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Modification of electrophoretic deposition of chitosan–bioactive glass–hydroxyapatite nanocomposite coatings for orthopedic applications by changing voltage and deposition time

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Abstract

This article presents electrophoretic depositions of chitosan (CS), bioactive glass (BG), and hydroxyapatite (HA) applied on titanium (Ti) substrate from ethanol-based suspension. The strategy was utilized to modify the deposition of particles with different values of sizes and Zeta potentials, and consequently obtain desirable nanocomposite coating. SEM studies showed that uniform distribution of particles was obtained on isolated substrate at pH 4.5. Moreover, modified deposition of BG microparticles (< 37 μm) and HA nanoparticles (< 150 nm) in chitosan matrix was reached by changing voltage and deposition time. The results of X-ray diffraction (XRD) revealed a composite with high content of HA was fabricated at pH 4.5, $V = 20$ V, and $t = 15$ min. The deposition mechanism at the initial and final times was significantly related to self-assembly of HA nanoparticles that chelated by cationic macromolecular chains and located on BG microparticles, and CS-coated particulates of HA nanoparticles, respectively. The results of potentiodynamic polarization and electrochemical impedance spectroscopy studies demonstrated that the CS–BG–HA composite coating acts as a barrier layer in corrected simulated body fluid (C-SBF).

Keywords: B. Nanocomposites; C. Corrosion; E. Biomedical applications; Electrophoretic

1. Introduction

The advanced design of orthopedic implant is one of the principal purposes in tissue engineering [1]. The well-known strategy to achieve desirable implant with suitable properties is utilizing surface engineering, i.e. using metal substrate as strengthening and in order to induce biomedical properties, its surface modified by biomaterials [2,3].

Optimization of bony and dental implant is under the influence of different parameters including: biomedical, corrosion resistance, adhesion strength, and mechanical stability properties [4]. Biomedical properties have been chosen as outstanding parameters for designing biological substitutes [5].

Among various biomaterials, bioactive glass (BG) is indicative of bioactivity. However, its disadvantages are the low tensile strength, fatigue resistance, and elastic module [6]. Hydroxyapatite (HA) can be chosen as biocompatibility symbol and its chemical composition is similar to the mineral part of bone and tooth tissue. Weak mechanical properties limit hydroxyapatite's application [7,8]. Several methods have been utilized to synthesize HA nanopowder [6–8].

Chitosan (CS) and its derivations have broad profitable properties such as biocompatibility, biodegradability, antibacterial, antimicrobial, coagulating, and drug delivery which have gained numerous attentions. Disadvantages of chitosan including weak mechanical properties, and low chemical and thermal stability [9–11]. Previous studies have shown that polymers such as chitosan lead to a sintering process of eliminating and smooth dispersion of particles which can obtain suitable coating [12,13].

Superb coatings can achieve by a composition process in order to gather advantageous properties of constituent biomaterial and also to limit their disadvantages. Nanocomposite

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coatings have more potential places for migration, segregation, adsorption, and nucleation of osteoblastic cells, as well as improving other applicable properties [14,15].

The growing interest toward application of electrophoretic deposition (EPD) in chitosan-based coating is ascribed to its simplicity, ability to produce smooth coating, low processing temperature, low cost, and high production rate [12,16,17]. The effective parameters on EPD were categorized into two groups: (i) those related to the suspension, and (ii) those related to the process [18].

In recent years, scientists have utilized numerous strategies to investigate modification of EPD process in order to obtain improved properties of composite coatings. Pishbin et al. [19,20] studied the influence of EPD parameters on obtained deposition of bioactive glass, chitosan–bioactive glass, and bioactive glass®/chitosan/nano-silver [21] via Taguchi method and introduced optimum coatings with suitable properties. Mahmoodi et al. [12] revealed that among alcoholic suspensions, the highest adhesion strength and corrosion resistance of hydroxyapatite–chitosan nanocomposite coating were yielded from ethanolic suspension.

Zhitomirsky et al. [17] introduced EPD of bioactive glass/polymer composite coatings with and without HA nanoparticle. The different EPD parameters affect on CS–BG–HA coating. These parameters should investigate in order to obtain optimum ternary nanocomposite coatings.

