

Investigation of Porous Silicon Nanocomposites with Hydroxyapatite Powder Solubility

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Abstract. In this work, precipitation of suspensions and colloidal solutions of hydroxyapatite (HAP), porous silicon (por-Si) and por-Si+HAP nanocomposites were studied by scanning electron microscopy and Raman spectroscopy. The precipitation was carried out from suspensions with different time exposure. The noticeable solubility of the nanocomposite powder in water is shown. © 2022 Journal of Biomedical Photonics & Engineering.

Keywords: nanocomposite; hydroxyapatite; porous silicon; colloidal solution scanning electron microscope; Raman spectroscopy.

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1 Introduction

Porous silicon (por-Si) nanocomposite with hydroxyapatite (HAP) is a promising basis of biomaterial for osteoplasty. HAP is a mineral phase of bone tissue, and ceramics based on HAP are widely used for the manufacture of bone and dental prostheses [1, 2]. In the treatment of bone tissue damage as a result of trauma or osteoporosis, to deliver HAP to the affected areas of bone, it is necessary to use transport porous particles saturated with substance, since pure HAP is practically insoluble in blood and plasma. The basis of such material can be por-Si, because of depending on the porosity, the por-Si can be both bioresistant and bioresorbable. The presence of a large number of nanoscale pores makes it possible to use por-Si as an effective matrix for creating nanocomposites, including those with hydroxyapatite [3–6]. The specific surface area, pore diameter and pore size distribution, as well as the nature and size distribution of porous particles, are important for performing the function of carrier matrices by geometric parameters regulated by synthesis conditions. The composition and condition of functional groups on the por-Si surface will depend on the anodizing conditions (current density, electrolyte composition, etc.), as well as on the choice of the brand of monocrystalline silicon [7, 8]. The current applications of por-Si for the transport of proteins, enzymes, drugs, etc. are shown [9–12]. In Ref. [6] por-Si is considered as a substrate for bone tissue growth, in Refs. [2, 7, 10, 11] por-Si nanoparticles are

proposed as transport for drug delivery, in Ref. [5] por-Si is used in prosthetics technology. However, the por-Si-hydroxyapatite system as the basis of a transport nanoparticle for use in osteoplasty is not enough covered in the scientific and technical literature. The most probable reason is the problem of solubility of the por-Si + HAP nanocomposite in physiological fluids. The good solubility of por-Si is due to its high reactivity due to the large free surface area. When filling the pores of the HAP, this surface will decrease, and the HAP does not dissolve in blood and plasma. Therefore, the issue of solubility of por-Si + HAP nanocomposite in water is relevant. It was previously shown that small por-Si pores are well filled with HAP nanoparticles, which are retained in them when por-Si is ground into powder [12, 13]. With satisfactory solubility, such particles can serve as transport for the delivery of HAP to the affected areas of the bone.

The aim of this paper is to study the change in the structure of the aqueous suspension of the por-Si + HAP nanocomposite powder over time to assess the possibility of its dissolution in physiological fluids.

2 Experimental Methods

2.1 Methods of Creating Samples

To obtain por-Si samples, the method of horizontal electrochemical etching was performed. Etching was carried out in water-alcohol solutions of hydrofluoric

