Electronic Supplementary Material (ESI) for Journal of Materials Chemistry

Supplementary Information

Experimental details:

Doc. 1. Surface modification of TiAlV and Titanium Sputtered Stainless steel wires.

The hydrothermal process carried out to generate nanofeatures on Ti has been extended to Ti alloys (TAV) as well as Ti coated Stainless steel rods to check the feasibility of applying this surface modification procedure to various metals/alloys. Identical hydrothermal conditions as used for metallic Ti have been adopted for this surface modification process. TiAlV alloy discs (Jayon surgicals Pvt Ltd, India) having a size of about 5mm diameter and 1 mm thickness were serially polished upto #4000 grit and used for the study. Sputter deposition of titanium on stainless steel wires of diameter 0.5 mm mounted on a rotating stage, in an inert Argon environment using a sputter coating unit (Model: EMI TECKK575X). This Ti coated SS wire was also hydrothermally modified as above to generate nanostructural features on its surface.

Doc. 2. Surface-area calculation by dye adsorption

Surface-area analysis of different nanomodified titanium surfaces was carried out using dye adsorption test. Titanium plates of equal dimensions with nanomodifications as well as control polished Ti were ultrasonically cleaned using distilled water and acetone and dried before experiment. Samples were immersed in 0.3 mM solution of a selected dye, viz., Eosin (Fisher scientific, USA) in ethanol for 48 hours. Samples were cleaned with ethanol after incubation with the dye, to remove any un-adsorbed dye from the surface of the samples. The dye adsorbed on to the nanomodified surfaces was desorbed by 0.1M KOH through repeated washing and the absorbance of the dye was recorded at 516 nm. The amount of dye adsorbed on each surface was determined from a standard plot of absorbance for various concentrations of dye. The quantity of dye adsorbed per cm^2 of the samples (Table 2) was derived from the surface-area of nanopolished control titanium calculated from AFM (ESI† Fig. S6). Keeping that surface area value as the reference, surface-area of nanomodifed titanium plates was calculated using the amount of dye adsorbed/cm^2.

Results and discussion

Doc.1. Surface modification of TiAlV and Titanium Sputtered Stainless steel wires.

Preliminary experiments on the hydrothermal processing of Ti alloy discs and Ti deposited on SS wire were carried out under similar experimental conditions as done for metallic Ti plates. Close resemblances were noticed between the structures generated on TAV and Ti. The nanoleafy pattern obtained on TAV discs was essentially similar in morphology to the leafy pattern on Ti plates (ESI† Fig. S3B - Structure 1), while the porous architecture was not very well defined (ESI† Fig. S3C - Structure 2). The nanorod-like structure formed on TAV displayed a more needular, whisker-like geometry (ESI† Fig. S3D - Structure 3).

Sputter deposited Ti on stainless steel (SS) wires upon hydrothermal treatment using identical conditions as above, yielded three different nanostructural features as represented in ESI† Fig. S4. Treatment using 1M NaOH at a temperature of 200°C for 4 h (as for the nanoleaves on metallic Ti) produced a broader, leaf-like foliate structure (Fig. S4D), while 0.5M NaOH at 175°C for 2 h (as for nanoporous on Ti) yielded a mesh-like porous nanostructure (Fig. S4E). The same alkali concentration at 250°C for 5 h gave a crystalline deposition of titania submicron structures on the material surface (Fig. S4F). This implies that a critical optimization of the processing conditions would help to fine tune the nanostructure morphology generated on metallic/alloy surfaces, suiting various applications.

Doc.2. Surface area analysis

Surface area of various Ti samples with nanomodification was calculated by measuring the amount of dye adsorbed on their surfaces with respect to control polished Ti. The concentrations of dye adsorbed on various surfaces are summarized in Table 2. From the surface area calculated (Table 1), it was observed that all the nanosurface modified samples have an increased surface area in comparison to nanopolished Ti surface, thereby providing a quantitative proof for increased surface area due to nanostructuring. Surface area value of polished Ti was found to be 1.069 ± 0.298 cm^2 from AFM. Nanorods showed the highest amount of dye adsorption as well as the surface area amongst all the Ti samples, which can be attributed to its vertically aligned 1D structure (9.626 ± 0.484 cm^2). Nanoleaves also displayed a higher surface area close to that of nanorods in the range of 8.180 ± 0.322 cm^2, while nanoporous structures showed a higher surface energy value (5.498 ± 0.364 cm^2) in comparison with the polished Ti.

Doc.3 Apoptosis assay of Human umbilical cord vein endothelial cells (HUVECs) cultured on various Ti surfaces

FITC-Annexin-V was used to detect cells undergoing apoptosis and Propidium Iodide (PI) for necrotic cells. The negative control is used to define the basal level of apoptotic and dead cells. ESI† Fig. S7 shows the flow cytogram of FITC-Annexin-V/ PI staining of HUVEC grown on various modified Ti surfaces and control polished Ti in comparison to a negative control. Our results revealed that there is no considerable cell apoptosis or necrosis for HUVECs on any of the modified Ti samples in comparison to the negative control even after 72 h of incubation.

Samples	Concentration of dye adsorbed (μg/cm^2)
Nanoleaves	6.96 ± 0.301
Nanoporous	5.58 ± 0.572
Nanorods	8.84 ± 0.530
Control Ti	2.46 ± 0.683

Table S1. Concentration of Eosin dye adsorbed per cm^2 area of different nanomodified and control Ti surfaces.