



Photodegradation of methyl orange and 2,3-butanedione on titanium-dioxide nanotube arrays efficiently synthesized on titanium coils

Vance Jaeger^a, Winn Wilson^b, Vaidyanathan (Ravi) Subramanian^{a,*}

^a Department of Chemical and Materials Engineering, University of Nevada, Reno, NV, USA

^b Department of Civil and Environmental Engineering, University of Nevada, Reno, NV, USA

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ABSTRACT

This work presents the synthesis, characterization, and application of titanium dioxide nanotube arrays (T-NT) prepared on titanium coils by anodization. A comparison of the physical, photoelectrochemical, and photocatalytic properties of T-NT on coil, mesh, and foil architectures is reported. The application of T-NT on helical coils to UV–vis initiated photodegradation of pollutants in aqueous and gaseous phases is discussed. The T-NT on coil shows better photoactivity compared to T-NT on other geometries such as foil and mesh. A 30% increase in the photodegradation of methyl orange in the aqueous phase is noted with T-NT on coils compared to T-NT on mesh. T-NT on coils also demonstrate photodegradation of a model pollutant 2,3-butanedione (diacetyl) in the gaseous phase. The T-NT grown on the coil architecture offer several advantages such as significantly minimized dark spots, highly reduced recombination centers, as well as adjustable spacing and dimensions for tuning photo(electro)catalytic activity. This configuration can be useful in other non-photocatalytic applications as well.

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1. Introduction

Titanium dioxide (TiO₂) has been widely studied as a photocatalyst for light-assisted remediation of environmentally toxic pollutants [1–8]. Irradiation of TiO₂ produces charged species that facilitate redox reactions at the photocatalyst surface [9–13] (and several other articles from different groups). Summarily, the process involves the formation of oxidative species, such as hydroxyl radicals under irradiation, which break-down toxic pollutants to relatively benign and eco-friendly product(s) [14]. Eventually, the treated product may be discharged into the environment safely. Recently, ordered TiO₂ architecture has attracted significant attention as a photocatalyst. Of particular interest has been 1-D ordered titanium oxide nanotubes (T-NT) which have demonstrated interesting optical, catalytic, and electrocatalytic properties for various photo-related applications [15–18]. The synthesis of these T-NT is often carried out by the process of anodization of Ti followed by heat treatment to facilitate phase transformation. One of the main reasons this nanotube architecture has been promising compared to films made of granular TiO₂ is the improved separation of

charged species realized with T-NT, attributable to highly reduced grain boundaries [19,20].

A review of recent literature shows that the anodization of titanium metal as a substrate results in the formation of T-NT with similar features, uniform dimensions, and high surface area [21–23]. The substrate transparency and geometry (such as foils, wires, and meshes) have been identified as key physical features that dramatically influence photoactivity of T-NT [24–27]. Earlier, we have demonstrated the benefits of producing nanotubes on a non-planar wire-type architecture [28]. Non-planar architecture offers the benefit of better light capture than a planar substrate, more efficient utilization of expensive titanium metal, and the possibility to eliminate the use of overlying expensive ad-atoms (atoms of elements that are added to assist a primary catalyst to enhance catalysis) for improving photoactivity. However, a significant challenge to the current preparation method for the T-NT is that a large volume of electrolyte is consumed during the anodization step, especially with non-planar geometries. Preparing nanotubes using small volume of electrolyte can be highly cost-effective.

Yet another relevant aspect of T-NT is its application as a photocatalyst in the degradation of environmental pollutants. An analysis of the literature in this area suggests that T-NT (i) effectively photodegrades a variety of pollutants [29,30], (ii) demonstrates better photodegradation kinetics compared to TiO₂ particulate films [19,20], and (iii) does not lose its photocatalytic activity after several cycles in operation [17]. However, the pollutants studied so far are limited to the aqueous phase only. An investigation of

* Corresponding author at: Chemical and Metallurgical Engineering Department, Room 310, LMR 474, Mail Stop 388, University of Nevada, Reno 89557, USA.
Tel.: +1 775 784 4686; fax: +1 775 327 5059.

E-mail address: ravisv@unr.edu (V. (Ravi) Subramanian).

the performance of T-NT in the photodegradation of gaseous phase pollutants has just started and is yet to be fully explored [31,32]. Particularly, the potential improvements realized by growing T-NT on non-planar Ti substrates in the gaseous phase photodegradation have not yet been examined.

We present three interesting findings in this work. Firstly, we demonstrate T-NT grown on a new non-planar helical coil-type architecture using the process of anodization and a comparison of the physical (length and diameter) and optical (absorbance) properties of these T-NT with T-NT prepared on foil and mesh. Secondly, the ability of the T-NT grown on these coils to perform photocatalytic degradation of representative pollutants in the aqueous as well as gaseous phases, the kinetics of the degradation process, and the superior performance of T-NT on coils with respect to T-NT on foils and mesh are discussed. Finally, a comparative analysis of TiO₂ nanoparticulate films and T-NT performance on different architectures and a discussion highlighting the benefits of T-NT formed on coils is also presented.