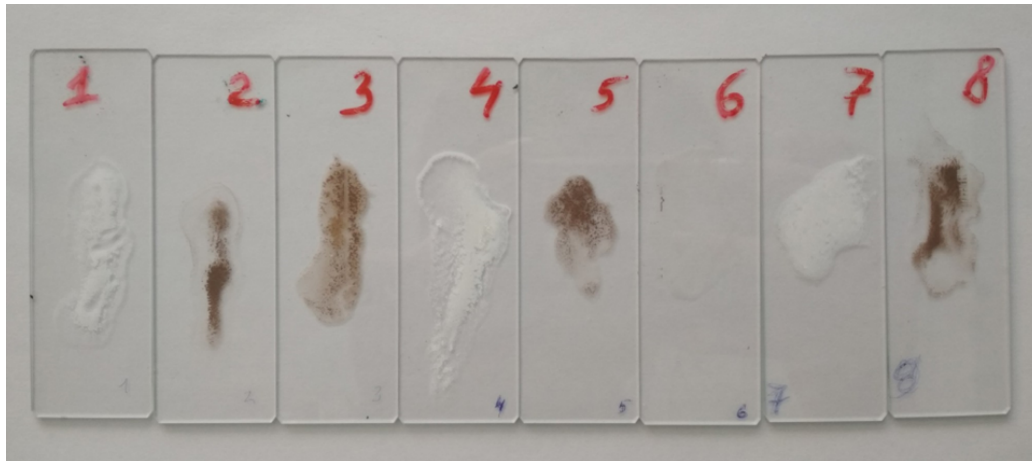


Fig. 1 The samples for the study: No. 1 HAP sediment from an aqueous suspension on the first day; No. 2 Por-Si + HAP sediment from aqueous suspension on the first day; No. 3 Por-Si sediment from aqueous suspension on the first day; No. 4 HAP sediment from aqueous suspension after a week; No. 5 Por-Si+HAP sediment from aqueous suspension after a week; No. 6 Por-Si sediment from aqueous suspension after a week; No. 7 HAP sediment from aqueous suspension in a month; No. 8 precipitation of Por-Si + HAP from aqueous.

acid for 20–30 min at an anode current density of 10 mA/cm^2 . To create nanocomposites, hydroxyapatite powder (HAP) was used, which was obtained by precipitation of the bone mineral component from a demineralizing solution [14]. The HAP is deposited on a substrate from a suspension of HAP powder in ethyl alcohol or water. The deposition time was 30 min until the sample was completely dry. Por-Si and nanocomposite powders were made by mechanically separating the porous layer from the substrate and grinding it in a mortar. Based on the powders, aqueous suspensions (colloidal aqueous solutions) of por-Si, HAP, por-Si + HAP and its precipitation samples were made.

2.2 Methods of the Nanoparticles Dissolution Processes Investigation

Solubility was tested after 1 day, 1 week, and 4 weeks. At the end of the time, the suspension of each sample was planted on a slide until completely dry.

The obtained precipitation samples were studied by scanning electron microscopy (SEM) on a FEI QUANTA 200 microscope and Raman spectroscopy on a Horiba Jobin Yvon LabRam HR-800 spectrometer with a spectral resolution of 2 cm^{-1} in the 400–500 nm region, and about 1 cm^{-1} in the 500–600 nm; signal registration was carried out by a cooled CCD matrix. The excitation was carried out by an Ar^+ laser at a wavelength of 488 nm.

3 Results

Fig. 1 shows glasses with the studied precipitation of suspensions. Here we can see that the precipitate of pure HAP has not been changed qualitatively either in a week

or a month (No. 1, 4, 7), the precipitate of pure por-Si has become completely transparent after a week (No. 3 and No. 6), and the nanocomposite por-Si + HAP only has become slightly more transparent (No. 2, 5, 8). More precisely, an area of a more transparent solution appeared, while at the same time a darker and opaque part was preserved. This indicates that sufficiently large particles are present in the nanocomposite solution even after a month of exposure, while in the pure por-Si solution, they are practically absent after a week of exposure. This result is confirmed by the analysis of precipitation images obtained with a scanning electron microscope. Figs. 2–6 show SEM images of sediment samples from suspensions with different exposure times and their Raman spectra.

Table 1 Sample description.

Sample #	Type of sediment	Exposure time
s1	HAP from an aqueous suspension	1 day
s2	Por-Si + HAP from an aqueous suspension	1 day
s3	Por-Si from an aqueous suspension	1 day
s4	HAP from an aqueous suspension	1 week
s5	Por-Si + HAP from an aqueous suspension	1 week
s6	Por-Si from an aqueous suspension	1 week
s7	HAP from an aqueous suspension	1 month
s8	Por-Si + HAP from an aqueous suspension	1 month

