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Factors affecting preparation of photocatalytic TiO_2 metal membrane with reactive nano-structured tubes

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ABSTRACT

A photocatalytic TiO_2 metal membrane embedded with large surface area of anatase crystallites was successfully fabricated by anodization technique. The nano-structured anodized TiO_2 membrane was characterized using SEM and XRD techniques and the operational parameters to fabricate such as anodization time and applied anodic potential were also investigated. Regular nanotubular arrays were obtained using a KH_2PO_4 electrolyte with 0.35 wt. % NH_4F and 25 V of applied potential by anodization. By the SEM and XRD patterns, the anodized TiO_2 membrane showed the enhanced photocatalytic properties of anatase phase.

Keywords: Photocatalytic; Nanotubular; Anodization; TiO_2 membrane, Anatase; Organics removal

1. Introduction

Anodization is generally known as a useful method for modifying the surface structures to obtain nanoporous or nanotubular structures [1–6]. The surface of 'valve metals' (Ti, Al, Ta, Nb and so on) is instantaneously covered with a native oxide film when these metals are exposed to oxygen containing environment and can be used for fabricating ordered pore array [7,8]. The fabrication of nanoporous metal oxide templates with well-defined cylindrical pores and variable pore spacing has attracted considerable fundamental and technological interests. Self-organized nano porous TiO_2 structures have a large potential in view of their large surface area. Potential applications include use as biomaterials and photocatalysis for water and wastewater treatment [9–11].

Photocatalytic technologies for environmental purification have been developed to eliminate refractory organic contaminants. Yet, the use of aqueous suspensions of photocatalysts in practical applications is limited, because they require separation following treatment. Considerable work has been performed to develop immobilized TiO_2 catalysts on various substrates, such as thin films and membranes, for use in many applications [12]. The photocatalytic activity of immobilized TiO_2, however, is low due to exfoliation of the deposited TiO_2 thin film and to reductions in the effective surface area that is to be illuminated [13]. The catalytic efficiency and long-term durability of catalyst-polymeric membrane composites tend to counteract each other, wherein efficient hydroxyl radical production leads to degradation of the polymer matrices that embed the catalysts, such as TiO_2. The objective of the current study is to create a nano-structured membrane without deposition or coating with TiO_2 powders on membrane surface, but rather to form self-organized nano-structured photocatalytic nanotubes that serve as the basis for a photocatalytic nano-structured TiO_2 metal membrane. We evaluate the

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water permeability of this membrane and its photocatalytic performance with respect to organics decomposition and bacteria inactivation in aqueous solutions.

2. Materials and methods

2.1. Membrane fabrication

The nanotubular membrane was fabricated from a sintered titanium pipe (diameter: 16 mm, length: 10 mm). Prior to anodization, the sintered titanium pipe was ultrasonically cleaned in deionized water and acetone. For fabrication, we used an electrolyte composition of 1 M potassium phosphate monobasic (KH_2PO_4), 0.15 M NH_4F, and 0.2 M citric acid. Anodization was performed at 10°C using titanium as the anode and tantalum as the counterpart electrode. Schematic diagram for anodization is shown in Fig. 1.

2.2. Evaluation of photocatalytic activity of nanotubular TiO_2 membrane

Humic acid (HA) was selected as the model pollutants (Aldrich, USA). Stock HA solution (1000 mg l^{-1}) was prepared, as described [14]. The initial pH was adjusted after addition of the stock solution. The temperature of the prepared solution in the reactor was maintained at 20 ± 1°C with a thermostat. Photolysis of the TiO_2 membrane was initiated by exposing the reactor to UV irradiation. Every 20 and 30 min, a sample was withdrawn for COD_{Cr} and TOC analysis. Cellulose nitrate membrane filters (Whatman Plc., England) that had a pore size of 0.2 μm were used to remove solid particles from the samples. The UV/TiO_2 membrane system comprised a 64 W UV lamp, a pH meter, and a TiO_2 membrane filtration device. The working volume of the photoreactor was 8 l. UV illumination was provided by a 64 W, low-pressure mercury vapor lamp (UV-A type) that had a maximum light intensity output of 375 nm. The TiO_2 membrane had an effective photoreaction area of 4 × 58.4 cm^2. The solution temperature of the interior photoreactor was maintained by a thermostatic water bath. The initial pH of the solution was adjusted by adding an appropriate amount of 0.1 N NaOH and 0.1 N H_2SO_4.

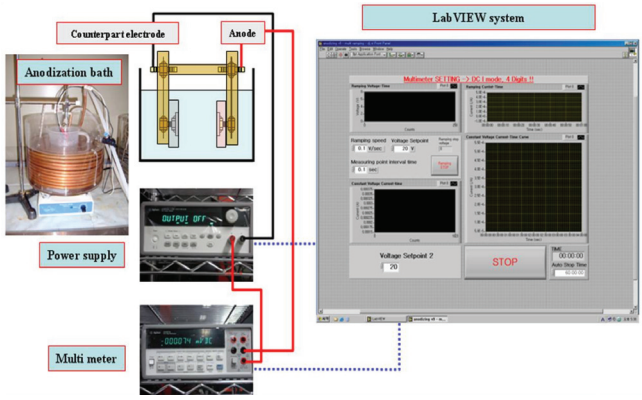

Fig. 1. Schematic diagram of anodization apparatus.

