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Supporting Information

Enhancing Surface Characteristics of Ti-6Al-4V for Bio-Implants Using Integrated Anodization and Thermal Oxidation

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1. **External surface morphologies of smooth, rough, anodized-smooth and anodized rough samples.**

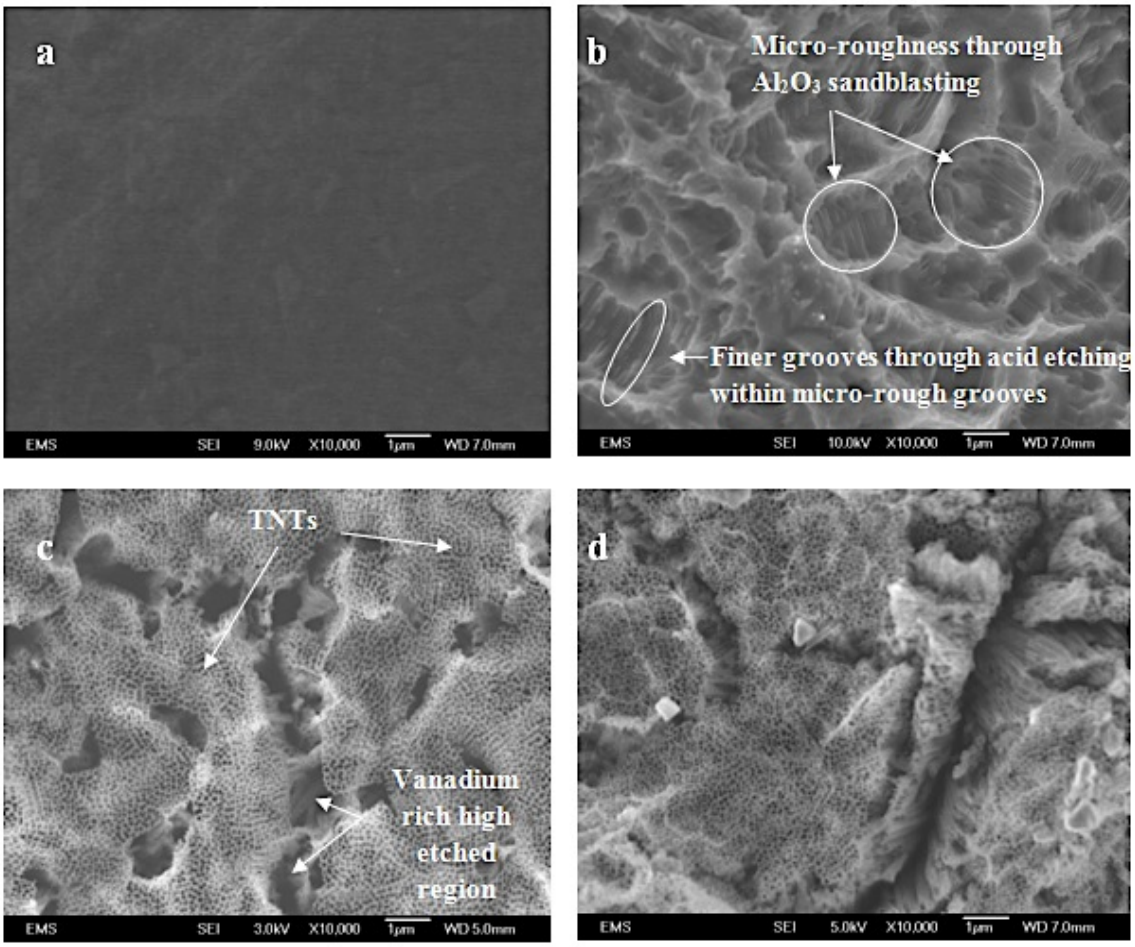

Figure S1. FE-SEM images of Ti-6Al-4V samples before TO possessing different surface topographies with X10k magnification and 1 μm scale a) smooth, b) rough (sandblasted with Al_2O_3, and acid etched in H_2SO_4 and H_2O_2), c) anodized smooth, and d) anodized rough; Anodization was performed in a solution mixture of EG, NH_4F, and H_2O at 60 V for 4 hours.

