

## A study of porous silicon and hydroxyapatite nanocomposite suspensions obtained by laser ablation and mechanically

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In this work, a porous silicon–hydroxyapatite nanocomposite was studied as a base for a promising biomaterial for osteoplasty. The mechanical method for creating nanocomposites is complicated and inefficient. Using the laser ablation method, there were obtained regular-shaped particles smaller in size than those obtained mechanically. The powder solubility in water was also investigated.

**Keywords:** porous silicon, hydroxyapatite, laser ablation, nanocomposite powders, probe microscopy.

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Among various drug nanocarriers, nanocomposites based on porous silicon (*por*-Si) are considered the most promising [1]. Porous silicon stimulates the growth of osteoblasts (young cells of bone tissue) 15–20 nm in size and affects the phase of bone mineralization. The prospects for the use of these carriers are determined by their abundance, biocompatibility and biodegradation [2]. The smaller is the nanocomposite grain size, the better is the functioning of bone tissue cells. Due to the presence of a great number of nanosized pores, porous silicon may be used as an efficient matrix for creating nanocomposites, including those containing hydroxyapatite (HAP) [3]. Notice that there exists a problem of low HAP solubility in water and biological fluids. Creation of a nanocomposite based on *por*-Si can help provide the required drug concentration in the body.

In this study, porous silicon was obtained from wafers of monocrystalline *p*-type silicon by using anodic electrochemical etching in a vertical cell containing a 1:1:1 solution of HF, H<sub>2</sub>O, and C<sub>2</sub>H<sub>5</sub>OH. As the electrodes, graphite was used. Dissolution of silicon atoms in the process of anodic etching was controlled by the electrochemical cell current due to better controllability of the porosity and thickness of the porous layer [4]. Samples of polished-surface single-crystalline silicon were etched for 15 min at the current density of 10 mA/cm<sup>2</sup>. Such a mode of etching allows obtaining nanoporous silicon with the pore diameter of < 1 μm.

The hydroxyapatite powder was fabricated by precipitating the mineral component of bone from a demineralizing solution with the particle sizes of 20–80 nm. The hydroxyapatite chemical formula is Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub>. To obtain the *por*-Si+HAP nanocomposite, porous silicon was saturated with aqueous solution of hydroxyapatite [5].

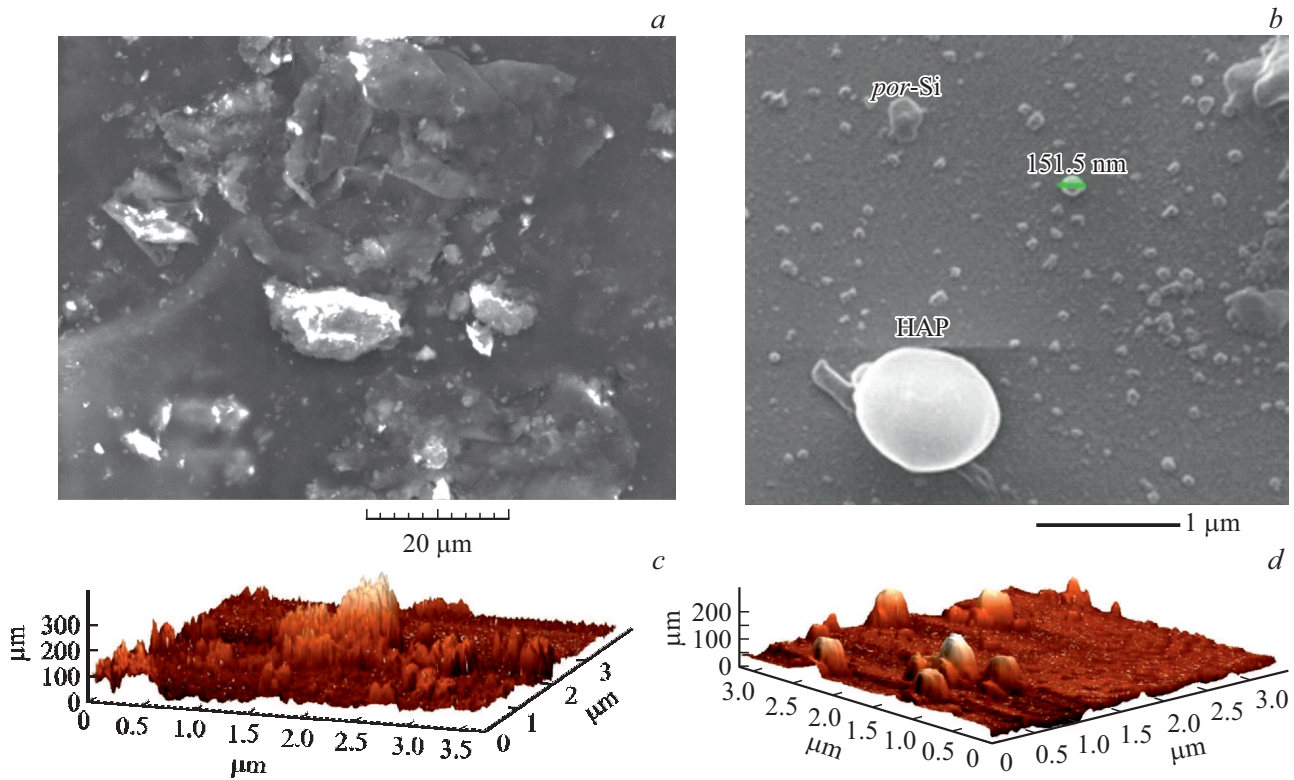
The *por*-Si+HAP nanocomposite powder was prepared by mechanically separating the porous silicon layer from the substrate with subsequent crushing. The disadvantages of this method are the possibility of powder contamination

