Functional Thin Films and Surfaces
Room Town & Country C - Session C4-FrM

Photo- and Electrochemically Active Surfaces

Moderators: Peter Kelly, Manchester Metropolitan University, UK, **Carlos Tavares**, University of Minho, Portugal

9:00am **C4-FrM-4 Shedding Light on Implant Biointerfaces: Designing Innovative Photocatalytic Coatings Towards Cell-Assisting and Bacteria-Killing Functions on Titanium**, ***Valentim Barão (vbarao@unicamp.br)***, *B. Nagay, C. Dini, H. Pantaroto,* University of Campinas (UNICAMP), Brazil **INVITED**

A significant concern emerging from current Implant Dentistry is the increasing prevalence of peri-implant infections and the lack of consensus on the most effective therapeutic technique to treat such diseases. Therefore, new strategies for peri-implant biofilm control are urged to be developed to guarantee the long-term predictability of the implant treatment. Within the context of photochemical processes, the development of photocatalytic coatings and photofunctionalized surfaces can be alternatives for reducing the biofilm formed on and assisting cellular interactions with dental implants. Targeting these optimal biological functions, the outstanding concept of photofunctionalization and photocatalysis for environmental decontamination, using the well-known crystalline titanium dioxide (TiO_2) coating as a photocatalyst, have shed light on scientists to the use of this strategy for biomedical implant application. Nevertheless, the use of photocatalysis for implant rehabilitation is still in its infancy. The main challenge of using TiO_2 as a photocatalyst for biomedical purposes is that, because of its wide band gap, TiO_2 can only produce bactericidal reactive oxygen species by ultraviolet (UV) light, which is harmful to human health due to its fast absorption by DNA. To overcome this limitation, photocatalytic coatings consisting of visible light-responsive photocatalysts have been developed for using with implants therapy. For this, to reduce the band gap to a level compatible with visible light ($\lambda \geq 400$ nm), it is necessary to resort to alternative strategies, such as elemental doping with metals and anions. Therefore, this presentation aims to approach multifunctional coatings for biomedical implants using the concepts of photocatalysis under UV and visible lights and the antibacterial mechanisms of biocompatible metals. We will also discuss the UV photofunctionalization on pre-osteoblastic cell differentiation and mineralization potential. In addition, the modulation of key inflammatory markers by UV-modified surfaces will also be addressed. From a clinical perspective, the use of light might be an effective strategy to reduce biofilm-related diseases and accelerate the wound healing of dental implants.

9:40am **C4-FrM-6 Hematite and Titania Thin Films: Energy and Environmental Applications (Virtual Presentation)**, ***Josef Krysa (Josef.Krysa@vscht.cz)***, University of Chemistry and Technology, Czechia **INVITED**

Titania (TiO2) and hematite (α-Fe2O3) have potential applications as semiconducting photoanodes for either hydrogen production *via* photoassisted water electrolysis or photoelectrochemical (PEC) oxidation of water pollutants. The advantages of TiO2 are high stability, nontoxicity, and low price. However, it absorbs only a very small part of sunlight (3% of the total power). On the other hand, iron oxide (α-Fe2O3) has a favourable band gap (2.0 – 2.2 eV), which enables absorption of a substantial fraction of solar light, resulting in the theoretical maximum power conversion efficiency of 27 %. This has created much interest in the past, which has been rekindled by the advent of new thin film preparation and texturization methods. Limitations are the non-ideal position of the conduction band, *i.e.* too large an electron affinity for spontaneous water reduction, low minority carrier diffusion length, surface states that can mediate recombination, low stability in acidic media, and photocorrosion. We have recently fabricated Sn-doped hematite (Fe2O3) films by aerosol pyrolysis (AP) on fluorine doped tin oxide (FTO). Photosensitivity had an onset around 650 nm and maximum incident photon to electron conversion efficiency (IPCE) was 0.21 at 400 nm. The aim of the present work was to check whether the capping with TiO2 can be used for corrosion protection of such films.

