BIPHASIC CALCIUM PHOSPHATE BIOCERAMICS DOPED WITH NANOMETALS

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Introduction

Over many years of research, a number of types of materials have been developed and used for various medical purposes, including bone replacement. Calcium phosphate bioceramics (CPs) occupies an important place among them. Its advantages are mainly porosity and high biocompatibility. Because of the similarity in chemical composition of natural apatites in bones, hydroxyapatite and other CPs not irritate the surrounding tissue, does not cause acute or chronic inflammation and stimulate bone repair processes, that enables the creation of chemical bonds at the implant-bone interface. Additionally, CPs biomaterials have exceptional sorption properties and can also intake a variety of isomorphic substitutions in both anionic and cationic subnet, without destroying the basic unit cell. Owing to the above features, it is possible to create new materials for specific applications.

Biphasic calcium phosphate bioceramics (BCP) are commonly used in medicine. Their structure is a combination of stable hydroxyapatite and restorable tricalcium ortho-phosphates. Phases can be mixed in different ratios depending on product's purpose. There is a possibility to make modifications of these materials using ions and nanoparticles. The doping of BCPs with antimicrobial substances may be beneficial in maintaining sterility both at the time of foreign body adaptation and in the postoperative wound healing process [1, 2]

Materials and Methods

One of the main aims of this work was obtaining hydroxyapatite, tricalcium ortho-phosphate and biphasic calcium phosphate bioceramics through applying the wet method. Two sets of reagents were used: $Ca(OH)_2$ and H_3PO_4 or $Ca(NO_3)_2$ and $(NH_4)_2HPO_4$. Physicochemical analysis of prepared materials included determination of molar ratio Ca/P, FT-IR spectroscopy and X-ray diffraction (XRD). The analysis of selected structure parameters such as porosity, pore's volume, weight loss, shrinkage and density were also conducted. Silver nanoparticles (AgNPs) were prepared by chemical reduction of $AgNO_3$ by varied reducing and stabilizing substances. The presence and average particles size of AgNPs were monitored by UV-Vis spectrometry and Dynamic Light Scattering method (DLS). Then, pure BCPs were modified by the "*in situ*" method with silver nanoparticles. Subsequently, preliminary bioactivity tests were performed on all obtained materials in fluids simulating a living organism.

Results and Discussion

As a result of the carried out syntheses, hydroxyapatite (HAp) was obtained with Ca/P molar ratio equal to 1.75. It means that it is a material with excess of calcium. In the case of calcium orthophosphate(V) (TCP), the ratio is 1.71, which is much higher than expected. However, XRD analysis confirmed that only the TCP phase is present in the sample. The occurrence of a higher Ca/P molar ratio may be related to the possibility that some of the phosphate(V) ions were substituted by other ions, such as carbonate CO_3^{2-}, which contributed to the increase of the ratio. In the case of biphasic bioceramics (BCP), the Ca/P molar ratio was determined to be 1.53 and is within the expected range. It is worth noting that the Ca/P molar ratio of bone is reported as 1.70, dentin as 1.62, and enamel as 1.64. This is associated with multiple ion inclusions in these structures [1].

The mass loss in the samples after calcination is at a similar level for HAp and BCP (2.95% and 3.33%, respectively), and is significantly lower in the TCP sample (1.53%).

The synthesis of silver nanoparticles resulted in monodisperse nanoparticles with average size up to 100 nm and narrow size distribution. The location of the absorption maximum of the nanoparticles did not change significantly after about several weeks from the date of preparation of the colloids, indicating the high stability of the nanoparticles over time.

FIG. 1. Test molds of pure BCP before modification with nanometals.

Incubation of nanosilver doped materials under conditions simulating a living organism showed no change in pH and conductivity during the 21-day incubation time. It indicates the stability of the materials and no negative effect on bioactivity.

Conclusions

It can be concluded that development of methods for the preparation of bioactive, metal-modified biphasic calcium phosphate bioceramics can be an important step towards creating a new generation of bioactive materials for applications in biomedicine:

1. The use of different ratios of TCP:HAp allowed us to determine the best ratio for pure and nanosilver doped BCP materials.
2. The Ca/P molar ratio of the obtained BCPs indicates that non-stoichiometric products were obtained.
3. The density and porosity of the investigated materials are within the range desired for implant materials and therefore they can be design as for substitutes for hard tissues.
4. Immersion in simulated fluids does not adversely affect the properties of the tested calcium phosphates, the lack of changes in pH and conductivity during incubation in conditions stimulating a living organism allows their potential use in a living organism.

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References

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