



RESEARCH ARTICLE

PLATINUM –COATED TITANIUM NANOTUBES -ENHANCING THE CORROSION RESISTANCE AND BIOMINERALIZATION

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ABSTRACT

Background: Titanium has long been the preferred material for oral rehabilitation due to its excellent mechanical properties and biocompatibility. However, despite its widespread clinical success, implant failures remain a significant concern, primarily due to peri-implant diseases. Studies indicate that over 56% of implants experience complications over time, highlighting the need for improved materials or treatment strategies. While surface modifications to enhance osseointegration by creating bioactive surfaces have shown promise, there remains a need to improve the antimicrobial properties of implant materials. This study explores a novel approach of coating platinum onto the titanium nanotube arrays leveraging its inherent antimicrobial properties, to enhance both biological performance and corrosion resistance.

Materials and Methods: Titanium surfaces were anodized to fabricate platinum-doped TNA on titanium alloys, aimed at promoting bioactivity and improving osseointegration. Platinum, known for its antimicrobial and antioxidant properties, was sputtered onto the nanotubes to further support healing and reduce microbial colonization. Surface morphology was analyzed using scanning electron microscopy (SEM), and electrochemical tests were conducted to assess corrosion resistance. Biom mineralization potential was evaluated by immersing the samples in Dulbecco's Modified Eagle Medium (DMEM) with fetal bovine serum (FBS) for seven days. ATR-IR spectroscopy was used to confirm the formation of biomimetic structures.

Results: SEM images revealed uniformly aligned platinum-doped nanotubes with partial coverage by platinum nanospheres. Corrosion resistance tests demonstrated enhanced stability of the platinum-coated TNA. Immersion studies showed a flower-like biomimetic morphology resembling water lettuce, confirmed by ATR-IR spectroscopy to be formed by proteins and calcium phosphate molecules.

Conclusion: In conclusion, platinum-coated titanium nanotube arrays (TNA) enhance antimicrobial properties and corrosion resistance, improving implant performance. This innovative approach offers potential for reduced microbial colonization and better osseointegration, providing a promising solution to reduce implant failures and improve long-term outcomes in oral rehabilitation. Further clinical research is needed.

Keywords: Titanium Nanotube, Platinum, Corrosion Resistance, Periimplant Diseases

INTRODUCTION

Titanium has become the cornerstone material for

oral rehabilitation due to its remarkable biocompatibility, mechanical strength, and corrosion resistance. Its widespread application in dental and

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orthopedic implants has been driven by its ability to integrate with bone tissue effectively, a process termed osseointegration. Despite these advantages, the long-term success of titanium implants is often compromised by peri-implant diseases, which include peri-implant mucositis and peri-implantitis. These conditions, characterized by inflammation and bone loss, remain a significant challenge in implantology.¹ Addressing this issue necessitates innovative approaches to enhance both the bioactivity and antimicrobial properties of implant surfaces.

Surface modification techniques, such as anodization techniques have been extensively studied to improve osseointegration. Anodized titanium nanotube arrays (TNA) have garnered considerable interest due to their unique ability to mimic natural bone structure and provide a favorable environment for cell attachment and proliferation.² These nanostructures not only promote osteogenesis but also offer opportunities for incorporating antibacterial agents, addressing a critical limitation of conventional titanium implants.

Recent advancements have focused on incorporating antimicrobial elements such as silver, zinc, and copper into titanium nanotube arrays (TNA) to prevent bacterial colonization.^{3,4} However, these materials often present challenges, including cytotoxicity and limited long-term efficacy.⁵ Unlike silver-based coatings, which raise concerns over bacterial resistance, platinum (Pt) offers a unique antibacterial mechanism that does not rely on ion release. Platinum, a noble metal known for its biocompatibility, antimicrobial properties, and antioxidant activity, has emerged as a promising candidate for implant surface modification. Its catalytic activity promotes the generation of reactive oxygen species (ROS), such as superoxide radicals and hydrogen peroxide, which induce oxidative stress in bacterial cells, damaging essential biomolecules and leading to cell death. Furthermore, Pt-coated surfaces modify surface charge and wettability, reducing bacterial adhesion and biofilm formation.⁶ These attributes make Pt an ideal choice for next-generation implant coatings, ensuring long-lasting antibacterial efficacy without concerns over ion release or cytotoxicity.

