Controllable preparation of a nano-hydroxyapatite coating on carbon fibers by electrochemical deposition and chemical treatment

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ABSTRACT

A nano-hydroxyapatite (HA) coating with appropriate thickness and morphology similar to that of human bone tissue was directly prepared onto the surfaces of carbon fibers (CFs). A mixed solution of nitric acid, hydrochloric acid, sulfuric acid, and hydrogen peroxide (NHSH) was used in the preparation process. The coating was fabricated by combining NHSH treatment and electrochemical deposition (ECD). NHSH treatment is easy to operate, produces rapid reaction, and highly effective. This method was first used to induce the nucleation and growth of HA crystals on the CF surfaces. Numerous O-containing functional groups, such as hydroxyl (–OH) and carboxyl (–COOH) groups, were grafted onto the CF surfaces by NHSH treatment (NHSH-CFs); as such, the amounts of these groups on the functionalized CFs increased by nearly 8- and 12-fold, respectively, compared with those on untreated CFs. After treatment, the NHSH-CFs not only acquired larger specific surface areas but retained surfaces free from serious corrosion or breakage. Hence, NHSH-CFs are ideal depositional substrates of HA coating during ECD. ECD was successfully used to prepare a nano-rod-like HA coating on the NHSH-CF surfaces. The elemental composition, structure, and morphology of the HA coating were effectively controlled by adjusting various technological parameters, such as the current density, deposition time, and temperature. The average central diameter of HA crystals and the coating density increased with increasing deposition time. The average central diameter of most HA crystals on the NHSH-CFs varied from approximately 60 nm to 210 nm as the deposition time increased from 60 min to 180 min. Further studies on a possible deposition mechanism revealed that numerous O-containing functional groups on the NHSH-CF surfaces could associate with electrolyte ions (Ca^{2+}) to form special chemical bonds. These bonds can induce HA coating deposition and improve the interfacial bonding strength between the HA coating and NHCH-CFs. The results of this study and the proposed preparation of uniform and dense nano-HA coating provide theoretical and practical guidance for future investigations of active HA coatings on fiber materials for medical products and implants. This work also lays the foundation for the wider use of HA-coated CFs/HA composite implants in clinical application.

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1. Introduction

The human bone tissue and vertebrate skeletal systems are primarily composed of HA ($Ca_{10}(PO_4)_6(OH)_2$) [1]. HA presents excellent osteoconductivity, biocompatibility, and bioactivity because of its biological nature compared with traditional medical titanium alloys, silicone rubber, etc. [2]. After HA is implanted into the human body, calcium and phosphate ions dissociate from it to be absorbed by the body, thereby contributing to the growth of new bone tissue [3]. Despite its obvious benefits, however, the wider application of HA ceramic in biomaterials is highly restricted because of the friability and poor flexural strength of the pure material [1,4]. Several reinforcing materials have been introduced to improve the overall mechanical properties of pure HA ceramic. Silk and cellulose fibers, for example, have been applied as templates to induce and control the growth of HA crystals to form

fiber/HA composites [5]. Among the known fibers, carbon fibers (CFs) are rarely used.

One-dimensional CFs possess a unique structure and excellent mechanical properties, including high strength, high modulus, and low density [6]. CFs are biologically inert, non-toxic, remain stable in the human body, and cause no rejection. Thus, CFs are ideal reinforcing materials that allow compatibility between the material and body tissue. Previous studies [7,8] have indicated that the mechanical properties of fiber-reinforced composite materials could be improved using ceramic-coated fibers. The application of these fibers would reduce the impact caused by differences in the thermal expansion coefficients of fibers and the substrate. This characteristic prevents degradation of the fiber/substrate interface at elevated temperatures. Such an approach could also improve the interfacial compatibility between the two materials and increase bonding strength [9]. The presence of HA crystals on fiber surfaces can effectively enhance osteoprogenitor cell attachment [10]. Hence, HA-coated CFs have been considered one of the best reinforcing materials for pure HA ceramic. HA coating on CFs

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could be used as a mid-layer between the HA substrate and CFs to reduce the gradient of thermal stress on the phase boundary between the materials [11–13].

Several coating techniques, such as sol–gel, biomineralization, and electrochemical deposition (ECD), are frequently used to deposit HA coatings on CF surfaces [14–16]. Ślósarczyk et al. studied an HA coating prepared by sol–gel on the surfaces of PAN-based CFs; the HA crystals exhibited flocculent distribution [14]. Huang et al. proved that a calcium phosphate (CaP) coating on the CF surfaces can be achieved by biomineralization and HNO_3 treatment. However, the main components of the CaP coating included plate-like $CaHPO_4 \cdot 2H_2O$ instead of HA [9]. The thickness, structure, morphology, and composition of HA coatings on CF surfaces are difficult to control. Experiments cannot satisfy the growth conditions of HA crystals when HA coatings are prepared on CF surfaces. Therefore, investigating active HA coatings on the surface of CFs is of theoretical and experimental significance.

Among the coating techniques available, ECD is a promising method to prepare coatings. ECD is widely used in commercial pure Ti, Ti–6Al–4V, and CF-reinforced carbon (C/C) composites because of its moderate preparation conditions, easy operation, low instrumentation costs, and controllable process parameters [17,18]. Control of the thickness, chemical constitution, and structure of the resultant coating, by ECD can result in the outstanding biological performance of the produced HA coating [19–24]. Unfortunately, ECD is rarely used to deposit HA coatings on CFs because of the lack of a proper method to clamp the CFs during deposition. Moreover, HA coatings are not easily formed at the center of a bundle of CFs because of the hydrophobicity of the CF surface. Thus, we designed a special fixture for clamping CFs to prepare a nano-HA coating on CF surfaces by ECD. As we intend to apply for a patent of the special fixture, this device is not specified in this paper.

