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Fabrication of hydroxycarbonate apatite coatings with hierarchically porous structures

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Abstract

Hierarchically porous hydroxycarbonate apatite is known to have a high bioactivity to regenerate bone, but its application in bone graft substitutes has been restricted due to its poor mechanical properties. This drawback has been addressed by (i) depositing calcium carbonate coatings on Ti6Al4V substrates by electrophoresis; and (ii) converting the coatings to hydroxycarbonate apatite coatings with hierarchically porous structures by treatment with a phosphate buffer solution (PBS). After soaking calcium carbonate coatings in PBS for 1 day, calcium-deficient hydroxycarbonate apatite nanocrystals are deposited on the surfaces of calcium carbonate particles via a dissolution–precipitation reaction. The aggregation of the nanocrystals produces plate-like hydroxycarbonate apatite. Mesopores with a pore size of ~3.8 nm and macropores or apertures with an aperture size of ~1 μm are formed within and among the plates, respectively. After soaking for 9 days, the pore size of mesopores decreases and the mesopores disappear partly due to the crystal growth of hydroxycarbonate apatite. Simulated body fluid immersion tests reveal that the good in vitro bioactivity of hydroxycarbonate apatite coatings is attributed to the calcium deficiencies in apatite lattice and the hierarchically porous structures.

Keywords: Apatite coating; Porous structure; Calcium carbonate; In vitro bioactivity

1. Introduction

Hydroxycarbonate apatite is a major component of the hard tissues of animals, and the corresponding synthetic material has been used as an artificial bone graft substitute due to its being biocompatible, bioactive, osteoconductive, nontoxic, noninflammatory and nonimmunogenic [1,2]. However, hydroxycarbonate apatite bulk has poor mechanical properties, including lower fracture toughness and higher elastic moduli in comparison with human bone [3], so its clinical applications have been limited. This drawback can be overcome by depositing hydroxycarbonate apatite on the titanium alloys, which exhibit excellent mechanical properties under load-bearing conditions [3,4]. This method combines the mechanical advantages of titanium alloys with the excellent bioactivity of hydroxycarbonate apatite.

The bone-forming bioactivity of biomaterials is associated not only with their chemical composition and crystallinity, but also with their textural properties, such as pore size, pore volume and pore structure [5,6]. The appropriate porosity allows the ingrowth of bone tissue to achieve full integration with the living bones [7]. The ideal porous structures of biomaterials must be composed of (i) mesopores or micropores, to promote cell adhesion, adsorption of biologic metabolites and resorbability at a controlled rate to match that of tissue repair; and (ii) macropores, to enable tissue ingrowth and nutrient delivery to the center of the regenerated tissue [8–10]. In addition, a wide pore size distribution can create favorable local conditions that lead to the nucleation and growth of carbonate apatite [11]. Although the template or surfactant synthesis is an available means of preparing porous bioactive materials,

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such as hydroxyapatite [12,13] and bioactive glass [5,14], this method has two main disadvantages: (i) calcinations to remove the templates or surfactants will impair partly the porous structure and decrease the surface area; and (ii) the remaining templates or surfactants will contaminate the final samples and reduce their bioactivity.

Here we report a new and simple synthesis strategy to fabricate hydroxycarbonate apatite coatings with hierarchically porous structures that consists of a two-stage application route: the deposition of calcium carbonate particles on Ti6Al4V substrates by electrophoresis and the conversion of calcium carbonate coatings (CCCs) to hydroxycarbonate apatite coatings (HCACs) by treatment with a phosphate buffer solution (PBS). This method of preparing HCACs has three innovations: (i) no structure-directing agents will contaminate the final products and deteriorate the bioactivity; (ii) HCACs with a poor crystalline structure are chemically more similar to the biological apatite, and the surface area is larger than that of conventional hydroxyapatite coatings; and (iii) HCACs exhibit a good in vitro bone-forming bioactivity.

2. Experimental

A 4.24 g quantity of sodium carbonate (Na_2CO_3) and 5.33 g of calcium chloride ($CaCl_2$) were each dissolved in 200 ml of deionized water. With magnetic stirring, the Na_2CO_3 solution was added dropwise to the $CaCl_2$ solution, yielding a milky suspension, which was then stirred for 1.5 h at room temperature. The products (calcium carbonate) were filtered off, washed with deionized water and dried in an oven at 60 °C for 48 h.

