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Electrodeposition of carbonate-containing hydroxyapatite on carbon nanotubes/carbon fibers hybrid materials for tissue engineering application

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Abstract

Carbon nanotubes/carbon fibers hybrid materials (CCF) were used as templates to deposit carbonate-containing hydroxyapatite (CHA) by ultrasound-assisted electrodeposition method. The morphology and microstructure of CCF and CHA on CCF were characterized by X-ray diffraction, scanning electron microscopy, Transmission electron microscopy, Energy dispersive X-ray spectroscopy, Raman spectroscopy, Fourier transform infrared spectroscopy, X-ray photoelectron spectroscopy and Thermogravimetric analysis. The results showed that the CCF was composed of carbon fibers and in situ grown carbon nanotubes. The carbon nanotubes were grown along the radial direction of the carbon fibers with a straight morphology and exhibited a loose structure. The CHA enwrapped the in situ grown carbon nanotubes of CCF, then infiltrated into the loose structures of the carbon nanotubes and finally covered the CCF entirely with a particle shape. By thermogravimetric analysis, the CHA on CCF displayed more deposition weight than that on carbon fibers without carbon nanotubes.

Keywords: Carbon fiber; Carbon nanotubes; Electrodeposition; Hydroxyapatite

1. Introduction

Due to the donor shortage for autografts, potential risk of disease transmission in allografts and immunological responses, artificial bone scaffolds have become indispensable supplemental materials for bone implantation [1]. Therefore, much attention has been devoted to artificial biomaterials which could mimic the structure and properties of natural bone.

Hydroxyapatite is an important inorganic material for application in bone implants, which has excellent biocompatibility and similar composition to human bone tissue [2–4]. Hydroxyapatite has the ability to bond directly to bone tissue without an intervening fibrous layer [5]. However, the intrinsic brittleness and poor mechanical property of hydroxyapatite restrict its clinical application. To overcome this problem, many attempts have been made to combine hydroxyapatite with biocompatible fibers, which could mimic the collagen fiber/hydroxyapatite composite structure of natural bone. Several fibers such as silk fiber [6], cellulose fiber [7], self-assembled peptide nanofiber [8] and carbon fiber(CF) [9] have been used to combine with the hydroxyapatite to form fiber/hydroxyapatite composites. Among these fibers, CF are considered as excellent materials for combining with hydroxyapatite due to strong mechanical properties and biocompatibility [10]. Many researchers have confirmed that the bone could grow on the exposed CF without any inflammation [11–13]. For the research on CF/hydroxyapatite materials, Dorner-Reisel et al. prepared CF/hydroxyapatite composites using hot pressing method. They found that the reinforcement of hydroxyapatite with CF enhanced the resistance against microabrasion [11]. Slosarczyk et al. found that the properties of CF/hydroxyapatite composites depended significantly on the type of functional groups existing on CF surface [12]. Wu et al. synthesized nanosized CF/hydroxyapatite composites in simulated body fluid. They found that the composites had high mechanical strength [9]. Wan et al. used the surface modified CF as the templates for the growth of hydroxyapatite. They found that surface treatment of CF in nitric acid promoted the mineralization and changed the morphology of hydroxyapatite formed on CF [13]. Beside CF materials, carbon nanotubes have

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emerged as very promising materials to combine with hydroxyapatite because they have low density, excellent mechanical property, good corrosion resistance and biocompatibility [14–16]. Liao et al. studied the formation of hydroxyapatite on multi-walled carbon nanotubes with bamboo periodicity and found that the carboxylic groups on the surface of carbon nanotubes acted as the coordination bonds for chelating of calcium in hydroxyapatite crystals [17]. Jandt et al. reported the biomimetic growth of hydroxyapatite on carbon nanotubes-protein hybrid materials. They found that the carbon nanotubes controlled the orientation of nuclei and the crystal growth of hydroxyapatite [18]. In brief, the CF and carbon nanotubes could be used to improve the mechanical and biological properties of the hydroxyapatite. However, there are few researches relating to the growth of hydroxyapatite on carbon nanotubes/CF hybrid materials (CCF).

