Synthesis and Characterization of Photocatalytically Active Titania Nanotubes

Elizabeth Ranney and Johannes Schwank*
Department of Chemical Engineering, University of Michigan, 2300 Hayward, Ann Arbor, MI 48109-2136 (USA)
*schwank@umich.edu

Introduction

Titania nanotubes are of particular interest because of their applications in photocatalytic water splitting. Titania is a photosensitive material and offers a wide band gap. In addition, a nanotube structure allows for an increased surface area per volume ratio. Titania nanotubes can be synthesized by anodic oxidation, which results in uniform arrays of nanotubes perpendicular to the substrate surface. Previous work indicates that the geometries and properties of titania nanotubes can be controlled by the synthesis conditions [1][2]. It is suggested that the nanotube wall thickness determines the effectiveness of titania nanotubes on a thick titanium substrate to split water for hydrogen production [3]. The goal of this study is to systematically explore and optimize synthesis conditions of titania nanotubes and characterize their properties for use as a catalyst.

Materials and Methods

In a clean room environment, a 500 nm layer of titanium was deposited via E-beam evaporation onto 1 in. by 3 in. glass microslides. To anodize the titanium, a microslide area of approximately 3 cm^2 was immersed in 40 mL of electrolyte with a platinum cathode. The electrolytes tested contained 0.35, 0.5, or 1.0 wt. % sodium fluoride, and the balance equal amounts of deionized water and glycerol by weight. The anodizations were performed at room temperature and constant voltage for an average of 15 minutes using an Agilent DC power supply. The current was monitored using an Agilent Data Acquisition/Switch Unit system and Agilent BenchLink Data Logger software.

The resulting titania nanotubes were viewed under a Philips XL30 Field Emission Gun Scanning Electron Microscope (SEM). Energy Dispersive Spectroscopy (EDS) compositional analysis was also performed using the SEM. In addition, the titania nanotubes were characterized with a JEOL 2010F Field Emission Gun Analytical Electron Microscope (AEM) operated at 200 kV. The AEM was used to obtain transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) images, and diffraction patterns. Experiments to determine the photocatalytic abilities of titania nanotubes are also performed. An array of titania nanotubes was immersed in a methylene blue solution. Oxygen was bubbled into the solution while the sample was exposed to ultraviolet (UV) light from a 100W Hg lamp. The degradation of the methylene blue was measured at varying time increments using a photospectrometer.

Results and Discussion

The work presented here demonstrates that amorphous titania nanotubes can be formed not only on titanium metal foils, but also on thin film titanium substrates. Within the range of synthesis variables explored, it proved possible to control nanotube diameters, wall thicknesses, and lengths by varying electrolyte fluoride content, anodization time, and applied electrical potential (Figure 1). For example, increasing the fluoride concentration resulted in smaller nanotube diameters. Higher fluoride concentrations and/or longer anodization times resulted in consumption of most of the titanium substrate and led to the formation of optically transparent nanotubes. This is useful for tailoring the nanotubes to specific catalytic reactions, such as the photocatalytic decomposition of methylene blue (Figure 2).

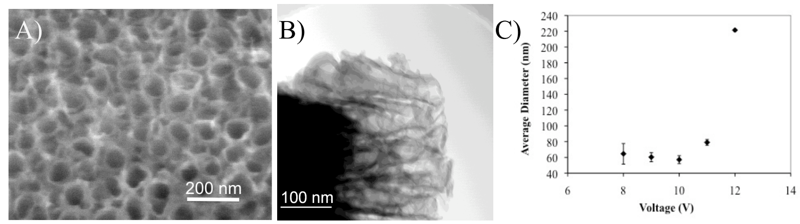

Figure 1. A) Top-view SEM image of titania nanotubes, B) side-view STEM image, and C) nanotube diameter as function of varying applied electrical potential.

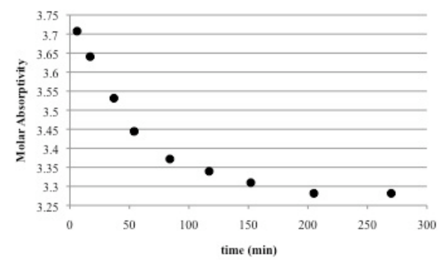

Figure 2. Molar absorptivity at 664 nm showing the degradation of methylene blue under UV light catalyzed by a titania nanotube sample synthesized in electrolyte containing 0.5 wt. % sodium fluoride.

Significance

Optically transparent titania nanotubes formed from thin titanium films can be more easily implemented in high temperature photocatalytic systems. In addition, these titania nanotubes can contain catalytically active metals if super-filled by incipient wetness impregnation.

References

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