



Anodized titania nanotube array microfluidic device for photocatalytic application: Experiment and simulation



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ABSTRACT

Microfluidic photocatalytic reactors have advantages over conventional bulk reactors such as large surface-area-to-volume ratio and high control of fluid flow. Although titania nanotubular arrays (TNA) have shown enhanced photocatalytic degradation compared to nanoparticle films in a batch reactor configuration, their application in a microfluidic format has yet to be explored. The photocatalytic performance of a microfluidic reactor with TNA catalyst was compared with the performance of microfluidic format with TiO₂ nanoparticulate (commercial P25) catalyst. The microfluidic device was fabricated using non-cleanroom based soft lithography, making it suitable for economical large scale manufacturing. The photocatalytic performance was evaluated at different flow rates ranging from 25 to 200 μL/min. The TNA microfluidic system demonstrated enhanced photocatalytic performance over microfluidic TiO₂ nanoparticulate layers, especially at higher flow rates (50–200 μL/min). For instance, 12 μm long TNA was able to achieve 82% fractional conversion of 18 mM methylene blue in comparison to 55% conversion in case of the TiO₂ nanoparticulate layer at a flow rate of 200 μL/min. A computational model of the microfluidic format was developed to evaluate the effect of diffusion coefficient and rate constant on the photocatalytic performance. The improved performance of the TNA photocatalyst over the nanoparticle film can be attributed to higher generation of oxidizing species.

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1. Introduction

Water based pollutants are a big concern and serious challenge in both developed and developing nations. Photocatalytic environmental remediation has been widely investigated for the degradation of water based pollutants [1]. Recently, nanomaterials such as nanoparticles, nanowires and nanoporous films have been applied to photocatalytic reactions due to their interesting properties over bulk materials. Many studies have used photocatalysts in the form of a powder. However, the use of powdered photocatalysts necessitates their downstream recovery, which can be costly. The immobilization or growth of photocatalysts as a film eliminates this drawback. Many studies involve conventional macroscale reactors

with limited mass transport and poor photon transport. This can potentially limit the degradation performance of the system [2–4]. The use of microfluidic system has the potential to reduce such aforementioned reactor limitations.

Microfluidic systems have inherent advantages such as large surface to volume ratio, smaller diffusion distance, uniform irradiation over the whole catalytic surface, self-refreshing property [5] and large mass transfer efficiency [6,4]. Microfluidic photocatalytic reactors have demonstrated higher photocatalytic efficiency compared to conventional reactors. For example, Lei et al. reported reaction rate constants in microreactors to be 100 times more than in bulk reactors [3]. In bulk reactors, there is a loss of photons reaching the photocatalyst surface due to scattering effects in the liquid [7]. In contrast, in microfluidic reactors, the thin layer of liquid over the catalyst ensures that less photons are lost due to scattering. Microfluidic reactors can also be used for rapid screening of photocatalysts [4,8].

Of the semiconductor materials studied for photocatalytic environmental remediation, titanium dioxide (e.g., nanoparticles, nanowires, nanotubes) is widely used due to its desirable

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properties. Titanium dioxide has successfully demonstrated photocatalytic degradation of a wide spectrum of metallic and organic pollutants [9]. Titania nanotube arrays (TNA) synthesized by anodization have received interest in last few decades in areas such as sensing, drug-delivery, energy conversion/storage, and catalysis, for example [10–12]. Macak et al. reported the use of high-aspect ratio TNA for enhanced photocatalytic properties compared to TiO₂ nanoparticulate layers [13]. Although the TNA layer was five times shorter than the P25 nanoparticulate layer, it still exhibited enhanced photocatalytic performance compared to the latter. In their study, the photocatalytic experiments were performed in a batch reactor configuration. Most of the current literature on photocatalytic microfluidic systems involve TiO₂ nanoparticle film as a photocatalyst [14,15,3,16,17]. Subsequently, a more efficient degradation system could be realized by integrating TNA in a microfluidic system. Moreover, microfluidic devices integrated with TNA can potentially be used for other applications such as photocatalytic syntheses of chemicals such as L-pipecolic acid, for example [18].

A potential disadvantage with current microfluidic photocatalytic degradation systems is that the microfluidic devices needed are often complex and difficult to fabricate especially when clean-room techniques are involved. This is especially critical when a large-scale array of microfluidic channels is required [4]. For example, previous reports on microfluidic photocatalytic devices used clean-room techniques to fabricate the mold for the microfluidic device [14,3,6] or to pattern the photocatalyst substrate [2] or CNC milling to pattern the substrate [19]. In contrast, in this study the microreactor mold was fabricated using laser patterned polymethyl methacrylate (PMMA) sheets [20,21] and polydimethylsiloxane (PDMS) was used to fabricate the device. A widely used material for microfluidic devices, PDMS, has desirable properties such as optical transparency, chemical inertness, and easy and rapid fabrication [22,17].