In this work, the CCF prepared by grafting carbon nanotubes onto CF was used as templates for the growth of hydroxyapatite. CCF could not only combine the advantages of carbon fibers and carbon nanotubes but also avoid the agglomeration of carbon nanotubes because the carbon nanotubes are in-situ grown on carbon fibers. In addition, the carbon nanotubes are grown along the radial direction of the CF and are connected with each other, which could provide a loose and porous structure and favor the infiltration of the subsequent hydroxyapatite crystals. In addition, to further improve the phase stability, solubility and bioactivity of hydroxyapatite, the stoichiometric hydroxyapatite was substituted with carbonate ion, forming carbonate-containing hydroxyapatite. The carbonate-containing hydroxyapatite was synthesized on CCF using ultrasound-assisted electrodeposition method, forming carbonate-containing hydroxyapatite coated CCF (H-CCF). The morphology, microstructure and chemical composition of the H-CCF were investigated.

2. Materials and method

2.1. Sample preparation

Schematic of the preparation procedure of H-CCF is shown in Fig. 1. The CF used in this work was polyacrylonitrile (PAN)-based fiber with a mean diameter of 7 μm. The CF was laminated to form CF felts with a density of 0.45 g/cm^3. For preparing CCF, the CF felts were impregnated with Ni $(NO_3)_2 \cdot 6H_2O$ dissolved in acetone (1.5 wt.%) for 10 h and vacuum dried. Then the CF felts were introduced into a chemical vapor deposition furnace and heated at 1273 K under Ar atmosphere. Methane was used as the carbon source gas of the carbon nanotubes. The deposition time is 2 h. Finally, the samples were treated at 2273 k for 3 h under vacuum. For preparing carbonate-containing hydroxyapatite, the ultrasound-assisted electrodeposition was carried out on the CCF using a two-electrode electrochemistry system. The electrolyte solution was consisted of 1.0 mmol/L $NH_4H_2PO_4$ (analytical grade) and 1.67 mmol/L $Ca(NO_3)_2 \bullet 4H_2O$ (analytical grade) solutions with a pH value of 4.5. A constant current of 5 mA was applied. The deposition time was 1 min and 10 min. Ultrasound was introduced by an emitting device with a frequency of 45 kHz and power of 100 W. The carbonate-containing hydroxyapatite was also deposited on CF using same method, forming carbonate-containing hydroxyapatite coated CF (H-CF). H-CF was acted as a reference in this work.

2.2. Characterization

The morphologies of CCF and H-CCF were observed using a scanning electron microscope (SEM, SUPRA55). An attached energy dispersive X-ray spectroscope (EDS) was used to analyze the element composition. The detailed structure of the CCF was examined using a transmission electron microscope (TEM, Tecnai F30G^2). TEM samples were prepared by sticking a single CCF to the copper collar using conducting resin. After solidification for 12 h, the samples were observed by TEM. The schematic of the sample for TEM observation was shown in Fig. 2. The crystalline structures of H-CCF were analyzed by an X-ray diffraction (XRD, X'Pert PRO) with a Cu Kα radiation source at 40 kV and 35 mA. The structural characteristics of the CCF and H-CCF were examined by a Raman spectroscope with

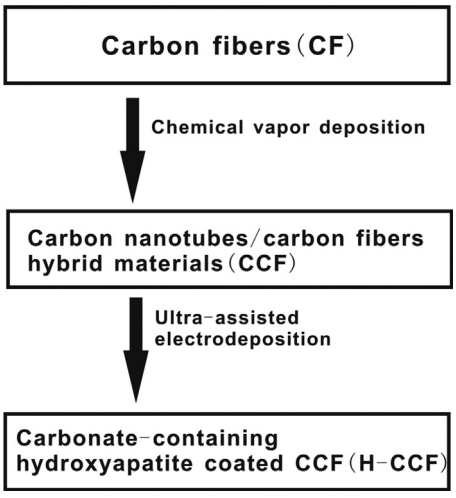

Fig. 1. Schematic of the preparation procedure of H-CCF.

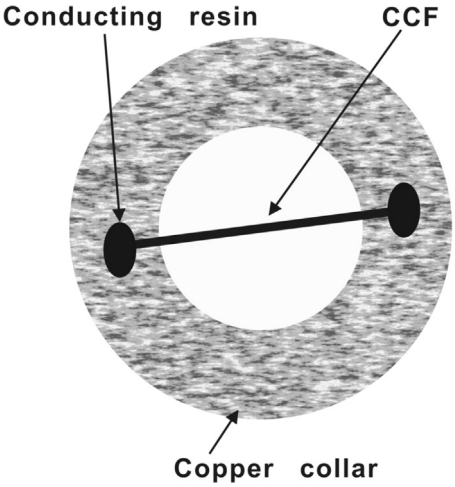

Fig. 2. The schematic of the sample for TEM observation.