2.3. Analyses

HA concentration, expressed in terms of chemical oxygen demand (COD) and total organic carbon (TOC) concentration were measured with a DR 2010 (Hach Co., USA) and TOC analyzer (Shimadzu 5000, Japan) using a combustion infrared gas analysis method, respectively. To analyze the surface and vertical morphologies and the length of titanium oxide nanotubes, top view, profile, and bottom view were observed by field emission scanning electron microscope (FE-SEM S-4700, Hitachi, Japan). Characterization of the fabricated membrane was observed by X-ray diffractometry (XRD: D-Max 2200, Rigaku Co. Ltd., Japan) excited with Cu Kα radiation at 45kV and 100 mA.

3. Results and discussion

3.1. Effect of operational parameters for nano structured cylindrical tubes fabrication

Fig. 2 shows the FE-SEM top view and cross sectional images of titanium oxide nanotubes as a function of anodization time. Only small differences were

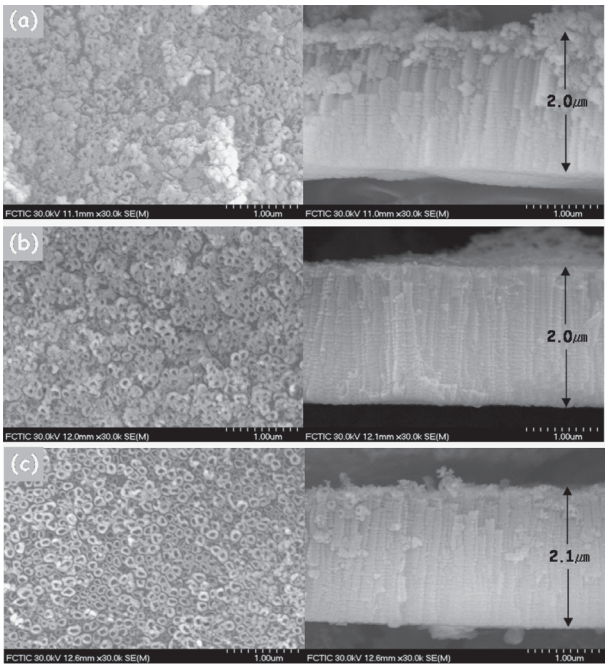

Fig. 2. FE-SEM top view and cross sectional images of titanium oxide nanotubes at 20 V for (a) 5 h, (b) 10 h and (c) 15 h.

observed in the range from 5 to 15 h of anodization time. Longer anodization time at constant anodic potential had little affected to the increase of nanotube length, however, it improved the shape resolution of nanotube in aqueous electrolyte. By-product precipitation was observed, possibly resulting from poor diffusion out of the titanium etched portion on the top of nanotube.

The anodization is started from F^-(aq) ion conducted to anode by anodic potential. The anodic potential is driving force of nanotubes growth. As an important operational parameter for anodization, the variation of anodic potential, multi step voltage method (MSVM) enabled anodized TiO_2 membrane to wipe out undesired oxide layer on top of the nanotubes as well as to acquire higher growth rate of titanium oxide nanotubes. Fig. 3 shows the variation of current transient by multi step voltage method during anodization. Fig. 4. shows the SEM of titanium dioxide nanotube by MSVM. We can find an increase the length of nanotubes as well as the reduction of breakdown in high anodic voltage potential. The current sharp peaks come from voltage steps to increase length of nanotubes and to eliminate undesired oxide layer on top of the nanotubes.

The photocatalytic efficiency of the anatase type TiO_2 crystal structure is known to be most effective compared other crystal forms such as rutile. Fig. 5 shows the XRD patterns of untreated Ti membrane and anodized nano-structured TiO_2 membranes with and without heat treatment. Heat treatment condition for fabricated nano-structured membrane was 500°C for 30 min. The XRD pattern for untreated Ti membrane (Fig. 5c) and nano-structured TiO_2 membrane without heat treatment (Fig. 5b) shows that they consist mostly of titanium (100), (002), (101) and (103). The titanium peaks originated from the Ti substrate. Anatase and rutile peaks were weakly presented and were not clear, which means that little crystalline structure was produced in TiO_2 membranes without heat treatment. After heat treatment at 500°C for 30 min, peaks of titanium oxide with anatase type of crystal structure are found in the XRD pattern, indicating a transition state from titanium to titanium oxide (Ti_xO_y). The anatase structure increased after heat treatment at 500°C. The peaks of anatase phase at 2θ near 25°, 47°, 54° and 55° are observed in the XRD pattern (Fig. 5a), which correspond to planes (101), (200), (105) and (211), respectively. Crystallites were primarily comprised of anatase.

