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Cellulose acetate/hydroxyapatite/chitosan coatings for improved corrosion resistance and bioactivity

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ABSTRACT

Cellulose acetate (CA) nanofibers were deposited on stainless steel plates by electrospinning technique. The composite of hydroxyapatite (HAP) nanoparticles and chitosan (CHI) was coated subsequently by dip-coating. The structure and morphology of the obtained coatings were investigated by Fourier transform infrared spectroscopy and scanning electron microscopy. The stability of the coatings in physiological environment was studied using electrochemical polarization and impedance spectroscopy. The CA nanofibers were embedded in the HAP/CHI coating and the resulted composite film was densely packed and uniform on the substrate. The in vitro biomineralization study of the coated samples immersed in simulated body fluid (SBF) confirmed the formation ability of bone-like apatite layer on the surface of HAP-containing coatings. Furthermore, the coatings could provide corrosion resistance to the stainless steel substrate in SBF. The electrochemical results suggested that the incorporation of CA nanofibers could improve the corrosion resistance of the HAP/CHI coating. Thus, biocompatible CA/HAP/CHI coated metallic implants could be very useful in the long-term stability of the biomedical applications.

1. Introduction

Metallic implants have dominated the market of orthopedic and dental surgeries in the past several decades. The corrosion properties of metallic implants under physiological environments have been extensively studied [1–4]. Corrosion resistant coatings are used on the implants to enhance their stability and limit undesirable release of metallic ions [5]. Among the metallic implants, stainless steel (SS) is a popular choice for orthopedic surgeries such as fracture fixation because it is cost effective and easy handling [1,6,7]. Therefore, improvement of the bioactivity and corrosion resistance of SS implants is important for clinical uses.

Hydroxyapatite (HAP) coatings on the metallic implants can increase their corrosion resistance and enhance their biological interaction with the tissues around the implanted areas [6,8,9]. It is well known that HAP is a biocompatible and bioactive material, which is the main mineral component in bone and teeth [10]. Various methods have been used to coat HAP on implants [11–13]. Among these methods, dip-coating is a facile technique which can be used to modify the implant surface with HAP [13,14]. Furthermore, dip-coating is able to coat complex shapes and process at low temperature. The combination of bioactive polymers and HAP is one of the popular choices for coatings [15]. The addition of polymer could improve the interface between HAP and the implant. Chitosan (CHI) is a biocompatible natural polymer and it can improve osteoblast mineralization [16]. The coating of HAP with CHI was suggested to be both biocompatible and antimicrobial [7,17]. Cellulose acetate (CA) based nanofiber mats have been studied for their bioactivity for bone healing applications [18]. The bioactivity could be improved after deposition of calcium phosphate on the CA nanofibers [19].

The aim of this study is to develop a homogeneous coating with good corrosion resistance and bioactivity. We prepared an organic–inorganic composite coating by deposition of CA and HAP/CHI subsequently, as shown in Fig. 1. The CA nanofibers were deposited on the SS plates by the electrospinning method. The HAP/CHI composite was applied by dip-coating technique. The morphology, structures and functional groups of the resulted coatings were examined. The corrosion stability of the coatings on the SS plates in the simulated body fluid (SBF) was investigated by electrochemical polarization and impedance spectroscopy [3,20]. In addition, the samples were further analyzed for their in vitro bioactivity using SBF.

2. Experimental procedure

2.1. Materials

HAP nanoparticles were purchased from Alfa Aesar Tianjin Chem Ltd. (Tianjin, China). CHI (medium Mw, 85%–90% deacetylated, Shanghai Ruji Biotech Company) and CA (average Mw 100,000, bound acetic acid of 54.5–56.0 wt.%, intrinsic viscosity of 300–500 mPa s, Sinopharm

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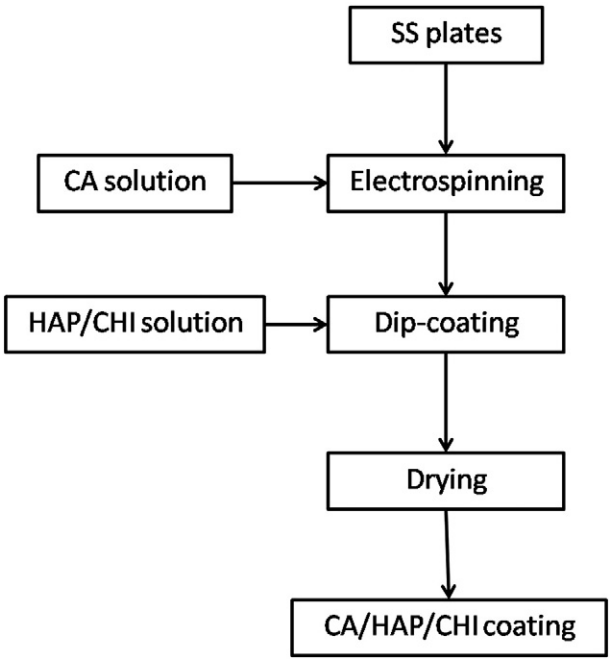

Fig. 1. Scheme for the preparation of CA/HAP/CHI coatings.

