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A COMPREHENSIVE REVIEW OF FABRICATION AND CHARACTERIZATION METHODS OF HYDROXYAPATITE

C. LUNG[1*], D. MARCONI[1,2*], T. FEHER[1*]

ABSTRACT. This synthesis article expands on the applications of hydroxyapatite (HA) coatings on titanium dioxide (TiO_2) substrates for biomedical applications, focusing on the methods of deposition and their impact on the material's properties. Various techniques, including sol-gel, electrochemical deposition and ultrasonic spray-pyrolysis are discussed because of their ability to enhance the mechanical resistance, biocompatibility and osteointegration of implants. The analysis methods used are X-Ray Diffraction (XRD), Scanning electron Microscopy (SEM) and Fourier Transform Infrared Spectroscopy (FTIR). They provide insights into the structural, chemical and physical characteristics of the HA coatings. The results indicate that these hybrid coatings significantly improve the performance and longevity of implants in orthopedic and dental applications.

Keywords: *Hydroxyapatite, Titanium Dioxide, Biomedicine, biocompatibility, Osteointegration, Sol-Gel dip-coating, Electrochemical Deposition, Ultrasonic Spray Pyrolysis, X-Ray Diffraction, Scanning Electron Microscopy, Fourier Transform Infrared Spectroscopy, hybrid coatings*

INTRODUCTION

Biomaterials are on the receiving end of a great deal of attention in the scientific community because a suitable biomaterial is capable of replacing, rebuilding and restructuring human tissue for long term use, without an excess of negative effects, whether they be toxic or inflammatory [1]. In applications such as bones replacements we are often looking for a material that will offer the appropriate

[1] *Babes-Bolyai University, Physics Faculty, M. Kogălniceanu No. 1, 400084, Cluj-Napoca, Romania.*
[2] *Department of Molecular and Biomolecular Physics, National Institute for Research and Development of Isotopic and Molecular Technologies, Cluj-Napoca, Romania.*
[*] *Corresponding authors: claudiu.lung@ubbcluj.ro, daniel.marconi@itim-cj.ro, tudorfeher@gmail.com*

balance between good mechanical resistance and good biological properties [2] In the following synthesis article, we will present past studies that included the use of titania (TiO_2) as substrate, together with a hydroxyapatite (HA) coating.

Such thin coatings present a good biocompatibility, bioactivity and osteoconductivity, which makes them ideal for improving the properties of implants used in orthopedy or stomatology [3]. Deposition methods influence the structure, properties and performance of thin layers with biomedical applications. Out of the broad range of deposition methods that are used at the moment, each one of them present their own advantages and challenges that allow us to use them in various applications in which we [4] will give the thin layers the properties that we need [1].

Next, we will discuss simple and hybrid layers of hydroxyapatite, several deposition methods, such as the sol-gel, electrochemical deposition and ultrasonic spray pyrolysis methods. We will also delve into the characteristic of analysis methods: X-Ray diffraction (XRD), Scanning Electron Microscopy (SEM) paired with energy dispersive X-Ray analysis (EDX) and Fourier Transform Infra-Red Spectroscopy (FTIR).

LITERATURE STUDY

The selection of the deposition methods depends in the range of applications that we require for the thin layer and on the properties of the deposited materials. For biomedical applications, the roughness of the titanium surfaces plays a major role in adhesion with the bone tissue [4]. It is proven that matching the roughness of the surface of the implant results in an improvement of the mechanical proprieties of the bone-implant interface, compared to a smoother surface. Furthermore, this offers a greater porosity that will improve the osteointegration between the bone and the implant [5].

Hydroxyapatite thin layers have been studied in the context of a single substrate or in the one of a hybrid substrate that has multiple constituents in its composition. There are many studies that investigate the deposition of hybrid layers on titanium substrates. It was discovered that hybrid thin layers can be deposited successfully, without traces of foreign contaminants. Titanium Oxide, which is the protective layer that naturally occurs on titanium was created, in this instance, by micro arc oxidation and the hydroxyapatite was deposited through plasma electrolysis and gel electrophoresis [2].