In this work, we demonstrate the use of self-ordered TNA for photocatalytic degradation in a microfluidic reactor. The degradation performance of TNA was also compared to P25 TiO₂ nanoparticle films in a similar microfluidic format. The degradation kinetics of a model pollutant (methylene blue) in a microfluidic channel with TNA vs. P25 TiO₂ particles as catalyst under solar irradiation (AM 1.5, ~100 mW/cm²) was used in this study. Most of the existing work on microfluidic photocatalytic system, however, have been done under UV light [2,6,17], limiting the practical application.

We have also developed a model using COMSOL Multiphysics to examine how convection and diffusion of the reactant/pollutant molecules affect the performance of the microfluidic surface reactor system. Although models have been developed to understand the nature and reaction kinetics between a photocatalyst and reactant in batch reactors [23–26], a model that would explain the behavior of such a system in a microfluidic flow based scenario has yet to be explored.

2. Experimental

2.1. Preparation and characterization of TNA and P25 film

Titania nanotube arrays were synthesized by electrochemical anodization similar to an earlier reported protocol [27,28]. In short, Ti foils (0.02032 cm thick) were cut into 3 cm × 2 cm and anodized under sonication (Branson 5510 ultrasonic bath) in an electrolytic solution consisting of ethylene glycol (Fisher Scientific, Waltham, MA), deionized (DI) water (2 wt.%) and ammonium fluoride (0.5 wt.%, Fischer Scientific) at 30 °C bath temperature. One side of the Ti foil was masked using Kapton tape to restrict oxide

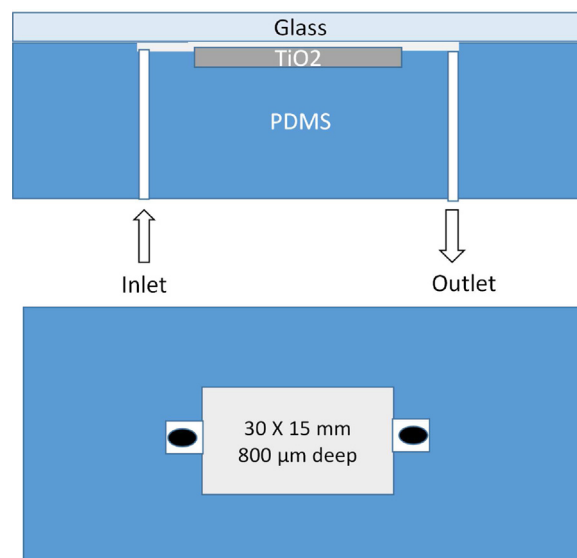


Fig. 1. Top and side view of the microfluidic device.

growth to only one side of the Ti strip. A two electrode configuration with platinum (Pt) mesh as the cathode was used for anodization. The anodization was carried out at an applied potential of 60 V (D.C.) (Agilent, E3647A) for different time intervals (60 min for long tubes, 30 min for medium tubes and 15 min for short tubes). The thus formed TNA were rinsed with DI water, air-dried and cut to the dimension of the microfluidic channel. The TNA samples were subsequently annealed in an atmosphere of N₂/H₂ (2% H₂) at 500 °C (1.6 °C/min ramp rate) for 2 h.

The P25 films were prepared by doctor blade method [29]. A fine paste of Degussa P25 was made with dilute nitric acid (pH 3–4) using a mortar and pestle. Scotch tape (3M) was used as a mold to form a film the same dimensions of the channel (30 mm × 15 mm) on a Ti foil. Subsequently the P25 film was calcined in air for 2 h at 450 °C. The morphology of the thus formed P25 TiO₂ and TNA films were characterized using a field emission scanning electron microscope (SEM) (Hitachi, S-4800). The crystalline properties of the films were examined using X-ray diffraction (Rigaku MiniFlex 600) with CuKα radiation ($\lambda = 0.1542$ nm) from $2\theta = 20\text{--}80^\circ$ with a step size = 0.01° and dwell time = 0.5°/min.

2.2. Fabrication of microfluidic channel and integration of TNA substrate

The microfluidic device was fabricated by soft lithography similar to a previous procedure [30]. A laser was used to create the mold for the microfluidic channel on a PMMA sheet (800 μm thick) and transferred onto a plastic petri dish. The dimensions of the channel are as shown in Fig. 1. A 20 mL mixture of PDMS (base to curing agent ratio – 1:10) was poured onto the mold and cured at 60 °C for 4 h to create the PDMS layer. Subsequently, inlet and outlet channels were bored onto the PDMS channel. Then the thin film catalyst (TNA or P25 film) was embedded (using a double-sided tape) into the PDMS channel. The TNA or P25 layer was placed facing the glass slide. The glass slide was bonded to the PDMS layer via corona surface treatment for 4 min and subsequently baked at 60 °C for 2 h [31].

2.3. Evaluation of the photocatalytic degradation

The photocatalytic degradation of the device was evaluated using methylene blue (MB) as a model pollutant. This dye is non-biodegradable and commonly used in the textile industry. As

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