

HYDROXYAPATITE COATINGS ON TI SUBSTRATES BY SIMULTANEOUS PRECIPITATION AND ELECTRODEPOSITION

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Abstract

This paper presents the results obtained by analyzing hydroxyapatite (HA) coatings electrodeposited onto titanium plates. Instead of using a solution containing both calcium and phosphorus ions, the present approach starts with just one precursor in the electrolysis cell, and the other precursor is being added while an electrochemical potential of -1500 mV is simultaneously applied. By alternating the order of precursor addition, the Ti substrate surface was modified and the differences were evidenced using XRD, SEM, Raman and AFM. For all samples, needle-like crystals of HA grouped as hemispheres on the substrate surface. There is no significant difference, regarding morphology and hemisphere size, between the samples prepared at 1h deposition time, regardless of the precursor addition order; by contrast, the sample deposited for 4h presented a higher density.

Introduction

The properties of HA, such as its chemical composition and crystal structure, bearing close similarity to the mineral component in human bones and teeth, together with its excellent biocompatibility, make it one of the most suitable implant materials used in orthopedics and dentistry. However, in terms of mechanical properties HA has low strength and high brittleness, which make it unsuitable for use as load bearing implant [1]. Because of this, HA is being used as coating material for metallic implants, such as titanium [2]. Many methods have been developed for depositing HA coatings on metal substrates, including the electrochemical deposition method, having several advantages such as a good stoichiometric ratio [3]. When using this method, the regular approach is to prepare the electrolyte solution so that it contains both calcium and phosphorus ions [4]. In the present work, the electrochemical deposition of HA on Ti substrates started with just one precursor in the electrolysis cell, while the second was added gradually with the simultaneous application of a -1500 mV electrochemical potential.

Experimental

Analytical grade calcium nitrate tetrahydrate $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (Sigma Aldrich) as 1.75 mM solution and diammonium phosphate $(\text{NH}_4)_2\text{HPO}_4$ (Merck) as 1.05 mM solution were used as Ca and P precursors, respectively. The Ca:P molar ratio between the solutions was 1.67, corresponding to stoichiometric HA. Bidistilled water was used for all experiments.

Titanium discs of 1 cm in diameter were cut from an as-received pure titanium plate. The discs were polished using SiC sandpaper of different grit sizes and a felt with alumina paste, washed with industrial soap solution and bidistilled water and placed in ethanol/acetone mixture 50:50 for 30 minutes in an ultrasonic bath. Before the experiments the discs were rinsed with bidistilled water and dried.

The electrochemical setup consisted in a PGZ 301 potentiostat, 3 electrodes and a glass cell with heating mantle connected to a thermostat set at 80°C. The titanium discs were used as cathode, after being inserted in a Teflon support (active surface = 0.28 cm²). The anode was a Pt plate (active surface = 0.8 cm²) and the reference electrode was the Ag/AgCl (sat. KCl) electrode.

50 mL of one precursor was placed inside the glass cell, then, the dropwise addition of the second precursor started simultaneously with the chronopotentiometric experiment. The parameters used for the electrodeposition of HA on the Ti discs and the nature of the added precursor are presented in Table 1.

Table 1. Synthesis parameters for HA samples obtained through electrochemical deposition

Sample name	Temperature (°C)	Time (h)	E (mV)	Added precursor
HAe1	80	1	-1500	P
HAe2	80	4	-1500	P
HAe3	80	1	-1500	Ca

The HA modified Ti discs were studied using various characterization techniques. X-ray diffraction patterns were recorded using a PANalytical X'Pert Pro MPD Diffractometer with Cu anode, working parameters 45 kV and 30 mA.

Images of the samples were obtained using a Phillips Inspect S scanning electron microscope. The discs were fixed with double adhesive tape on the SEM holders.

Atomic force microscopy was performed on a MultiView 2000 scanner from Nanonics Imaging Ltd., in intermittent mode, using 20 nm radius tip. The same platform was used in combination with the proper module for recording Raman spectra (excitation wavelength was 514 nm).

Results and discussion

The XRD patterns of the three samples are presented in Figure 1. In all three cases, the formation of crystalline HA is confirmed, the standard reflections being evidenced in comparison to the 00-009-0432 JCPDS file. The crystallinity degree improves as the deposition time increases (A and B spectra). By adding the Ca precursor to the P precursor (C spectrum), the crystallinity degree improves even more. A strong preferential orientation along the c crystallographic axis can be observed, an effect which is more obvious for the samples deposited within 1h. In case of the sample deposited within 4h, the crystallographic plane (211) presents a higher intensity.

