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Enhanced photoelectrochemical-response in highly ordered TiO₂ nanotube-arrays anodized in boric acid containing electrolyte

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Abstract

We examine the photoelectrochemical properties of highly ordered titanium dioxide nanotube-array photoanodes, fabricated by anodization of titanium in a nitric acid/hydrofluoric acid electrolyte, with and without the addition of boric acid. Under UV–Vis illumination the photocurrent densities achieved with TiO₂ nanotube-arrays fabricated in the H₃BO₃–HNO₃–HF electrolyte are a factor of seven greater than the TiO₂ nanotube-array samples obtained in the commonly used HNO₃–HF electrolyte, indicating the ability to control the photoelectrochemical response of the highly ordered nanotube arrays by tailoring the electrolyte composition. For 560 nm long boric-acid fabricated nanotube arrays, a photoconversion efficiency of 7.9% is achieved upon a 320–400 nm illumination at an intensity of 98 mW/cm², with hydrogen generated by water photoelectrolysis at the power-time normalized rate of 1708-μmol/h W (42 ml/h W). The resulting nanotube-arrays demonstrate excellent photocorrosion stability, with no detectable degradation in photoconversion properties over 6 months of testing. While the titania bandgap is not suitable for high visible spectrum efficiencies, the high photoconversion efficiency achieved under UV illumination indicates the suitability of the highly ordered nanotube-array architecture for hydrogen generation by water photoelectrolysis.

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1. Introduction

The photoelectrochemical properties of a semiconductor are critically dependent upon its nanoscale surface structure. For example, it has been reported that nanoporous GaP and SiC photoelectrodes show a significant enhancement in photocurrent quantum yield for absorbed light in comparison to photoelectrodes having a flat geometry [1–3]. In dye-sensitized solar cells, the use of mesoporous nanocrystalline TiO₂ electrodes results in higher solar-to-electrical conversion efficiencies as compared to nanoparticle electrodes [4,5]. Further, it is widely recognized that the ability of a given semiconductor to generate hydrogen and oxygen by water photoelectrolysis is critically dependent upon the interfacial contact characteristics between the semiconductor and the electrolyte solution. Earlier work of the authors has shown that a highly ordered TiO₂-nanotube array architecture, obtained by anodization of a starting titanium film in a fluoride containing electrolyte, has remarkable gas sensing [6], photocatalytic [7], and photoelectrolysis properties [8] that make the material platform worthy of further consideration.

Electrochemical anodization of metals and semiconductors is a relatively simple process for creating precisely engineered semiconductor nanostructures. Highly ordered, self-organized nanoporous materials such as aluminum [9,10], silicon [11–13], titanium [14–16], zirconium [17], tin [18], and InP [19] have been created by electrochemical anodization. Anodization variables including electrolyte composition and pH, applied potential, temperature and etching time can influence the morphologies and properties of the resultant semiconductors, and thus these parameters generally affect the photogenerated charge carrier transport within the porous material-electrolyte network. It has been established from our previous studies [14,20] that the inner pore diameters of the titania nanotubes are primarily determined by applied potential; pore sizes ranging from 20 to 110 nm can be obtained with, respectively, potentials ranging from 10 to 25 V. The electrolytic cell temperature has been found to control the wall thickness of the resulting nanotubes, and to a smaller but still significant extent the length of the nanotubes [8]. The duration of the anodization significantly affects the nanotube length, and to a smaller effect pore size and wall thickness [20,21].

Electrolyte composition plays a critical, and as of yet essentially unexplored role in determining the resultant nanotube-array nanoarchitecture and, potentially, its chemical composition. Electrolyte composition, and its pH, determines both the rate of nanotube-array formation, as well as the rate at which the resultant oxide is dissolved. For example, our previous studies showed that nanotube-arrays greater than 500 nm in length could not be obtained using a pure HF–H₂O electrolyte [14]. However, nanotubular arrays up to 6500 nm in length can be made using a KF–H₂SO₄–H₂O system [20,21]. In all cases, a fluoride ion containing electrolyte is needed for nanotube-array formation.

In this paper, we examine the resulting photoelectrochemical characteristics of TiO₂ nanotube arrays anodized in a nitric/HF acid based electrolyte with and without the addition of boric acid; results are presented in comparison to a TiO₂ film made by 500 °C annealing of a Ti foil, the same as used to fabricate the titania nanotube arrays from. As will be detailed, we find that the addition of boric acid to the electrolyte results in a significantly enhanced photochemical response.

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