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Electro-Assisted Deposition of Calcium Phosphate on Self-Assembled Monolayers

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ABSTRACT

Calcium phosphate (CaP) ceramics are used in orthopedics and dentistry due to their excellent biocompatibility and osseointegration. Here, the electro-assisted deposition of CaP on two different self-assembled monolayers (SAMs), 2-mercaptoacetic acid (MAA) and 2-mercaptoethanol (ME), was studied both at short (up to 3 min) and long (2 hours) deposition periods on well-defined evaporated gold surfaces. It was found that the end group of the monolayer has a major effect on the growth of the CaP coating. The deposition was slower and less electrically efficient on MAA SAM, but surface cracking was essentially eliminated due to reduction of the crystallographic mismatch. The carboxylic acid may facilitate CaP growth by attracting Ca^{2+} ions to the surface, which could explain the higher amount of side reactions occurring at the beginning of the deposition.

1. Introduction

Calcium phosphate (CaP) is the major component of the bone. It represents a family of materials consisted of various phases, among others, hydroxyapatite (HAp), α- and ß-tricalcium phosphate (TCP), and octacalcium phosphate (OCP) [1]. One of the major challenges in biomaterial research during the last decades has been implant design as a means of accelerating post-surgery bone healing. As a result, several methods have been developed for coating implants with CaP in order to enhance their fixation. Since the Food and Drug Administration (FDA) approved CaP-based cements containing specifically HAp, OCP and TCP for human use in the 1990s, these phases have become prevalent in coatings as well [2]. HAp is especially popular since it bears the greatest similarity to biological apatite, both in crystallographic structure and Ca/P ratio [3].

Today, plasma spraying (PS) is the most common technology used commercially for coating implants with CaP. Since the early 1990s, however, much interest in electrodeposition of CaP has evolved due to the advantages it offers, such as non-line-of-sight coating and lower residual stresses [4–9]. The electrodeposition of CaP from aqueous solution is driven by cathodic potential, which causes the elevation of pH and thus the deprotonation of phosphate species to form insoluble CaP [3]. This process has been studied mostly on reactive metals, primarily on titanium and its alloys. For example, Gopi *et al.* [10] studied the film composition of electrodeposited CaP on stainless steel. They suggested that in acidic aqueous solution containing calcium and phosphate ions, the electrochemical and chemical reactions that follow the deprotonation of phosphate first yield the deposition of dicalcium phosphate dihydrate (Brushite, DCPD) while OCP is deposited more slowly. This was then reversed when the pH increased. Montero-Ocampo *et al.* [11] studied the CaP coating on titanium alloy at varied controlled potentials. They showed that the kinetics of CaP precipitation was enhanced by sufficiently negative potentials. The latter determined the structure of the coating. Eliaz *et al.* studied the effect of surface mechanical and chemical pre-treatments on electrodeposited CaP. It was shown that the current transient during deposition was affected by the surface pre-treatment, consequently resulting in different surface morphologies of the coating [12].

The electrocrystallization of CaP on titanium has also been studied. Eliaz *et al.* [3] investigated the nucleation of CaP on titanium and concluded that it involved two stages: instantaneous nucleation and 2D growth followed by progressive nucleation and 3D growth. Nucleation commenced at −0.84 V (*vs.* SCE) while potentials that were more negative than −1.26 V were required for enhanced growth. Mass transport was found to have only secondary effect on the deposition process. Grubač *et al.* [13]

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concluded based on fitting of the current-time transients to various nucleation and growth models that instantaneous nucleation, 3D growth under diffusion control took place. Metikoš-Huković *et al.* [14] showed that the chronoamperometry (CA) of $CaHPO_4$ nucleation on Mg-alloy deviated from instantaneous nucleation with 3D growth, while its nucleation on glassy carbon was progressive, followed by 3D growth.

As described earlier, the course of crystal growth reactions and the properties of the electrodeposits are markedly influenced by many parameters, such as surface pretreatment, bath composition, oxygen level, pH, stirring, the applied potential (or current density), temperature, and cell geometry. In addition, defects on the surface play a major role in the nucleation and growth of electrodeposits [3]. Namely, in order to thoroughly investigate the nucleation and growth processes, it is essential to work with well-defined and reproducible surfaces. The latter are relatively easy to form by self-assembled monolayers (SAMs).

It has been shown that surfaces modified by SAMs bearing various functional end-groups had a significant effect on the chemical precipitation and nucleation of CaP [15–19]. Ordinarily, the end-group of the monolayer was chosen to mimic the biomineralization process in the body, where the growth of HAp is associated with the organization of the collagen fibers. Thus, it is believed that interfacial interactions between HAp and the functional groups on the side-chains of the collagen molecules are crucial in this process. Accordingly, various SAMs terminated with hydroxyl (OH), sulfonic acid (SO_3H), phosphate (PO_4H_2) and carboxylic acid (CO_2H) have been studied [15–18]. Some of the negatively charged end-groups were found effective in promoting the mineralization process from solution and affected the texture of the CaP coating [18]. Yet, there is an active discussion in the literature regarding which SAM is most beneficial. To the best of our knowledge, SAMs have never been studied in the context of CaP electrodeposition.