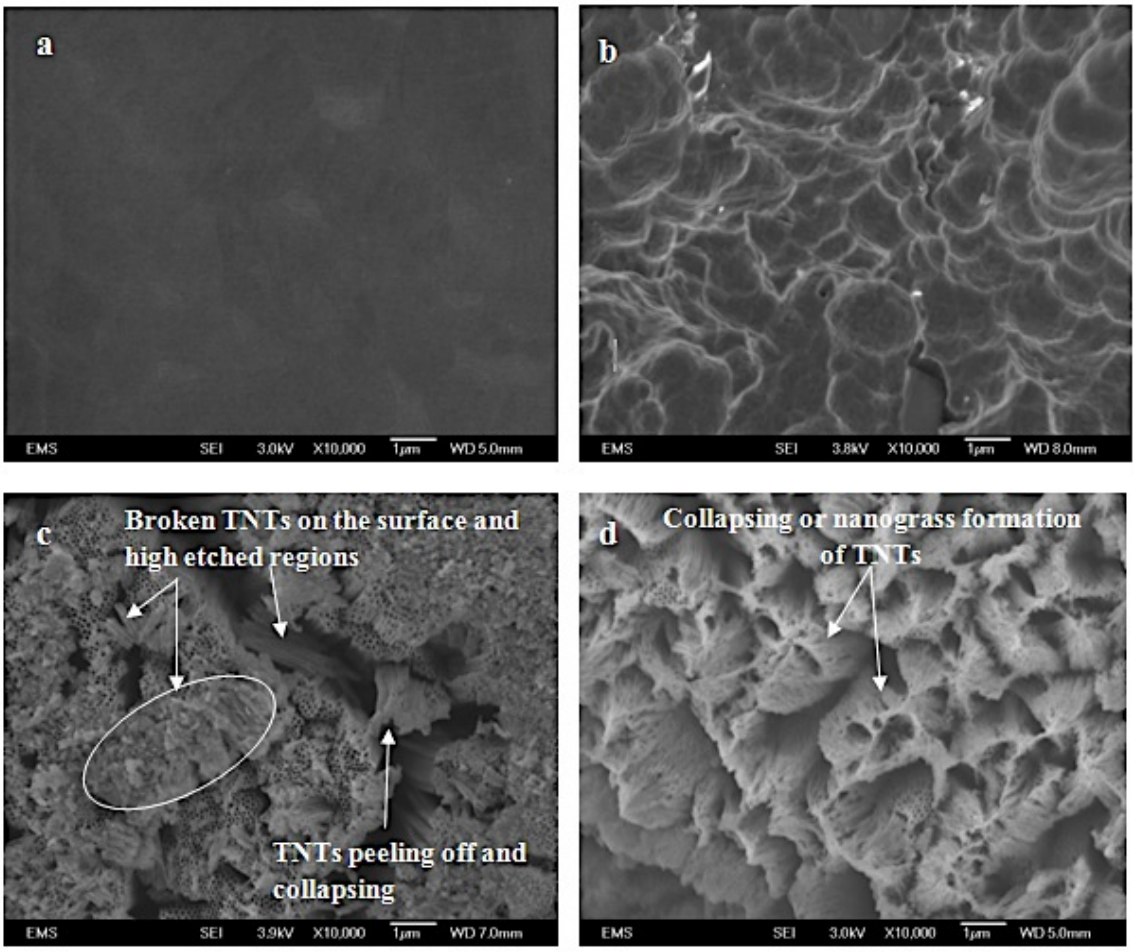

Figure S2. FE-SEM images of Ti-6Al-4V samples after TO (450 °C, 3 hours) possessing different surface topographies with X10k magnification and 1 μm scale a) smooth, b) rough sample, c) anodized smooth, and d) anodized rough; Rough and anodized samples were prepared using same condition as that in Figure S1.

