

## HYDROXYAPATITE NANOPOWDERS AND THEIR CHARACTERIZATION OWING TO ELECTRON WORK FUNCTION MEASUREMENTS

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**Abstract:** Nanoparticles of hydroxyapatite (HAP) are in use to prepare nanostructured ceramics for bioimplants. Their biocompatibility depends particularly on osteoblast adhesion on the material surface. The adhesion is the result of the competition of attractive and repulsive forces between the cell and the surface of bioimplant [1]. The repulsive force has typically an electrical origin. Therefore, an electrical charge of the bioimplant surface, particularly of the nanoparticles that are employed to fabricate the implant could have a great influence on adhesion of the cells.

The mechanical-chemical technology to reach hydroxyapatite nanoparticles is achieved. The sizes of the particles have an influence on their electron work function (actually, the surface charge). The particles sized to 20-40 nm are characterized with the lower energy that is necessary to escape the electron. This means that the smaller particles (20-40 nm) have a more positive surface charge in contrast with the larger particles sized to 100-1000 nm.

The larger particles have greater capability for conglomeration, that could influence morphology of HAP nanoparticles based implant.

The different values of the electron work function (surface charge) could affect adhesion of the cells by human organism on the HAP based bioimplants surface.

### Introduction

Nanoparticles of hydroxyapatite (HAP) are in use to prepare nanostructured ceramics for bioimplants. Their biocompatibility depends particularly on osteoblast adhesion on the material surface. The adhesion is the result of the competition of attractive and repulsive forces between the cell and a surface of bioimplant [1]. The repulsive force has typically an electrical origin [1]. Therefore, electrical charge of the bioimplant surface, particularly of the nanoparticles that are employed to fabricate the implant could have a great influence on adhesion of the cells.

Because HAP is a material that has an energy gap, the external mechanical pressure varies the latter and as the result density of charged surface states. On the other

hand the size of the nanoparticle because of its "capillarity" has a strong correlation on the pressure.

So, the surface charge of the HAP nanoparticle could correlate to its size.

In addition to the above, electrical communications between HAP nanoparticles depended on their charge could provide conglomeration, that affect fabrication quality of the implant and its surface morphology.

The surface charge delivers an electrical field that affects escaping of electrons from the surface. Because of this the charge could be estimated owing to measurement of the electron work function ( $\phi$ ).

Because of the above the present paper is directed to detect  $\phi$  of HAP nanoparticles to meet correlation with their sizes and conglomeration.

### Materials and Methods

The nanoparticles of HAP were fabricated due to mechanical-chemical technology. For this powders of  $\text{Ca}(\text{H}_2\text{PO}_4)_2$  – (class pure for analysis) and CaO (class – for spectral analysis) were mixed with water in a mortar during 10-30 minutes. Mechanical activation (4-10 minutes) of mixtures was provided in a planetary mill owing to rotation of a titanium drum (850 revolutions/minute) filled with titanium carbonitride balls. The obtained particles were selected by grids within fractions.

To verify the size of the particles, a transmission electron microscopy (TEM) was employed. The transmission electron microscope JAM-2010 (Japan), having voltage 200 kV and resolution 0.27 nm was in use.

To verify HAP origin of nanoparticles X-ray diffraction (DRON-3 equipment, Cu-cathode, radiation was filtered by the Ni-filter, tube voltage – 30 kV, anode current – 8 mA, speed of a counter/detector – 2 grad/min, vertical aperture height – 0.5 mm) was applied. The nanopowders had typical spectra of crystalline HAP.

Infra red spectroscopy was applied to test chemical content of nanoparticles. Measurements were done owing to spectrometer Specord -75 DR in a range 400...4000  $\text{cm}^{-1}$ . The specimens that were mixed with annealed KBr powder and pressed in tablets. Photoelectron spectroscopy (ultraviolet range) was

employed to estimate  $\phi$ . For this the nanopowders were mixed with ethanol to reach a cream-like emulsion. The latter was deposited on a glass wafer and dried during 1 hour at room temperature and atmosphere. After that the specimens were placed in an photoelectron emission spectrometer [3] for measurements at vacuum condition ( $10^{-4}$  Pa). The values of  $\phi$  were estimated with the uncertainty that did not exceed  $\pm 0.04$  eV.

