Fig. 5, the appropriate combination of the aforementioned two methods makes it possible to obtain the final silicon dioxide particles with a narrow size distribution (the deviation of the diameter is less than 3%), a perfect spherical shape, and a smooth surface.

The SEM image of the packing of these particles into an opal-like structure is shown in Fig. 6.

4. CONCLUSIONS

In this work, we have investigated the conditions of synthesis of monodisperse colloidal silicon dioxide microparticles by a combined method in which heterogeneous hydrolysis of tetraethoxysilane in the presence of the amino acid is used together with the Stöber method. We have determined the hydrodynamic, thermal, and concentration parameters of the synthesis of SiO_2 particles with sizes ranging from 20 to 100 nm (the deviation of the particle size is approximately 5%). The optimum conditions for further growth of these particles with the use of the multi-stage Stöber method have been determined. The silicon dioxide particles synthesized by the combined method have average diameters in the range 200–300 nm, a nearly perfect spherical shape, and a smooth surface.

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