

Bioactive Titanate Nanostructures Fabricated by  
Hydrothermal-Assisted Anodization

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In recent years, titanate nanomaterials have drawn much attention because of their widespread applications in, for example, dye-sensitized solar cells, photocatalysts, lithium ion batteries, and bone implants. Pertaining to bone implants, the formation of nano structured titania and titanate layers on titanium are promising to improve the bioactivity and biocompatibility of titanium. Many synthetic methods to fabricate titania and titanate nanostructures have been investigated such as sol-gel method, hydrothermal method, chemical vapor deposition, electrodeposition, and anodization. Hydrothermal method (HT) and anodization possess advantages over other methods because they are simple and cost-effective and can be used for mass production of titania/titanate-based nanostructures.

Highly crystalline titania/titanate nanostructures can be prepared by HT because the dissolution-recrystallization mechanism of HT is effective to grow nanocrystals. Although the HT method can easily produce highly crystalline nanostructures, the growth rate of the nanostructures is low. Alternatively, anodization can be used to fabricate self-organized titania nanostructures with higher growth rate than the HT method. However, titania nanotubes prepared by anodization are amorphous; high-temperature annealing is required to increase their crystallinity.

Herein, we combined the HT with conventional anodization to overcome these problems. Figure 1 shows the experimental equipment for hydrothermal-assisted anodization. In this research, one-step hydrothermal anodization (HTA)<sup>1</sup> and two-step anodization hydrothermal treatment (AHT)<sup>2</sup> were proposed to synthesize bioactive titanate nanostructures. In HTA, rapid formation of highly crystalline nanostructures was realized by combining the advantages of hydrothermal treatment and anodization. Multiple reactions including recrystallization/dissolution and electric field-enhanced oxidation/dissolution result in HTA providing wide working windows for both anodic oxidation and dissolution of titanium. The effects of reaction temperature, applied current, and electrolyte concentration were studied. Crystalline sodium titanate nanowires [Figure 2 (a)] with an average length of 1.0  $\mu\text{m}$  were synthesized at a growth rate of 500  $\text{nm h}^{-1}$ , and a titanium surface with a roughness of ca. 1.5 nm was obtained by HTA. Immersion of the nanowires in simulated body fluid to examine their bioactivity shows that porous nanoflakes of crystalline hydroxyapatite were deposited after 1 week.

In AHT, crystalline calcium titanate nanobricks [Figure 2 (b)] of width 45–75 nm and length 125–275 nm were prepared by treating regular anodized titania nanotubes in HT environment for 12 h. Calcium titanate nanobricks also shows excellent hydroxyapatite forming

ability. We consider that these hydrothermal-assisted anodization methods will provide general approaches to synthesize morphology/phase-controllable titanate nanostructures, which promote the investigation on the anodization process in the field of electrochemistry.

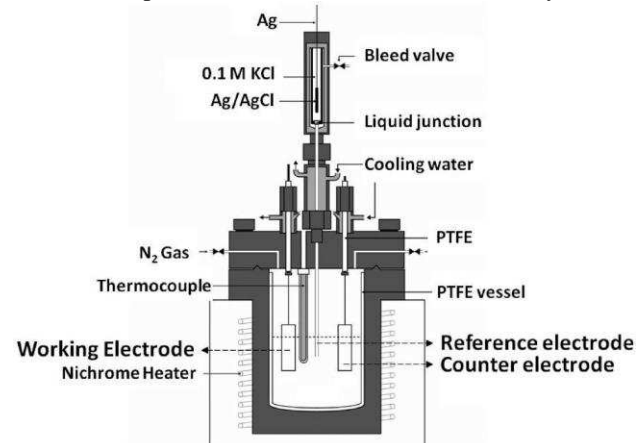


Figure 1. Schematic diagram of the experimental equipment used for hydrothermal-assisted anodization.

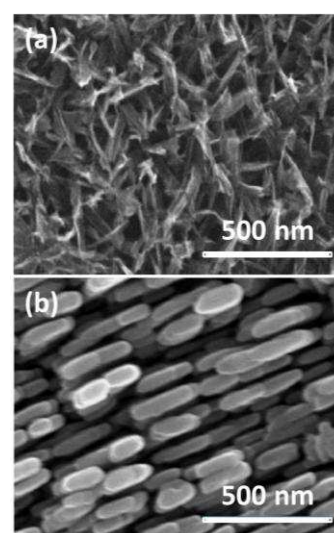


Figure 2. (a) SEM image of sodium titanate nanowires fabricated by one-step HTA at 150 °C for 2 h in 5 M NaOH electrolyte with an applied current of 5.0  $\text{mA cm}^{-2}$  and (b) SEM image of brick-like calcium titanate nanostructures prepared by immersing the aligned titania nanotubes array in saturated  $\text{Ca}(\text{OH})_2$  solution at 150 °C for 12 h.

Reference

1. J. Phys. Chem. C, 2012, 116 (14), pp. 8054–8062.
2. Electrochemistry Communications, 2012, 22, pp. 101–104.