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Self-Organized, Free-Standing TiO_2 Nanotube Membrane for Flow-through Photocatalytic Applications

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ABSTRACT

In the present work we show a simple and robust fabrication process of a dense and free-standing membrane consisting of vertically oriented, both-side-open TiO_2 nanotubes. This membrane structure allows direct, size-selective, flow-through photocatalytic reactions with a very high efficiency.

Synthesis and characterization of one-dimensional nanostructures, in particular nanotubular symmetries, have attracted significant scientific and technological interest in the last decades. Such structures proved to be very efficient when using them for sensing applications, as catalysts in fuel cells or as templates for secondary material nanotube/nanowire formation.

Beginning with the discovery of carbon nanotubes,[1] a series of approaches to produce nanotubular structures other than carbon, such as the well-known cases of alumina[2] or titania,[3] have been explored. Among them special attention has been directed to TiO_2 due to its unique functional properties, such as increased photocorrosion resistance,[4] high photoconversion efficiency,[5,6] and the suitability as a material for purification of water and air.[7,8] Particular interest has been given to the self-organized electrochemical growth of TiO_2 nanotube layers on Ti, as it leads to an array of closely packed vertically aligned tubes. Recently, several attempts were carried out in order to understand the formation mechanism and to increase control over the morphology of these nanotubes.[9−11] Wider applications, however, have been hampered by the fact that the nanotube layers are attached to the metallic Ti substrate and the tubes are closed at their bottoms.

In the present work we describe the preparation of a free-standing TiO_2 membrane by a simple three-step process: (i) growth of a high aspect ratio TiO_2 nanotubular layer on Ti, (ii) selective dissolution of the metallic substrate, (iii) opening of the closed tube bottom by selective chemical etching. For the first step, a nanotubular layer of a thickness of >100 μm was grown electrochemically by controlled anodization of a Ti foil in a fluoride-containing ethylene glycol.[12] This leads to a dense array of aligned TiO_2 nanotubes, as shown in Figure 1a,b, attached to the Ti substrate. From Figure 1a it is evident that the array consists of very regular tubes with a diameter of 160 ± 30 nm and a wall thickness of 20 ± 5 nm. The layer is overall 145 μm thick and has very smooth walls typical of nanotubes grown in organic electrolytes.[10]

In order to separate the TiO_2 tube layer from the metallic Ti substrate, we selectively dissolved the metal by a treatment in water-free CH_3OH/Br_2 solution.[13] After this process, a free-standing nanotubular layer is obtained (see Figure 1e) that has an opaque appearance and easily can be handled by tweezers or other microhandling tools. However, it is evident from scanning electron microscopy that the bottom of the nanotubes after this process remains closed (Figure 1c). To open the closed bottoms, the wet nanotube layers were exposed (bottom side down) for 30 min to HF vapors. This procedure leads to preferential HF gas condensation at the tube bottoms and therefore causes etching of the TiO_2 layer at the bottom end.[14] The process is remarkably reliable and reproducible and leads to a bottom morphology of the nanotube layers as shown in Figure 1d. Clearly, some minor inhomogeneity in the bottom morphology is introduced, but overall the vast majority of the nanotubes are open and possess an appearance similar to the top.

In order to demonstrate the functionality of the membranes in terms of permeability and photocatalytic activity, the membranes were mounted on a PVC holder as shown in Figure 2b. The round membranes of 1 cm diameter were glued along their perimeter on a 0.5 cm diameter opening in the holder using epoxy resin.