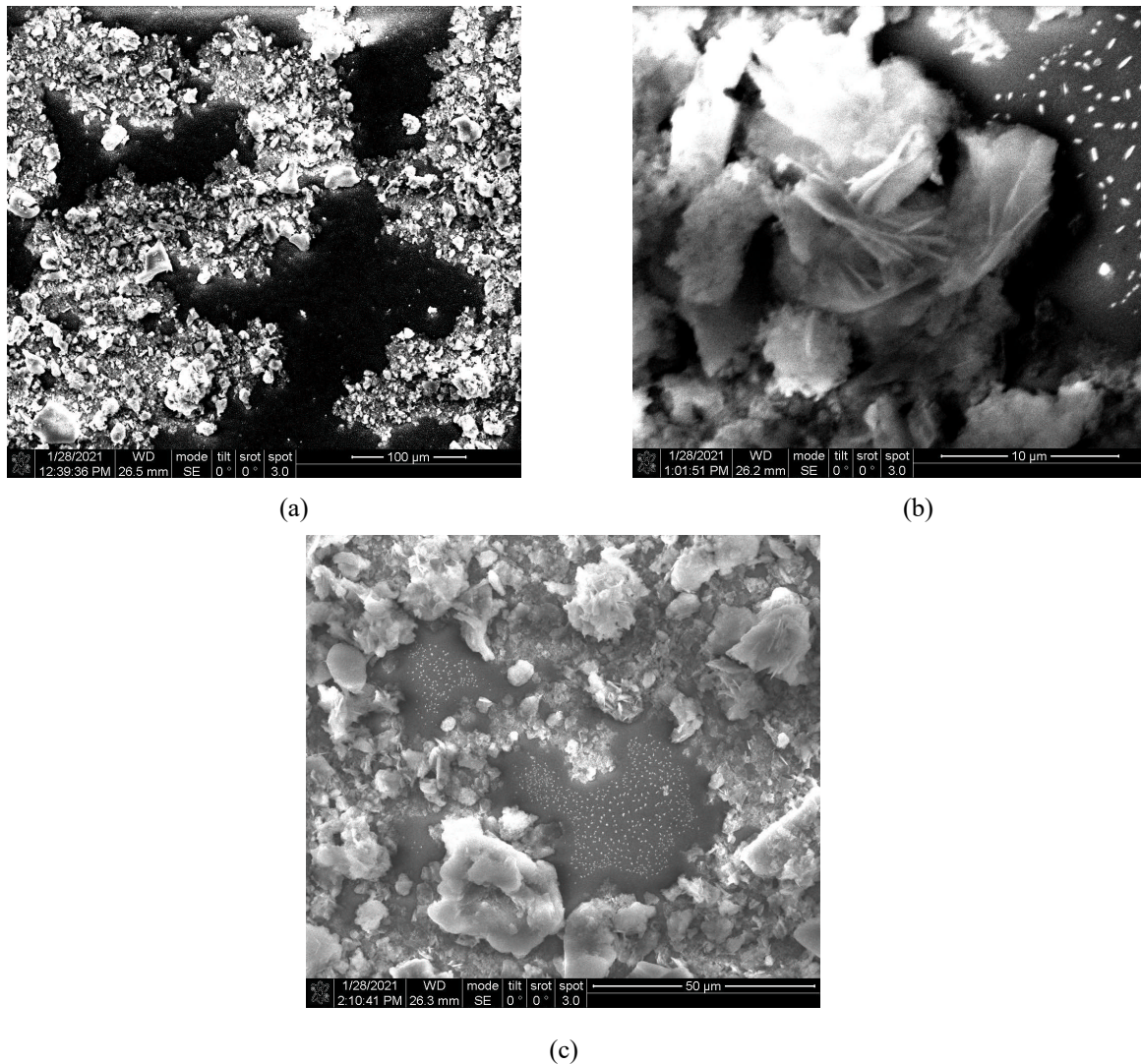


Fig. 2 SEM images of HAP suspension precipitation on the day of its manufacture (a, b) and after a week of exposure (c). Ruler size a) 100 μm , b) 10 μm , c) 50 μm .