2. Experimental

2.1. Synthesis of T-NT on a coil architecture with highly reduced electrolyte volume and characterization of the T-NT

Titanium wire (99.7%) of O.D. 0.25 mm was obtained from Alfa Aesar and cut into lengths of 22 cm. The lower 20 cm of the wire was tightly and helically coiled around a 6 mm O.D. glass rod. The remaining 2 cm was bent into a crook that would allow easy attachment to an alligator clip. Two different configurations were used for the anodization. Configuration 1 was used for the plates and mesh. For this configuration a platinum flag electrode was placed in the solution 4 cm away from the bulk titanium. A volume of 300 ml of solution was used in a 500 ml beaker. This configuration is described in detail in earlier articles [33,34]. The samples were prepared using this method so that the photoactivity of T-NT on mesh and foil can be fairly compared with the newer method.

Configuration 2 was used strictly for the coils. In this method, the coils were placed around 1.5 mm I.D.–4 mm O.D. glass tube of 10 cm length. A 15 cm × 1 mm O.D. platinum wire was inserted into the inside of the glass tube, and 4 cm of the wire was allowed to hang out of the bottom of the tube. A slight bend was placed in the wire to keep the glass tube from slipping down the wire. The glass tube along with the titanium coil and the platinum wire were placed in a 25 ml graduated cylinder filled with 25 ml of the anodization solution. A schematic and a picture of the setup used for anodization of Ti with the coil configuration are shown in [Supporting information S1](#). For both configurations, a bias of 20 V, 36 V, or 60 V was applied to the electrodes, and the anodization was carried out for different durations with the vessels in an ultrasonication bath. For anodization over 30 min, the water in the bath was changed at 30 min into the process to minimize heat-related deviations. After anodization, the coils were washed with DI water and allowed to dry overnight. All samples were annealed under a N₂ atmosphere at 550 °C for 2 h at a ramp rate of 4.5 °C/min.

2.2. Surface and photoelectrochemical characterization

The post-anodization and heat treated samples were characterized using scanning electron microscope (Hitachi S-4700 FE-SEM). Several sections of the coil samples were imaged in order to determine whether the proper and uniform structure of the nanotubes were present, as well as to measure the dimensions of the nanotubes. The nanotubes were further characterized for crystalline structure using XRD and indexed to JCPDS files. The analysis was

performed by glancing angle X-ray diffraction equipment. The photoelectrochemical responses of the T-NT on different Ti configurations were measured using an Autolab potentiostat/galvanostat. A 1 M NaOH solution was used as the electrolyte in the photoelectrochemical measurements with Ag/AgCl as the reference and Pt wire as a counter electrode. For photoelectrocatalysis, external bias was varied between +0.0 V and +0.6 V vs. Ag/AgCl in steps of 0.1 V. For photovoltage measurements, intermittent irradiation was performed with the lights on for 50 s and lights off for 50 s. The scan voltage for chronoamperometric (*I*–*t*) studies was maintained at +0.0 V. Photocurrent densities determined from these measurements are normalized to the exposed geometrical area of the catalyst.

2.3. Photocatalytic degradation of aqueous and gaseous phase pollutants

2.3.1. Aqueous phase methyl orange (MO) photodegradation

An aqueous solution of 40 μM MO was prepared for testing the photocatalytic activity of the nanotubes. Photodegradation experiments were performed using 7 ml of the dye solution. The T-NTs were kept immersed in the cell with the MO. Continuous illumination of the T-NT immersed dye solution was performed for 30–120 min. A Newport® xenon light source (Part #366902) with an output of 500 W was used for photoillumination of methyl orange. The lamp source has an irradiation profile similar to natural solar radiation with light intensities extending from far UV to visible and infrared. A 0.5 M CuSO₄ solution was used to cut-off the far UV and reduce the intensity at the catalyst surface to 90 mW/cm². The details of the setup used here are based on an earlier work [35]. The distance between the light source and the sample was maintained constant at 3 cm to ensure that the light intensity at the catalysts surface is identical for all experiments (a luxmeter was used to confirm that the light intensities are the same). The photoreactor, geometrical area of illumination of the reactor (4 × 1 cm²), and the volume of aqueous dye used (7 ml) in the photoreactor is the same for all experiments. The photocatalysis results are normalized to the illuminated geometrical area of the catalyst. Dye samples were withdrawn at regular intervals and then tested for UV–vis absorbance. The MO photodegradation was estimated from the decrease in the absorbance at 470 nm. The photocatalytic activities of T-NT on different geometries were tested in a similar manner. More details of the photocatalyst testing procedure including additional information on the apparatus are reported in an earlier work [17].

2.3.2. Gaseous phase diacetyl photodegradation

T-NT on Ti was placed in a quartz glass tubing of 20 cm length and an I.D. of 6 mm and an O.D. of 10 mm. The quartz tubes were incorporated into a flow system using polyethylene as the carrier hoses. The quartz tubes that carries the vapors were placed vertically alongside a cooling jacket containing a 450 W light source (Part #7825-34), powered by an Ace Glass® 450 W power supply. The light source emitted radiation stretching mainly between UV and visible light (40–48% UV, 40–48% visible, and balance IR). A 250 ml fluted Erlenmeyer flask containing approximately 3 g of 2,3-butanedione (diacetyl) was used as the source of pollutant. The diacetyl was carried by dry ambient air through the glass tubing containing the titanium coils. The volumetric flow rate of the carrier gas was determined and maintained constant by a flow gauge connected at the carrier gas entrance, and the motive for the gas flow was provided by a vacuum pump. After passing through the tubing, the gas was condensed using a dry ice and acetone trap. A mass balance was performed on the fluted Erlenmeyer flask and the water trap to determine conversion.

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