The properties of CF surfaces remarkably affect the depositional quality of the HA coating [25,26]. CF surfaces are treated to change the properties of the fibers and improve the deposition of the HA coating. For example, the surfaces of para-aminobenzoic acid-treated CFs can achieve a granular HA coating by biomineralization [9]; the CFs were oxidized at 300–700 °C to obtain a larger specific surface area and limited acceleration of HA deposition [25]. While such treatments are effective to some extent, the nonuniform distribution of HA crystals on the CFs remains a problem, and low crystal density obtained has not been improved significantly. The coating stability may be affected and cannot meet requirements for bone apposition if the coating thickness was too low. Thus, modifying CF surfaces is a significant endeavor.

In this study, the growth of HA crystals was enhanced by treating CFs with three oxidizing solutions to introduce O-containing functional groups to the CF surfaces. Optimal treatment with mixed solution of nitric acid, hydrochloric acid, sulfuric acid, and hydrogen peroxide (NHSH) was obtained after comparing and analyzing the types and numbers of surface functional groups found on the CFs before and after treatment. A nano-hexagonal rod-like HA coating with controllable structure, morphology, and thickness was successfully prepared on the CF surfaces by combining NHSH treatment and ECD. A similar uniform and dense HA coating has not been observed in previous works. The rules of how different oxidation methods affect the morphology, uniformity, and density of the HA coating, as well as a possible deposition mechanism of the HA coating during ECD, were also discussed. The results of this study provide theoretical and practical guidance for future investigations active nano-HA coatings on fiber materials for medical products. This work also lays the foundation for the wider use of HA-coated CF/HA composite implants in clinical applications.

2. Materials and methods

CFs (TohoTenax Co., Ltd., with diameter of 7–9 μm) were manufactured from a polyacrylonitrile precursor through a carbonization process. During chemical treatment, the CFs were first cleaned ultrasonically and sequentially by acetone, alcohol, and distilled water at
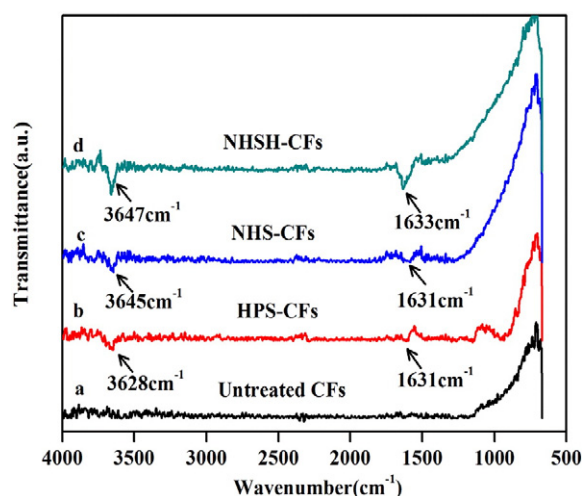

Fig. 1. FTIR spectra of CFs: (a) untreated; (b) treated with hydrogen peroxide solution (HPS); (c) treated with mixed acid solution of nitric acid, hydrochloric acid, and sulfuric acid (NHS); (d) and treated with mixed solution of nitric acid, hydrochloric acid, sulfuric acid, and hydrogen peroxide solution (NHSH).

room temperature. Then, the cleaned CFs were divided into four groups of the same mass to determine the influence of different CF oxidizing treatments on HA deposition. Three groups of CFs were treated with different oxidizing solutions, and the last sample was dried and left untreated. The oxidizing solution for the first group was hydrogen peroxide solution (HPS), the second group was treated with a mixed acid solution of nitric acid, hydrochloric acid, and sulfuric acid (NHS), and the third group was treated with NHSH. The three groups of CFs were treated at 80 °C for 2 h, cleaned with distilled water, and then submerged separately in NaOH solution at 60 °C for 24 h. Finally, the CFs were cleaned with distilled water until a constant pH was achieved and then dried for later use.

CFs and graphite electrodes have been reported to act as the cathode and parallel anode, respectively, in ECD. The electrolyte solution consisted of 3.80×10^{-4} mol/L $NH_4H_2PO_4$, 6.35×10^{-4} mol/L $Ca(NO_4)_2$, and 0.10 mol/L $NaNO_3$ [27]. Initial pH of the electrolyte solution was adjusted to pH 6.00 ± 0.02 with nitric acid solution and ammonia water. After initiation of ECD, the treated and untreated CFs were deposited separately at a constant current of 5 mA, and the temperature was controlled to 99 ± 1 °C. All four groups of CFs were deposited for 60, 120, or 180 min. The electrolyte solution was renewed every 60 min,
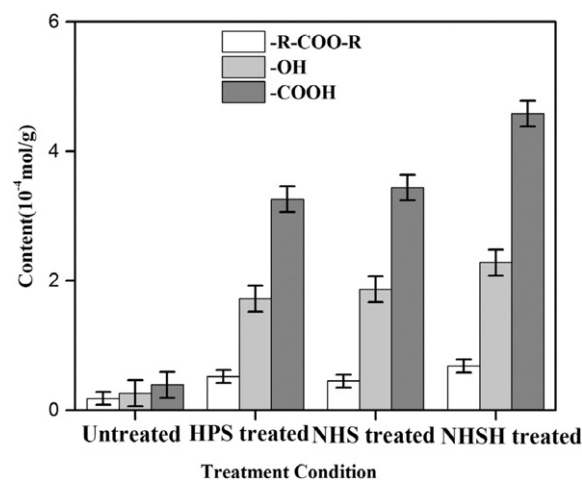

Fig. 2. The amount of –COOH, –OH, and –R–COO–R groups on the CF surfaces treated with different chemical methods.