The present study investigates a novel approach of doping TNA with platinum to develop a multifunctional implant surface. By combining the osteogenic potential of TNA with the antimicrobial efficacy of platinum, this strategy aims to address the dual challenges of bacterial infections and peri-

implant diseases. The incorporation of platinum through sputtering not only enhances antimicrobial properties but also improves corrosion resistance, a critical factor for the longevity of titanium implants in the oral environment.

To assess the effectiveness of this approach, platinum-doped TNA surfaces were analyzed using scanning electron microscopy (SEM) to examine surface morphology and subjected to electrochemical testing to evaluate corrosion resistance. Biomineralization studies were conducted by immersing the samples in Dulbecco's Modified Eagle Medium (DMEM) with fetal bovine serum (FBS), providing insights into their bioactivity. Additionally, ATR-IR spectroscopy was used to confirm the formation of biomimetic structures. This study builds upon previous research demonstrating the potential of nanostructured titanium surfaces for enhanced osseointegration, while addressing the critical need for antimicrobial functionality.⁷ By harnessing the unique properties of platinum, this surface modification presents a promising strategy to reduce implant failures and enhance the clinical success of titanium-based oral rehabilitation. Further investigations could lead to the development of next-generation implant materials with improved biological integration, mechanical performance, and long-term durability.

MATERIALS AND METHODS

Sample Preparation

A 2 mm thick commercially pure titanium (Cp-Ti) sheet was obtained from M/s Uniforce Engineers, Chennai, India. The sheet was mechanically cut into 15 mm × 20 mm × 2 mm samples. To prepare the surface for electrochemical anodization, the samples were ground using silicon carbide paper with varying grit sizes. Ultrasonic cleaning was then performed using acetone and double-distilled water to remove surface contaminants. Following a previously reported method, the cleaned samples were etched using Kroll's reagent (a mixture of 7.5 mL water, 1.5 mL concentrated sulfuric acid, and 1.5 mL hydrofluoric acid) for 10 seconds. The etched samples were then rinsed thoroughly with double-distilled water and left to air-dry at room temperature before further processing.⁸

Electrochemical anodization was performed at room temperature using an electrolyte solution of 0.5 M sodium fluoride and 1 M orthophosphoric acid. A cleaned Cp-Ti sample functioned as the anode, while platinum served as the cathode in a two-electrode electrochemical setup. The process was conducted

under a constant voltage of 30 V for 90 minutes to facilitate nanotube formation. Following anodization, the sample was rinsed thoroughly with double-distilled water and air-dried at room temperature. To improve nanotube stability, the samples were sintered at 400°C for 3 hours, enabling the formation of the anatase phase. Finally, a thin platinum layer was sputtered onto the TNA surface for 45 seconds at 20 mA using a JEC-3000FC Auto Fine Coater.⁹

The surface topography of the platinum-sputtered TNA (Pt-TNA) samples was analyzed using a scanning electron microscope (SEM, JOEL-JSM-IT800), equipped with energy-dispersive X-ray spectroscopy (EDS, Oxford Instruments) for elemental composition analysis.¹⁰ Additionally, the functional groups present on the Pt-TNA surfaces were identified using Attenuated Total Reflectance-Infrared Spectroscopy (ATR-IR, Spectrum Two). Electrochemical corrosion behavior was assessed using electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization analyses, conducted on a CHI 730E electrochemical workstation. A three-electrode electrochemical setup was used, consisting of a saturated calomel electrode (SCE) as the reference electrode, a graphite rod as the counter electrode, and the sample as the working electrode. Corrosion studies were performed in simulated body fluid (SBF) solution, following our previous methodology. To stabilize the open circuit potential (OCP), the sample was immersed in SBF for 1 hour before testing.

For EIS analysis, a 10 mV sinusoidal voltage was applied within a frequency range of 0.01 Hz to 100 kHz, with results represented using Nyquist and Bode plots. Data fitting and equivalent circuit modeling were conducted using ZSimpwin software (Princeton Applied Research, USA). Potentiodynamic polarization studies were performed over a ± 250 mV potential range, recorded against SCE at a scan rate of 1 mV/s. The corrosion potential (E_{corr}) and corrosion current density (i_{corr}) were derived from the polarization curves, with the Stern-Geary equation used to calculate the corrosion current density.¹¹

