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Synthesis and characterization of nanobelt-shaped Na, F and carbonate multi-substituted hydroxyapatite

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ABSTRACT

Na, F and carbonate multi-substituted hydroxyapatite (NFCH) with nanobelt shape has been synthesized using a combined method of ultrasound-assisted electrochemical deposition and ion exchange. The morphology, microstructure and in-vitro bioactivity of the NFCH are analyzed. The results show that the nanobelt-shaped NFCH are 5–40 nm in thickness, 250–700 nm in width and tens of micrometers in length. The nanobelt-shaped NFCH is oriented randomly and interlocked with each other on carbon/carbon composite substrates. The nanobelt-shaped NFCH could induce the precipitation of apatite layers with Ca/P molar ratios of 1.34–1.51 on its surface in simulated body fluid, exhibiting excellent in-vitro biocompatibility. The nanobelt-shaped NFCH should have potential application as reinforcement phase for bioactive coatings or as scaffold for tissue engineering.

1. Introduction

Hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) is routinely used in the structural repair of bone defects owing to the fact that it is the basic component of the natural bone and possesses osteo-conductive properties [1]. Compared with micro-sized hydroxyapatite, nano-sized hydroxyapatite exhibits several advantages due to both the nanometer scale topography and the inherent calcium phosphate chemistry. The nano-sized hydroxyapatite could significantly enhance osteogenic gene expression and promote osteoclastic activities, leading to the improvement of bone remodeling [2]. The shape of nano-sized hydroxyapatite significantly affects its physical, chemical and biological properties [3]. Several kinds of shapes for nano-sized hydroxyapatite have been synthesized, such as needle shape [4], plate shape [5], spherical shape [6] and rod shape [7]. To our best knowledge, the synthesis of nanobelt-shaped hydroxyapatite has not been reported. In this work, we reported a nanobelt-shaped hydroxyapatite synthesized by a combined method of ultrasound-assisted electrochemical deposition (UED) and ion exchange (IE). In addition, to further improve the phase stability, solubility and bioactivity of hydroxyapatite, the stoichiometric hydroxyapatite was substituted with Na ion, F ion and carbonate ion, forming Na, F and carbonate multi-substituted hydroxyapatite (NFCH). The NFCH closely resembled the inorganic phase of human bone whose structure was calcium phosphate apatite substituted with a wide range of ions [8]. The morphology, microstructure and in-vitro bioactivity of the nanobelt-shaped NFCH were investigated.

2. Experimental

Carbon/carbon composites (CC) with a density of 1.78 g/cm^3 were chosen as substrates for preparing nanobelt-shaped NFCH. The CC substrates were put into UED equipment and served as cathode. The graphite plate acted as anode. The electrolyte was composed of 0.5 mmol/L of $NH_4H_2PO_4$, 0.85 mmol/L of $Ca(NO_3)_2 \cdot 4H_2O$ and 0.85 mmol/L of $NaNO_3$. The deposition was carried out using the following conditions: current of 20 mA, temperature of 333 ± 1 K, ultrasound frequency of 45 kHz, ultrasound power of 100 W and deposition time of 15 min. After the UED process, the samples were put into 0.1 mol/L of NaOH solution for 24 h at 333 K and then immersed into 0.1 mol/L of NaF solution for 48 h at 323 K. Then the samples were taken out of the solutions, rinsed with deionized water and dried. The products on the CC substrates were characterized by scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), X-ray diffraction (XRD), Raman spectroscopy (Raman), Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS). Simulated body fluid (SBF) immersion test was used to investigate the in-vitro biocompatibility. The detailed information of the SBF test could be found elsewhere [9].

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3. Results and discussion

The SEM micrographs of the products on the CC substrates are shown in Fig. 1. Large quantities of belts are observed. The belts are randomly oriented and are interlocked with each other. The belts are 5–40 nm in thickness, 250–700 nm in width and tens of micrometers in length. Some positions of the belts exhibit a semi-transparent structure due to the extremely thin thickness, as denoted by the arrow in Fig. 1b.

XRD and Raman are used to analyze the products on the CC substrates. For the XRD pattern (Fig. 2a), all of the strong peaks can be indexed to hydroxyapatite. No peaks from other phases could be detected, indicating the high purity of the products. By Raman analysis (Fig. 2b), four characteristic Raman peaks for PO_4^{3-} groups in hydroxyapatite are viewed, including ν_1 PO_4^{3-} mode at 964 cm^{-1}, ν_2 PO_4^{3-} mode at 433 cm^{-1}, ν_3 PO_4^{3-} mode at 1049 cm^{-1} and ν_4 PO_4^{3-} mode at 589 cm^{-1}. In addition, the Raman spectrum also shows the presence of carbon peaks generating from the CC substrates, including *D* peak (in-plane disorder) at 1359 cm^{-1}, *G* band (in-plane lattice vibration) at 1585 cm^{-1} and 2D peak (three dimensional order) at 2705 cm^{-1}.