The nanopowders were stored during 6 months at room conditions and after that the transmission electron microscope IEM – 1200 EX – IEOL, (120 keV) was employed to estimate the typical size of HAP conglomerates.

## Results

The typical TEM image of the obtained particles is presented at the Figure 1.

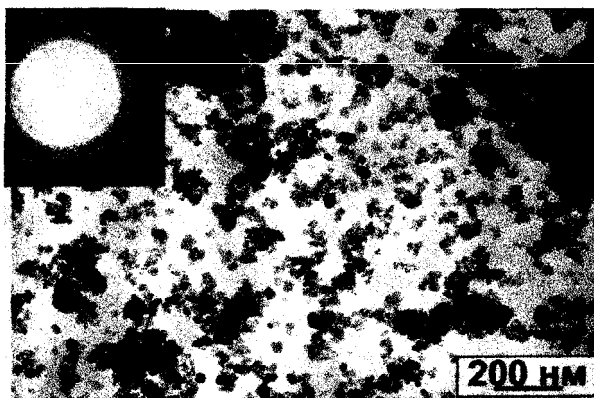


Fig. 1. Typical TEM image of the particles

The typical X-ray diffraction spectra of the particles are presented in Figure 2.

The typical infrared spectra of the particles are presented in Figure 3. The specimens demonstrated absorption in a vicinity of a P-O bond oscillations that were the same as for the apatite. There were absorption peculiarities at  $885\text{ cm}^{-1}$  and at  $1420 - 1460\text{ cm}^{-1}$ , that related to deformation and valence oscillations of C-O bonds, correspondingly. This meant that the particles consisted of both HAP and carbonates and had a content similar with a biological HAP having  $\sim 7.4\%$  of carbonates [2]. Carbonates were probably provided from an environment.

The typical scanning electron microscopy image of the conglomerate is presented in Figure 4.

The magnitudes of  $\phi$  were directly proportional to the typical sizes (X) of the nanoparticles (Figure. 5).

A derivation of the emission current (I) to a photon energy (hv) demonstrated a sharp maximum at 5.2 eV

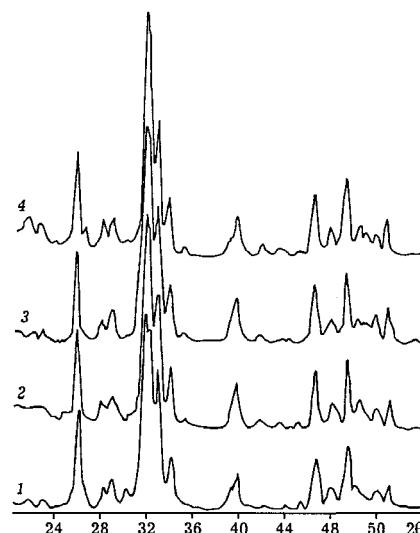


Fig. 2. Several typical X-ray diffraction spectra of the powders of nanoparticles.

for the powders sized to  $\approx 20 - 60\text{ nm}$ . However the particles belonged to the range of size  $\geq 100\text{ nm}$  indicated the maximum at 5.5 eV that had a scattered structure (Figure 6)

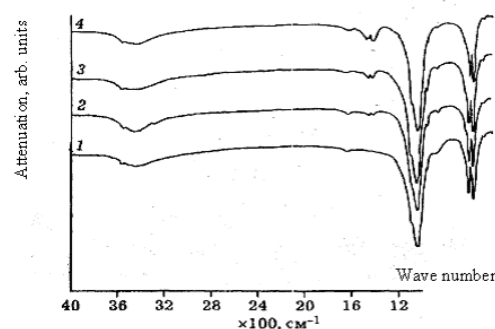


Fig. 3. Typical infrared spectra of the powders of nanoparticles

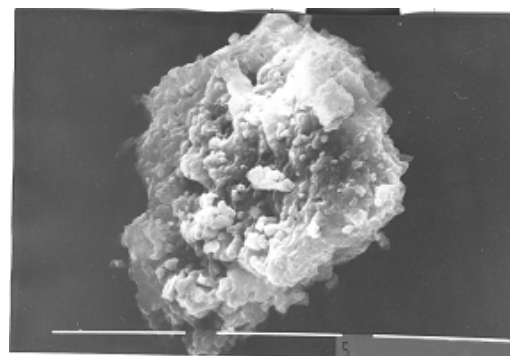


Fig. 4. Typical conglomerate (scale 1 mkm)

The typical size ( $X^*$ ) of the conglomerate positively correlated on  $\phi$ . (Figure. 7).

