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Composition and properties of porous silicon nanoparticles with deposited cinnarizine

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Abstract. As a result of our work samples of nanopowders of porous silicon with the deposited cinnarizine were obtained and technique of the chemical deposition of cinnarizine into the porous layer was elaborated. The obtained structures of porous silicon can be used for delivery of various therapeutic agents starting from small molecules of the preparations up to the large peptides/protein therapeutic agents while controlling composition of the surface and morphology of the porous layer. Nanopowder of porous silicon was obtained by mechanical and ultrasound grinding of the porous silicon wafers. Using transmission electron microscopy, infrared and ultraviolet spectroscopy morphology and composition of the porous silicon samples were studied. According to the results of transmission electron microscopy (TEM) a presence of both crystalline and amorphous phases was determined. Chemical composition and types of the bonds in the porous silicon layer was studied according to the data of infrared (IR) spectroscopy. The data on ultraviolet (UV) allowed to determine the energy of the possible direct transitions in nanostructures. Adsorption and desorption processes in nanostructures were studied.

Keywords: mesoporous silicon, nanopowders, nanopowders, spectroscopy, cinnarizine, systems of drug delivery

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Состав и свойства наночастиц пористого кремния с осажденным циннаризином

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Аннотация. В результате работы были получены образцы нанопорошков пористого кремния с осажденным циннаризином и отработана методика химического осаждения циннаризина в пористый слой. Полученные структуры пористого кремния могут быть использованы для доставки различных терапевтических средств, от малых молекул препаратов до больших пептидов/белковых терапевтических препаратов при управлении составом поверхности и морфологией его пористого слоя. Нанопорошок пористого кремния был получен механическим и ультразвуковым измельчением пластин пористого кремния. Методами просвечивающей электронной спектроскопии, инфракрасной спектроскопии и ультрафиолетовой спектроскопии исследованы морфология и состав образцов пористого кремния. По результатам исследований просвечивающей электронной микроскопии определили присутствие в образцах как кристаллической, так и аморфной фазы. Химический состав и типы связей в слое пористого кремния был определен по данным инфракрасной спектроскопии. По данным ультрафиолетовой спектроскопии были определены энергии возможных прямых переходов в наноструктурах. Исследованы процессы адсорбции и десорбции на наноструктурах.

Ключевые слова: мезопористый кремний, нанопорошки, наночастицы, спектроскопия, циннаризин, системы доставки лекарств

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Introduction

Now one of the most prospective areas for the application of porous silicon proves to be biomedicine. Therefore an interest to porous silicon from the viewpoint of biomedicine problems is due to its good biocompatibility and high specific surface as well to the possibility of modification of the surface chemical properties and controlling of the porous layer morphology. Porous silicon can be well used for the delivery of various therapeutic agents starting from the small molecules of the drugs up to the large peptides/protein preparations while controlling surface composition and morphology of the porous layer. Drug preparations made on the basis of silicon nanostructures show the main properties advanced to systems of directed drug delivery: a slight release of the drug agent after attainment of the predetermined goal, as well a possibility of paranteral dosing, in particular, intravenous injection. Therefore, an experience in the use neuroprotective and neurotrophic preparation of cinnarizine for the patients with neurologic disorders in post-Covid period is of a great interest [1–4]. Goal of the work is a formation of the structures of porous silicon – cinnarizine type and the study of their features, investigations of its composition and sorption-desorption process of cinnarizine from the surface of porous silicon.

Materials and Methods

Samples of porous silicon were obtained by anodic electrochemical etching of single-crystalline silicon with *n*-type conductivity having specific resistivity of 0.2 Ohm·cm in the alcoholic solution of hydrofluoric acid with an addition of hydrogen peroxide. Nanopowder of porous silicon was obtained first by mechanical separation of the porous layer with its further grinding in the alcohol solution with the use of ultrasound for 10 minutes [4].

Morphology and microstructure of the samples were studied by transmission electron microscopy with the use of transmission electron microscope Libra120 (CarlZeiss, Germany, CKPNO VSU). Chemical composition of the samples was determined with IR-Fourier spectrometer Vertex Bruker 70 with an attachment for the measurement of absorption/transmission in thin-film samples. Optical properties of the samples were investigated by ultraviolet spectroscopy in the range of 190–190 nm with the use of spectrometer LAMBDA 650 produced by Perkin Elmer company.

To study optical properties of the samples in the UV-range specially elaborated approach method was employed applying a technique for surveying of reflection spectra [5]. This technique makes it possible to obtain information concerning the films and layers deposited/formed on the optically denser and bulk substrates. In order to study the features of sorption/desorption of cinnarizine to/from the surface of porous silicon the wafers of silicon with por-Si layers were placed in 0.1 M solution of HCl, containing 0.5 mg/cm^3 of cinnarizine. The volume of the media was 100 cm^3. Tests of dialyzate (5 ml) were sampled every 30 minutes. In order to determine cinnarizine content spectrophotometry technique in the UV-range (254 ± 2 nm) was applied with the use of spectrophotometer SF-2000. Cinnarizine concentration in solutions was determined by the calibrating curve. Release of cinnarizine from the surface was studied by dialysis technique applying semi-permeable cellophane membrane also using spectrophotometer technique.