The chemical compositions and functional groups of the products on the CC substrates were analyzed by EDS, XPS and FTIR (Fig. 3). EDS spectrum not only reveals the presence of elements that constitute the hydroxyapatite structure (O, Ca, P) but also exhibits F and Na elements with clear peaks. XPS survey scan shows same elements to EDS results (Fig. 3b). The atom percentages of the Ca, P, Na and F elements are 15.16%, 10.31%, 1.88% and 4.33%, respectively. The high resolution XPS spectra of Ca 2p, P 2p, Na 1s and F 1*s* are shown in Fig. 3 c, d, e and f, respectively. The spectrum for Ca 2p is doublet with a primary peak at 347.2 eV and a secondary peak at 350.9 eV whereas the spectrum for P 2p exhibits a single peak at 133.2 eV. The binding energy values for Ca and P are characteristic of the element in the normal oxidation states (Ca^{2+} and P^{5+}). The Na 1s peak is located at 1071.9 eV, which is in agreement with the position of Na-substituted hydroxyapatite reported by other researchers [9]. The F 1s peak is positioned at the fingerprint for fluorine in F-substituted hydroxyapatite (684.5 eV). By FTIR analysis (Fig. 3g), characteristic bands for hydroxyapatite owing to PO_4^{3-} functional group are detected, including ν_4 $PO_4^{3-\,-}$ vibration at double bands of 569 cm^{-1} and 608 cm^{-1} as well as ν_3 PO_4^{3-} vibration at 1039 cm^{-1}. The presence of OH^- functional group for the hydroxyapatite could be confirmed from the stretching vibration at 3434 cm^{-1} and 2926 cm^{-1}. The information relating to the CO_3^{2-} incorporation in the hydroxyapatite structure could be viewed at

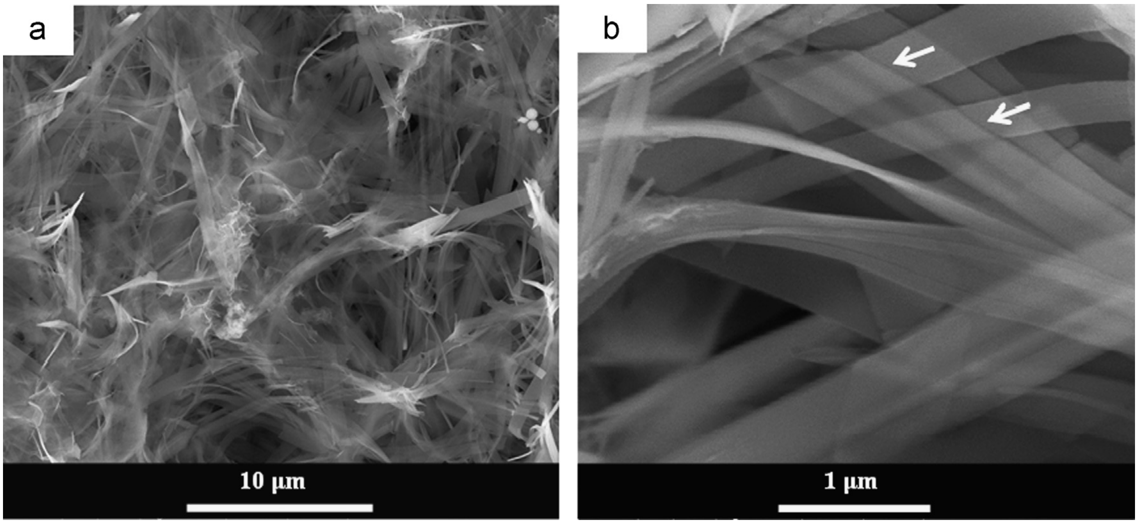

Fig. 1. SEM micrographs of the products on the CC substrates, (a) low magnification and (b) high magnification.

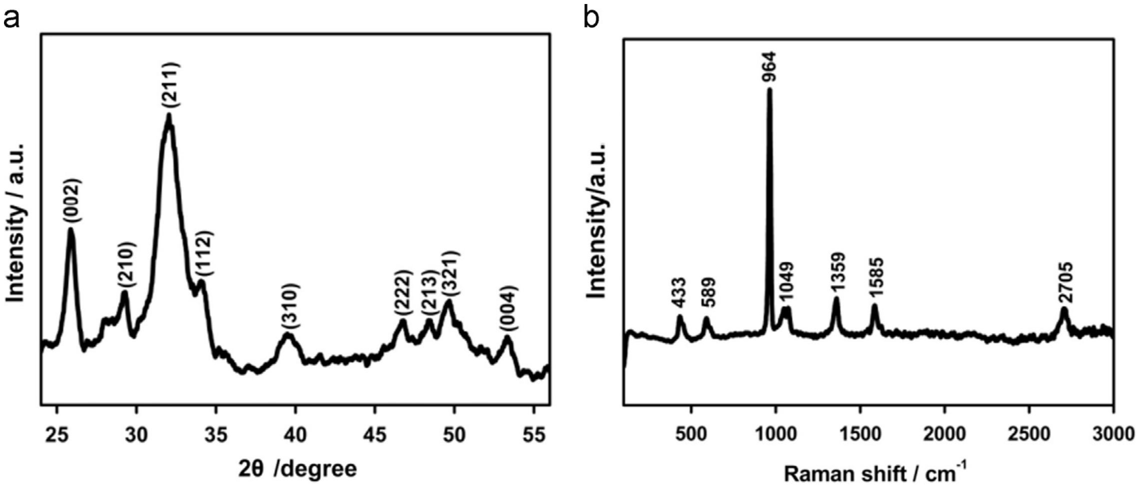

Fig. 2. XRD pattern and Raman spectrum of the products on the CC substrates, (a) XRD pattern and (b) Raman spectrum.