Medical Engineering & Physics 33 (2011) 887–892

Contents lists available at ScienceDirect

Medical Engineering & Physics

journal homepage: www.elsevier.com/locate/medengphy

Realization and efficiency evaluation of a micro-photocatalytic cell prototype for real-time blood oxygenation

Marco Rasponi[a,*], Tania Ullah[b], Richard J. Gilbert[b], Gianfranco B. Fiore[a], Todd A. Thorsen[c,1]

[a] Dipartimento di Bioingegneria, Politecnico di Milano, Piazza Leonardo da Vinci 32, 20133 Milano, Italy
[b] Department of Mechanical Engineering, Massachussetts Institute of Technology, 77 Massachussetts Avenue, United States
[c] Lincoln Laboratory, Massachussetts Institute of Technology, 77 Massachussetts Avenue, United States

ARTICLE INFO

Article history:
Received 8 January 2010
Received in revised form
15 September 2010
Accepted 11 October 2010

Keywords:
Photocatalytic cell
Microfluidics
Fluid oxygenation
Titanium dioxide
PDMS
Methylene blue
Electrochemically assisted photocatalysis
Dye degradation
Water dissociation

ABSTRACT

A novel, miniaturized, high-efficiency photocatalytic cell, able to work in dynamic conditions, has been designed and validated in this study. Microfluidic channels were molded out of polydimethylsiloxane (PDMS) by means of standard soft lithography techniques, so as to work as photocatalytic cells, where the coupling of anatase titanium dioxide thin films and platinum electrodes, allows an electrically assisted photocatalytic reaction to produce dissolved oxygen gas from the water content of flowing fluid (e.g. blood). The thin films were deposited onto quartz glass substrates at room temperature (300 K) using reactive radio-frequency sputtering with a titanium metal target. The photocatalytic activity was evaluated through reduction rate of methylene blue solution. The results of the current study, as a proof of concept, have shown that the device can generate oxygen at a rate of 4.06 μM O_2/(cm^2 min), thus extending its possible application range to the full oxygenation of flowing venous blood.

1. Introduction

The breakthrough work of Fujishima and Honda in 1972 [1], in which they achieved ultraviolet light-induced water cleavage with the use of titanium dioxide (TiO_2) in an electrochemical cell, has drawn considerable attention in recent years to the "acceleration of a photoreaction by the presence of a catalyst" [2] or photocatalysis. Photocatalysts work by the following principle: the material absorbs energy from photoexcitation, leading to the creation and separation of electrons and holes. Such a charge separation can generate electrical work through an external load or can be used to drive chemical (redox) reactions [3]. Research on photocatalysis has explored the decomposition of organic pollutants and microorganisms, the superhydrophilic self-cleaning properties of surfaces, and the photosplitting of water, among other applications. Semiconductors can act as photocatalysts because of their electronic structure and TiO_2, in particular, has been a popular choice. It is non-toxic and mechanically stable, can be fabricated at low-cost, and the anatase phase of TiO_2 has a bandgap of approximately 3.2 eV, ideal for excitation by light in the ultraviolet range.

Since the photocatalytic activity of TiO_2 is influenced by the crystal size, crystal structure, crystallinity, and surface hydroxylation, the synthesis of phase pure nanocrystalline anatase TiO_2 is challenging [4]. The most commonly tested compounds for decomposition through the photocatalysis are phenols, chlorophenols, pesticides, herbicides, benzenes, alcohols, dyes, pharmaceutics, humic acids, organic acids, and others.

In the last few years, researchers have been investigating the effects the photocatalytic activity of TiO_2 has on blood [5–8]. In particular, blood oxygenation can be obtained by splitting water molecules contained in plasma and thus allowing the combination of O_2 with hemoglobin molecules. In a previous work [6], a photocatalytic cell (PC) was developed, which was able to oxygenate bovine blood. More recently, a simpler PC was designed and used with human blood [8], even if the oxygenation was reached in static conditions.

Based on the idea of overcoming the previous limitations of blood oxygenation, we present in this work the development of a novel miniaturized PC able to operate on a flowing medium. The cell is made of biocompatible materials, thus making it possible to extend its application range to blood oxygenation. A pure anatase

* Corresponding author. Tel.: +39 0223993377.
E-mail addresses: marco.rasponi@polimi.it (M. Rasponi), tania_u@mit.edu (T. Ullah), rgilbert@mit.edu (R.J. Gilbert), gianfranco.fiore@polimi.it (G.B. Fiore), thorsen@LL.MIT.EDU (T.A. Thorsen).
[1] Tel.: +1 781 981 5227.

1350-4533/$ – see front matter © 2010 IPEM. Published by Elsevier Ltd. All rights reserved.
doi:10.1016/j.medengphy.2010.10.008

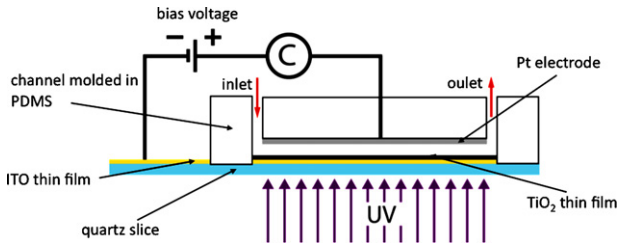

Fig. 1. Schematic representation of the photocatalytic cell system. A PDMS microchannel, where liquid flows through input and output ports, is bonded on a pretreated quartz slice. An ITO/TiO_2 junction is in fact deposited on the quartz surface. The top wall of the channel is covered by a Pt electrode, connected directly to the ITO layer, thus closing an electrical circuit.

