

# Defect-Engineered TiO<sub>2</sub> for Coupling Biofunction and Electrochemical Stability

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Among metallic biomaterials, titanium exhibits exceptional ability to integrate stably with living tissues, owing to the unique physicochemical nature of its surface.<sup>1,2</sup> Its passive oxide film governs interfacial chemistry and plays a determinative role in biofunctionality. From an electrochemical perspective, titanium oxide (TiO<sub>2</sub>) acts as an *n*-type semiconductor. However, the relationship between the biofunctionality of the passive TiO<sub>2</sub> film and its semiconducting properties remains underexplored.

Recent photoelectrochemical investigations<sup>3</sup> have revealed that the semiconducting properties of the passive film change dynamically in various electrolytes. This film has been proposed to underpin the unique biofunctionality of titanium. These findings imply that conventional surface treatments, including anodization, acid etching, and hydrothermal oxidation,<sup>4</sup> may influence biological responses by modifying the *n*-type semiconducting behavior of the titanium oxide film. Most treatment methods introduce extrinsic dopants and leave residual chemical species on the surface. The incorporation of such impurities can alter the intrinsic relationship between the semiconducting properties of the passive film and its biological function.

To address this issue, self-doped TiO<sub>2</sub> was fabricated on titanium via hydrothermal oxidation in hydrogen peroxide. This additive-free approach enabled the intrinsic effects of semiconducting behavior to be studied independently. Thin-film X-ray diffraction and Raman microspectroscopy identified partial reduction of Ti<sup>4+</sup> to Ti<sup>3+</sup>, consistent with the formation of oxygen-deficient states characteristic of *n*-type semiconductors. Treatment conditions were varied to control the defect level.

Moderate treatment produced a pronounced *n*-type character while preserving electrochemical passivity, whereas prolonged treatment yielded thicker, cracked films with reduced semiconducting response. The modified surfaces exhibited antibacterial activities against *Porphyromonas gingivalis* and *Aggregatibacter actinomycetemcomitans* and promoted in vitro osteogenic functions, including upregulation of the redox-responsive genes *Hic-5* and *Sod2*. These results demonstrate that defect-mediated *n*-type semiconducting properties are closely linked to biofunctionality, and that tuning self-doping to moderate levels is the key for co-optimizing the biological performance and corrosion resistance of titanium.<sup>5</sup>

## References:

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