Literature findings have shown that a hybrid combination of the two aforementioned deposition techniques can give pure hydroxyapatite from a stoichiometric perspective on the outside layer and an intermediate layer of Titanium Oxide [6], that offers the appropriate mechanical properties and a good biostability, in the corrosive environment of the human body [7]. Another advantage of a hybrid substrate is the improvement of the osteoblastic activity of titanium implants, respectively the capability of improving the capability of improving the activity and the proliferation of the osteoblastic cells in the human body, that are responsible with the regeneration of bone tissue [2]

For us to further elaborate this synthesis article on the theme of deposition oh thin layers of hydroxyapatite on titania substrates, we will discuss the specifical details presented in the literature, respectively deposition methods and analysis methods.

Ultrasonic Spray Pyrolysis for Hydroxyapatite Deposition

The ultrasound spray pyrolysis method stands out among others as a promising method of deposition of HA thin films on TiO_2 substrates due to her ability to produce layers that are homogenous and have a controlled thickness and composition. The method consists in the atomization of a precursor substance in fine droplets, that are then further transported by a carrier gas on the heated substrate where they undergo the process of pyrolytic decomposition and form a solid thin layer [3]. This allows for a precise control on the chemical and phasic composition of the deposited films, thus improving the limitations of the plasma deposition techniques, that often suffer of a poor stoichiometry of the sample and of inhomogeneous phases of HA. The deposition parameters such as the concentration of the precursor solution, the temperature of the substrate and the deposition time are meticulously controlled to optimize the properties of the film [8].

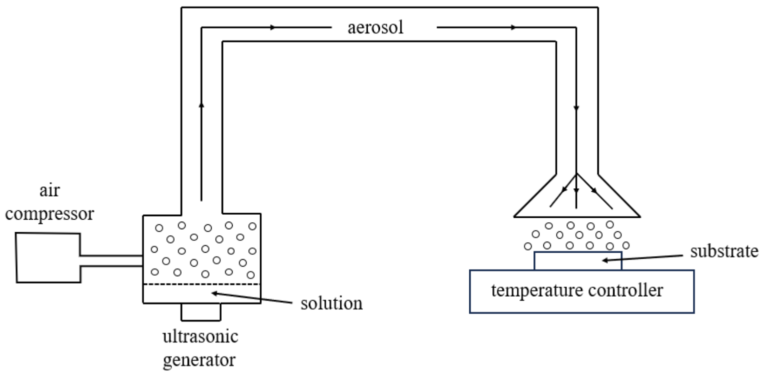

Fig. 1: Schematic of Ultrasonic Spray Pyrolysis coating method

Among the advantages that were mentioned above, the method has its' own specific limitations. One of them is the necesary thoroughness and meticulosity in the preparation of a precursor substance. It is important for it to display an appropriate degree of viscosity to ensure an efficient vaporization, but too great of a viscosity might cause the vaporizer to jam [8]. Another limitation is the difficulty in obtaining a uniform layer on a substrate of large dimensions and irregular surface [3], as the variation of the diameter of the droplets and the homogeneity of the flow of the gas can lead to non-uniform areas of the thin film [8].

Sol-Gel method for HA deposition

The Sol-Gel method is a chemical deposition method used to create solid materials out of molecules suspended in a solution as precursors. The process consists of the transition of a liquid system that takes the name of "sol" into a solid substance, the "gel". In the case of HA, the precursors are generally calcium and phosphates, which are dissolved in a solvent, together with a catalyzing agent that has the role of forming bonds with the precursor ions in order to prevent the precipitation or premature conglomeration. Moreover, the adjusting of the concentration of the sol can increase or decrease the deposition time.