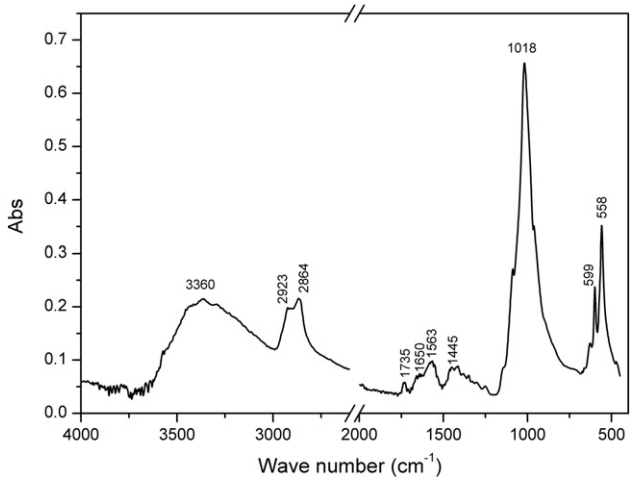

Fig. 3. ATR-FTIR spectrum of the CA/HAP/CHI coating.

Chemical Reagent Co. Ltd.) were used as provided. The type 304 stainless steel plates (0.5 mm thick) were provided by Huatai Metal Materials Co. Ltd. (China). All of the other chemicals were chemically pure grade or above and were used without further purification. De-ionized water was used to prepare the solutions.

2.2. CA nanofiber coatings

The mixture of dimethylacetamide (DMAc) and acetone had previously been used in the electrospinning of CA [18,21]. Briefly, CA (16% w/v) was dissolved in 2:1 (v/v) acetone and DMAc under stirring conditions. For electrospinning, the CA solution was placed in a 20 ml plastic syringe with a blunt needle tip and a voltage of 20 kV (Tianjin Dongwen High Voltage Power Supply Co. Ltd., China) was applied between the needle tip and the ground collector. Before the coating process, SS specimens were polished using silicon grit carbide paper (100–1000 grits) and were then washed with ethanol followed by water. The dried SS plates were placed on the ground collector at a distance of 15 cm from the needle tip. After electrospinning for 1 h, the collected fiber mats were dried in vacuum at room temperature.

2.3. HAP/CHI and CA/HAP/CHI composite coatings

The HAP powder (3.6 g) and CHI (1.2 g) were added to a beaker containing 48 ml water, 5 ml ethanol and 1 ml Tween-80. The mixture was stirred for 6 h to form a homogeneous slurry. The SS samples were dipped into the HAP/CHI solution and extracted with a withdrawal speed of 2 mm/s using a motorized stage. The SS plates with the CA nanofiber mats were dip-coated after the process described above and the obtained samples were denoted as CA/HAP/CHI coatings. After the dip coating process, the plates were dried in a hot-air oven at 80 °C for 4 h.

2.4. Characterization

2.4.1. Functional group and morphological characterization

The functional group characterization was examined using Fourier transform infrared spectroscopy (FTIR, VERTEX 70, Bruker, Germany) with the wavenumber range of 4000–400 cm^{-1}. The samples were mounted on the stage and the spectrum was collected using an attenuated total reflectance (ATR) module.

The morphology of the samples was observed using scanning electron microscopy (SEM) in a Nova Nano SEM instrument (FEI, the Netherlands) working at 5 kV. Prior to SEM observation, all the samples were sputter coated with gold to increase the conductivity.

2.4.2. Bond strength measurements

The bond strength of the coatings was examined using a universal tester (AG-100KN, Shimazu, Japan) according to the previous study [22]. The SS plates with coatings were glued to another piece of SS plate using epoxy resin. After the resin was cured, the samples were pulled with the speed of 1.0 mm/min until the coatings were peeled off.

2.4.3. In vitro biomineralization process

The SBF was prepared and the pH value was adjusted to 7.4 [3]. In vitro biomineralization of the CA, HAP/CHI and CA/HAP/CHI coated SS plates in physiological environment was investigated by immersing

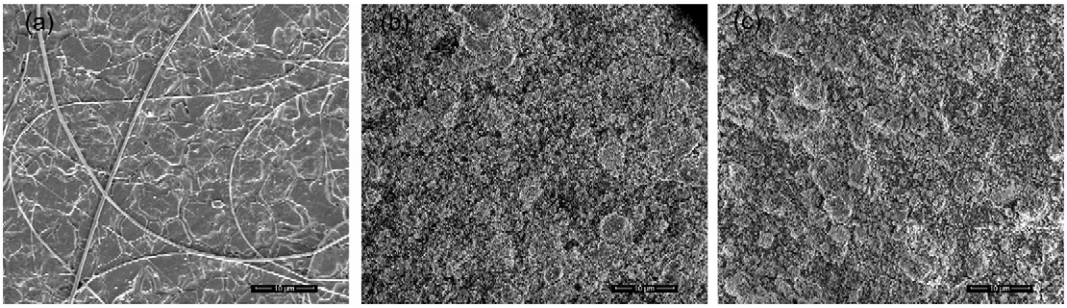

Fig. 2. Scanning electron micrographs of the coatings (a) CA (b) HAP/CHI and (c) CA/HAP/CHI.