## Discussion

TEM images confirm that the employed technology to fabricate particles is capable to provide the nanoparticles sized to 10-1000 nm. (Figure 1).

The X-ray diffraction spectra demonstrated that the nanoparticles crystalline lattice corresponds to the HAP origin (Figure 2).

The infrared spectroscopy evidenced that the chemical content of the particles is also similar to the crystalline HAP (Figure 3).

Keeping the powders at the room conditions induces their conglomeration as could be watched from the scanning electron microscopy images (Figure 4).

Because  $\phi$  was directly proportional to  $X$  (Figure 5) the greater particles are characterized with higher energy to escape electrons. By this reason one could predict that the mechanical pressure that shapes he surface of the particle induces the negative electrical charge on the HAP nanoparticle surface.

Taking into account that  $dI/d(h\nu)$  demonstrates a sharp maximum at 5.2 eV for the powders sized to  $\approx 20-60$  nm and a scattered structure for the particles belonged to the range of size  $\geq 100$  nm (Figure 6), one could conclude that correlation of  $\phi$  on  $X$  was stipulated by the alteration of charge density of states depended on  $X$ .

Moreover the typical size ( $X^*$ ) of the conglomerate positively correlated on  $\phi$ . (Figure 7)

The sizes of the particles were spread stastically within the fractions, indeed. Therefore they had different electrical charge and due to electrical communication were gathered within conglomerates after storage.

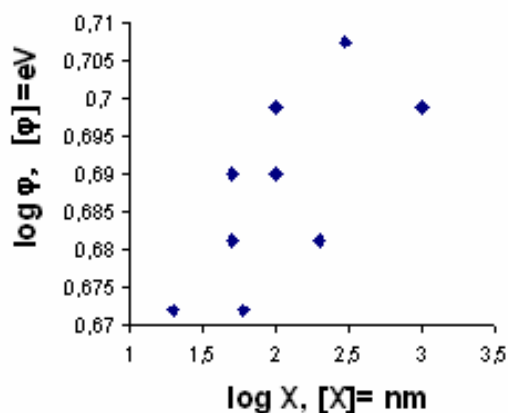


Fig. 5. Correlation of  $\phi$  on  $X$ .

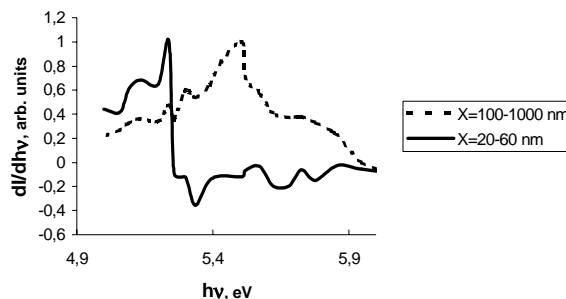


Fig. 6. Typical derivations  $dI/dhv$  for different ranges of  $X$ .

## Conclusions

The reached mechanical-chemical technology allows to fabricate the HAP nanoparticles.

Their sizes has the influence on their electron work function (actually, the surface charge). The smaller particles (20-40 nm) are characterized with the lower energy that is necessary to escape the electron. This means that the smaller particles (20-40 nm) have a more positive surface charge in contrast with the lager particles (100-1000 nm).

The lager particles have greater capability for conglomeration.

## Acknowledgement

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## References

- [1] Biomaterial science. Ratner B.D. (Ed.) et al. Academic Press. London 1996.
- [2] Chaikina M. V., Khlusov I. A., Karlov A. V., Paichadze K. S.. 'Mechanochemical synthesis of non-stoichiometric and substituted apatites with nanoparticles for using as biocompatible materials'. *Khimiya v interesakh ustojchivogo razvitiya* (in Russian) No. 12, 2004, pp. 389-399.
- [3] Akmene R.J., Balodis A.J., Dekhtyar Yu. D. Markelova G.N., Matvejevs J.V., Rozenfelds L.B., Sagalovijs G.L., Smirnovs J.S., Tolkačovs A.A., Upmiņš A.I. Exoelectron emission spectrometre complete set of surface local investigation. *Poverhnost. Physica, Himiya, Mehanika* (In Russian) N. 8, 1993.,pp. 125.-128.