Results and Discussion

Figure 1 represents TEM-image and electron-diffraction pattern of the obtained porous silicon powder. To make phase analysis with the use of external standard in order to analyze electron-diffraction pattern previously obtained value of the device constant was used.

Results of TEM showed the presence of as crystalline (points at the electron-diffraction pattern) as amorphous phase of silicon (rings at the electron-diffraction pattern) in the powder. Size of the particles according to TEM data was of ~ 5 nm.

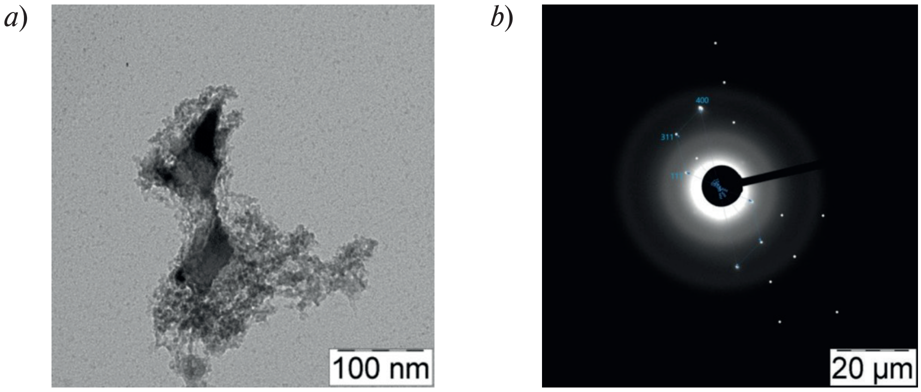

Fig.1. TEM image of the porous silicon powder (*a*) and electron-diffraction pattern of the porous silicon powder (*b*)

IR-spectra of the samples with the deposited cinnarizine are presented in Fig. 2. Comparative analysis of IR-spectra for the samples of original porous silicon and those ones after cinnarizine deposition demonstrated the presence of cinnarizine on the surface of porous silicon. Position of the distinctions in IR-spectra for the deposited drug agents was determined with the use of AIST database: Spectral Database for Organic Compounds, SDBS [6].

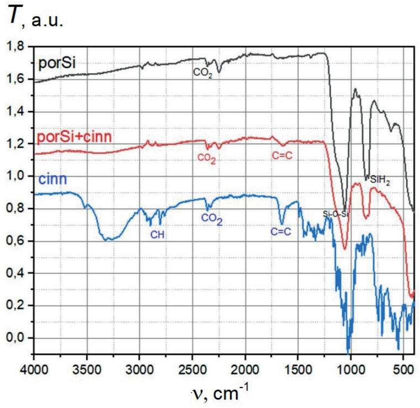

Fig.2. IR transmission spectra of porous silicon with the deposited cinnarizine and reference samples: cinnarizine powder and original porous silicon

While comparing spectrum of the obtained sample with the standard spectrum of cinnarizine it was found that after cinnarizine deposition into porous silicon new peaks appeared in the spectrum, corresponding to those ones of cinnarizine: 2959 cm^{-1} and 2936 cm^{-1}, corresponding to the valence vibrations of C—H bond in alicyclic compounds; 1597 cm^{-1}, corresponding to the valence vibrations of C=C bond in aromatic ring, 1134 cm^{-1}, corresponding to the valence vibrations of C—N bond; 999 cm^{-1} and 962 cm^{-1}, corresponding to the valence vibrations of =CH bond. Note that in the spectra of all the samples one can clearly observe the bands characteristic of porous silicon Si-Si (616 cm^{-1}), Si-O-Si (1060 cm^{-1}), Si-H$_x$ (805 cm^{-1}) [7].

In order to know the mechanism of optical absorption in porous layers formed by electrochemical etching with the use of the software package OPUS Bruker and taking into account Lambert-Bugger formula:

$$T = \exp\left[-D\right],$$

where T is transmission, D — optical density, transmission-reflection spectra were reconstructed into absorption spectra. Dependences $(D\cdot h\nu)^2$ on the quanta energy for single-crystalline Si are presented in Fig. 3, as well those ones for porous silicon samples; the latter ones were calculated from the spectra of specular reflection with the use of of Kramers-Kronig relations [8]. Graphical analysis allowed to reveal separate parts with linear dependence of $(D\cdot h\nu)^2$ on the quanta energy. This can indicate at the presence of the direct allowed transition in this spectral range (Fig. 3). Linear extrapolation of these parts in the spectra to the value makes it possible to determine the energy of direct transitions which are characteristic for these samples.

