SYNTHESIS OF NANOAPATITE CRYSTALS

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Abstract Synthesis of nanocrystalline hydroxyapatite (HAp) by coprecipitation is presented. It is shown that the addition of PolyAcrylicAcid (PAA) acts as a crystal-growth inhibitor. In this way, needle-like nanoapatite crystals with a length of less than 100 nm are obtained. The obtained nanoparticles do not agglomerate in solution, which is believed to be due to the bonding of PAA to the surface of the apatite nanocrystals. The nanoparticles are stable into solution and they can be tailored for different applications such as coatings, composites, densified apatite and cements by controlling the size and the reactivity of the particles.

Introduction Hydroxyapatite (HAp) polycrystalline ceramic is used for orthopaedic and dental implants because it closely resembles native tooth and bone crystal structure. HAp ceramic is featured by its brittleness (fracture toughness: $\sim 0.6\text{--}1.5$ MPa m^{1/2}) [1]. Therefore, in spite of its bio-activity with human bone tissue, its use is limited. Recently, attention has been focused on nanocrystalline or nanocomposite materials, which demonstrated improvement of mechanical properties and/or machinability and superplasticity [2].

In this paper we show our results of nanocrystalline HAp obtained by coprecipitation. It is a common low-cost method in powder synthesis and finds widespread use because of its simplicity and easily controllable processing, in terms of both the preparative reactions and the characteristic of the reaction product.

Experimental The procedure for preparation of nanoapatite crystals has been described previously [3, 4]. Starting materials are Ca(NO₃)₂ 4H₂O, (NH₄)₂HPO₄, NH₄OH (all from Merck). A series of experiments were conducted to determine the optimal pH, ageing temperature and addition rate. Synthesis was performed under N₂

atmosphere to avoid CO₂ contamination, which can result in a (partially) carbonated hydroxyapatite.

HAp was prepared according to the following reaction:

The pH and temperature were registered continuously. The former was kept constant by computer-controlled NH₄OH addition. Using a second pump the reactant was added droplet-wise. A mechanical mixer was used during experiments. Nanoparticle syntheses were performed using three different amounts of PolyAcrylicAcid (PAA) addition: 0, 5 and 11.5 wt % PAA compared to HAp.

The samples were characterised using X-ray diffraction (Philips Xpert), infra red (IR) spectroscopy (in KBr tablets, Perkin Elmer), scanning electron microscopy (SEM – Jeol JSM 840) and transmission electron microscopy (TEM – Jeol 2000 FX). The particle size distribution was measured as a function of time using dynamic light scattering (DLS – Malvern 4700).

Results and discussion

The concentration of reactants, the pH, the addition rate of phosphate, temperature had to be optimised for the nanocrystal synthesis. It was found that at room temperature using a pH of 10.5 and low addition rates it is possible to obtain a solution containing nanoparticles. The solution was not stable; the particles started to agglomerate strongly and the crystals grew further (Ostwald Ripening). Already during DLS measurement, agglomeration was noticed and large particles could be observed. After some days, SEM micrographs show large needle-like and plate-like crystals on tens of micrometer in size.

Therefore, it was decided to use a suitable additive to prevent growth. From several options PAA chosen and added to a calcium-nitrate solution in an amount of 5 wt % compared to HAp. Other parameters were kept constant. The nanoparticles were filtered and dried at 120°C. X-ray diffraction of the particles only shows lines that can be attributed to hydroxyapatite (JCPDS – 09-0432)(Fig. 1).

FIGURE 1. X-ray diffraction pattern of the solution synthesised in presence of 5 wt% PAA and dried at 120 °C.

a)

b)

c)

FIGURE 2 TEM micrographs of nanoapatite particles synthesised in presence of 5 wt% of PAA at different magnifications: a) 20000; b) 50000; c) 150000.

FIGURE 3. IR spectrum of apatite nanoparticles synthesis with 5 wt% PAA after drying at 120 °C.

TEM showed needle-like apatite crystals with a length of about 20 nm and a width of about 1–2 nm. Even at a high magnification (150000X) the apatite nanoparticles do not show sharp edges, suggesting that the apatite nanoparticles are covered by PAA. The IR spectrum of the dried powder showed bands at 1418 cm^{-1} , 1455 cm^{-1} , 1566 cm^{-1} , 1638 cm^{-1} and 2930 cm^{-1} , which indicated the presence of PAA, Fig. 3. The DLS measurement showed an average particle size of 80 nm. When we stirred the diluted solution or put it in an ultrasonic bath the solution had a vague bluish colour. From this we conclude that some agglomeration of the needle-like particles occurs which easily break-up by ultrasonic bath treatment or mechanical mixing.

A higher amount of PAA (11.5 wt%) was used for a third experiment. In this case spherical nanoparticles of about 5 nm were obtained, which were strongly agglomerated.

References

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