RESULTS

The surface topography and elemental constituents of TNA and Pt-TNA are provided in Figure 1. The anodized surface exhibits consistently aligned vertical nanotubes. At higher magnification, the nanotubes appear to fuse together, forming a uniform structure. The resulting EDX profile of TNA (Figure 1b) confirms the presence of Ti, O, and P. The incorporation of phosphate ions in the nanotubes

is beneficial for the bone mineralization process. In contrast, Pt-TNTA (Figure 1c) displays a uniform distribution of platinum deposits on the TNA surface. The rim of the nanotubes remains visible, with partial coverage of sputtered Pt (Figure 1d). Despite Pt deposition, the nanotubular structures retain their integrity, indicating that the sputtering process does not significantly alter their morphology.²

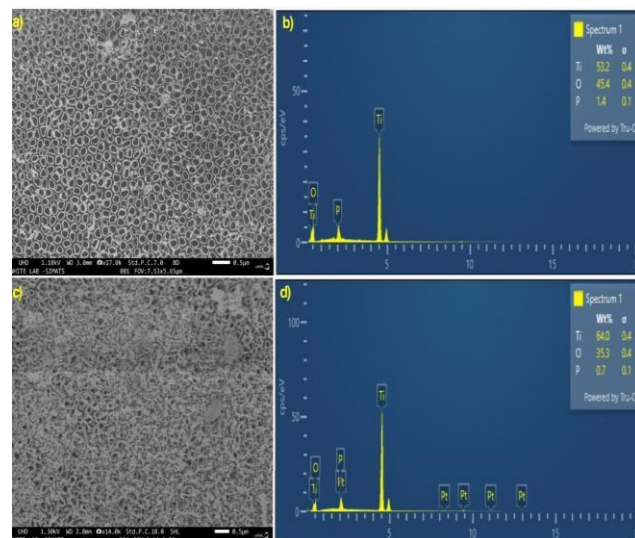


Figure 1. Surface Morphology and Elemental Analysis of Titanium Nanotubes and Platinum Sputtered Titanium Nanotubes

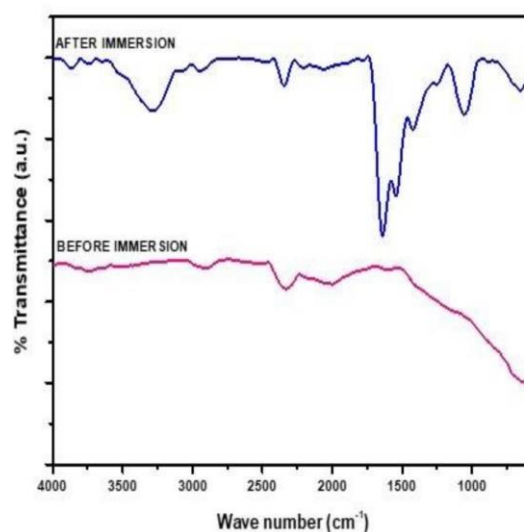


Figure 2. FTIR Analysis of Surface Modifications Before and After Immersion

The FTIR spectrum presented in the image compares the material before and after immersion in a specific solution. The x-axis represents the wavenumber (cm^{-1}), indicating the vibrational frequencies of molecular bonds, while the y-axis represents the percentage transmittance, showing how much

infrared light passes through the sample. Before immersion, the pink curve appears relatively featureless, suggesting a minimal presence of functional groups absorbing IR radiation. However, after immersion, the blue curve exhibits significant peaks, particularly in the range of 1600 cm^{-1} to 1000 cm^{-1} .¹³ These peaks likely correspond to phosphate (PO_4^{3-}) or carbonate (CO_3^{2-}) groups, which are commonly associated with biomineralization. The observed spectral changes indicate surface modifications or the deposition of biomolecules and minerals after immersion. This suggests that the material undergoes chemical transformations, potentially forming a bioactive or mineralized layer, which could be beneficial for biomedical applications such as bone integration or bio-coatings.

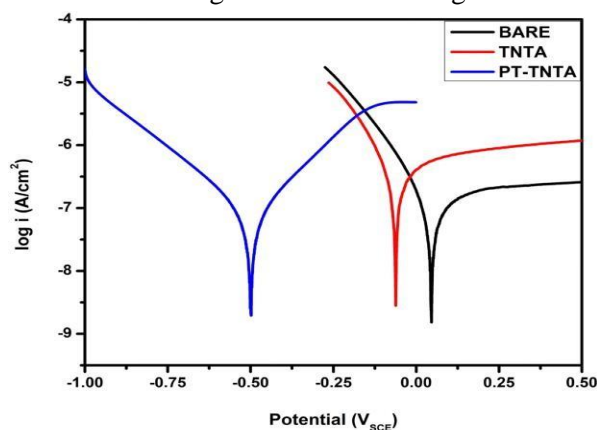


Figure 3. Polarization curves for Bare Titanium, Titanium Nanotube and Platinum Nanotube