The purpose of the present work is to modify electrophoretic deposition of chitosan–bioactive glass–hydroxyapatite coating on titanium substrate by investigating the effective parameters such as pH, voltage, deposition time, and isolation process. The optimum composite coatings with desirable properties are presented. We expected this study paves way for yielding suitable composite coatings with broader applications.

2. Experimental procedures

2.1. Materials

The following chemicals were purchased from Sigma-Aldrich: medium molecular weight chitosan (MW = 80 kDa) with a degree of deacetylation of about 85%, acetic acid (> 98%), ethanol, SiO_2, Na_2CO_3, $CaCO_3$, $Ca(NO_3)_2 \cdot 4H_2O$, and P_2O_5.

2.2. Synthesis of bioactive glass

Bioactive glass microparticles were produced by a melting technique described in Ref. [22]. To obtain a submicron powder in size the range of up to 37 μm, as-synthesized bioactive glass was dried and sieved.

2.3. Synthesis of hydroxyapatite

HA nanoparticles were prepared by a sol–gel method. $Ca(NO_3)_2 \cdot 4H_2O$ and P_2O_5 powders were separately added to ethanolic solutions and both of them were stirred for 30 min. Afterwards, they were mixed and achieved solution was stirred for 1 h to insure the completion of the reactions. The production was kept at room temperature for 24 h to gel formation. Then, the gel container was exposed at 80 °C for 24 h to dry. The heat treatment was performed at 600 °C for 5 h with heating rate of 10 °C min^{-1} to attain hydroxyapatite powder. To obtain a nano-HA, as-synthesized HA was dried and sieved.

2.4. Preparation of suspension and EPD

Dilute chitosan solution was prepared by dissolving 0.5 g L^{-1} chitosan in 1% acetic acid solution and stirred for 24 h at room temperature. To prepare suspension, 1 g L^{-1} BG and 0.4 g L^{-1} HA powders were added in different ratios of mixed ethanol–water solvent. Prior to EPD, the suspension was sonicated for 20 min after stirring by magnetic stirrer for 90 min. The pH level of suspension was adjusted by diluted hydrochloric acid.

Commercially pure titanium (1 mm × 20 mm × 35 mm) and stainless steel type 316L (1 mm × 21 mm × 37 mm) electrodes were used as deposited and counter electrode, respectively.

The distance between the cathode and the counter electrode was 15 mm. DC power source was used at constant voltages of 20 and 30 V in suspension at 21 ± 2 °C. In some cases, preparation stage was processed to isolation process in which an isolating tape was used on the back of electrodes (anode and cathode). Deposition was performed at different amounts of pH, voltage, deposition time, as well as with and without isolation process in ethanolic suspension. The deposited samples were dried overnight.

2.5. Characterization of deposits

To study the microstructural features and verify the quality of the coatings, scanning electron microscopy (SEM, JXA – 840, JEOL) was used. The thickness of nanocomposite coating was measured by coating thickness gauge (Electrometer 456) and the medium value was presented.

The crystalline structures of coating were analyzed by X-ray diffraction (XRD, 3003 PTS, Seifert) with Cu-K_α radiation ($\lambda = 1.54$ Å) using the 2θ range of 10–80° with step size of 0.04° and a count rate of 50 s per step.

FT-IR spectroscopy (FT-IR, Nexus 870, Thermo-Nicolet) was used to characterize intermolecular bindings between components of coating in the wavenumber of 4000 − 400 cm^{-1}. A multi-meter (Fluke 189) was used for online monitoring of the current density vs. time. All curves were plotted in $V = 20$ V and $t = 15$ min at different pH levels.

In order to investigate the electrochemical corrosion behavior, uncoated and coated samples were evaluated by electrochemical polarization and impedance spectroscopy experiments in corrected simulated body fluid (C-SBF) at room temperature. C-SBF solution was prepared according to the procedure described by Kokubo et al. [23]. A three-electrode cell with a saturate calomel electrode (SCE), a working electrode (the sample) and a counter electrode (Pt plate) were used. The working electrode with an exposed