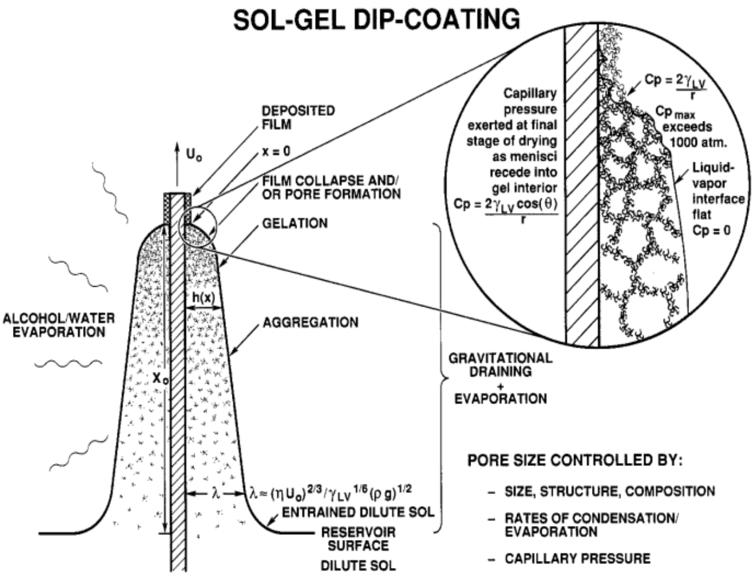

Fig. 2: Schematic of sol-gel dip-coating method [9]

Next, the sample undergoes a process of hydrolysis and polycondensation, that results in the formation of a colloidal suspension in the substance – the so called "sol". This is later distributed in the substrate, and one method to do so is represented in diagram: Dip-Coating. This is later heat treated, and a matrix will be formed and converted into a solid substance.

The sol-gel process takes places at temperatures that are generally lower than other deposition methods, thus minimizing the thermal stress that the sample is exposed to. On another side, the preparation of the precursors in the sol gel method is very rigorous and time consuming, which could become very resource intensive for a larger scaling of this operation [2].

A hybrid layer of hydroxyapatite and TiO_2, deposited through the sol-gel method presents improvements in the mechanical resistance of the thin film with the substrate and of the cellular fixation density, compared to a single substance layer. Furthermore, it was found to be bioactive through the apparition of needle-like hydroxyapatite when submerged in a solution that stimulates biological fluid [4].

Advanced Sol-gel HAP coatings on titanium

Moreover, other research groups focused on optimizing the sol-gel process through the introduction on TiO_2 interlayers, to increase the coating adhesion and integrity.

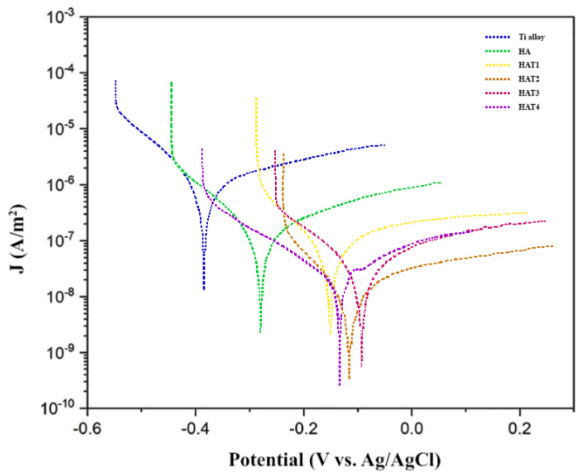

Fig. 3: Polarization Curve obtained through potentiodynamic testing [6]

The researchers were able to produce monophasic, crystalline hydroxyapatite films through pretreating Ti_6Al_4V samples with thermal oxidation, sol-gel coating and anodization. Some of the observed advantages of this deposition method are high protective properties in simulated body fluid, demonstrated low corrosion rates, improved adhesive strength and they are free from cracks [6].

Critical parameters for the sol-gel deposition process have been identified, such as the pH value, aging time and sintering temperature. Another benefit of including the TiO_2 interlayers is the fact that the issue of mismatching thermal expansion coefficients has been alleviated, reducing the formation of cracks. The enhanced corrosion resistance has been proven through potentiodynamic tests, which shows that such coated implants are more suitable for long term applications.

In Figure 3, we can observe how the polarization curve obtained through potentiodynamic testing has shifted towards higher values of the corrosion potential [6], which indicates a lower tendency for the material to corrode. The curve labelled *Ti alloy* shows the highest corrosion current for the lowest corrosion potential, indicating low corrosion resistance. The red curve shows that for a hydorxyapatite coated sample, the corrosion potential increases and the current decreases, both of them being a desirable trait for better corrosion resistance. The HAT samples represent different thickness of titanium and hydroxiapatie bilayer coatings. Here we can see that the introduction of bilayer coatings acts as a barrier against corrosion, further reducing the parameters.

