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Improved bio-physical performance of hydroxyapatite coatings obtained by electrophoretic deposition at dynamic voltage

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Abstract

This study investigates the effects of the electrophoretic deposition process (EPD) at dynamic voltage on the physical and biological characteristics of hydroxyapatite (HA) coatings. HA powder is synthesized and used for preparation of HA/ethanol suspension which is subsequently characterized by X-ray diffraction (XRD), energy-dispersive spectroscopy (EDS), Fourier transform infrared spectroscopy (FT-IR), zeta potential and particle size analyses. Samples are prepared from commercially pure titanium (CP-Ti) substrates and coated with HA using EPD at dynamic voltage that keeps a constant depositional rate by adjusting the current and electrical field during the process. The HA-coated samples are dried and sintered at 800 °C for 2 h to densify the coatings. The XRD, scanning electron microscopy (SEM), EDS and adhesion tests are used to characterize the coated samples. The cross-sectional SEM images indicate that the thickness of coatings enhances as the current increases from 0.07 to 0.35 mA. The coatings are more uniform, packed and non-cracked at lower currents while HA particles start to arrange in a highly porous structure and show non-uniform, cracked and non-stable coatings as the current increases. The results also demonstrate that the best adhesions for the coatings are obtained at lower currents of 0.07 and 0.15 mA. Morphological studies and cell biological experiments are conducted using MG63 cells cultured on the HA-coated sample with the best overall physical performance. The number of attached and proliferated cells on the selected HA-coated sample is higher than on the non-coated titanium sample and culture plate used as control. There are significantly higher ALP activity and better cytoskeleton organization of cells on the HA-coated sample. This study shows that the EPD process at dynamic voltage can influence the structure and morphology of the coatings; therefore, substrate engineering can be used to improve and control cell–substrate interactions.

Keywords: Hydroxyapatite coating; Electrophoretic deposition; Dynamic voltage; Physical performance; Biological response

1. Introduction

Instability is the number one cause for bone implants' failure [1]. The key step to obtain a stable implant is a direct structural and functional connection between the bone tissue and the surface of the implant material which involves optimal cellular and molecular interaction at bone–material interface [1–4]. The initial stability and rigid fixation of the implant would secure long-term durability which reduces the rate of revision surgeries and health care costs [5]. Much research has been performed to chemically or structurally modify the surface of an implant material to gain an optimized reaction at the interface [5,6]. Owing to close similarity in composition and structure to natural human bone, hydroxyapatite (HA) has been widely used over the years as one of the most bioactive materials [4,7]. Pure HA has poor mechanical properties [8,9], hence, it has been used as coatings on the surface of metallic materials in order to combine the strength and toughness of the substrate with the bioactivity of HA [6,10,11]. It is also suggested that the application of HA coatings will improve

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corrosion resistance of the underlying implant material and reduce metallic ion release at the same time as promoting its bone bonding ability [5,9].

Many coating techniques have been investigated in order to deposit HA coating on the surface of metallic substrates including plasma spraying [12], sol–gel [13], ion beam dynamic mixing, pulse laser deposition, biomimetic coating [14], and electrophoretic deposition [15]. However, there are many limitations in the current coating methods which include non-uniform coating formation over geometrically complex surfaces, thermal decomposition of HA, formation of non-uniform metastable phase of HA during the high temperature process [15,16], sluggishness of the process, low crystallinity and poor adhesion of the coating on the substrates [7]. Therefore, there has been an increasing interest in the application of other techniques in recent years [17].

Electrophoretic deposition (EPD) process, on the other hand, is a fairly rapid and inexpensive method that exhibits some advantages over other alternative processes. Some of these advantages are simplicity of the method, ability to form complex shapes and patterns, control over the thickness and morphology of the coating, low temperature, ability to produce a composite layer and most importantly applicability for medical purposes [15–17]. Moreover, it is now well established that the particle size and the state of agglomeration of ceramic powders are important factors for the quality of the coating. Agglomerate-free structures made from close-packed fine particles can be densified at lower sintering temperatures. An important advantage of electrophoretic processing is that agglomerates can be separated by pre-sedimentation. Owing to the insulating properties of the deposit, the electric field provides a higher deposition rate in defect regions, resulting in better packing and uniformity of the deposit [18].