2. Surface composition of rough and anodized-rough Ti-6Al-4V samples

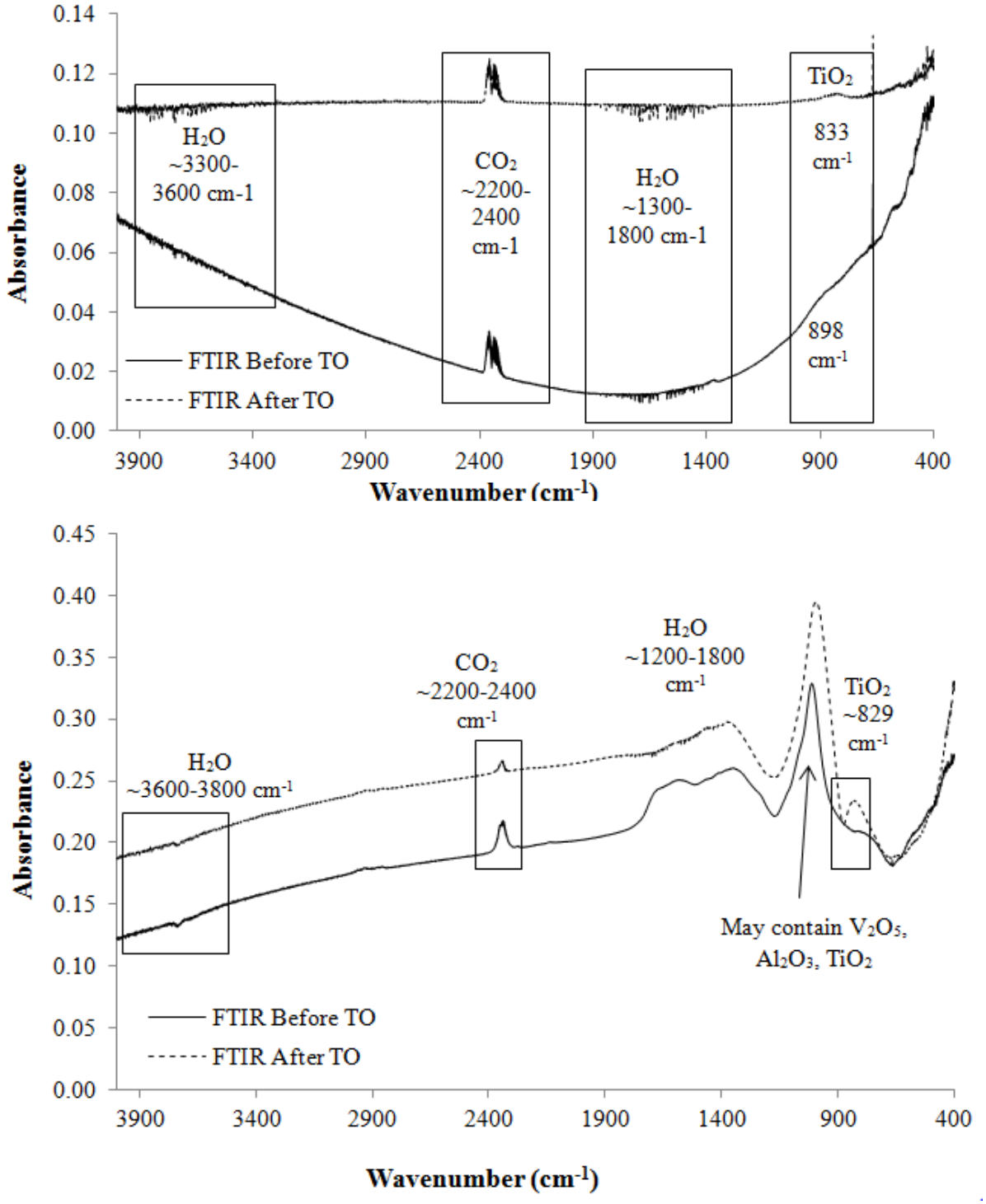

Figure S3. FTIR spectra of rough (a) and anodized-rough (b) Ti-6Al-4V samples before (solid line) and after (dashed line) thermal oxidation at 450 °C for 3 hrs.

3. Surface TiO_2 crystallinity of smooth Ti-6Al-4V samples

Ti-6Al-4V samples were first polished and then were divided into three groups: control, 450 °C and 600 °C heat-treated samples for 3 hours (step by step procedure is provided in the experimental section of manuscript). To investigate the surface crystallinity of TiO_2 formed from thermal oxidation, grazing incidence X-ray diffraction (GIXRD) was performed (details are provided in the revised manuscript).

Figure 4S shows the GIXRD spectrum of control, 450 °C and 600 °C heat-treated samples along with the PDF#'s for titanium, anatase and rutile. It is observed that i) the rutile peaks at 2-theta of 27.447 (110) and 54.323 (211) appear for Ti-6Al-4V 600 °C heat-treated samples, and ii) the rutile peak intensities at 2-theta of 36.086 (101), 39.187 (200), and 62.742 (002) increase for 600 °C heat-treated samples when compared to 450 °C heat-treated samples, indicating crystallization of TiO_2 to rutile. Previously, E. Gemelli *et al.* performed XRD on heat-treated Ti-6Al-4V samples at temperatures ranging from 400-800 °C for much longer durations than thiat used in this study, that is 48 hours. No anatase peak at 2-theta of 25.303 (1 0 1) was observed for 400 °C treated samples; however, similar to this study, there was a peak observed at about 2-theta of about 38.1, which indicates the presence of anatase TiO_2. [1] Additionally, H. Guleryuz *et al.* investigated similar behavior of heat-treated Ti-6Al-4V samples at 600 °C for much longer duration than the one used in here, that is for 12 and 48 hours. A relatively low intensity was observed at 2-theta of 25.303 (1 0 1) for anatase and 27.447 (110) for rutile even after 12 hours of heat-treatment. [2] The above mentioned studies corroborate the GIXRD analysis performed in this study, which indicates the presence of anatase from

the peak observed at 2-theta of 37.790 (0 0 4), albeit without a peak at 2-theta of 25.303 (1 0 1).