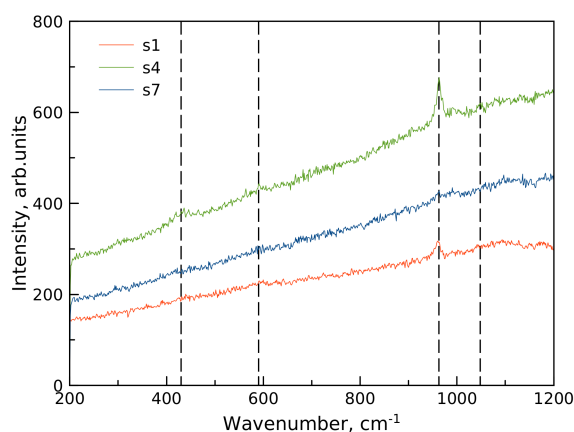


Fig. 3 Raman spectra of HAP suspensions precipitation with different exposure times: on the day of the preparation (s1), after a week (s4), and a month of exposure (s7).

Fig. 1 (a–c) shows the precipitate of the HAP suspension on the day of its preparation (a, b) and after a week of exposure (c). It can be seen that the precipitate contains two different fractions: agglomerates of large irregularly shaped particles and clusters of evenly distributed smaller particles, which have approximately the same size (0.3–0.4 μm) and a more regular form. In some agglomerates, the structure of bone tissue (b) is visible because of the natural origin of the HAP powder from the bone demineralizing solution. In the sediment from the suspension after a week of exposure (b), the agglomerates look looser, which indicates their gradual dissociation. At the same time, the average size of small particles in clusters does not change noticeably.

Fig. 3 shows the Raman spectra of samples s1, s4, s7. Vertical dotted lines indicate the position of the Raman lines in the HAP spectrum from the Ref. [15]. The analysis of the Raman spectra (Fig. 3) shows that there is no peak corresponding to the HAP in the HAP sediment spectrum of the suspension with a monthly exposure (sample s7). This may also indicate the gradual destruction of HAP agglomerates.