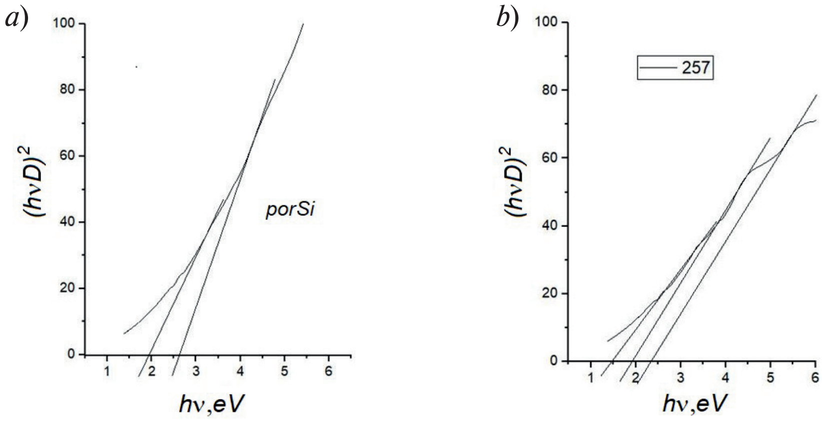

Fig.3. Dependences of $(D\cdot h\nu)^2$ on the quanta energy for original porous silicon (*a*) and porous silicon with the deposited cinnarizine (*b*)

Applying tangents concept one can determine the following possible direct transitions in the range of 2.3—2.5 eV for light powders, corresponding to nanocrystals with the size of ~2 nm, according to [9], and to transition of 1.8—2 eV, corresponding to the particles with the size of ~3 nm, for more heavy fractions of mesoporous silicon nanopowders. Basing on the obtained dependences for the samples with the deposited cinnarizine one can also determine direct transition in the range of 1.5 eV, which can be associated with the features of cinnarizine optical absorption, or formation of its bonds with silicon, or either with more large silicon nanocrystals.

During the study of cinnarizine adsorption on the surface of porous silicon (Fig. 4) it was found that for the time of adsorption equal to 30 minutes cinnarizine concentration on the wafers of meso- and macroporous silicon was of 1.1 mg/cm^3 (Fig. 4). While increase of the adsorption time cinnarizine concentration was slightly reduced up to 1.00 mg/cm^3, respectively. Thus, the optimal time for cinnarizine adsorption is of 30 minutes.

While cinnarizine desorption from the surface of silicon wafers with por-Si layer it was determined that for 45 minutes of the experiment cinnarizine concentration in the hydrochloric acid medium of 0.1 M concentration equal to 0.70 mg/cm^3 (Fig. 4, *b*). The obtained results showed the availability of the mesoporous silicon usage for the preparation of the carriers drug agents with a durable action.

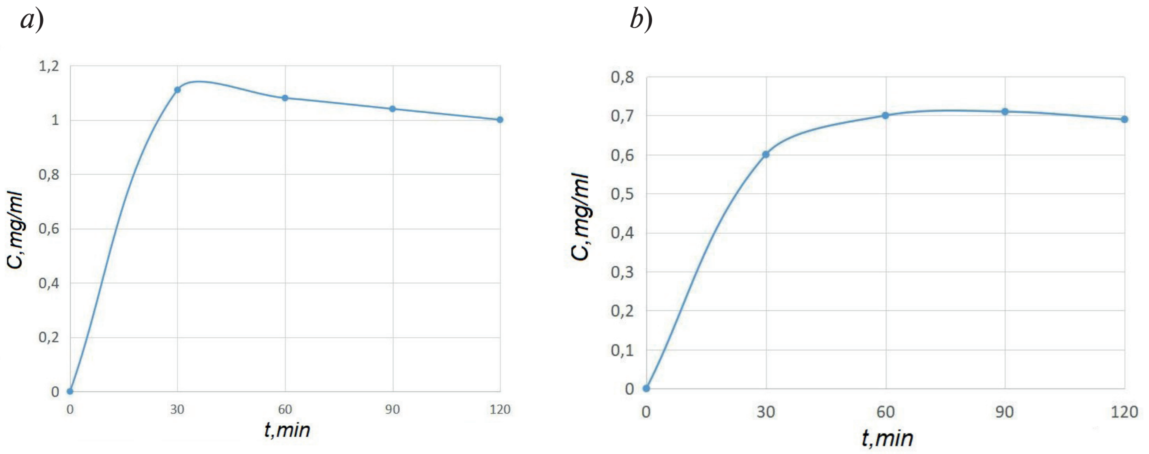

Fig. 4. Dependence of cinnarizine concentration on: (*a*) the time of deposition on the surface of porous silicon and (*b*) on the time of desorption from the surface of porous silicon

Conclusion

As a result of the performed investigations samples of the porous silicon nanopowders with a diameter of less than 5 nm and the deposited cinnarizine were obtained in the work. Data of the transmission electron microscopy helped us to determine a presence of both crystalline and amorphous phase in the sample. Using infrared spectroscopy chemical composition of the porous layer was determined as well as the types of bonds in this layer. It was shown that Si-O, Si-H_x, Si-OH and Si-Si bonds are present in the porous layer as well those ones characteristic of cinnarizine. According to UV-spectroscopy possible direct transitions were determined with the energy of 1.8 eV and 2 .3 eV for the original porous silicon and the additional transition at 1.5 eV for the sample with the deposited cinnarizine. It was ascertained that cinnarizine on the surface of porous silicon is most efficiently sorbed and desorbed for the time of 30–45 minutes.

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