The polarization curves in the image illustrate the electrochemical behavior and corrosion resistance of three different surfaces: bare (black), TNA (red), and Pt-TNA (blue). The bare surface exhibits the most negative corrosion potential (E_{corr}) and the highest corrosion current density (i_{corr}), indicating greater susceptibility to corrosion. In contrast, the TNA and Pt-TNA curves shift towards more positive potentials, demonstrating enhanced corrosion resistance due to the formation of a protective nanotubular oxide layer. The Pt-TNA surface shows the lowest i_{corr} , signifying the best corrosion protection among the three. The shift in the anodic branch of the Pt-TNA curve further suggests improved electrochemical stability, likely due to the catalytic and passivating effects of platinum. Overall, the results indicate that TNA enhances corrosion resistance compared to bare titanium, while Pt-TNA provides the highest level of protection, making it a promising material for biomedical and electrochemical applications.¹⁴

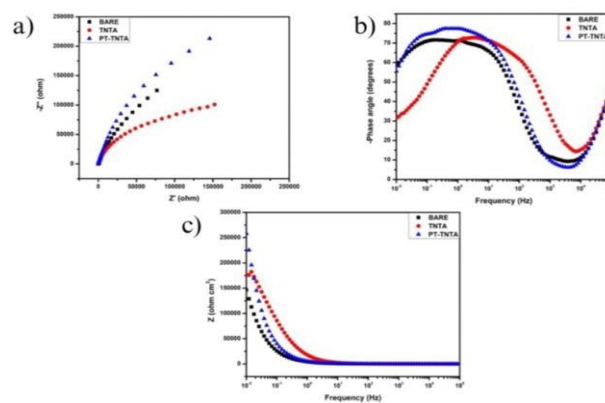


Figure 4. Electrochemical impedance spectroscopy (EIS) analysis of BARE, TNTA, and PT-TNTA samples: (a) Nyquist plot, (b) Bode phase angle plot, and (c) Bode magnitude plot.

Figure 4 presents three electrochemical impedance spectroscopy (EIS) plots—(a) Nyquist, (b) Bode phase, and (c) Bode magnitude—comparing the electrochemical behavior of BARE (black squares), TNA (red circles), and PT-TNA (blue triangles) samples. The Nyquist plot (a) depicts the real (Z') and imaginary (Z'') impedance components, showing the highest impedance for PT-TNA, followed by BARE and TNA, indicating increased charge transfer resistance and improved corrosion resistance. The Bode phase plot (b) illustrates the phase angle versus frequency, with PT-TNA exhibiting the highest peak phase angle, suggesting enhanced capacitive behavior. The Bode magnitude plot (c) demonstrates impedance variation across frequencies, where PT-TNA maintains the highest impedance at low frequencies, indicating superior barrier properties. Overall, the PT-TNA modification enhances electrochemical performance, likely improving corrosion resistance and surface stability.¹⁵

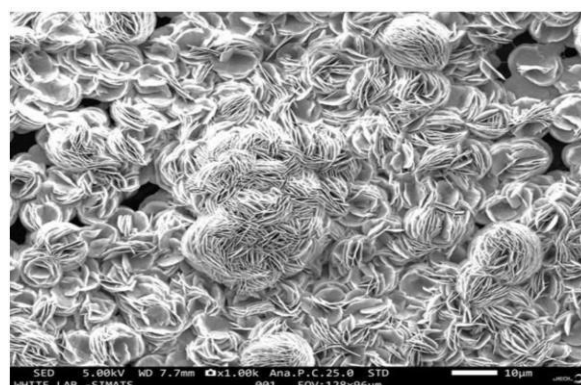


Figure 5. SEM Image of Pt-TNA Surface Morphology After 7 Days of Immersion in DMEM and FBS Solution

The Figure 5 illustrates a SEM micrograph of Pt-TNTA after immersion for 7 days in DMEM and FBS solution, captured at 1000× magnification with a 10 μm scale bar. The image reveals nanoplatelet-like apatite structures that have merged to form a distinct flower-like morphology. This hierarchical architecture suggests the progressive precipitation of calcium phosphate compounds, along with amino acids and proteins, resulting in structurally ordered apatite formation. The incorporation of phosphate within the nanotubes facilitated strong conjugation with calcium ions from the DMEM and FBS solution, leading to the development of biologically active apatite complexes integrated with amino acids and proteins. This surface transformation indicates enhanced bioactivity, potentially beneficial for biomedical applications.¹⁶