with the crushing media material, and long duration and high energy consumption of the process [6]. After that, the samples were deposited onto a glass slide and examined with scanning probe microscope (SPM) „Integra Tomo NT-MDT“ and scanning electron microscopes (SEM) „Vega 3-T Scan“ and „FEI Quanta 200“. The mechanical method produces large particles most of which are 10–15 μm in size (Fig. 1, *a*). They get combined with other particles thus forming large irregularly-shaped clusters. The structure of powder particle surfaces is of the loose character due to a large number of pores (Fig. 1, *c*).

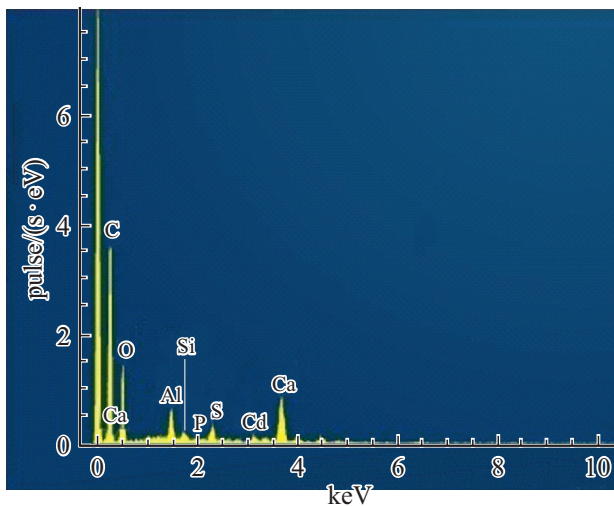
For comparison, the *por*-Si+HAP nanocomposite powder was prepared by laser ablation of the porous layer [7]. The process of laser ablation proceeds when high-power laser radiation is focused onto a solid target surface. Ablation was performed using pulsed fiber laser Raycus 20W with the wavelength of 1064 nm, scanning speed of 20 mm/s, pulse repetition rate of 25 kHz, output power of 16 W in water, and pulse duration of 100 ns. Particles of the powder fabricated by laser ablation have a more rounded shape (Fig. 1, *d*). In the process of ablation, hydroxyapatite particles fly out of large pores. They merge with each other thus forming large clusters. The major part of the powder consists of small particles 0.27–0.53 μm and less in size (Fig. 1, *b*).

The presence of hydroxyapatite in silicon pores was confirmed by examining the powder by X-ray energy-dispersive microanalysis. The powder consists of the hydroxyapatite components, namely oxygen, calcium and phosphorus, as well as of silicon (see Fig. 2 and the Table). The amount of carbon is large because of destruction of graphite electrodes during etching. This confirms the presence of HAP in the silicon pores. The presence of other elements confirms the natural origin of the material from which hydroxyapatite was fabricated.

