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Synthesis of silicon dioxide hollow spheres

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The hollow spherical particles of silicon dioxide have been synthesized by hydrolysis of dimethyl dichlorosilane (DMDCS) on the surface of spherical aerosol particles of DMDCS solution in nonpolar solvents. The formation conditions for spherical particles with prespecified structure and morphology have been determined. The phase and chemical composition as well as the morphology of the particles have been examined by X-ray diffraction, Auger electron spectroscopy, scanning electron microscopy, and atomic force microscopy.

Полые сферические частицы диоксида кремния синтезированы путем гидролиза диметилдихлорсилана (ДМДХС) на поверхности сферических частиц аэрозоля раствора ДМДХС в неполярных растворителях. Определены условия формирования частиц с заданной структурой и морфологией. Фазовый и химический состав и морфология полученных частиц исследованы методами рентгеновского фазового анализа, оже-спектроскопии, растровой электронной и атомной силовой микроскопии.

The benefits provided by application of dispersed solids that can add new functionalities to various materials stimulate the interest of researchers in establishing a mechanism of their formation (nucleation, subsequent growth of nuclei, aggregation, agglomeration, ageing, etc.) [1, 2]. One of the important advances attained in the last years is a controlled synthesis of micro- or nanosized hollow particles [2–9] that can simultaneously perform a number of useful functions. Possessing a complete set of properties that are peculiar to the materials with a highly developed surface (sorption and catalytic activity), the hollow particles can be used as temporary carriers of therapeutic agents such as polypeptides, antibodies, enzymes, small medical molecules of nucleic acids (encapsulation) [10–13]. The strength properties of solid hollow particles can be used to protect photosensitive agents against light exposure and dyes against drying. By using a time-controlled breakup of a mixture that contains various chemical agents, it is possible to obtain intermediate or final process products [14–16]. A substance encapsulated in a particle cavity can be deprotected by mechanical or thermal breaking of the particle or its contacting with a solvent. The structured materials of this kind may be used as catalyst carriers, air flow tracers or stuff storage media.

The studies conducted using the regular structures of metal clusters (e.g. Au, Pt [17–18]) encapsulated in inorganic shells have shown significant changes in their physical and some chemical properties. However, application of such materials is restricted since the existing techniques used to provide homogeneous and regular shell structures and control their thickness and porosity are developed insufficiently. In this work, we have considered the manufacturing principles of such materials and methods of their realization taking as an example the synthesis of silicon dioxide hollow nanospheres being widely used as a highly dispersed agent for production of high-performance adsorbents and drugs.

The initial material solution was dispersed using an ultrasonic disperser at the frequency of 2.64 MHz. The particle sizes were varied in the 0.1 to 0.5 mm range. The aerosol particles were transported by

dry air flow at room temperature. The partial pressure of water vapors and temperature in the reactors were set in the 20°C to 50°C range using heaters. As the initial liquid for aerosol formation, we have used neat DMDCS and its solution in a hydrophobic solvent (heptane and carbon tetrachloride). The solution concentration was varied within the whole concentration range at 5 % (v/v) increments. The synthesized product was separated from the solution by centrifugation and decantation with subsequent washing with acetone to limit agglomeration. The residual solvents and moisture were removed by heating up to 130°C at a rate of 10 deg/h under residual pressure of 10^{-1} Pa or in the oxygen flow in the temperature range from about 350°C to 500°C.

The chemical composition of samples prepared by evaporation of a low-concentrated suspension of silicon dioxide particles on the polished surface of silicon single crystal was determined by Auger electron spectroscopy (JEOL JAMP 10S Auger-microprobe, Japan), X-ray phase analysis was carried out using a DRON-3M X-ray diffractometer. The sample morphology was studied by scanning electron microscopy and atomic force microscopy.

As a basis for designing a synthetic process of hollow spherical particles, we have used the following general approaches.

Hollow spherical particles may be formed as a result of chemical reactions between two substances at their interface that has a spherical shape. Such a reaction shall result in formation of a particle of insoluble or low-soluble shell-forming compound or its precursor. The literature data available show that the most easily reproducible methods for these purposes are based on chemical reactions at the liquid-gas (or vapor) or liquid-liquid interfaces. The less frequently used methods are based on the ability of some inorganic substances to form a stable interfacial layer upon their adsorption on a surface of polymer globules (e.g. polymer beads in emulsions) [1, 2]. Those methods also include the formation techniques of porous and hollow ceramic particles by a sol-gel method that is usually used in combination with emulsification procedures.

