Photocatalytic microfluidic reactors utilizing titania nanotubes on titanium mesh for degradation of organic and biological contaminants

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ABSTRACT

Microfluidic reactors have gained considerable interest for photocatalytic degradation of contaminants in water. These systems have advantages such as large surface-area-to-volume ratio and high control of fluid flow, yet still suffer from drawbacks due to limited mass transport associated with laminar flow. The use of titania nanotubes synthesized on a mesh substrate shows improved photocatalytic performance in comparison to nanotubes synthesized on a foil substrate in a microreactor. At the lowest flow rate (25 μL/min), the area normalized fractional conversion of methylene blue increased from 20% for foil to 46% in the case of nanotubes on mesh. The enhanced photocatalytic performance of the mesh is due to shorter diffusion distance and induction of flow perturbation. Also, the radially outward oriented nanotubes formed over the circumference of the titanium wire leads to the efficient capture of both reflected and refracted light. The device was also applied for inactivation of *Escherichia coli* O157:H7. At a flow rate of 50 μL/min, the titania nanotubes on a mesh microreactor were able to achieve >99% inactivation of *E. coli* under AM 1.5 ($\approx$100 mW/cm^2) simulated solar light.

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1. Introduction

According to estimates, 1.2 billion people lack access to safe drinking water, which contributes to the death of 3900 children daily [1]. Hence, access to clean water is a worldwide concern. In both industrialized and developing nations, chemical and biological contaminants are finding their way into water bodies due to increasing human activity [1]. Cleanup and reuse of polluted wastewater is an attractive solution to some of these issues. Low-cost and high-efficiency water remediation technologies are needed to achieve the same [2]. Conventional wastewater treatment technologies such as adsorption or coagulation merely concentrate the pollutants present by transferring them to other phases [2]. Other conventional methods such as sedimentation, filtration, chemical, and membrane technologies are expensive and potentially generate toxic secondary pollutants [1].

Advanced Oxidation Processes (AOP) could solve some of the issues associated with conventional water treatment methods. These processes work by the generation of transitory highly reactive oxygen species (ROS) for mineralization of chemical and biological pollutants present in water [2]. Among these AOPs, photocatalytic environmental remediation employing semiconductor photocatalysts has been widely applied for water-based pollutants [2,3]. Nanomaterial semiconductor photocatalysts have been used due to their interesting properties over bulk materials. Many studies have used powdered photocatalysts suspended in solution [4,5]. However, the use of powdered photocatalysts necessitates their downstream recovery. This can lead to increased operational and capital costs [5,6]. Also, the use of powdered catalyst particles limit the depth of penetration of light due to strong adsorption and scattering [7,8]. The immobilization or growth of photocatalysts as a film on a substrate eliminates many of these drawbacks [6].

Microfluidic reactors (microreactors) have been increasingly applied to water remediation over conventional macroscale reactors [9,10]. This is because conventional macroscale reactors have limitations due to mass transport and poor photon management [5]. In the case of microreactors, the thin layer of liquid over the catalyst ensures lesser photons are lost due to scattering [11]. Microreactors can be advantages over conventional

macroscale reactors due to large surface to volume ratio, smaller diffusion distance, and large mass transfer efficiency [12]. Microfluidic photocatalytic reactors have been reported to have higher photocatalytic efficiency compared to conventional reactors [10]. Current microfluidic formats face a major drawback due to limited mass-transport associated with laminar flow [5]. To overcome this limitation, Li et al. reported the use of a fiberglass coated with P25 titanium dioxide nanoparticle (TNP) layer for the degradation of methylene blue (MB) [5]. The new design, incorporating the same catalyst (TNP), but on a geometrically different substrate (fiber) yielded higher degradation over a conventional microreactor platform involving P25 TNP layer embedded on a flat surface.

Titanium dioxide (TiO_2) has been widely applied to photocatalytic degradation of chemical and biological pollutants [6,13–15]. Titania nanotube arrays (TNA) are of particular interest due to their simple synthesis and improved ability to transport photogenerated charges as compared to their TNP counterpart [16]. Titania nanotube arrays have shown to have enhanced photocatalytic properties compared to TNP layers in a macroscale batch reactor configuration [17]. Further, by electrochemical anodization, TNA can be synthesized on different titanium (Ti) metal substrates, having varied geometries (e.g., thin wires [8], meshes [16], and curved surfaces [18]).

TiO_2 based catalysts in the form of TNA [11] and TNP [5,10,19] have been applied in microreactors for photocatalytic degradation. We recently reported the application of TNA synthesized on a foil (TNA_{foil}) for degradation of MB in a microreactor [11]. The TNA_{foil} had enhanced photocatalytic performance over P25 TNP layer when used in a microfluidic format.

Although TNA_{foil} has shown promising results for photocatalytic applications, the use of metal foils has limitations (such as the opacity, inefficient use of Ti, and reduced flexibility). As an alternative, metal meshes provide an approach that allows for high flexibility, efficient Ti utilization, and transparency. Such a format has shown to be effective in applications such as dye-sensitized solar cells [20].

