Available online at www.sciencedirect.com
ScienceDirect
Acta Biomaterialia 5 (2009) 3178–3191
Acta BIOMATERIALIA
www.elsevier.com/locate/actabiomat

The effect of surface treatment on the surface texture and contact angle of electrochemically deposited hydroxyapatite coating and on its interaction with bone-forming cells

Noam Eliaz [a,*], Sharon Shmueli [a], Irena Shur [b], Dafna Benayahu [b], Daniel Aronov [c], Gil Rosenman [c]

[a] *Biomaterials and Corrosion Laboratory, School of Mechanical Engineering, Tel-Aviv University, Ramat Aviv, Tel-Aviv 69978, Israel*
[b] *Department of Cell and Development Biology, Sackler Faculty of Medicine, Tel-Aviv University, Ramat Aviv, Tel-Aviv 69978, Israel*
[c] *School of Electrical Engineering, Tel-Aviv University, Ramat Aviv, Tel-Aviv 69978, Israel*

Received 2 February 2009; received in revised form 26 March 2009; accepted 1 April 2009
Available online 10 April 2009

Abstract

This work demonstrates the effects of both surface preparation and surface post-treatment by exposure to electron beam on the surface texture, contact angle and the interaction with bone-forming cells of electrochemically deposited hydroxyapatite (HAp) coating. Both the surface texture and the contact angle of the ground titanium substrate changed as a result of either heat treatment following soaking in NaOH solution or soaking in H_2O_2 solution. Consequently, the shape of the current transients during potentiostatic deposition of HAp changed, and the resulting coatings exhibited different surface textures and contact angles. The developed interfacial area ratio *Sdr* and the core fluid retention index *Sci* were found more reliable than the mean roughness R_a and the root-mean-square roughness Z_{rms} in correlating the adhesion of the coating to the metal substrate and the cellular response with surface texture. The NaOH pretreatment provided the highest surface area and induced the highest cell attachment, even though the H_2O_2 treatment provided the highest hydrophilicity to the metal substrate. Electrodeposition at pH 6 was found preferable compared to electrodeposition at pH 4.2. The ability to modify the cellular response by exposure to unique electron-beam surface treatment was demonstrated. The very high hydrophilicity of the as-deposited HAp coating enhanced its bioactivity.

Keywords: Hydroxyapatite coating; Electrochemistry; Surface texture; Contact angle; Cell attachment; Titanium

1. Introduction

A key factor for successful fixation of cementless implants used for joint reconstruction is the establishment of a stable interface between the implant and bone. Coating of the implant with osteoconductive hydroxyapatite (HAp, $Ca_5(PO_4)_3(OH)$) is a well-known method for achieving such fixation [1]. The coating can improve the biocompatibility of orthopaedic implants by blocking the diffusion of poisonous elements from the metal into the body, as well as reducing the friction coefficient between the implant and its biological surroundings [2]. HAp is capable of enhancing bone growth across a gap around an implant in both stable and unstable mechanical conditions, and even converting a motion-induced fibrous membrane into a bony anchorage [3,4].

Several methods are available for the application of HAp coatings onto metal substrates. While plasma spraying is by far the most commonly used technique for orthopaedic implants, other techniques such as dip coating, sputtering, sol–gel, electrophoretic deposition and electrochemical deposition have attracted much interest in recent years. Because the thermal expansion coefficients of HAp

* Corresponding author. Tel.: +972 3 6407384; fax: +972 3 6407617.
E-mail address: neliaz@eng.tau.ac.il (N. Eliaz).

1742-7061/$ - see front matter © 2009 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.
doi:10.1016/j.actbio.2009.04.005

or tricalcium phosphate (TCP, $Ca_3(PO_4)_2$) are larger than those of Ti-based metals ($11–15 \times 10^{-6}$ vs. $8–10 \times 10^{-6}$ cm cm^{-1} K^{-1}, respectively), it is not easy to obtain good coatings on metals by processes that involve high temperatures [5].

Eliaz et al. [6–13] have reviewed the advantages of electrodeposition of HAp and studied different aspects of electrocrystallization of HAp on commercially pure Ti (CP-Ti) and Ti–6Al–4V, including the effects of bath pH and operating conditions, nucleation and growth, structure, chemistry and surface morphology, corrosion behaviour and in vivo performance. In one of these studies [7], the need for improving the adhesion of the coating to the substrate, on one hand, and accelerating the bone growth during the first few days post-operation, on the other hand, was noted.