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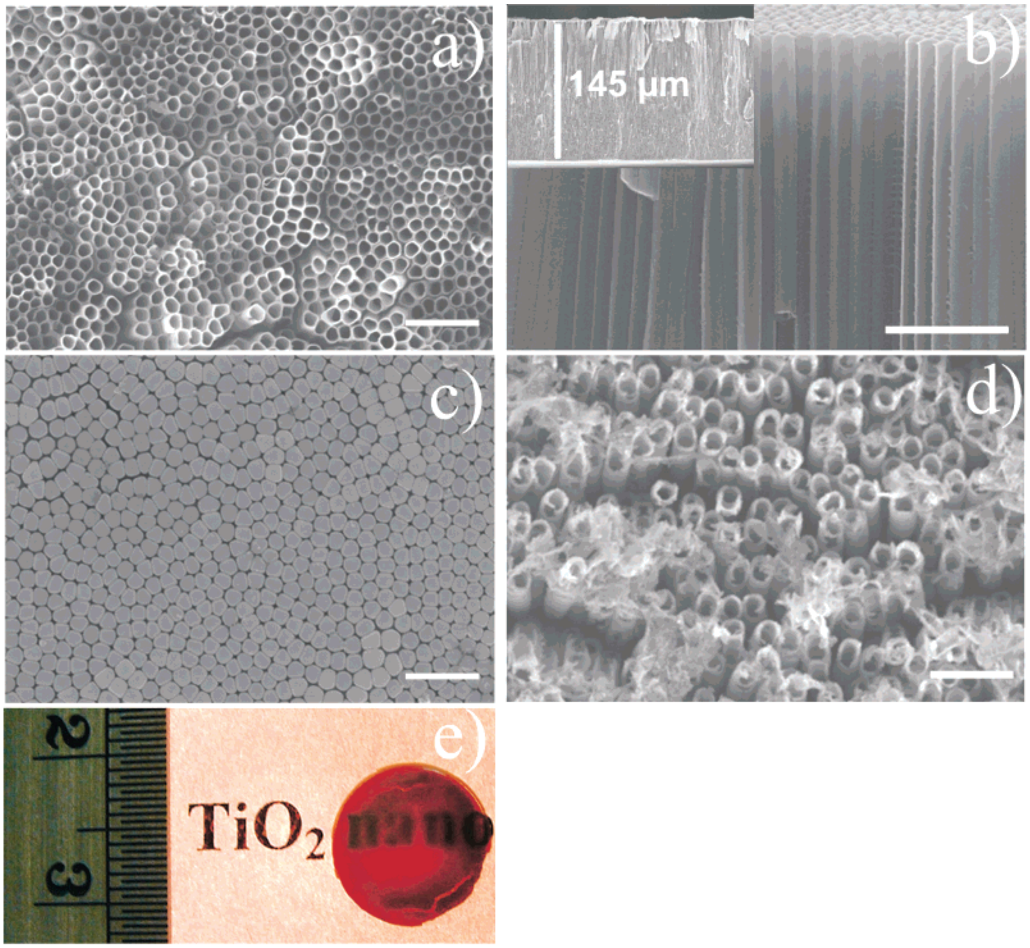

Figure 1. SEM images of the TiO_2 nanotube layer formed in ethylene glycol + 0.2 M HF at 100 V for 10 h anodization: (a) top view; (b) cross section. After selective substrate dissolution, an opaque free-standing layer with closed bottoms (SEM image Figure 1c) is obtained. By selective etching, the bottoms can be opened (SEM image, Figure 1d) producing a free-standing membrane (optical image in Figure 1e). The inset in (b) shows the total thickness of the TiO_2 nanotube layer. The bar in all the images corresponds to 1 μm.

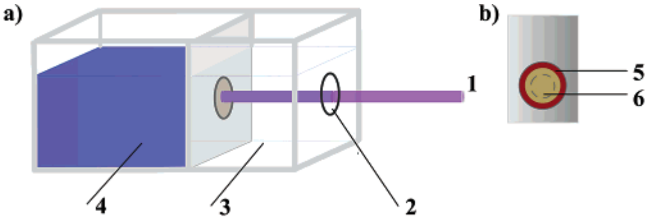

Figure 2. Schematical representation of the setup used for flow-through photocatalytic experiments. The chamber on the right is filled with distilled water, the chamber on the left is filled with MB, and between them a TiO_2 membrane is glued on a holder with an opening (1, laser; 2, quartz window; 3, distilled water; 4, MB; 5, epoxy glue; 6, TiO_2 nanotubular membrane).