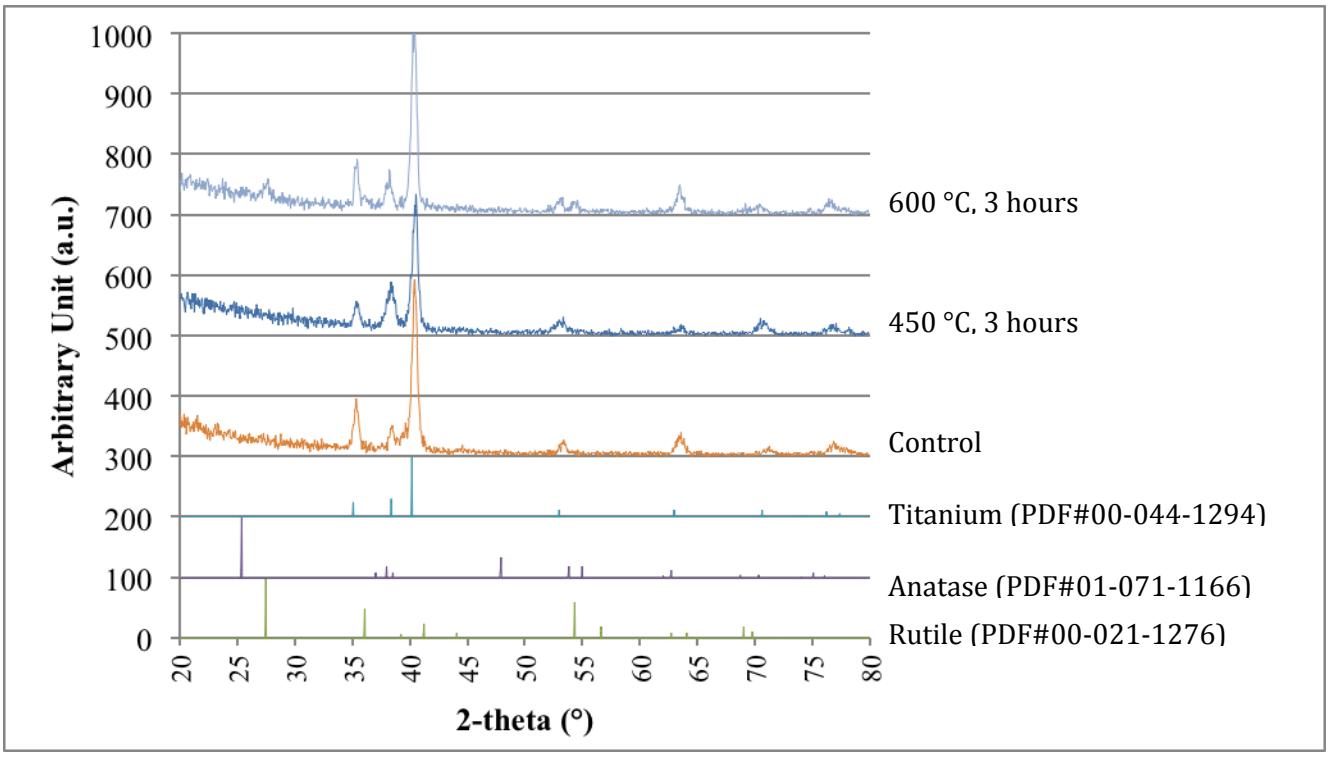

Figure S4: GIXRD spectra of Ti-6Al-4V for control (non-treated sample), 450 °C and 600 °C heat-treated samples for 3 hours in ambient environment. XRD baselines for titanium, anatase TiO_2, and rutile TiO_2 are also provided.

References

1. Gemelli, E. and N.H.A. Camargo, *Oxidation kinetics of commercially pure titanium.* Matéria (Rio de Janeiro), 2007. **12**: p. 525-531.
2. Guleryuz, H. and H. Cimenoglu, *Oxidation of Ti–6Al–4V alloy.* Journal of Alloys and Compounds, 2009. **472**(1–2): p. 241-246.