AP hematite films on FTO were covered by titania films fabricated by spray-pyrolytic coating. Spray pyrolysis of TiO2 used as precursor a 0.2 M ethanolic solution of titanium di-isopropoxide bis-acetylacetonate. AP hematite layers coated with TiO2 show that with increasing thickness (increasing number of passes of the spray nozzle) of the TiO2 coating the photoelectrochemical response decreased. This is due to TiO2 increasingly taking part in the solid liquid interface. This is also reflected in the photocurrent onset shifting to more negative potentials. The Faradaic efficiency (f) of the photocorrosion reaction in 1 M sulphuric acid decreased from 0.47 % (for an unprotected hematite electrode) to 0.17 % for that covered with spray coated TiO2 layer (but decreased photoresponse).

10:20am **C4-FrM-8 Multifunctional Coatings for Maritime Applications**, ***José Castro (uc2021120076@student.uc.pt)***, University of Coimbra, Colombia*; M. Lima, I. Carvalho, M. Henriques,* University of Minho, Portugal*; S. Carvalho,* University of Coimbra, Portugal

The main transportation system in the world commerce are ships and their problems could be critical, affecting the world economy. Corrosion and biofouling are considered like common issues associated to maritime components and those must be prevented to avoid possible damage, pollution or functional performance losses and hence, economical and environmental drawbacks. In this context, some products have been applied to minimize dead times in maintenance in ships, and hence extend its productive time. Tributyltin (TBT) paint was the most used solution before 2008, however it was banned since then. With this lack, multifunctional coatings seem to be a good option to replace TBT. Zirconium (oxy)nitrides doped with Cu obtained by Magnetron Sputtering technology, could gather the desired properties in maritime applications. The films were sputtered over SS316L substrates, material used largely in the naval industry, among others. Cu_xO_y and Zr(O)N coatings were deposited as control samples, and these helped to disclose features and mechanisms in Cu-Zr(O)N films. The properties of films were assessed by SEM, EDS, XRD, AFM, and OCA measurements. Also, EIS and potentiodynamic polarization tests were performed in NaCl (3.5% wt.) solution for 24 h to simulate seawater exposure. XPS were done before and after corrosion test to establish the action of copper and its reactivity with artificial seawater. Also, copper ionic release was studied in seawater by ICP-OES. Bacterial inactivity, which is directly related with the antibiofouling surface potential, was evaluated by inhibition halo tests. The results revealed that Cu did not react with Zr(O)N directly during deposition process. This demonstrates the influence of Cu in Zr(O)N was promote gaps among film's columns boundaries, affecting other films properties such as surface energy, roughness, and wettability. Concerning corrosion tests, Cu deteriorates the Zr(O)N chemical strength against seawater. On the other hand, ZrON film exhibited an antibacterial action with the Cu inclusion, though after the chemical activation. The Zr(O)N films were unable to capture enough oxygen to oxides the copper during the deposition process. With the additional availability of oxygen from the chemical activation process, the Cu inside the ZrON film, can react to form CuO. The Cu^{2+} ions releasing had no influence on the antibacterial film action. The presence of CuO was vital to get an antibacterial comportment. The obtained results shown the first sight of the potential of Cu-Zr(O)N films to be applied as a unique coating to avoid biofouling and corrosion under seawater exposure and replace TBT paint in maritime components.

Author Index

Bold page numbers indicate presenter

— B —
Barão, V.: C4-FrM-4, **1**
— C —
Carvalho, I.: C4-FrM-8, 1
Carvalho, S.: C4-FrM-8, 1
Castro, J.: C4-FrM-8, **1**
— D —
Dini, C.: C4-FrM-4, 1
— H —
Henriques, M.: C4-FrM-8, 1
— K —
Krysa, J.: C4-FrM-6, **1**
— L —
Lima, M.: C4-FrM-8, 1
— N —
Nagay, B.: C4-FrM-4, 1
— P —
Pantaroto, H.: C4-FrM-4, 1