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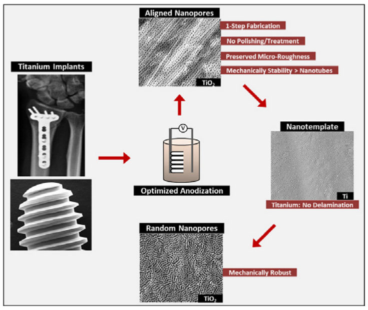
Bridging the gap: Optimized fabrication of robust titania nanostructures on complex implant geometries towards clinical translation

Tao Li [a,b,c], Karan Gulati [a,b,d,*], Na Wang [c], Zhenting Zhang [c], Sašo Ivanovski [a,b,d,*]

[a] School of Dentistry and Oral Health, Griffith University, Gold Coast, QLD, Australia
[b] Menzies Health Institute Queensland (MHIQ), Griffith University, Gold Coast, QLD, Australia
[c] Department of Prosthodontics, School of Stomatology, Capital Medical University, Beijing, People's Republic of China
[d] The University of Queensland, School of Dentistry, Herston, QLD 4006, Australia

GRAPHICAL ABSTRACT



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ABSTRACT

Electrochemically anodized titanium surfaces with titania nanostructures (TNS; nanopores, nanotubes, etc.) have been widely applied as therapeutic bone/dental implant modifications. Despite the numerous advancements in the field of electrochemical anodization (EA), in terms of translation into the current implant market, research gaps in this domain include the lack of fabrication optimization, performed on a substrate of conventional implant surface/geometry, and inadequate mechanical stability. In the current study, we investigate the role of substrate pre-treatment on achieving desired nanotopographies for the purpose of reproducing optimized nanostructures on the complex geometry of commercial implant surfaces, as well as in-depth mechanical stability testing of these nano-engineered coatings. The results confirmed that: (a) substrate polishing/smoothening may be insignificant with respect to fabrication of well-ordered and high quality TNS on micro-rough implants with preserved underlying micro-roughness; (b) optimized outcomes can be successfully translated onto complex geometries characteristic of the current implant market, including dental implant abutments and screws (also applicable to a wider implant market including orthopaedics); (c) mechanical stability testing revealed improved modulus and hardness values as compared to conventional nanotubes/pores. We believe that such optimization advances the existing knowledge of titanium anodization and anodized implants towards integration into the current implant market and successful clinical translation.

1. Introduction

Titanium is the ideal material choice for hard tissue fixation devices, such as orthopaedic and dental implants, due to

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* Corresponding authors at: The University of Queensland, School of Dentistry, Herston, QLD 4006, Australia

E-mail addresses: k.gulati@uq.edu.au (K. Gulati), s.ivanovski@uq.edu.au (S. Ivanovski).

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its corrosion resistance and favourable biocompatibility [1]. In order to augment implant surface bioactivity and promote both early integration and long-term success, Ti surfaces have been modified at the macro, micro and nanoscales. Indeed, this represents one of the major research foci in the domain of orthopaedic/dental implants over the past few decades [2]. Extensive research has been performed towards tailoring the surface chemistry and topography of current Ti implants at the micro-scale, in order to enhance bone apposition at the implant interface [3]. However, since cellular function is often dictated by the interaction with the extracellular matrix at the nanoscale level, recent research focus has shifted towards enhancing surface bioactivity using nano-scale features [4,5]. Among the various nano-engineering techniques used for Ti surface modification, electrochemical anodization (EA) stands out due to its ability to facilitate fabrication of self-organized TiO_2 nanostructures (TNS, nanotubes or nanopores) via a simple, cost-effective and tailorable approach [6].

Numerous *in vitro* and *in vivo* studies have established that TNS are capable of promoting osseointegration and soft-tissue integration, as well as imparting antimicrobial and immunomodulatory properties, compared with conventional macro- or micro-rough Ti orthopaedic/dental implants [7–9]. Furthermore, the hollow architecture of the pores/tubes allows for the loading and local release of various therapeutics directly within the bone microenvironment, in order to target adverse conditions such as infection, inflammation or poor integration [7–11]. Typically, the EA of the titanium surface is carried out in aqueous/organic electrolyte containing fluoride ions and water, by applying a constant voltage or current to the electrochemical cell [12]. By optimizing electrolyte composition (ageing, water/fluoride content, pH) and anodization conditions (voltage, current, time), high quality and mechanically stable TNS can be fabricated with high-aspect ratio and tuneable dimensions [13,14].

In clinical dentistry, micro-roughness is regarded as the current ‘gold standard’ surface for achieving enhanced osseointegration, hence its preservation may be beneficial when further augmenting bioactivity through nanoscale modification [8]. Despite our ability to influence the EA process through various optimizations, it is still questionable whether pre-treatments of Ti surfaces (polishing and multi-step anodization) play a role in improving the stability of TNS, especially on geometrically complex Ti surfaces characteristic of clinically utilized implants. Keeping all other parameters constant, in the current study, we focused on substrate preparation and its influence on the EA of micro-rough titanium, which represents a considerable portion of the commercial implant market.