TiO_2 thin film was obtained, and its photocatalytic activity was evaluated by degradation tests of methylene blue dye (MB) in aqueous dissolution. Finally, tests on bovine blood were carried out to evaluate the performance of the PC in terms of oxygenation rate.

2. Methods

2.1. Photocatalytic cell (PC) design

The photocatalytic cell is composed of (1) a microfluidic channel molded out of polydimethylsiloxane (PDMS); (2) a platinum (Pt) electrode that is exposed to the liquid flowing through the channel and by means of which a bias potential can be maintained; (3) an anatase TiO_2 thin film deposited onto a conducting indium tin oxide (ITO) thin film to form a semiconducting TiO_2/ITO junction.

A bias potential can be maintained across the height of the channel by means of the Pt electrode, deposited as thin film onto the PDMS that constitutes the top of the channel, and the ITO film that is beneath the TiO_2. In Fig. 1 a schematic representation of the functioning mechanism of the PC is sketched, showing electrodes, the path of the flowing liquid and the ultraviolet (UV) light source. The photocatalytic reaction takes place in the flowing liquid within a microchamber, whose design relies on a thin rectangular cross-sectioned channel (4.5 mm wide × 25 mm long × 0.1 mm high).

Studies have found that the photocatalytic efficiency can be increased by creating ITO/TiO_2 junction [8]. An applied bias voltage across the ITO/TiO_2 junction enhances the migration of the electron/hole pairs to the surface of the TiO_2 film where further oxidation of water can take place. The bias voltage also conducts away the electrons generated when the TiO_2 film is irradiated by UV light and minimizes the recombination process of electron and holes that can slow down the photocatalytic reaction [9–11].

2.2. PC development

2.2.1. Side-walls: PDMS microchannel

The microchannel was molded in PDMS using established soft lithography methods [12]. Silicon molds containing the outlines of the channel in positive relief were fabricated by spinning negative photoresist (SU8-50; MicroChem) at 1000 rpm for 60 s onto silicon wafers followed by exposure to UV-radiation through a transparency mask printed with the channel outlines. The molds were pretreated with a silanizing agent (chloro-trimethyl-silane, Aldrich), and PDMS (Sylgard 184, Dow Corning) (10:1 ratio of elastomer to curing agent) was spun 60 s at 1110 rpm onto them up to a thickness of 100 μm. After curing for 3 h at 80°C, the solidified PDMS within the channel region was peeled away to create a void through which the fluid can flow. Fig. 2A shows the steps required to obtain the 100 μm layer.

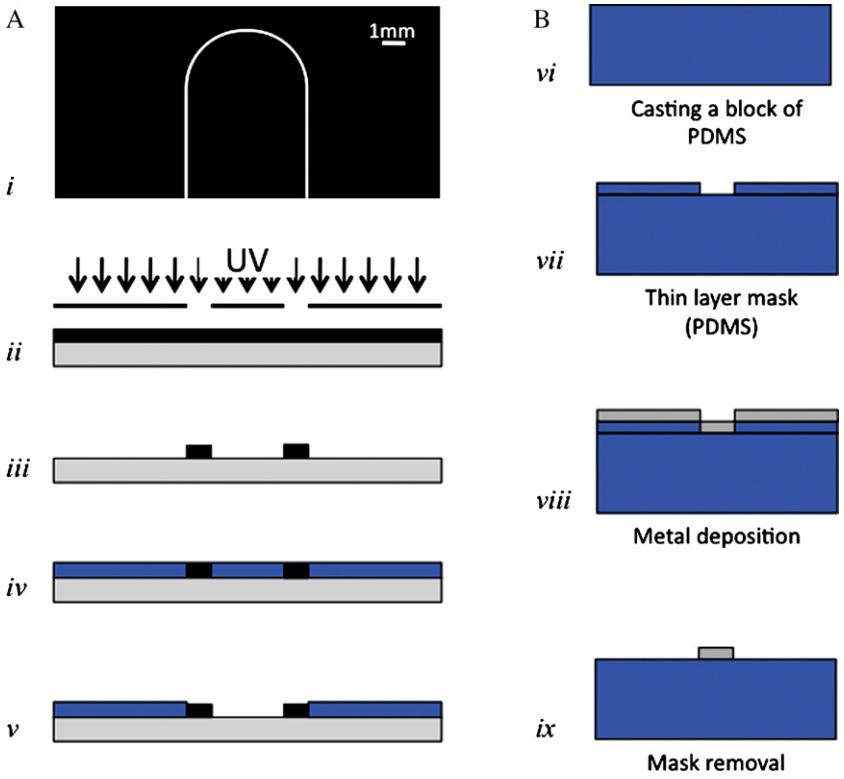

Fig. 2. Microfabrication process developed to realize the PDMS microchannel (A) and the patterned Pt electrode (B). The mask, in which only the patterns borders are drawn, (*i*) is brought into soft contact with the wafer covered with a 100 μm film of SU-8 resist (*ii*); the photoresist is exposed and developed to reveal the channel outline (*iii*); a 100 μm thick layer of PDMS is spun onto the wafer and cured (*iv*); the PDMS in the channel region is peeled away (*v*). A 5 mm thick layer of PDMS cured overnight (*vi*) is masked with a thinner PDMS layer (*vii*) and placed in a RF sputterer for Ti/Pt deposition (*viii*). After mask removal, a T-shaped Pt electrode is patterned (*ix*).