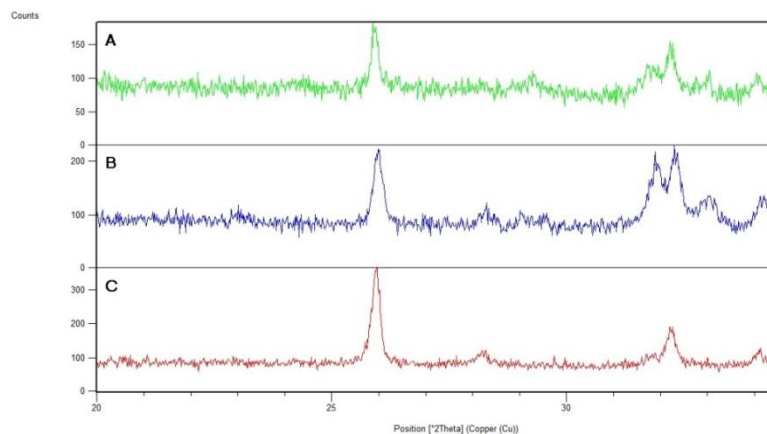


Figure 1. XRD patterns of the samples: A = HAe1, B = HAe2 and C = HAe3

The Raman shift spectra of the HAe3 sample is presented in Figure 2. The very strong peak corresponding to the PO_4 ν_1 vibration at 961 cm^{-1} , characteristic for HA [5], can be observed in this case as well. Other indications that the electrodeposited material is HA are the weakly defined peaks observed in the areas $430\text{--}450\text{ cm}^{-1}$ and $580\text{--}600\text{ cm}^{-1}$, characteristic for HA doubly and triply degenerated bending modes of the PO_4 group.

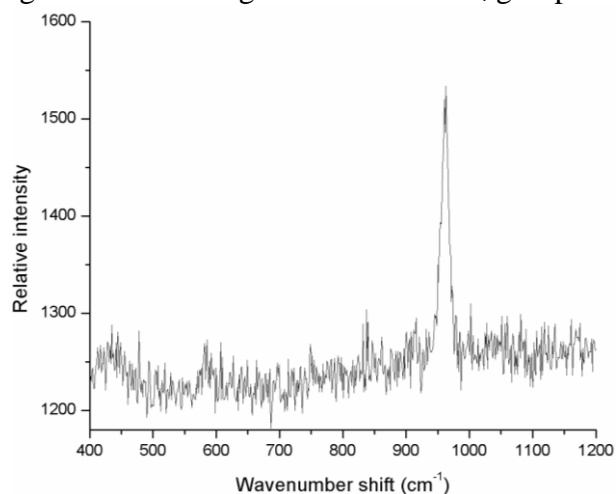


Figure 2. Raman shift spectra of the HAe3 sample

SEM images recorded for the three samples are presented in Figure 3. Sample HAe1 consists of micrometric needle-like crystals with spherical arrangement, displaying lengths of less than $5\text{ }\mu\text{m}$.

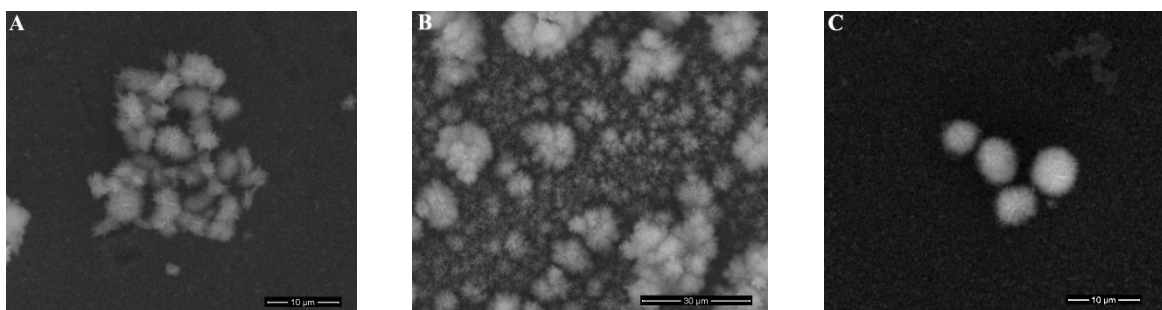


Figure 3. SEM images of the samples: A = HAe1, B = HAe2, C = HAe3

By comparison, sample HAe2 shows the same structure and arrangement of the crystals, the difference being that the number of crystals forming the spherical arrangements is higher in this case. Furthermore, due to the increased deposition time, the amount of deposited HA is larger and its distribution more uniform.