DISCUSSION

The proposed platinum-doped titanium nanotube array (TNA) structure offers adaptive features crucial for enhancing cell interactions with implant materials. Its vertically aligned nanotube topography provides a significantly larger surface area compared to flat titanium surfaces, a feature that has been shown to address limitations of current clinical implants.¹⁷ This enhanced surface area creates additional sites for cell interaction, particularly at the extracellular matrix level, and may mimic the pore size of natural bone, which is essential for bone cell response.^{18,19} Moreover, the bioactive layer formed by inward growth TiO₂ nanotubes demonstrates improved adherence to the titanium metal, addressing challenges associated with weak interfacial bonding observed in existing ceramic coatings.^{20,21} The increased surface energy of these nanostructures promotes interactions with proteins like vitronectin and fibronectin, which are critical for specific cell adhesion and improved osseointegration.^{22,23}

Additionally, the platinum coating not only enhances the biomineralization potential but also provides antimicrobial and antioxidant properties, further supporting the healing process and reducing microbial colonization. Yu et al.²⁴ demonstrated that anatase TNA optimally supports cell adhesion, proliferation, and differentiation while reducing inflammatory responses.²⁵ In addition to the above TNA-modified implant surface, we have sputtered it with a noble metal such as platinum.

Hence, this study presents compelling evidence in favor of using platinum as a monometallic coating for implants, in contrast to conventional bimetallic or alloy-based coatings.

Platinum, as a noble metal, possesses unique chemical and electrochemical properties that contribute to its superior biocompatibility, corrosion resistance, and antibacterial potential. One of the key advantages of platinum is its exceptional chemical inertness, which prevents undesirable interactions with biological tissues and bodily fluids, ensuring long-term stability and reducing the risk of adverse immune responses. This property is shared among noble metals such as gold and silver, but platinum's superior corrosion resistance further enhances its suitability for biomedical applications.²⁶ Unlike other metals, platinum does not readily oxidize or degrade, even in aggressive physiological environments, thereby maintaining the structural integrity of the implant over extended periods.^{27,28}

Electrochemically, a monometallic platinum coating eliminates the presence of a galvanic pair, thereby preventing the preferential oxidation of a more reactive metal. While bimetallic coatings can facilitate controlled ion release, they also introduce the risk of accelerated degradation of the less noble component due to galvanic coupling.^{29,30}

This effect is particularly pronounced in silver-based systems, where the presence of platinum enhances silver ion release, improving antibacterial efficacy but potentially shortening implant longevity.³¹ By utilizing pure platinum, these degradation risks are avoided while maintaining its inherent antibacterial properties and biocompatibility. Additionally, concerns regarding unintended inflammatory reactions or unpredictable biological responses from alloying elements are minimized.

Although bimetallic nanoparticles and coatings have garnered interest for their synergistic antibacterial effects, the potential for bacterial resistance to monometallic nanoparticles—especially silver—remains a concern. While Ag-Pt and Au-Pt bimetallic systems have demonstrated improved antimicrobial performance, monometallic platinum coatings offer a stable, long-term alternative without the complications of silver ion release or the risk of bacterial resistance development.³²

Furthermore, platinum coatings eliminate uncertainties related to compositional variations and structural inconsistencies, which can influence the biological response of bimetallic systems.^{33,34} While the present study demonstrates the potential of platinum-coated titanium nanotube arrays (TNA) as surface modification in improving antimicrobial

properties and corrosion resistance, limitations include the need for long-term clinical validation and potential cost implications. Future research should explore the biological interactions of platinum coatings over extended periods and optimize deposition techniques for uniform coverage. Additionally, *in vivo* studies are essential to confirm the long-term stability, osseointegration efficiency, and resistance to peri-implant diseases in real-world applications.

CONCLUSION

In conclusion, platinum-coated titanium nanotube arrays (TNA) surface modification shows significant promise for enhancing both antimicrobial properties and corrosion resistance, addressing key challenges in oral implantology. The incorporation of platinum improves the biological performance of titanium implants, offering potential for reduced microbial colonization and enhanced osseointegration. The findings suggest that platinum-coated TNA could provide a viable solution to reduce implant failures and improve long-term outcomes in oral rehabilitation, warranting further research and

clinical exploration.

Declarations

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Conflict of Interest

The author declares that he has no conflict

Ethical Approval

Not Applicable

Informed Consent

Not Applicable

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