Electrophoretic deposition of hydroxyapatite coatings

The electrophoretic deposition of hydroxyapatite is another promising method of obtaining appropriate thin coatings on titanium bone implants [10]. Tests have been run by researchers to determine the optimum deposition voltage for a likeable outcome of a stable and uniform hydroxyapatite layer. The tests have been conducted at 20, 30 and 40 V dor 30 minutes in HAP suspension. Out of the three different depositions, the one at 30V gave the best results, after being evaluated for their thickness, morphology and electrochemical properties [11]. They have also exhibited the best corrosion resistance, showed fewer defects, higher compaction and remained intact for the longest period when being in contact with simulated body fluid.

The samples were studied using various analytical techniques, such as Field Emission Scanning Electron Microscopy (FE-SEM), Energy Dispersive Spectroscopy (EDS), X-ray Diffraction (XRD), and Fourier Transform Infrared Spectroscopy (FTIR).

In the FE-SEM image below, one can observe that the 20V sample displayed a more porous structure, whereas the other structures are more compact. At large voltages, such as 40V, large crystals that cause cracks in the thin film appeared as well [11].

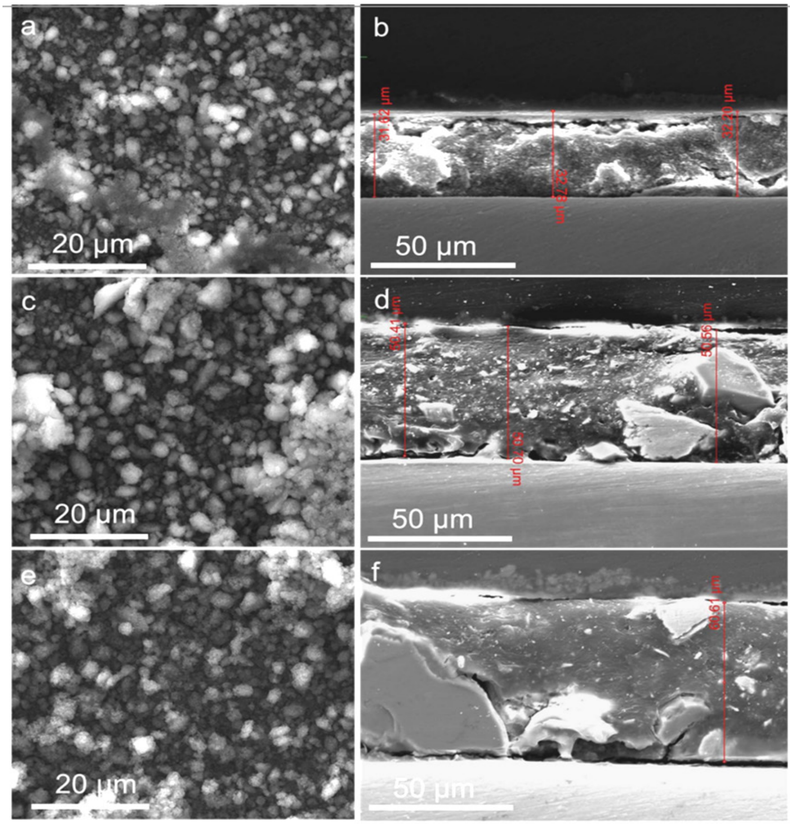

Fig. 4: FE-SEM Images in plane view and cross-sectional area of the HA coatings, deposited at 20V (a),(b), 30V (c),(d) and 40V (e),(f) [12]

Electrochemical method for hydroxyapatite deposition

This deposition method presents significant advantages in the deposition of HA on titania substrates. It offers a great control over the substrate thickness and ensures a uniform coverage, even if the substrate has a complex shape from a geometric perspective. This method allows for the doping with different ions in order to improve the biological characteristics of the sample [5]. Furthermore, this process leads to the formation of thin films with a really good adherence to the titania substrate, which is really important for the durability of titanium implants [13].