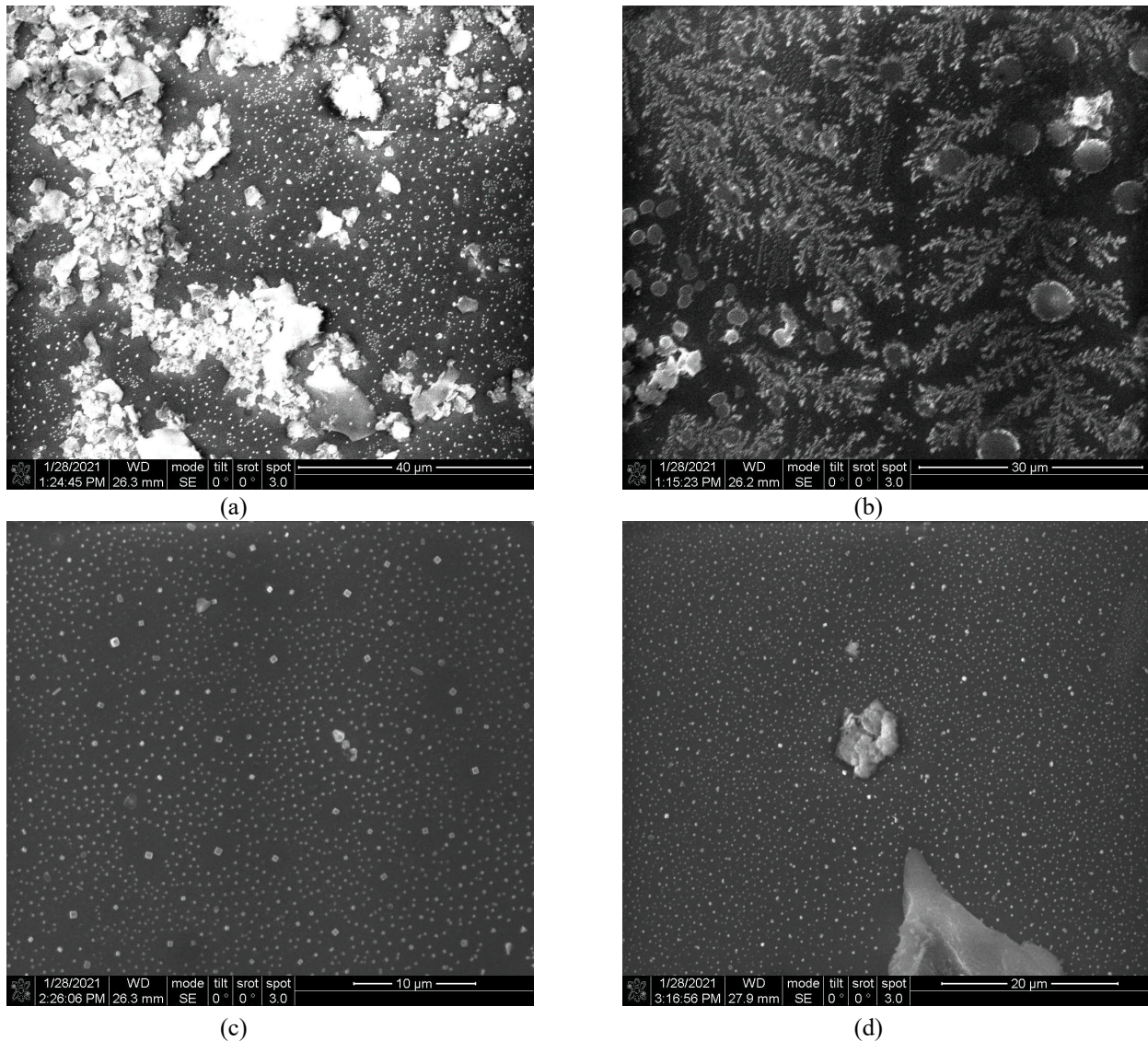


Fig. 4 SEM images of PC + HAP suspension sediments (a, b, c, f); (a, b) suspension sediment on the day of the preparation; c) after a week of exposure; d) after a month of exposure. Ruler size a) 40 μm , b) 30 μm , c) 10 μm , d) 20 μm .

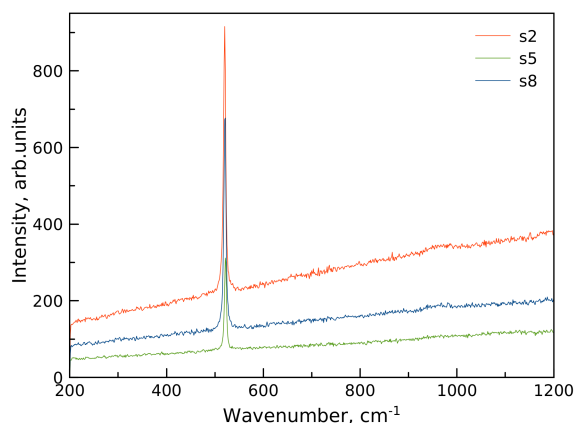
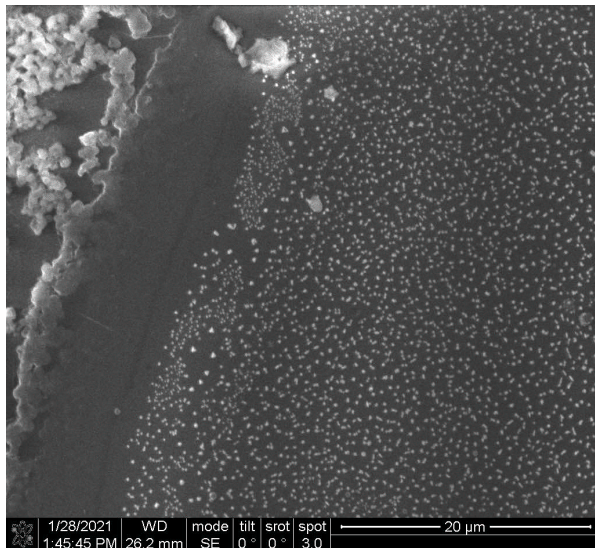


