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Mini Review

Extending the Down Limit of Pore Size of Anodic TiO_2 Nanotube Arrays

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Abstract

Anodic TiO_2 nanotubes prepared by anodization of titanium metal substrates is one of the most investigated structures of TiO_2 due to their excellent performances as functional materials in various fields. Pore diameter has great influence on the performances of anodic TiO_2 nanotubes in application. A number of works have been carried out in the fabrication of anodic TiO_2 nanotubes with pore diameter ranging from several nanometers to several hundred nanometers. This minireview focuses on the impact factors influencing the pore diameter of anodic TiO_2 nanotubes and the efforts on decreasing the pore diameter of highly ordered TiO_2 nanotube arrays in the past two decades.

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Introduction

Anodization of so called "valve metals" has long been employed to grow a nanoporous oxide layer on the metal substrate including aluminum [1], titanium [2], etc. Since the first report of the formation of anodic TiO_2 in 1999 by Zwilling and co-workers [3], there have been extensive studies on the morphology control and application of TiO_2 nanotube arrays [4-7]. As known, application performances of anodic TiO_2 nanotube arrays largely depend on their pore sizes. Small pore TiO_2 nanotubes can have much better performance compared with large pore nanotubes due to higher specific surface areas and size effect [8,9]. As reported by Varghese et al. [8], the hydrogen sensitivity of anodic TiO_2 nanotubes with 22nm pore diameter was about 200 times more sensitive than 76nm pore diameter nanotubes.

Various experiments have shown that pore diameter of anodic TiO_2 nanotubes depends on anodizing parameters including applied voltage, anodizing current density, aqueous or nonaqueous based electrolytes used, concentration of ammonium fluoride, content of water, as well as humidity and temperature [10]. Generally, it is widely accepted that the pore diameter of anodic TiO_2 nanotubes has a positive quasi-linear relationship with applied voltage. Small pore nanotubes were produced at low voltage, while large pore nanotubes were grown at high voltage. However, a semi-empirical study on TiO_2 nanotubes grown in ethylene glycol containing 2 wt% H_2O and 0.3 wt% NH_4F by Su et al. [11,12] showed that the porosity of porous anodic metal oxide has an exponential relationship with applied voltage and decreased with increasing voltage, which led to a result that the pore diameter of anodic TiO_2 nanotubes did not increase with applied voltage monotonically but has a maximum value at a critical voltage determined by other anodizing parameters such as electrolyte used.

The work by Bauer et al. [13] on anodic TiO_2 nanotubes grown in H_3PO_4/HF electrolyte showed that the pore diameter of TiO_2 nanotubes was 120nm at 25V, which decreased to 15nm as the anodization voltage dropped to 1V. However, when the applied voltage was lower than 1V, no evidence of nanotube growth was found.

Many research works have demonstrated that pore size of anodic TiO_2 nanotubes grown in nonaqueous solution such like ethylene glycol and glycerol could be much smaller than those grown in aqueous solution [14]. It is suggested that the diffusion of H^+ cations produced at the pore base via dissociation of water to the pore mouth and bulk electrolyte was greatly influenced by the viscosity of the electrolyte. In a nonaqueous solution with higher viscosity, the small diffusion rate of H^+ cations leads to relative low concentration at the pore mouth, which reduces the chemical dissolution of tube wall of anodic TiO_2, resulting in small pore nanotube arrays. While in a nonaqueous solution such like ethylene glycol and glycerol, the content of water added could also has an impact on the pore diameter of anodic TiO_2 nanotubes. Generally, the pore diameter increases with increasing water content as the viscosity decreases.

Pore diameter of anodic TiO_2 nanotubes could also be adjusted by varying fluoride concentration and temperature [15,16]. Usually, high concentration of fluoride causes severe chemical dissolution of pore mouth and widening of pore diameter. In a similar way, high temperature can enhance the reaction rate of chemical dissolution, and high humidity can cause absorption of water from the surrounding environment leading to higher water content in electrolyte, both leading to widening of pore diameter.

Since the pore diameter of anodic TiO_2 nanotubes was determined by several factors, it is difficult to obtain nanotubes with ultrasmall pore size by simply adjusting a single factor. That might be why for more than one decade, the smallest pore size of anodic TiO_2 nanotube arrays was limited by 15nm. In a recent work by Qin et al. [10], the influences of concentration of ammonium fluoride, viscosity of solution, amount of adding water and applied voltage on the anodic growth of small pore TiO_2 nanotubes are studied systematically. Ultrasmall pore highly ordered nanotube arrays with pore size down to 6nm were obtained in ethylene glycol solution containing relative high content of NH_4F and low content of water at an applied voltage of 3V in a sealed electrolytic cell isolated from the surrounding humid environment.

Conclusion

This paper reviews recent developments on the formation of small pore anodic TiO_2 nanotubes under various conditions. The pore diameter of anodic TiO_2 nanotubes was determined by applied voltage and current density, nonaqueous or aqueous solution, water content and fluoride concentration, humidity and temperature. In order to fabricate TiO_2 nanotubes with ultrasmall pore size, all interconnected relating parameters should be taken into account. This provides a way for the precise control of the anodic TiO_2 nanotube morphology and extending of the pore diameter of anodic TiO_2 nanotube both in the down limit and the up limit.

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Conflict of Interest

The authors declare no conflict of interest.

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