The method proposed in this work has distinct advantages against the methods where solid templates are used. The synthesis of such solid templates requires development of particular procedures that sometimes are more complicated. Besides, there is a need in a procedure of their removal

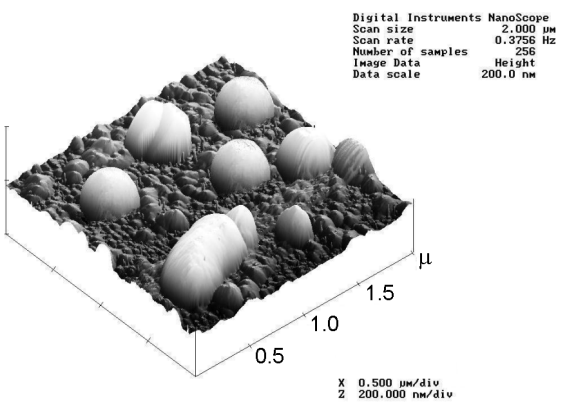

Fig. 1. AFM image of aerosol sphere-like nanoparticles precipitated and dried on the polished surface of single-crystal silicon.

(e.g. burning, acid etching) and such treatment may result in damage of the template structure. The liquid templates can be removed at low temperatures by evacuation and such an approach makes it possible to encapsulate drug components which are unstable at high temperatures or interact with liquids that are used to remove the solid templates.

Fig. 1 shows the nanosized spherical particles of silicon hydroxide precipitated from the alcohol solution and dried on a flat polished surface of single-crystal silicon wafer. The real surface is oblate to some extent and this indicates its deforming upon precipitation on the flat crystal face. The synthesized material consisted of hollow spherical particles of silicon dioxide of 40 nm to 10 µm in diameter. Fig. 2 shows the bar graph for distribution of the hollow nanoparticle diameters. About 80 % of the particles were of 100 to 500 nm in diameter. The thickness of hollow particle shells was correlated with the pre-specified concentration of the active component in a solution. The shell thickness was evaluated with the use of the micrographs of debris obtained by grinding the spherical particles in an agate mortar. When the DMDCS solution concentration was increased from 5 % to 40 %, we have observed clearly an increase in the shell thickness by 10 to 20 % of the particle external diameter and a decrease in the particle porosity. At $C_{DMDCS} \geq 40$ % by volume, we observed a substantial decrease in the number of regularly shaped particles until their complete disappearance. The specific surface area of the synthesized material was 40 to 80 m^2/g, as measured by argon adsorption.

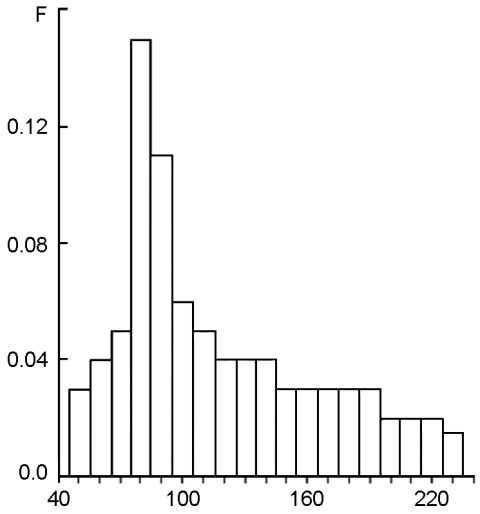

Fig. 2. Distribution of diameters for the silicon dioxide hollow nanospheres.

The Auger spectra of the samples prepared by annealing for 15 min at 350°C show the high intensity peaks of silicon (in the oxidized form) and oxygen and a low intensity peak of chlorine (Fig. 3a). The chlorine peak may result from the presence of DMDCS residues on the surface of hollow spheres. After annealing of the synthesized spheres in oxygen atmosphere for 30 min, the chlorine peak disappears (Fig. 3b).

The X-ray diffraction (XRD) patterns of the spherical nanoparticles have shown that the silicon dioxide spheres are in an amorphous state. There were no apparent peaks of crystalline SiO_2 and peaks of contaminating and intermediate phases in the XRD patterns.

The sample morphology studied by scanning electron microscopy shows (Fig. 4) that the highly dispersed material consists of spherical particles. The sphere sizes are varied in a wide range. The walls of some particles are partially destroyed (insets *1*, *2*, *3*) and this is an indication that the spheres have interior cavities. There are some intact particles of smaller diameters in the interior of one damaged sphere (inset 2).

In summary, using the dimethyl dichlorosilane hydrolysis on spherical surfaces of aerosol droplets of DMDCS solution in non-polar solvents, we have synthesized hollow spherical nanosized particles of silicon dioxide of about 100 to 500 nm in diameter, 40 to 80 m^2/g specific surface area and with a shell thickness of about 10 to 20 % of their external diameters. The method ensures the optimum conditions for formation of hollow spheres with a needed structure and morphology.