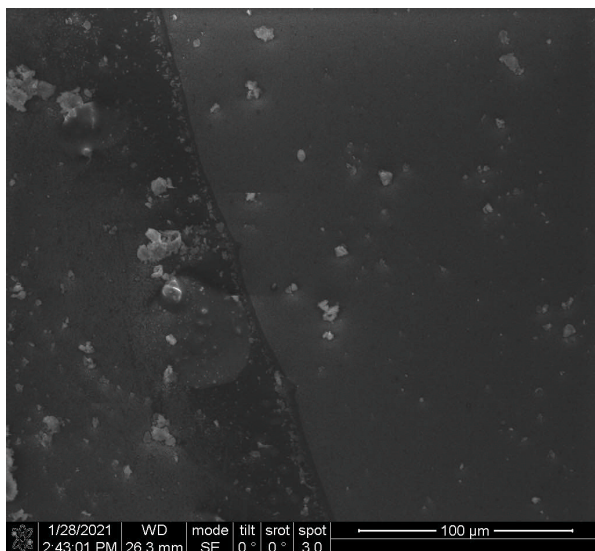
Fig. 5 Raman spectra of por-Si+ HAP suspension precipitation on the preparation day of (s2), after weekly (s5) and monthly exposure (s8).

Fig. 4 (a–d) shows the SEM images of the por-Si + HAP suspension precipitation on the preparation day (a, b), after a week (c) and a month (d) exposure. Here it is also possible to distinguish fractions of agglomerates of large, tens of micrometers, particles and clusters of uniformly distributed smaller ones with characteristic sizes of less than 1 μm . Among the small ones there are particles of regular square shape, which can be identified as silicon nanocrystals crystallizing in a cubic syngony (Fig. 4d). In addition, there is a phase of polycrystalline HAP in the form of characteristic “herringbone”. Its formation indicates that very small HAP particles are present in the suspension. When the sediment dries, they crystallize into needle-like nanocrystals, which are then “folded into a herringbone” into a supracrystalline structure in the hexagonal syngony characteristic of the $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ compound (for example, see Ref. [18]). These particles are released from nanoscale pores by grinding a porous layer saturated with HAP. A similar pattern is observed on the transverse

cleavage of a porous layer saturated with HAP from an aqueous solution after evaporation of the liquid from the pores. (Fig. 4b) [13]. Over the time, agglomerates of large particles gradually break down in the suspension (Fig. 4c, d). The number of small silicon particles also decreases, as evidenced by a noticeable decrease in the intensity of the peaks of the corresponding to silicon with a wave number of 520 cm^{-1} (Fig. 5).



(a)



(b)

Fig. 6 SEM images of por-Si suspension precipitation on the preparation day (a) and after a week (b) exposure. Ruler size a) 20 μm , b) 100 μm .

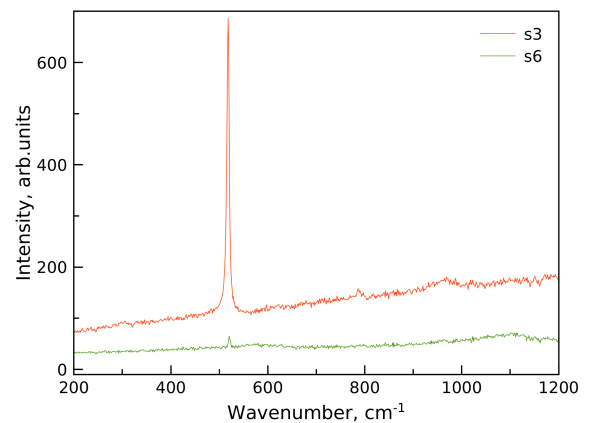


Fig. 7 Raman spectra of por-Si suspension precipitation on the preparation day (s3) and after a week of exposure (s6).

The same pattern of reduction in the number of silicon particles is demonstrated by samples of precipitation of pure por-Si suspensions both in the SEM images of Fig. 6 (a, b) and in the Raman spectra (Fig. 7), which is consistent with the data on the high solubility of porous silicon [16, 17].

4 Conclusion

The study shows that the powder of the por-Si + HAP nanocomposite is soluble in water, although to a lesser extent than the powder of the initial porous silicon without hydroxyapatite. This means that the particles of the por-Si + HAP nanocomposite can be used for HAP transport in biological fluids. Over the time, they dissolve in water, releasing nanoscale HAP particles in the pores. Therefore, we can conclude that porous silicon is a promising material for creating a biomaterial for bone implants and drugs for the treatment of osteoporosis on the basis thereof. The direction of further research should include determining the dissolution rate of the nanocomposite powder, its dependence on the size of nanoparticles in order to determine the optimal sizes of nanoparticles and the conditions for their manufacture.

Disclosures

All authors declare that there is no conflict of interests in this paper.

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