MULTIFUNCTIONAL BIOMATERIALS BASED ON NANOSTRUCTURED ANODIC TITANIUM DIOXIDE

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Introduction

An increasing number of bone implants determines an increased interest in developing novel implantable materials and improvement in currently used ones. One of the most commonly applied biomaterials in orthopedics and dentistry is titanium and its alloys. It is mainly due to their favorable properties, such as corrosion resistance, good biocompatibility, and decent mechanical properties [1]. However, the osseointegration process between the implant and the surrounding tissue, which happens through the natural titanium oxide (TiO₂), is inefficient. That is why scientists are applying various surface modifications, among which electrochemical oxidation (anodization) of metals seems promising [2]. The method is cost-effective and straightforward, and what is more important, it allows for synthesizing nanostructures with precisely controlled morphology. Such morphology, comprised of vertically aligned nanocontainers, not only provides a biocompatible surface for cells growth [3] but also enables for the incorporation of different compounds, e.g., drugs or antibacterial agents [4], growth factors, which ensures that such materials possess multifunctional properties [5,6].

Anodization was recently applied for three-dimensional substrates (3D –printed), which opens a wide range of new possibilities and challenges for synthesizing complex biocompatible biomaterials [7,8].

Materials and Methods

Anodic titanium oxide (ATO) layers on 2D Ti foil, Ti-based alloys (Ti13Nb13Zr and Ti15Mo), and 3D Ti substrates were prepared via the anodization process conducted in the ethylene glycol-based electrolyte with the addition of NH₄F and H₂O, under a constant voltage in the range between 40 and 100 V at 20°C. The obtained oxide layers were characterized by their physicochemical properties by using different methods, e.g., SEM, EDS, XRD, XPS, and contact angle measurements. 2D and 3D Ti samples were used as drug delivery systems, and their detailed characterization as drug carriers was provided. Some of the synthesized materials were also modified with Ag nanoparticles in terms of their antimicrobial properties. Finally, the biocompatibility of such layers was also examined.

Results and Discussion

Different anodization procedure was applied depending on the used substrate (Ti foil/cube or Ti-based alloy), which resulted in different morphologies of the obtained nanostructured oxides. Received ATO layers differed in the pore diameter and oxide thickness, which then impacted their properties, both physicochemical and biological. All anodized samples showed better wettability when compared with bulk substrates. Corrosion parameters differed for all of the examined materials. The surface properties of the examined biomaterials were compared with their biocompatibility. What is more, the successful deposition of silver nanoparticles on ATO layers was performed. Such modified materials were characterized by slightly better antibacterial activity towards Gram-positive and Gram-negative bacteria. ATO layers also presented enhanced osteoblast-like cells growth when compared to bare substrates. Finally, 2D and 3D samples modified with titanium dioxide were used as drug delivery systems for ibuprofen and/or gentamicin. It was proved that drugs could be successfully loaded and released from such materials. What is more, a kinetic model was fitted to the release profiles, describing the nature of the process in detail.

Conclusions

To sum up, it was shown that electrochemical oxidation of titanium-based materials leads to the efficient modification of the metallic surface of various initial geometries. Such biomaterials enhance cells adhesion and proliferation but also may be used as drug carriers. Combined with chemical changes with antibacterial agents, they gain also new properties, and thus, may be considered as multifunctional biomaterials.

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MATERIAL