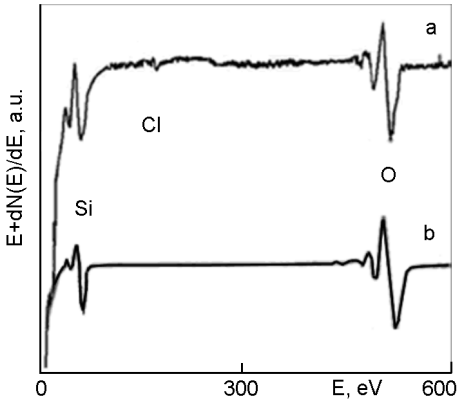

Fig. 3. Differential Auger spectra (0–600 eV) for (a) a film of SiO_2 particles deposited on a single-crystal silicon surface and (b) after annealing in the oxygen atmosphere.

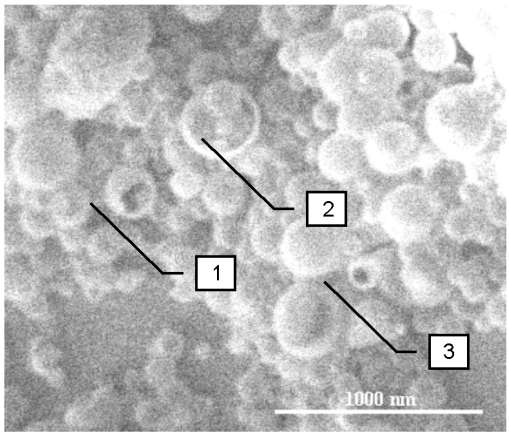

Fig. 4. SEM image of hollow spheres of silicon dioxide (insets *1*, *2*, *3*: hollow nanospheres with partially broken walls).

References

1. S.S.Berdonosov, O.I.Buzin, I.V.Melikhov et al., *Vestn. Mosk. Univ. Ser. 2: Khim.*, **39**, 134 (1998).
2. S.S.Berdonosov, I.A.Kabanov, I.V.Melikhov et al., *Vestn. Mosk. Univ. Ser. 2: Khim.*, **4**, 202 (2000).
3. U.S. Patent 20020004111 (2002).
4. U.S. Patent 6,225,361 (2001).
5. U.S. Patent 6,110,528 (2000).
6. Y.Gu, L.Chen, Zh.Li, Y.Qian et al., *Carbon*, **42**, 235 (2004).
7. Zh.Lou, Q.Chen, J.Gao at al., *Carbon*, **42**, 229 (2004).
8. L.Y.Chen, Y.L.Gu, L.Shi et al., *Solid State Commun.*, **130**, 537 (2004).
9. H.Shiho, N.Kawahashi, *Colloid. Polym. Sci.*, **278**, 270 (2000).
10. S.Phadtare, V.P.Vinod, K.Mukhopadhyay et al., *Biotechnol. Bioeng.*, **85**, 629 (2004).
11. W.Tan, K.Wang, X.He et al., *Med. Res. Rev.*, **24**, 621 (2004).
12. H.Jia, G.Zhu, P.Wang, *Biotechn. Bioeng.*, **84**, 406 (2003).

13. N.G.Balabushevitch, G.B.Sukhorukov, N.A.Moroz et al., *Biotechn. Bioeng.*, **76**, 207 (2001).
14. Y.Aoi, H.Kambayashi, E.Kamijo et al., *J. Mater. Res.*, **18(12)**, 2832 (2003).
15. Zh.Niu, Zh.Yang, Zh.Hu et al., *Adv. Funct. Mater.*, **13**, 949 (2003).
16. H.J.Ding, H.M.Wang, *J.Acoust. Soc.Am.*, **115**, 1414 (2004).
17. Zh.Liang, A.Susha, F.Caruso, *Chem. Mater.*, **15**, 3176 (2003).
18. K.S.Mayya, B.Schoeler, F.Caruso, *Adv. Funct. Mater.*, **13**, 183 (2003).

Синтез порожнистих сфер діоксиду кремнію

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Порожнисті сферичні частинки діоксиду кремнію синтезовано шляхом гідролізу диметилдихлорсилану (ДМДХС) на поверхні сферичних частинок аерозолю розчину ДМДХС у неполярних розчинниках. Визначено умови формування частинок із заданою структурою та морфологією. Фазовий та хімічний склад та морфологію одержаних частинок досліджено методами рентгенівського фазового аналізу, оже-спектроскопії, растрової електронної та атомної силової мікроскопії.