Investigation of porous silicon nanopowders functionalized by antibiotic Kanamycin, fluorophore Indocyanine Green

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Abstract. Porous silicon nanopowders for target drug delivery were obtained by electrochemical anodic etching in a hydrofluoric acid solution using the monocrystalline silicon n-type conductivity. Porous silicon powders were obtained by sonification of porous silicon layers. The powders were functionalized by antibiotic Kanamycin and fluorophore Indocyanine Green by the passive adsorption method. The peculiarities of absorption spectra in 190-600 nm region were revealed for functionalized porous silicon powders dispersions in water.

1. Introduction
Currently in modern Material Science is actively grown the field of creating porous materials with controlled parameters (pore diameter, the porosity, structure and thickness of the porous layer, the phase structure on the inner surface of the pores). Porous silicon (por-Si) and por-Si powders are one of the most promising advanced materials in bioengineering (targeted drug delivery, implants, photodynamic therapy, biosensors, etc. [1-3, 7-9].

A separate area of application of porous silicon in biomedicine currently is the use of porous silicon particles as carrier matrices for drug delivery. Creation of methods of drug delivery is one of the leading trends in modern pharmacology [4-6].

Currently, there are a lot of methods to fix the drug in a porous carrier: method of passive adsorption, electrostatic adsorption, chemical (covalent bonding), and etc. Passive adsorption method in the solution is most commonly used when working with porous silicon based carrier matrix. The method consists in immersing por-Si particles in a predetermined concentration of the drug solution. After the particle pore volume is filled with molecules of drug substance, functionalized particles can be prepared by centrifugation or filtration. The amount of drug substance to be filled is controlled by the concentration of the solution, the time of adsorption, as well as the porosity and pore size of the particles [10].

2. Materials and methods
Por-Si nanopowders were obtained in two steps. In the first step porous silicon nanolayers were obtained by electrochemical anodic etching in a hydrofluoric acid solution from the monocrystalline silicon n-Si(111) with 4.5 Ω·cm resistivity. The choice of process conditions (anodization current density of j = 80 mA / cm2, anodization time of t = 20 min) was based on the experience of previous studies [1]. In the second step por-Si nanolayers were removing by the ultrasonication process. After centrifugation the particles characterized of narrow range of size distributions. Based on SEM data, the particles characterized by the diameter of 300-500 nm. Basically, the particles are rectangular. Figure 1 shows typical size of obtained particles.

For functionalization of such prepared por-Si nanopowders the passive adsorption method was chosen. The nanopowders were immersed into saturated aqueous solution of Kanamycin (or of Indocyanine Green (ICG)) for 24 hours. Absorption spectra were acquired on a PE-5400UV UV–vis spectrophotometer (LLC “Ekohim”).
3. Experiment and results

To reveal the nature of the interaction between the functionalizing substances and particles of porous silicon (control functionalization of porous particles) spectrophotometry method was used. In order to show the result of functionalization, additional absorption spectra were taken: spectrum of the aqueous dispersion por-Si before functionalization, and also spectra of Kanamycin aqueous solution, IGG aqueous solution.

Figure 2 shows absorption spectra of Kanamycin, por-Si aqueous dispersion and aqueous dispersion of functionalized por-Si by Kanamycin. As can be seen from absorption spectra Kanamycin has absorption at 207 nm and 236 nm. Functionalized por-Si by Kanamycin also has absorption in the same ultraviolet region (194 nm and 244 nm) as Kanamycin. So the absorption bands are shifted relative to the solution of Kanamycin, which may indicate the interaction between the porous silicon and Kanamycin molecules.

![Figure 1. Morphology of por-Si particles fixed on Si substrate taken by SEM](image)

![Figure 2. Absorption spectra of Kanamycin, por-Si water dispersion and water dispersion of por-Si functionalized by Kanamycin](image)
Figure 3 shows absorption spectra of ICG, por-Si aqueous dispersion and aqueous dispersion of functionalized por-Si by ICG. ICG has a number of absorbance peaks: in the near-infrared region with a maximum absorption at 776 nm, at 710 nm and in the ultraviolet region at 213 nm, which corresponds to the typical absorption spectrum of Indocyanine Green. Spectrum of functionalized por-Si by Indocyanine Green has no peaks of absorbance. The main contribution to the signal strength makes the concentration of particles in the solution. That may indicate that the IGG molecules were not fixed on the surface of the porous silicon particles.

Such different nature of the interaction of molecules of Kanamycin and ICG with porous silicon is obviously related to the different composition of the functional groups of analytes. Thus, it is known from previous studies [9-10] that the porous silicon obtained in selected in this work conditions of preparation and post-processing are hydrophilic and contains hydroxyl groups on the surface. Molecules Kanamycin contain amino and hydroxyl functional groups. Therefore, an interaction between a hydrophilic molecule Kanamycin and hydrophilic surface of such prepared porous silicon is energetically favorable, which, in our opinion, is confirmed by absorption spectrum. Furthermore, fastening Kanamycin molecule onto the porous silicon surface by Kanamycin hydroxyl groups is preferred for the NH$_2$-group would be in the active form and could provide its therapeutic function. On the other hand, ICG molecules have many hydrophobic CH$_2$-functional groups, which disadvantageously interact with a hydrophilic porous silicon surface. Therefore, fixing the molecules on the particles of the porous silicon were not observed.

![Figure 3. Absorption spectra of ICG, por-Si water dispersion and water dispersion of por-Si functionalized by ICG](image)

4. Conclusion

Thus, Porous Silicon nanopowders were obtained by electrochemical etching. The analysis of the obtained data by scanning electron microscopy showed that the average sizes of obtained particles are 300-500 nm. The porous silicon obtained in selected in this work conditions of preparation and post-processing are hydrophilic and contains hydroxyl groups on the surface. As Kanamycin molecules contain amino and hydroxyl functional groups, interaction with por-Si surface is energetically favorable. ICG molecules have many hydrophobic CH$_2$-functional groups, which disadvantageously
interact with a hydrophilic porous silicon surface. Therefore, fixing the molecules on the particles of the porous silicon was not observed, which is confirmed, in our opinion, by spectrophotometry data. According to the results, you can make the following recommendations for the choice of the conditions for obtaining porous matrices carrier on the basis of porous silicon:

- porous silicon particles in the selected conditions are suitable for functionalization of molecules of antibiotic Kanamycin;
- for the functionalization of porous silicon by fluorophore Indocyanine Green adjusting of technological conditions is in need for changing the functional groups on its surface to the hydrophobic. Another line of research may be additional post-processing of porous silicon. Furthermore, the method of spectrophotometry in the UV range is an appropriate for rapid evaluation of functionalization process of porous silicon particles with target substances.

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