On another hand, due to the fact that this process is a line-of-sight one, it can result in a non-uniform coverage of substrates that have a complex geometry or deep grooves. The success of this deposition method relies heavily on the precise control of the compounds that make up the electrolyte, and any deviation from it can cause a non-stoichiometric deposition of HA or the presence of unwanted phases of the compound [13].

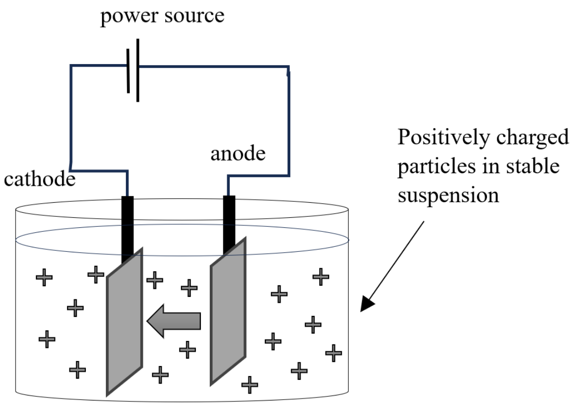

Fig. 5: Schematic of Electrochemical deposition method

Scanning electron Microscopy and Energy Dispersive X-Ray Analysis

Scanning Electron Microscopy (SEM) is a powerful analysis tool that is used for the study of the surface morphology of the thin films and their composition.

It works with the help of a thin, focused beam of electrons that will scan over the surface of the sample. As the electrons interact with the thin layer, they will be either backscattered or absorbed. If they are absorbed, they will cause the emission of secondary electrons, all of whom are later collected [14]. The secondary electrons are useful in the study of the topography of the sample, whilst the back-scattered electrons offer insights into the composition of the sample, their energy being correlated to the atomic number of the elements the material is made out of [15]. The analysis of the constituting elements takes the name of Energy Dispersive X-Ray analysis (EDX).

As seen in the SEM images below, this technique can give clear pictures of the morphology of the surface of the samples, its' uniformity, the film thickness and the orientation of HA crystals.

X-Ray Diffraction (XRD)

By measuring the intensity of diffracted X-Rays by a substance with a crystalline structure one can identify the phases of the material, its' crystallinity and other structural attributes, such as the presence of crystalline planes in the studied substance [16]. Using the information about the atomical composition of HA obtained through the analysis of the EDX spectrum of secondary electrons, and the information about the crystal planes present in the sample obtained through XRD one can find a clear overall picture of the composition of the deposited film, both from the point of view of the elements that it consists of and the one of the crystalline phases that are present [17].

Fourier Transform Infrared Spectroscopy (FTIR)

Is an analytical technique used to obtain a infrared-absorption spectrum of a solid, liquid or gas. It is useful especially in the identification of organic and polymeric substances, and it can sometimes be used for inorganic substances as well. The technique relies on the phenomena of absorption of IR radiation with frequencies specifical to the modes of vibration of molecules, creating a spectral fingerprint for each material [2].

The FTIR technique plays an important role in the analysis of thin HA layers, offering insights into their structure and chemical composition. It can identify the presence of specific structural groups, such as phosphate PO_4 that have absorption bands at frequencies of 560 cm^{-1}, 600 cm^{-1} and 1000-1100 cm^{-1}. Hydroxyl OH groups can be highlighted by a absorption peak at the frequency of 3570 cm^{-1} [18]. By analyzing the position of such peaks, one can confirm the presence of key constituents of HA.

CONCLUSIONS

In conclusion, through this synthesis article we have achieved a comprehensive exploration of the deposition techniques such as the Sol-Gel method, electrochemical deposition and ultrasound spray pyrolysis, highlighting their applicability in the context of deposition of thin HA layers, mentioning their advantages and limitations.

The complementary analysis techniques such as X-Ray diffraction, Fourier Transform Infrared Spectroscopy and Scanning Electron Microscopy play important role in the characterization of HA thin films. FTIR offers information on the chemical groups present in the sample, XRD about the crystalline planes and HA phases, all while SEM gives insights on the morphology and stoichiometry of the sample.

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