The holder was then placed as a separator wall in a two-compartment cell with quartz glass as shown in Figure 2a. A series of experiments was performed using a 2×10^{-5} M methylene blue (MB) solution as "model pollutant"[15] frequently used for photocatalytic studies. It decomposes on TiO_2 surfaces under the influence of photogenerated charge carriers either by direct oxidation[16] or by $^{\bullet}OH$ radicals formed by reaction of valence band holes with water.[17]

In a first experiment using the membrane structure, the permeation was tested by filling methylene blue in one compartment and distilled water in the second (Figure 3a). After 20 h in the dark, i.e., in absence of photocatalytic activity, the methylene blue is equally distributed in the left and the right cell (Figure 3b); in other words, the concentration gradients are equilibrated.

In the next set of experiments one of the chambers was filled with MB (either compartment 1 or 2) and the other with distilled water, and the surface of the membrane was illuminated with 50 mW/cm^2 UV light through compartment 1. Figure 3c shows a typical result for both types of experiments after 20 h of illumination. In all cases, the solutions on both sides are essentially colorless showing successful photocatalytical decomposition of MB. Considering a tube length of 145 μm, one would expect photocatalytic activity to be confined to the illuminated side with a penetration depth and charge carrier diffusion length of only a few micrometers.

To demonstrate this, one can consider the results of Figure 4. The results of spectrophotometric results are compiled for three cases of compartment 1 to compartment 2 loading, MB/water dark, MB/water illuminated, and water/MB illuminated, and considering that the kinetics of photodecomposition can be approximated by a first-order kinetics.[18]

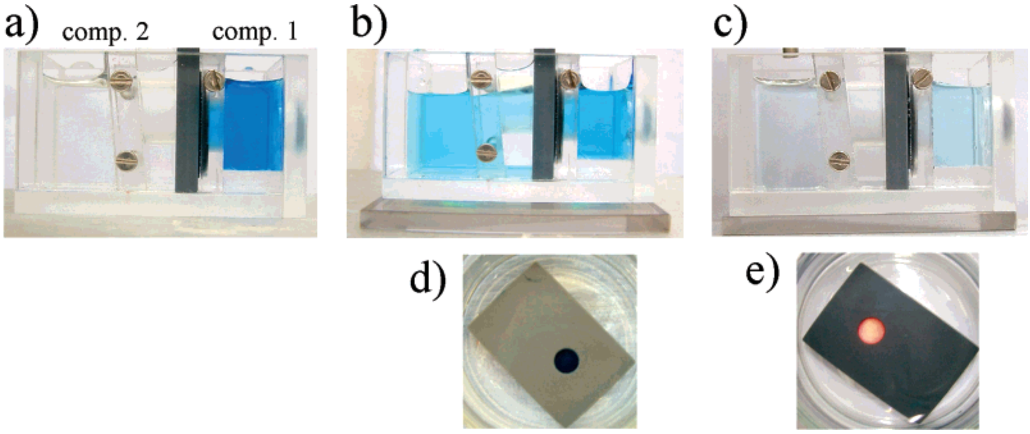

Figure 3. Experimental setup: (a) after filling compartment 1 with MB; (b) after 20 h in the dark (demonstrating that membrane is permeable); (c) after filling either compartment 1 or compartment 2 with MB and illuminating membrane for 20 h (demonstrating successful photocatalytic decomposition). Panels d and e show the holder with the membrane after the experiment b and after the experiment c, respectively.

