BIOACTIVE SILICA ENRICHED HAp COATING ON TITANIUM WITH NANOPATTERNED TiO_2 INTERMEDIATE LAYER

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Introduction

To enhance the bioactivity and osseointegration of metallic implants, a wide range of technologies has been offered to adjust the surface properties to specific needs. Such treatments include surface anodization [1] and coating with hydroxyapatite (HAp) [2] or enhancement of HAp formation [3]. The nanotubular structure of TiO_2 has been reported to increase significantly the titanium surface area and enhance the formation of HAp and the bond strength between the substrate and the coating [4]. Silica nanoparticles are considered to be an attractive material to improve the biocompatibility and biodegradability of HAp coatings [5]. It was reported that silica nanoparticles have an inhibitory effect on osteoclast differentiation and stimulatory effect on osteoblast differentiation [6].
In the present work, hydrothermal method was used to fabricate highly bioactive HAp coatings enriched with silica nanoparticles on titanium with anodized TiO_2 in the form of nanotubes and u-shapes as an intermediate layer.

Materials and Methods

The TiO_2 nanopatterns were prepared on 14x14 mm^2 titanium plates by standard two electrode anodization at room temperature in potentiostatic mode. The anodizing voltage was kept constant at 50 V during the process. One of the samples from each kind was annealed in oxidizing atmosphere at 600°C for 1 h, whilst the other substrate was left without annealing as a reference sample. In order to produce silica enriched HAp coatings, the hydrothermal process was carried out in an autoclave from stock solution containing: calcium salt hydrate, diammonium phosphate, calcium helating agent and soluble source of silicon.
The morphology and structure of as prepared specimens were characterized using X-ray diffraction, scanning electron microscope, proton induced X-ray emission, infrared and Raman spectroscopy. Changes in surface morphology were examined after 4 days of incubation in simulated body fluid.

Results and Discussion

FIG. 1 shows SEM images of TiO_2 arrays after the hydrothermal process. The research revealed different effect of surface nanopatterning, i.e. nanotubes or u-shapes, on morphology of HAp-SiO_2 coatings. Concerning the ability to induce hydrothermal crystallization of HAp and coating bioactivity, the best results were obtained for annealed nanotubes (B). In the case of unheated substrate with TiO_2 u-shapes, there was no coating formed on its surface after the synthesis (C). Subsequent heating slightly improved the deposition of HAp crystals, although not in order to form homogeneous and continuous coatings (B). The XRD and spectroscopic analysis confirmed the existence of well crystallized HAp and amorphous form of silica nanoparticles in the prepared specimens. The formation of nanosized silica particles within HAp matrix is based on Stober process by hydrolysing monomeric tetraethyl orthosilicate precursors in the presence of ammonia as a catalyst.

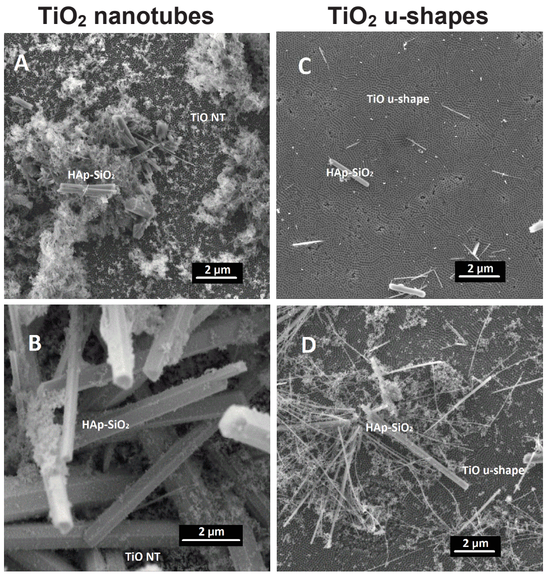

FIG. 1. SEM images of TiO_2 arrays with (B,D) and without thermal treatment at 600°C (A,C) after hydrothermal deposition of HAp coatings enriched with silica nanoparticles.

Conclusions

We demonstrate novel method for synthetizing highly bioactive crystalline HAp coatings enriched with nanoparticles of silica on nanopatterned titanium substrates. We also examined the effect of surface morphology and nature of TiO_2 nanotubes and u-shapes on hydrothermal crystallization of HAp-SiO_2 coatings. The synthesis allows to homogeneously cover the titanium substrate concerning complex geometry, as most of the implants possess. In this study, biodegradable properties of silica nanoparticles (with size ~25 nm) introduced into HAp matrix, can not only enhance nucleation rate of bone-like apatites and stimulate osteoblast differentiation, but also facilitate bone remodeling, being slowly replaced by newly formed tissue. The SBF test revealed high bioactivity of the synthesised coating on annealed TiO_2 nanotubes just after 4 days of immersion.

References

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