Certain surface treatments of the titanium substrate may allow these two goals to be achieved. For example, it has been reported that after soaking in an alkaline solution (e.g. 5 M NaOH at 60 °C for 24 h), a hydrated titanium oxide gel layer containing Na^+ ions is formed on the surface. A complementary heat treatment (e.g. 600 °C for 1 h) then dehydrates and densifies this layer, transforming it to amorphous sodium titanate with a porous network structure [13–18]. This phase is a precursor for amorphous calcium titanate, which induces nucleation of amorphous calcium phosphate, and then HAp. It was reported that NaOH treatment prior to electrodeposition in a modified simulated body fluid resulted in both a denser and a more uniform brushite ($CaHPO_4{\cdot}2H_2O$)/HAp coating [18]. It was speculated that the porous network of the titanium surface formed after the NaOH pretreatment provided more favourable sites for the nucleation of CaP. Soaking in NaOH per se has recently been found to be beneficial both with respect to improving the adhesion of the coating to the substrate and enhancing the bone growth around HAp-coated implants in rabbits [13].

Another treatment of the titanium substrate may be soaking in H_2O_2 [19–21], which results in formation of a relatively thick porous oxide layer on the titanium surface. In an aqueous medium, OH^- bonds to the Ti cation in TiO_2, forming Ti–OH groups, which may be either acidic or basic, depending on the pH of the electrolyte. Application of cathodic potential results in a relatively high concentration of OH^- ions in the vicinity of the cathode surface, thus locally increasing the pH and providing better conditions for the nucleation and growth of HAp.

Post-treatment of the HAp coating may also improve the cellular response. For example, the wettability and electric charge at a material surface affect both cell and bacterial adhesion. Cell adhesion, e.g. in the case of osteoblasts, is often better on hydrophilic surfaces [22,23]. There are several techniques for altering surface wettability, such as deposition of self-assembled monolayers [24], light-induced changes [25] and electrochemical methods [26]. In the present work, an innovative process was evaluated. In this treatment [27–31], low-energy electron irradiation leads to surface energy modification on the nanoscale. HAp is a *p*-type wide-band-gap semiconductor with originally positive surface band-bending and several electron/hole bulk and surface states. The energy of the primary incident electrons significantly exceeds the mobility gap in HAp ($E_g \sim 4$ eV), resulting in generation of electron–hole pairs. The traps of different origin located in the irradiated surface region lead to the capture of primary and secondary electrons and holes, which are thermalized on the scale of tens of angstroms. Because the electron mobility is higher than the hole mobility, holes may constitute hole surface traps, while electrons are localized by bulk states, thus creating a thin charged double layer near the surface (~0.5–5 nm deep). Consequently, the wettability is changed even without applying external electric fields or interlayer deposition. This process provides gradual modulation of the wettability over a wide range of contact angles, from hydrophilic to superhydrophobic, by variation of the incident electron charge. The process allows induction of either uniform or patterned wettability, without altering the topography, roughness or the phase state of the material. The tailored wettability state remains stable for at least one month in various environment conditions, such as air and high humidity. The process is reversible; the charge can be discharged by UV irradiation.

The objective of this work was to determine the effects of these three surface treatments (i.e. two pre-treatments and one post-treatment) on the surface texture, wettability and interaction with bone-forming cells in vitro of electrochemically deposited HAp.

2. Materials and methods

2.1. Sample preparation and electrodeposition

The substrate metal was CP-Ti Gr. 2, in the form of 5 mm thick sheet. Samples, 1×1 cm^2 in size, were cut and ground mechanically on SiC papers from P120 to P1000 grit. They were then washed with detergent and water, ultrasonically cleaned in acetone, recleaned ultrasonically in Millipore deionized (Milli-DI) water and dried in warm air.

Electrodeposition was carried out for 2 h at 90 °C, in a solution containing calcium nitrate $Ca(NO_3)_2$ and ammonium dihydrogen phosphate $NH_4H_2PO_4$, following the procedure described in detail elsewhere [11]. First, the effect of the initial bath pH was sought, therefore comparison was made between coatings deposited at either $pH_0 = 4.2$ or $pH_0 = 6.0$ (hereafter termed HAp4.2 and HAp6.0, respectively). The pH was measured by an InoLab pH/Oxi Level 3 meter (WTW), after the desired temperature had been attained. An EG&G/PAR 263A potentionstat/galvanostat was employed to maintain the cathode potential at −1.4 V vs. a saturated calomel electrode (SCE). The CorrWare/CorrView (v. 2.6b) software package from Scribner Associates was used for data acquisition and data analysis.

ID	Title	Pages
1129	The effect of surface treatment on the surface texture and contact angle of electrochemically deposited hydroxyapatite coating and on its interaction with bone-forming cells	14