A review on TiO$_2$ nanotube arrays: Fabrication, properties, and sensing applications

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Fabrication, properties, and sensing applications of TiO$_2$ nanotubes have been reviewed, and the highly ordered TiO$_2$ nanotube arrays made by anodic oxidation in fluoride-contained electrolytes highlighted. The effect of anodization parameters (electrolyte, pH, and voltage) on the titania nanotube size and shape were discussed. The excellent biocompatibility of TiO$_2$, the high orientation, the large surface area with tunable pore sizes, as well as the high electron transfer rate along with the nanotubes make TiO$_2$ nanotube array an ideal substrate for the sensor’s fabrication and application. The sensors based on the TiO$_2$ nanotube arrays for sensing hydrogen, oxygen, humidity, glucose and hydrogen peroxide all exhibited low detection limit, high stability, very good reproducibility and high sensitivity.

Nanostructural titania is one of the most widely studied materials due to its unique and excellent properties in optics, electronics, photochemistry and biology, as well as its applications in photovoltaic cells, photocatalysis, and sensors [1–3]. Among the various forms of nanostructural titania, nanotubular titania has attracted increasing interest due to its highly ordered structure and the convenient controlling of the size. Reviews have been given on the fabrication, properties, and applications of titania nanotubes in solar cells [4–6]. It is known that the sensors are increasingly demanded in medicinal, industrial, environmental applications. Sufficient sensitivity, high stability, short response time and long length of life are all key factors for a sensor’s application in practice. Generally, the performance of the chemical sensors is optimized by improving the electric properties of the sensor through modifying or selecting more ideal substrates with excellent morphology. With the advent of nanotechnology, it has become evident that nano-scale architectural features of the functional materials applied in sensing can yield superior and unexpected electric behaviors. Recently, TiO$_2$ nanotube arrays fabricated by anodization were applied in the fabrication of gas sensors and biosensors [3]. The highly uniform morphology, unique orientated growing property, and large surface area with controllable pore sizes as well as the facile fabrication make the titania nanotube array a promising functional material for application in sensors. Furthermore, the photovoltaic property of TiO$_2$ under UV illumination makes the sensors self-clean the contamination, resulting in a long length of life. Consequently, in this review we focus on the recent developments in the fabrication, modification, and sensing application of the anodized titania nanotubes, which would open up new avenues for the development of sensors.

1 Fabrication and modification of anodic titania nanotube arrays

TiO$_2$ nanotubes have been fabricated by various methods, such as electrode reactions [7], hydrothermal or solvotherma-
Fabrication of titania nanotube arrays by anodization

Fabrication of titania nanotube arrays via anodic oxidation of titanium foil in a fluoride-based solution was first reported in 2001 by Mor G K and co-workers [4]. The anodization of titanium is generally conducted in a two-electrode electrochemical cell with a platinum foil as cathode at a constant potential ranged from 5V to 25 V in aqueous electrolyte (pH ≤5) containing F−. Acetic acid, HNO3, H3BO3, H3PO4, H2SO4 or HSO4−, and citric acid were used to adjust the acidity [4,11–13]. The diameter of the nanotube arrays ranges from 15 nm to 140 nm and the length ranges from 200 nm to 1000 nm. The anodization can be roughly divided into three stages as shown in Figure 1 [14]: (1) the electrochemical oxidation of titanium surface results in the formation of the initial TiO2 barrier layer, corresponding to the first current drop; (2) TiO2 is chemically etched by fluoride ions through the formation of TiF6−2 as shown in Figure 1(c)), resulting in nanotube formation that corresponds to the current increase; and (3) the growth of nanotubes corresponds to a slow current decrease. The nanotube growth is determined by the equilibrium between anodic oxidation and chemical dissolution. The anodic oxidation rate is determined by the anodic potential, while the chemical dissolution rate is determined by the electrolyte acidity and F− concentration [4]. Research conducted by Grimes group [4] has shown that only in a certain F− concentration range can nanotube arrays be formed: from 0.05 to 0.3 mol/L in acidic solution. The anodic potential at which nanotubes are formed is related to the F− concentration, and higher potentials require electrolytes with higher F− concentration.

The formation of nanotubes strongly depends on the chemical dissolubility of the electrolytes. In strongly acidic solutions (pH < 1), both the nanotube growth rate and dissolution rate are increased, the anodization time generally is about 0.5 h, increasing the duration results in a more uniform nanotubular structure both in shape and size with not much change in the length of less than 500 nm [4]. Increasing pH decreases the chemical dissolution rate, and apparently prolongs the time needed to reach equilibrium between the rate of nanotube growth and the dissolution rate. In weak acid electrolytes, the nanotube length appears to be time dependent. Consequently, 4.4-μm-long nanotube arrays were obtained at pH 4.5 [4]. In the absence of chemical dissolution, anodization would finally be terminated with growth of the barrier layer, and no nanotubes could be formed in alkaline solution [14]. Low pH results in the formation of short nanotubes with clean morphology, while high pH results in long nanotubes that suffer from unwanted precipitates.

In comparison to aqueous electrolytes, much longer titania nanotube arrays can be fabricated in polar organic electrolytes due to the low chemical dissolution rate resulting from the minimizing water content [4]. Illustrative organic solvents include ethylene glycol (EG) [10], formamide (FA) [15], N-methylformamide (NMF) [15], dimethyl sulfoxide (DMSO) [16] and acetic acid [17]. A typical organic electrolyte solution contains 1wt%–5wt% water and 0.25wt%–0.6 wt% NH4F [15]. Anodization of titanium foil at 35 V for 48 h in FA based electrolyte formed 70-μm-long nanotubes with an outer diameter of ~180 nm and wall-thickness of 24 nm, while anodization at 60 V for 17 h in EG solution containing 0.25% NH4F formed 134-μm-long nanotubes (hexagonal packing, out diameter 160 nm, wall thickness 25 nm) [15].

Studies show that the use of EG as a solvent exhibits an extremely high titania nanotube growth rate of up to 15 μm/h [18]. A 17 h anodization at 20, 40, 50, 60, and 65 V in a fresh EG solution containing 0.3 wt% NH4F and 2 vol% H2O formed nanotube arrays at length of 5, 30, 45, 165, and 106 μm, respectively, while the 21, 48, and 96 h anodization obtained 188, 289, and 360-μm-long nanotubes, respectively. The maximum long individual nanotube array fabricated so far is over 1000 μm through anodizing 1.0 mm thick Ti foil at 60 V for 216 h in EG solution containing 0.6 wt%