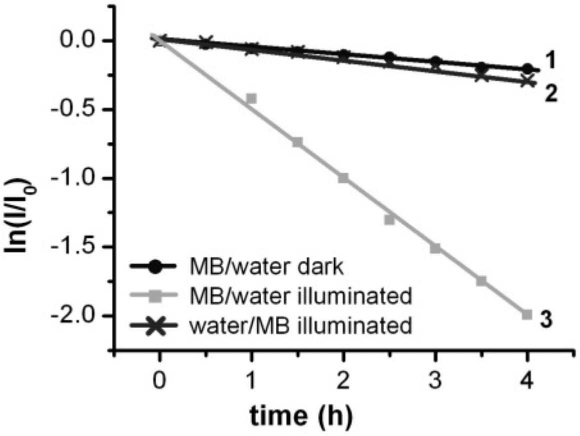

Figure 4. Evaluation of MB decoloration by photometric measurements. Measurements were always performed in the MB-containing compartment of the cell.

From the results, it is evident that the decay of the decoloration in the dark side of the compartment (curve 2) follows the plain diffusion case (curve 1). This rate is clearly slower than direct decomposition on the illuminated membrane (curve 3). Therefore, for the membrane produced here, the decomposition rate is determined by the diffusion rate, not by the rate of the photocatalytic process. In other words, complete pollutant removal is obtained by one flow-through cycle through the membrane (as all arriving reactants are immediately oxidized). Furthermore, the results show that MB decomposition indeed takes place only at the illuminated surface of the membrane.

In summary, we have demonstrated for the first time the direct fabrication of a flow-through TiO_2 nanotubular membrane that can be used as a photocatalytic microreactor. We believe that this TiO_2 membrane, fabricated using a simple electrochemical method, provides the key to a very broad range of applications. Compared to the case of self-ordered porous alumina, besides applications as a template or size-selective filter, the TiO_2-based structure can directly be used as a photoactive membrane for environmental cleaning or in biomedical applications due to the good biocompatibility of TiO_2.

Furthermore, considering that the size of the open channels can be adjusted over a range from 10 to 160 nm,[19] size selective highly defined nanotubular photoreactors can be constructed not only for pollution removal but also for biomedical applications or for controlling photodecomposition cascades[4] to a much higher extent than today.

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(12) To produce anodic TiO_2 nanotube layers, titanium foils (99.6% purity) with a thickness of 0.1 mm were first cleaned in acetone, 2-propanol, and methanol successively using an ultrasonic bath. Then the

substrates were rinsed with dionized (DI) water and dried in a nitrogen stream. Electrochemical anodization was carried out in a three-electrode cell; a Haber–Luggin capillary with Ag/AgCl (1 M KCl) was used as reference electrode, and platinum gauze served as a counter electrode. For the anodization we used a high-voltage potentiostat Jaissle IMP 88 PC. First the potential was ramped from open circuit potential (OCP) to 100 V with a sweep rate of 5 V/s followed by holding at 100 V for 10 h. The electrolyte was an organic electrolyte, ethylene glycol + 0.2 M HF.[11] All the experiments were carried out at room temperature.

(13) The TiO_2 nanotubular layers were separated from the Ti substrates by selective metal dissolution. The TiO_2/Ti specimens were immersed into a mixture of Br_2 and dry methanol (both Sigma Aldrich, 1:9 vol%) for 12 h under a dry N_2 atmosphere. This leads to a free standing nanotube layer floating in the etching solution. The layer can be seen by eye and captured by a grit or with tweezers. After being rinsed with methanol and distilled water, the layers were placed (closed tube side down) 1–2 cm above an open HF 48% bottle for 30 min. This leads to HF condensation at the bottom and preferential etching of the tube bottoms (i.e., the procedure opens the tubes).

(14) To open the oxide tubes bottoms the membranes were rinsed with DI water , placed in a Teflon grit, and mounted ~5 cm above the liquid surface of HF 48% (Merck) contained in a Teflon bottle. After 30 min the membrane was washed with DI water and dried in an Ar stream.

(15) Methylen Blue (from Merck) was used as a model pollutant in water with an initial concentration of 2×10^{-5} M. As UV light source a He-Cd laser with 325 nm wavelength and 50 mW/cm^2 output power was used. Percolation kinetics was followed by evaluating the MB absorbance at 668 nm using an Ocean Optics USB2000 spectrometer.

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