To deposit calcium carbonate coatings on the substrates, an electrophoretic cell using a titanium alloy (Ti6Al4V) as the cathode and a graphite plate as the anode was mounted, with the two electrodes about 10 mm apart. Before deposition, the substrates were abraded with 1000-grit SiC paper followed by treatment with a 1.0 mol l^{-1} H_3PO_4–1.5 wt.% HF solution for 20 min [15]. A calcium carbonate suspension with 1.25 g of solid powders in 250 ml of ethanol was prepared, and then dispersed ultrasonically for 30 min. The electrophoretic process was carried out at 90 V for 1 min by using 0.5 ml volumes of a 1.0 mol l^{-1} HCl solution as the additive [15].

After electrophoretic deposition, the CCCs were immersed into a beaker with PBS ($NaH_2PO_4 + Na_2HPO_4$), pH 7.4, and kept at 37 °C for 1–12 days. To maintain the pH value at 7.4, the PBS was replaced every day. The HCACs obtained from the CCCs were washed with deionized water, and dried in a convection oven at 37 °C for 48 h. The HCACs converted from CCCs by treatment with PBS for 1 and 9 days are termed HCAC01 and HCAC09, respectively. In order to obtain large enough amounts of hydroxycarbonate apatite to measure the porous structures by using N_2 adsorption–desorption isotherms, the calcium carbonate particles were immersed in PBS for 1 and 9 days respectively without depositing on the substrates.

A simulated body fluid (SBF) with ion concentrations approximately equal to those of human blood plasma has been used widely for in vitro assessment of the bioactivity of bioceramics and biocoatings [16]. Each HCACs was soaked in 25 ml of SBF, and kept at 37 °C. The SBF was prepared by dissolving reagent grade chemicals of NaCl, $NaHCO_3$, KCl, $K_2HPO_4 \cdot 3H_2O$, $MgCl_2 \cdot 6H_2O$, $CaCl_2$, Na_2SO_4 and $(CH_2OH)_3CNH_2$ into deionized water, and buffering it at pH 7.40 with hydrochloric acid. After given periods of time, the specimens were removed from the SBF, washed with deionized water and dried at room temperature.

Morphological observations of specimens were performed by transmission electron microscopy (TEM; CM200/FEG, Philips) and scanning electron microscopy (SEM; S-4800, Hitachi). The crystalline phases of the coatings were examined with X-ray diffraction (XRD; D/max-II B, Japan) using Cu K_α radiation. Fourier transform infrared spectra (FTIR; VECTOR22, BRUKER) were collected at room temperature using the KBr pellet technique. N_2 adsorption–desorption isotherms were measured with an automatic surface area and porosity analyzer (AUTOSORB-1-C, Quantachrome) at 77 K. The pore size distributions were derived from the desorption branches of the isotherms using the Barrett–Joyner–Halanda (BJH) method. At least four adsorption points in the relative pressure range $0.05 < P/P_0 < 0.30$ (where P_0 is the saturated vapour pressure) were used in the calculation of the BET surface area. The concentrations of phosphorus and calcium in SBF were determined using inductively coupled plasma optical emission spectroscopy (ICP-OES, Optima 5300DV, Perkin–Elmer). The thermal behavior of samples was examined by thermogravimetry (TG, STA449C, NETSCH) with a heating rate of 10 °C min^{-1}. The conversion percentages of calcium carbonate to hydroxycarbonate apatite can be calculated by the following formula:

$$X_{HA} = 1 - X_{HO} - \frac{M_{Ca} \cdot X_C}{M_C} \quad (1)$$

where X_{HA} is the percentage composition of hydroxycarbonate apatite, and M_{Ca} and, M_C are the molecular weight of $CaCO_3$ and CO_2, X_{HO} is the mass loss at 35–600 °C due to the elimination of H_2O and other absorbed species [17], and X_C is the mass loss at 600–800 °C due to the decomposition of calcium carbonate (Fig. 5).

3. Results and discussion

3.1. Structure of hydroxycarbonate apatite coatings

Fig. 1 shows the XRD pattern and FTIR spectrum of calcium carbonate particles prepared by chemical coprecipitation. The characteristic peaks of calcite (JCPDS card no. 86-0174) and vaterite (JCPDS card no. 72-0506) are shown in Fig. 1a. FTIR spectrum is also used to determine the phases of the calcium carbonate particles. The characteristic bands of vaterite are at 877, 744 cm^{-1}, while those of

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