The image of the HAe3 sample shows structures similar to the ones of the HAe1 sample, but the spherical arrangements are slightly larger and better defined. The crystal dimensions of the third sample are similar to the crystal dimensions of the first one, but the crystallinity degree is higher. Because of this, it can be presumed that adding the Ca precursor to the P precursor leads to more satisfactory results.

The AFM images of the three samples are presented in Figure 4. The maps of the HAe1 and HAe3 samples are 10x10 μm^2 , while the map of the HAe2 sample is 50x50 μm^2 because in this case the deposited material was much thicker and attempts to acquire maps with higher resolution failed. As expected from deposition time and SEM observations, maps A and C are similar, displaying likewise characteristics, with hemispheres as large as 2 μm . The same morphological characteristics can be seen in image B, but the structures are more densely packed, as a result of prolonged deposition time. Completing these information with the SEM data, it can be concluded that the electrochemically-controlled crystalline growth of the HA particles led to the formation of hemispheres attached to the Ti substrate.

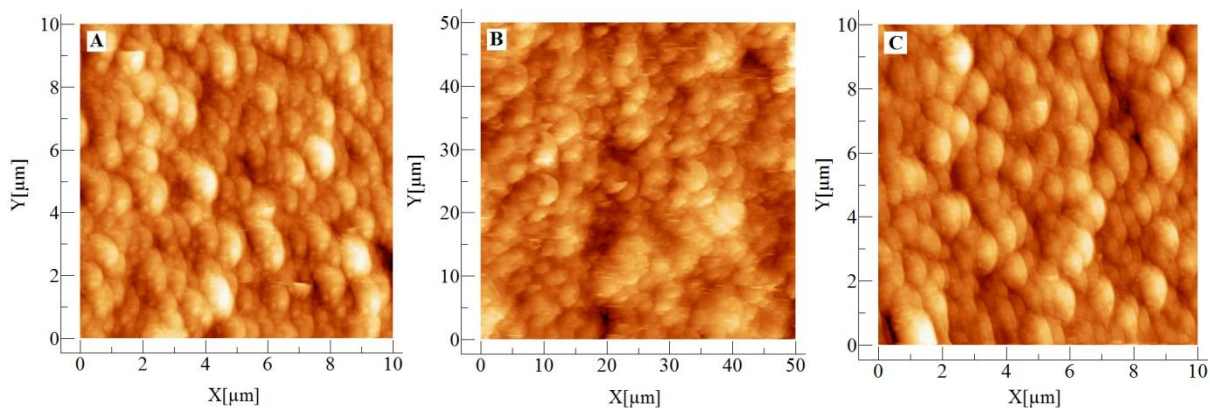


Figure 4. AFM images of the samples: A = HAe1, B = HAe2, C = HAe3

Table 2 shows the values calculated from AFM data. The presented values are: average roughness (Sa), root mean square roughness (Sq), maximum peak height (Sp), maximum valley depth (Sv), maximum peak to valley height (Sy), surface kurtosis (Sku), surface skewness (Ssk).

Table 2. Values obtained from AFM analysis

Sample name	Sa (nm)	Sq (nm)	Sp (nm)	Sv (nm)	Sy (nm)	Sku	Ssk
HAe1	51.88	65.81	252.56	-233.47	486.03	3.29	0.37
HAe2	282.30	355.20	1605	-1277.8	2882.8	3.08	0.10
HAe3	51.58	65.58	269.76	-219.26	489.02	3.3	0.35

The parameters values are similar for the HAe1 and HAe3 samples, which is to be expected, considering the observations previously presented (SEM and AFM). The values for the HAe2

sample cannot be compared to the values of the other two samples because the image had to be recorded on a larger surface.

Conclusion

Electrochemical deposition of HA on Ti substrates was successfully achieved in a novel manner, by adding just one precursor in the electrolysis cell, while the second precursor was added simultaneously with an applied electrochemical potential.

The samples prepared by reversing the order of precursor addition (HAe1 and HAe3 from Table 1) were analyzed using various physico-chemical methods, which revealed no significant morphological differences, but an increase in the crystallinity degree in case of the HAe3 sample. Both samples consist in hemispherical formations composed of needle-like crystals of HA, attached to the Ti surface.

The same methods were employed for the HAe2 sample, prepared the same way as HAe1, but with longer deposition time (4h, compared to 1h), and they indicated a denser deposition layer with similar morphology.

Future research will be directed towards improving the characteristics of the deposited material, aiming at higher degrees of uniformity, homogeneity and crystallinity, suitable for medical applications.

References

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