The objective of this work is to investigate CaP nucleation and growth on well-defined surfaces. Specifically, the electrodeposition of CaP was studied both on bare gold and on gold surfaces covered with 2-mercaptoacetic acid (MAA) and 2-mercaptoethanol (ME) SAMs. We found that the presence of ME has only a minor effect on the adhesion of the deposit. On the other hand, MAA SAM affects not only the nucleation, but also the growth rate of the coating and its final surface morphology.

2. Experimental

2.1. Chemicals

2-mercaptoacetic acid (MAA, 98%), 2-mercaptoethanol (ME, 98%), analytical grade sulfuric acid, calcium nitrate (99%), ammonium dihydrogen phosphate (98%), analytical grade sodium hydroxide, analytical grade hydrochloric acid, analytical grade sodium chloride, reagent grade sodium phosphate monobasic, and reagent grade calcium chloride anhydrous were purchased from Sigma-Aldrich. Deionized (DI) water (>18 MΩ cm) was used for all the experiments.

2.2. Instruments and programs

Electrochemical deposition (ED), chronoamperometry (CA) and cyclic voltammetry (CV) were carried out with a CHI-750B potentiostat (CH Instruments Inc., TX, USA). Electrochemical quartz crystal microbalance (EQCM, Advanced Wave Sensors, Valencia, Spain) was connected to a network analyzer (250 B/C, Saunders and Associates) and a potentiostat (BioLogic SP-150, France).

X-ray photoelectron spectroscopy (XPS) spectra were recorded using an Axis Ultra spectrometer (Kratos) and Mg-Kα radiation of 1486.71 eV. Data were collected and analyzed by a Vision processing program. The surface morphology was analyzed by an environmental scanning electron microscope (ESEM, Quanta 200 FEG, FEI).

The saturation indices (SI) were calculated for the different CaP phases using PHREEQC computational program. The procedure of such calculations is described elsewhere in detail [1].

2.3. Procedures

Preparation of the gold samples: evaporated samples of gold (15 nm Cr + 100 nm Au) on glass, 1.5 cm^2 in area, were used for ED. An AT-cut (Inficon, East Syracuse, NY, 1.27 cm^2), 5 MHz Au-coated quartz crystals were used for EQCM experiment. The samples were treated for 15 min in a UV/ozone apparatus (UVOCS, Philadelphia, US). They were then immediately immersed in 1 mM solution of either MAA or ME in ethanol overnight. This was followed by dipping the samples three times in DI water at ambient temperature. Evaporated gold samples for ED were annealed after the UV/ozone cleaner using a torch. CA experiments utilized a gold disc (2 mm in diameter) that was pretreated by electrocycling the electrode using CV. This was performed in 0.5 M sulfuric acid, from −0.5 V to 1.6 V, at a scan rate of 0.5 V s^{-1}, for 40 cycles.

Electrochemical cell: ED was carried out in a standard three-electrode cell (15 mL) in which platinum wire and an Ag/AgCl (3 M KCl) electrode were used as the counter and reference electrodes, respectively. Therefore, all potentials are given hereafter *vs.* this reference electrode.

EQCM: Prior to deposition of CaP, the entire EQCM cell was placed in a 37 °C water bath and allowed to equilibrate. The resonance frequency of the bare crystal in solution was then measured for 10 minutes, and the subsequent frequency shifts during CaP ED were referenced to the bare crystal in solution. Deposition was carried out in a three-electrode cell with the working electrode set at −1.0 V for two hours. A platinum counter electrode was used.

The electrolyte for deposition in both EQCM and ED was 0.61 mM $Ca(NO_3)_2$ + 0.36 mM $(NH_4)H_2PO_4$ in DI water. The pH of the bath was measured using an InoLab pH/Oxi Level 3 meter, and adjusted to pH 7.4 by addition of NaOH before the experiment started. The bath temperature was kept at 37 ± 0.1 °C by means of a hot plate with temperature control. ED was carried out by applying a constant potential of −1.36 V for 2 hours. After ED, the samples were washed in DI water. Finally, the samples were dried and stored in a Petri dish sealed in a polyethylene bag.

CA: After cleaning, the samples were immersed in 1 mM thiol solution in ethanol for one hour. The samples were carefully washed before transferring into the electrochemical cell. The current transient under constant potential of −1.36 V was recorded in solutions containing 0.1 M NaCl ("Blank") and 0.1 M NaCl with 0.61 mM calcium chloride and 0.36 mM sodium phosphate monobasic ("Low") at constant pH 7.4. Nitrate ions were eliminated in these CA experiments to avoid their contribution to the formation of hydroxyl ions. The solution was bubbled with argon for 10 min prior to the experiment.

CV: After cleaning, the samples were immersed in the deposition solution. The CV was carried out at a scan rate of 10 mV s^{-1}, from 0 to −1.5 V and back.

3. Results and Discussion

The electrochemical deposition (ED) of CaP is based on altering the pH in the vicinity of the electrode surface as a result of an applied negative potential. The pH change shifts the equilibrium into an unstable state where CaP precipitates. Therefore, the first step in this work involved calculation and characterization of the