

A Novel Two-step Electrochemical Approach for the Complete Filling of Cu₂O into TiO₂ Nanotube Arrays as An Anti-fouling Titanium Surface

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Abstract Titanium has great potential for application in the marine engineering due to its corrosion resistance, low density, and chemical stability, but titanium is also prone to suffer from marine biofouling, thus limiting its further development. Completely filling the interior of TiO₂ nanotube arrays, generated by electrochemical anodizing on the titanium surface, with Cu₂O, a biocide widely used in anti-fouling coatings, seems to be a promising approach for developing a novel biocidal anti-fouling titanium surface. The tubular structure of TiO₂ nanotube arrays not only loads a large amount of Cu₂O but also slows down its release rate in the marine environment. Herein, we devised an innovative and simple two-step electrochemical approach to completely fill TiO₂ nanotube arrays with Cu₂O. This approach involves a precise cathodic polarization to selectively enhance the bottom conductivity of TiO₂ nanotube arrays, followed by an optimized pulsed deposition to fill Cu₂O. EIS and Mott-Schottky plots results showed that after cathodic polarization of TiO₂ nanotube arrays at -1.7 V (vs.SCE) for 60 s in 1 mol/L (NH₄)₂SO₄ aqueous solution, the charge transfer resistance R_{bl} of the inner barrier layer decreased by two orders of magnitude, while the charge transfer resistance R_{nt} of the outer nanotube layer remained unchanged, and the carrier density increased by four orders of magnitude. The selective enhancement of the bottom conductivity of TiO₂ nanotube arrays resulted in the nucleation of Cu₂O at the bottom and growth along the bottom-to-top direction during pulse deposition. Laboratory anti-adhesion experiments demonstrated that the completely filling of Cu₂O into TiO₂ nanotube arrays showed remarkable effectiveness against marine bacteria ((99.51 ± 0.17) % for Bacillus sp.), marine diatoms ((99.60 ± 0.13) % for P. tricornutum), and barnacles ((100 ± 0) %). Furthermore, the completely filling of Cu₂O into TiO₂ nanotube arrays also exhibited a durable resistance to P. tricornutum adhesion for up to 49 days ((99.52 ± 0.15) %) in the laboratory and prevented barnacle settlement for 20 days in the marine environment. This preparation method of the complete filling of Cu₂O into TiO₂ nanotube arrays offers a promising and reliable strategy to address the marine biofouling problem of titanium.

Keywords titanium; TiO₂ nanotube arrays; Cu₂O; completely filling; anti-fouling performance