During the EPD process and under an applied current, charged particles from a stable colloidal suspension are deposited onto a charged electrode [19,20]. EPD has particularly been used with ceramic particles, since a range of porous and non-porous materials can be produced that have been employed as filters, porous carriers, and bioactive scaffolds [19,21]. Once a well-dispersed suspension is prepared, the applied voltage becomes a critical parameter [20]. By the application of constant voltage during the EPD process, the thickness of the deposited coating will increase and cause a non-constant electrical field which leads to the formation of a non-uniform coating on the electrodes. In fact, the coating itself is a non-conductive material, thus, the functional electrical field will decrease as the amount of deposited particles increases. This is the main drawback in the EPD process while using a constant voltage [21].

The present study aims to control and improve the structure, porosity, and adhesion of HA coatings by the application of the EPD process at dynamic voltage. The voltage is adjusted in a way to keep a constant current and optimum electrical field during the EPD process. Nano-meter sized HA powder is synthesized, characterized and electrophoretically coated on the surface of commercially pure titanium (CP-Ti) substrates. The coated samples are dried and sintered at elevated temperature to densify the coatings followed by characterization and adhesion tests. It is known that the quality of organic–inorganic interface is directly correlated to the interactions between the macromolecules produced by cells and structure of the substrates. Therefore, the most uniform, un-cracked coating with the highest adhesion on the substrate is selected and tested for its bio-performance. The biological performance is assessed through cell attachment, proliferation, alkaline phosphatase activity and morphological studies.

2. Materials and methods

2.1. Preparation of titanium substrates

Commercially-pure titanium (CP-Ti) sheet (McMaster-Carr Company, Los Angeles, CA) was used and cut in a way to have the same surface area ($10 \times 10 \times 1\ mm^3$). Each sample was mechanically grounded with a set of SiC papers followed by vibratory polishing with a vibrometer (Buehler, Lake Bluff, IL) to achieve a mirror surface finish. Subsequently the samples were cleaned with ethanol and distilled water, respectively, in an ultrasonic bath for 20 min. To increase surface roughness, the CP-Ti samples were etched and oxidized with a solution consisting of 10% nitric acid, 10% hydrochloric acid, 10% sulfuric acid and 10% H_2O_2 for 1 h. This treatment created small, nano-sized pits that increases the potential adherence of the HA powder on the surface of CP-Ti samples [15]. The samples were then submerged in a 5.0 mol/L NaOH aqueous solution at 50 °C for 48 h followed by washing with deionized water. Finally, before the EPD process, the samples were heated in an electric furnace at a heating rate of 1 °C/min, maintained at 600 °C for 1 h. The furnace was then cooled to room temperature.

2.2. Synthesis and characterization of HA powder

The HA powder was synthesized by the metathesis method (proposed by Hayek and Stadlman) [16] in a solution containing tetra hydrated calcium nitrate ($Ca(NO_3)_2 \cdot 4H_2O$) and di-ammonium hydrogen phosphate ($(NH_4)_2HPO_4$) with Ca/P ratio of 1.667. The reaction was as follows:

$$10\ Ca(NO_3)_2 + 6(NH_4)_2HPO_4 + 8NH_4OH \rightarrow Ca_{10}(PO_4)_6OH_2 + 6H_2O + 20NH_4NO_3$$

To obtain the HA powder, NH_4^+ and NO_3^- ions were removed by washing the precipitate repeatedly with water followed by drying in an oven at 100 °C for 24 h. The powder was calcinated at 1000 °C (heating rate of 5 °C/min) for 1 h in air atmosphere. HA powder was obtained by grinding with an agate mortar and pestle for 1 h and characterized by XRD (EQuniox 3000, INEL, France) and Fourier transform infrared spectroscopy (FT-IR-Bruker IFS 48, Germany).

2.3. Dynamic voltage EPD process

A suspension was made by adding 5 g of HA powder into 500 mL of ethanol (99.99%, Merck, Germany) and dispersed by adding 0.25% of carboxy-methyl cellulose (CMC, $[C_6H_7O_2(OH)_2OCH_2COONa]_n$). The suspension was

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