We report the use of TNA grown on a Ti mesh (TNA_{mesh}) for photocatalytic degradation of MB and inactivation of *Escherichia coli* O157:H7 in a microfluidic format. The microfluidic device was fabricated using non-cleanroom based technique which makes it suitable for large scale applications [21]. The degradation performance is compared to that of previously reported data using TNA_{foil} at different flow rates in a geometrically similar microreactor [11]. We also report the use of TNA_{mesh} for the photocatalytic inactivation of *E. coli*. TiO_2 based photocatalysts have been shown to have bactericidal and bacterial endotoxin decomposing capability [14,22–24]. The use of TNA for inactivation of pathogens in a flow through system has yet to be fully explored.

2. Experimental

2.1. Preparation and characterization of TNA on foil and mesh

Titania nanotube arrays grown on a titanium mesh were synthesized by electrochemical anodization similar to an earlier reported protocol [16]. In short, Ti gauze (50 mesh woven from 0.102 mm diameter wire, 64% open area) was obtained from Alfa Aesar and cut into 3 cm × 2 cm dimensions. The Ti gauze was first washed with isopropanol and DI water under sonication for 10 min each, and then electropolished in 1 °C glacial acetic acid/perchloric acid (9:1 volume ratio) at 60 V under sonication for 1 min [25]. The electrochemical anodization was carried out at an applied potential of 60 V (D.C.) (Agilent, E3647A) for 60 min. The thus formed TNA_{mesh} was rinsed with DI water, air dried and subsequently annealed in an atmosphere of N_2+2% H_2 at 500 °C

(1.6 °C/min ramp rate) for 2 h. The morphology of the thus formed TNA_{mesh} film was characterized using a field emission scanning electron microscope (SEM) (Hitachi, S-4800).

2.2. Fabrication of microfluidic channel and integration of TNA_{mesh} substrate

The microfluidic device was fabricated by soft lithography [21] similar to that reported in our earlier study [11]. In short, the mold was cut on a tape using a laser. Next, a polydimethylsiloxane (PDMS) mixture was poured onto the mold, and cured in an oven to create the PDMS layer. Subsequently, inlet and outlet channels were bored onto the PDMS channel and the TNA_{mesh} catalyst was embedded into the PDMS channel. Finally, a corona activated glass slide was bonded to the PDMS layer. A photograph of the microfluidic reactor is provided in the Supporting information (Fig. S1).

2.3. Evaluation of the photocatalytic degradation of methylene blue

The photocatalytic degradation of the device was evaluated using MB as a model pollutant. MB is a non-biodegradable dye and is used for characterizing photocatalytic performance [17,26,27]. The experimental setup used to evaluate the photocatalytic performance of the device is depicted in our earlier work [11]. In a typical experimental run, 5 mL of 18 mM aqueous solution of MB was injected through the inlet into the microfluidic device using a syringe pump (KD Scientific, Manassas, VA) via Tygon tubing (0.02 in./0.0508 mm inner diameter) at different flow rates ranging from 25–200 μL/min. The microfluidic device was irradiated with AM 1.5 simulated solar light ($\approx$100 mW/cm^2). The intensity of the light was measured at the surface of the microfluidic device using a handheld power meter (Nova, Ophir-Spiricon, UT). The degraded MB solution was collected and the concentration was determined by monitoring the change in characteristic absorption peak at λ = 664 nm using a UV–vis spectrophotometer (Shimadzu Corp., Japan). The fractional conversion was calculated by:

$$X(\%) = \frac{A_0 - A}{A_0} 100 \tag{1}$$

where A_0 is the initial concentration absorbance value, and A is the absorbance value of the degraded solution. The experiment was repeated in the absence of AM 1.5 light to evaluate the amount of MB adsorbed on the catalyst. The fractional conversion was normalized with respect to the substrate area exposed to normal incident light [8]. The results were compared to normalized fractional conversion of MB using a TNA_{foil} (12 μm and 7 μm nanotube lengths) reported in our earlier work [11].

2.4. Evaluation of the photocatalytic inactivation of E. coli

The photocatalytic inactivation of *E. coli* was evaluated using TNA_{mesh} in a microreactor as described above. *E. coli* O157:H7 (non-pathogenic strain, Catalog no. 700728, ATCC) was used to prepare different concentrations (1000 and 10,000 CFUs/mL) of *E. coli* in 1× PBS solution [28]. The concentration range of *E. coli* was chosen based on total coliform levels in municipal wastewater [29]. The experimental setup is the same as that for MB degradation mentioned previously. A 4 mL sample of the *E. coli* solution was taken in a syringe, 3 mL of which was injected using a syringe pump through the inlet into the microfluidic device. The flow rates were varied from 25–200 μL/min in the absence and presence of AM 1.5 simulated solar light ($\approx$100 mW/cm^2). The intensity of the light was varied from 10 to 100 mW/cm^2 to evaluate the effect on