Suspensions were prepared by mixing the powder of porous silicon or *por*-Si+HAP nanocomposite with distilled water. The number of particles (*N*) and their concentration



**Figure 1.** SEM (*a, b*) and SPM (*c, d*) images of particles obtained mechanically (*a, c*) and by laser ablation (*b, d*).



**Figure 2.** Elemental composition of the nanocomposite *por-Si*+HAP powder.

(*n*) in the suspension prepared by laser ablation were calculated by the gravimetric method:

$$N = \frac{3}{4} \frac{M}{\rho \pi R^3},$$

$$n = N/V,$$

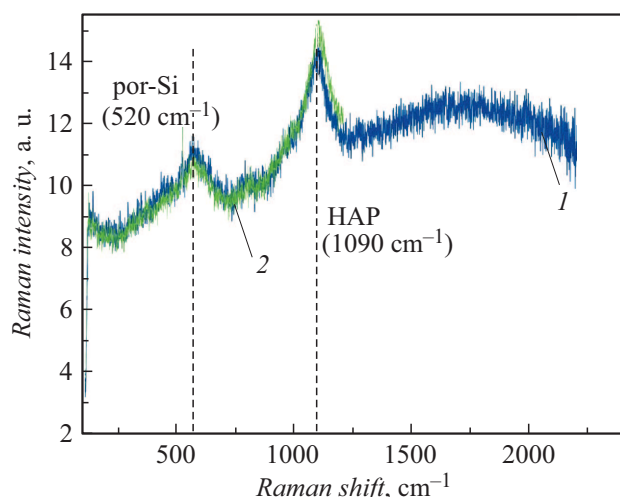
where *M* is the powder mass,  $\rho$  is the silicon density, *R* is the linear radius of the particle, *V* is the fluid volume.

Elemental composition of particles

Element	Percentage, at.%
C	64.63
O	29.19
Ca	3.32
Al	1.43
S	0.75
Cd	0.34
Si	0.28
P	0.06
Total	100.00

For a silicon wafer 6cm<sup>2</sup> in area and 6% in porosity, the weight of the powder is equal to the loss of wafer weight after laser ablation. Using this method, it is possible to obtain, in average,  $5 \cdot 10^{15}$  particles with concentration of  $1 \cdot 10^{14}$  cm<sup>-3</sup>.

Porous silicon is a soluble substance, while hydroxyapatite is unsolvable in biological fluids. The suspension obtained by laser ablation was, in addition, tested for solubility in distilled water by using Raman spectroscopy (RS). For this purpose, the suspension was deposited onto a glass slide. The Raman spectra were measured at setup MicroRaman LabRAM HR Visible on the day of ablation and five months later. Excitation was performed by an Ar<sup>+</sup> laser with a wavelength of 514.5 nm. The obtained Raman spectra are



**Figure 3.** Raman spectra of nanocomposite *por-Si+HAP* prior to (1) and after dissolution (2).

presented in Fig. 3. The peak near  $520\text{ cm}^{-1}$  corresponds to *por-Si* (the Si–C longitudinal valence oscillations), the peak in the vicinity of  $1090\text{ cm}^{-1}$  corresponds to HAP (molecular group  $\text{C}^{16}\text{O}_3$ , oscillation range of the B-type carbonate ions). The experimental data are in agreement with literature data [8,9].

The powder spectra measured prior to dissolution exhibits broad peaks of porous silicon 12 a.u. in intensity and hydroxyapatite 14.3 a.u. in intensity (curve 1 in Fig. 3). After dissolution, the HAP spectrum intensity increased ( $\sim 15$  a.u.). Intensity of the *por-Si* spectrum became lower ( $\sim 11$  a.u.), as well as the peak width (curve 2 in Fig. 3). This means that porous silicon dissolves with time and releases hydroxyapatite.

The results of this study may be used as a base for a technique for producing the *por-Si+HAP* nanocomposite with controllable content of HAP.

This article does not contain any studies involving human subjects.

### Conflict of interests

The authors declare that they have no conflict of interests.

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