Prior to EA, as-received titanium is often cleaned in order to remove surface-bound impurities. Furthermore, most EA is performed on smoothened Ti substrates, which enables improved ordering of TNS. Smoothening of the substrate is performed via chemical, mechanical and electro-polishing methods to remove surface artefacts, yielding a ‘flat-bed’ suitable for perpendicular growth of nanotubes/pores [15]. Although it has been shown that polishing results in mechanically stable anodic films, better ordering of tubes/pores and reduced surface defects, this does not necessarily apply for complex implant surface geometries [16]. In addition, nano-templated surfaces obtained by fabricating and removing the anodic film have gained much attention, and upon 2nd EA these can yield highly ordered nanostructures [17–18]. Interestingly, both surface polishing and two-step EA (anodize, remove, re-anodize) are routinely utilised for anodizing Ti (Fig. 1a), with applications ranging from therapeutic implants to solar cells and catalysis [13]. Indeed, the production of TNS for biological applications often involves polishing of the Ti substrate followed by a 2-step EA procedure, which can be detrimental towards preserving surface micro-roughness, as well as increasing overall costs (Fig. 1a).

For bone/dental implant applicability, the underlying implant macro- and micro-features are crucial for initial stability. Indeed, loss in active dimension due to polishing may compromise the initial implant fit and stability, which may lead to implant failure, especially in compromised conditions such as poor bone density [8]. Therefore, creating a dual topography with preserved existing micro-roughness and superimposed nanotubes/pores may be the ideal solution, as reported elsewhere [19]. Studies exploring such advanced hybrid structures often utilize multiple techniques (printing, patterning, etc.) followed by EA [20]. However, for clinical translation, it would be highly relevant to fabricate such ‘bioactive’ nano-scale features superimposed on a preserved micro-roughness typical of existing commercially utilized implants.

Planar titanium foil, which represents the most commonly researched substrate for applications involving biomedical titanium implants, represents an easy to manage surface. However, ‘real world’ commercially available implants are often curved with sharp edges (screws) and pins/wires/abutments (cylindrical), making nanoscale surface modification via EA far more complex. Complex geometries increase the chance of anodic film cracks and

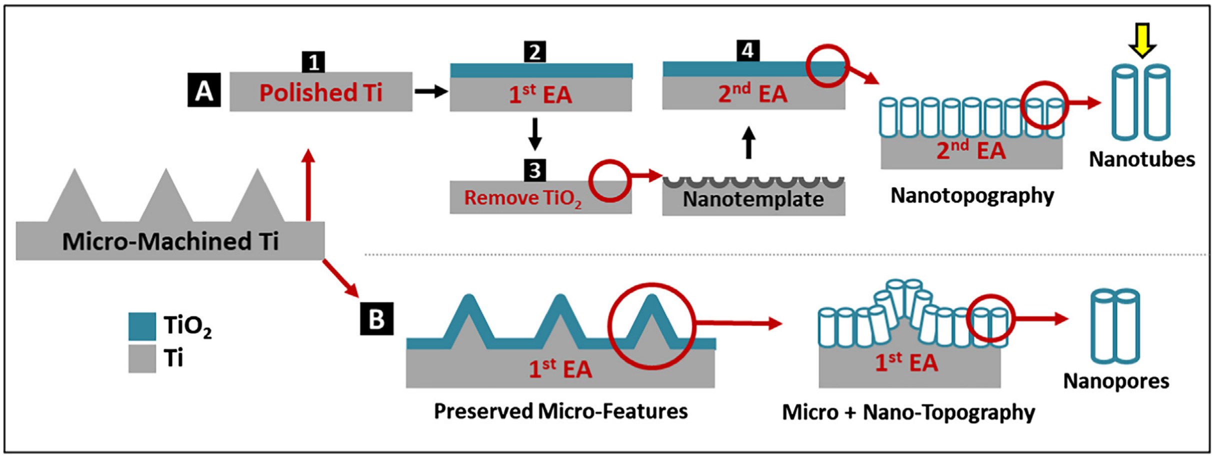

Fig. 1. Representation of the fabrication of nano-engineered Ti via electrochemical anodization (EA) on a micro-rough surface (images represent a cross-sectional view). (A) Conventional protocol: (1) polishing, (2) 1st EA, (3) removal of anodic film-nanotemplate, and (4) 2nd EA, yielding nanotubes which are more prone to damage/delamination due to space between individual tubes (yellow arrow). (B) Preserving underlying substrate micro-features and superimposing nanopores, via single step EA (under optimized conditions), yielding a dual micro-and nano-scale topography.