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LETTERS
TO THE EDITOR

Hydroxyapatite Nanoparticles Modified by Peroxide Groups

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Recently hydroxyapatite nanoparticles draw attention in connection with unique possibilities of their medical and biologic use. Hydroxyapatite as an organism component is almost the only inorganic material, which is not rejected as a foreign matter. Simultaneously it serves as a regulator of the calcium and phosphorus content in an organism. It seems of importance to impart antiseptic properties to the material, e.g., by introducing peroxide groups in it.

To study the possibility of the substitution of peroxide groups for hydroxide groups in hydroxyapatite, we have synthesized several samples, which were dried at 150°C, i. e. under the conditions of the full removal and decomposition of free hydrogen peroxide. Sample no. 1 was obtained by the hydrothermal treatment of hydroxyapatite (preliminary synthesized under the hydrothermal conditions) with a hydrogen peroxide solution at a temperature exceeding H_2O_2 stability limit. The X-ray patterns of the sample corresponded to hydroxyapatite with specific surface area S_{sp} 20 m^2/g. According to transmission electron microscopy (TEM), the sample consisted of needle-like particles of 30–100 nm in thickness.

Sample no. 2 was prepared in air by direct mixing calcium hydroxide (stoichiometric excess of 10%), orthophosphoric acid, and a hydrogen peroxide solution. Its phase composition corresponded to hydroxyapatite (S_{sp} 75 m^2/g). According to TEM, the main morphological elements of sample no. 2 are roundish slightly extended particles about 17 nm in thickness. Sample no. 3 synthesized without a $Ca(OH)_2$ excess also corresponded to hydroxyapatite. According to TEM, its main morphological elements are of the same size as those of sample no. 2. Specific surface area of sample no. 3 is 77 m^2/g.

Based on hydroxyapatite structural features, let us suppose that only one hydroxide group in the $Ca_{10}(PO_4)_6(OH)_2$ unit cell is capable to be replaced by a peroxide group. Then, according to the chemical analysis, 2% of unit cells in the first sample contain peroxide groups, 13%, in the second, and 26%, in the third.

Using the simplest model of a disperse substance in the form of a thin layer 1 g of which has a surface area equal to a substance specific surface area, we have estimated a share of surface crystallographic cells. We accepted in this calculation that the hexagonal *c* axis of a cell is parallel to the surface. In this case S_{sp}, layer thickness *d,* and density ρ of 3.08 g/cm^3 are related to each other as $S_{sp}d = 1/\rho$. Thus $d = na3^{1/2}$, where *a* 0.941 nm is the unit cell parameter, $a3^{1/2}$, its minimal thickness, and *n*, the number of cells, one of which is external. As a result we find that 10% of unit cells are external in the first sample, 38% in the second, and 39% in the third. These values agree well with the chemical analysis results.

To synthesize hydroxyapatite samples, we used analytically-pure grade $Ca(OH)_2$, 84.8% H_3PO_4, and 32.7% H_2O_2. Sample no. 1 was obtained by processing a mixture of 7.8084 g of $Ca(OH)_2$, 4 mL of H_3PO_4, and 74 mL of H_2O in an autoclave. The mixture was placed in a teflon test tube with a cover, which was placed in an autoclave (*V 0.5* L, made of stainless steel), heated at a mean rate of 100–150 deg/h to 240°C and exposed further at this temperature for 1 h at a pressure of 2.8 MPa. A reaction product was taken from the

autoclave, separated from the solution by centrifugation, and dried at 150°C for 1.5 h. To 9.98 g of the resulting substance 78 mL of a hydrogen peroxide solution were added, and the hydrothermal treatment at 240°C, centrifugation, washing by water, and drying at 150°C were repeated.

Sample no. 2 was prepared by express synthesis at room temperature under the conditions of fast mixing the same amounts of $Ca(OH)_2$ and H_3PO_4 with 74 mL of H_2O_2 solution followed by isolation, washing, and drying at 150°C.

Sample no. 3 was obtained similarly, but the initial amount of calcium hydroxide (7.1398 g) corresponded to the stoichiometric ratio of the reagents.

The X-ray phase analysis was fulfilled on a DRON 3 diffractometer with monochromatized FeK_α radiation. The X-ray patterns were solved using the ASTM card file.

Electronic microphotographs were taken on a Jeol JEM-107 electronic microscope. Samples were prepared by applying a drop of aqueous suspension on cells of a copper grid covered with a collodion film.

Specific surface areas were measured by the argon thermodesorption method with chromatographic recording. The training temperature was 110°C. Training was carried out in a vacuum. The error of the method was 4%.

Quantitative determination of peroxide groups was carried out by the volumetric titration with a 0.1 N solution of potassium permanganate.

The foregoing data suggest that hydroxyapatite is capable to be modified by peroxide groups both when treated by an H_2O_2 aqueous solution and when synthesized in an H_2O_2 medium. The possibility of obtaining at 240°C a sample containing 2 mol % of peroxide groups points to the sufficient stability of the substitution product. The maximal replacement of hydroxide groups is reached at the direct synthesis in the hydrogen peroxide medium, the quantity of entered peroxide groups appears comparable with the number of structural hydroxide groups in the surface layer.