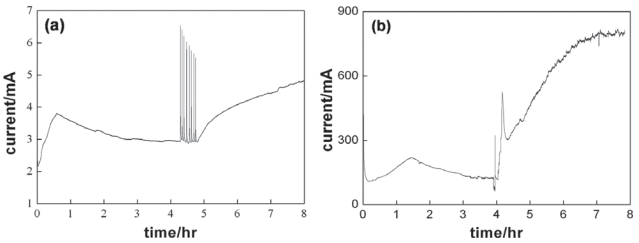

Fig. 3. Current transient curve during anodization in 1M KH_2PO_4 containing fluorine 0.15M aqueous electrolyte at 24 V for 8 h.

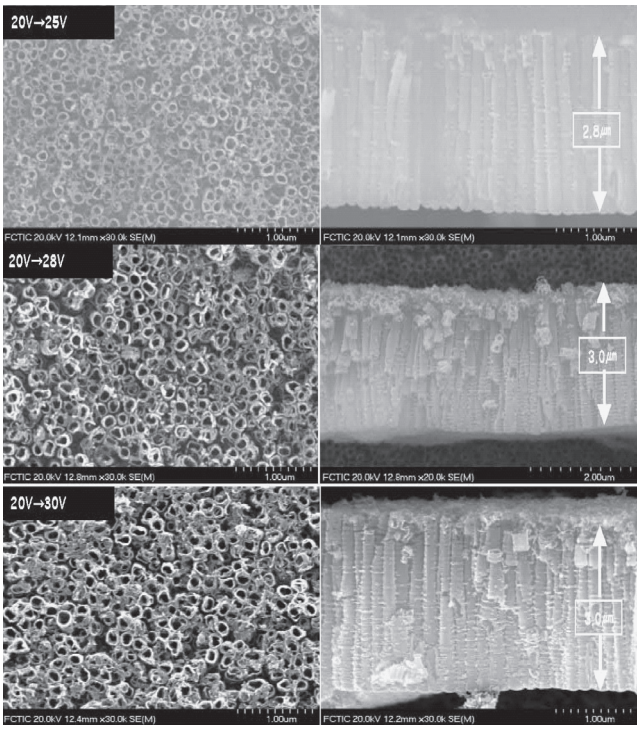

Fig 4. SEM of titanium dioxide nanotube by MSVM.

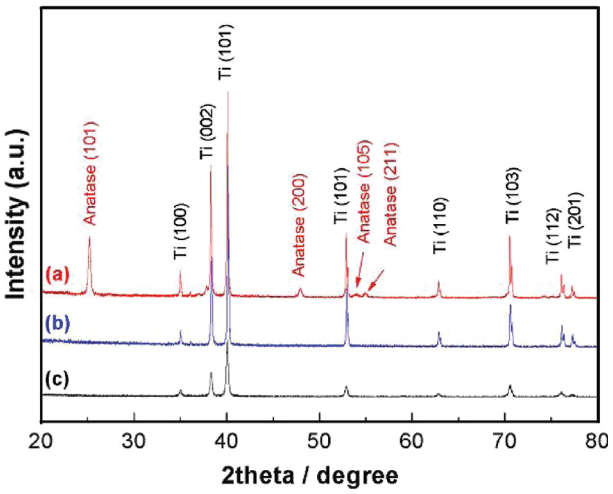

Fig. 5. XRD pattern of the nanotubular TiO_2 membrane: (a) nanotubular TiO_2 membrane after 30 min at 500°C, (b) nanotubular TiO_2 membrane, and (c) Ti membrane.

3.2. Photocatalytic activity of nanotubular TiO_2 membrane and flux behavior

The mechanism of photocatalysis in the presence of TiO_2 involves the enhanced formation of hydroxyl radicals, which actively participate in oxidation. Hydroxyl radicals have a significant effect on the chemical oxidation of organic compounds. Complete mineralization of many organic substances is possible in aqueous systems when sufficient hydroxyl radical levels are generated. The photocatalytic activity of the nanotubular TiO_2 membrane during removal of humic acid (HA) was investigated, as shown in Fig. 6. The nano-structured TiO_2 membrane with UV illumination showed much higher rate constants than that without UV illumination and without anodization as determined from the slopes of TOC and COD data. This high photocatalytic efficiency may be attributed to the crystal structures of anodized TiO_2 membrane. The anodized TiO_2 membrane with anatase type of crystalline nano-structure plays a significant role in the photocatalytic reaction for refractory organics removal. On the other hand, the treatment performance of TiO_2 metal membrane without annealing at 500°C for 30 min is similar to that of TiO_2 metal membrane without ultraviolet illumination. TiO_2 membrane with UV illumination showed reduced flux decline. Embedding with TiO_2 nanotubes on membrane surface appears to an effective method of maintaining good membrane permeability.

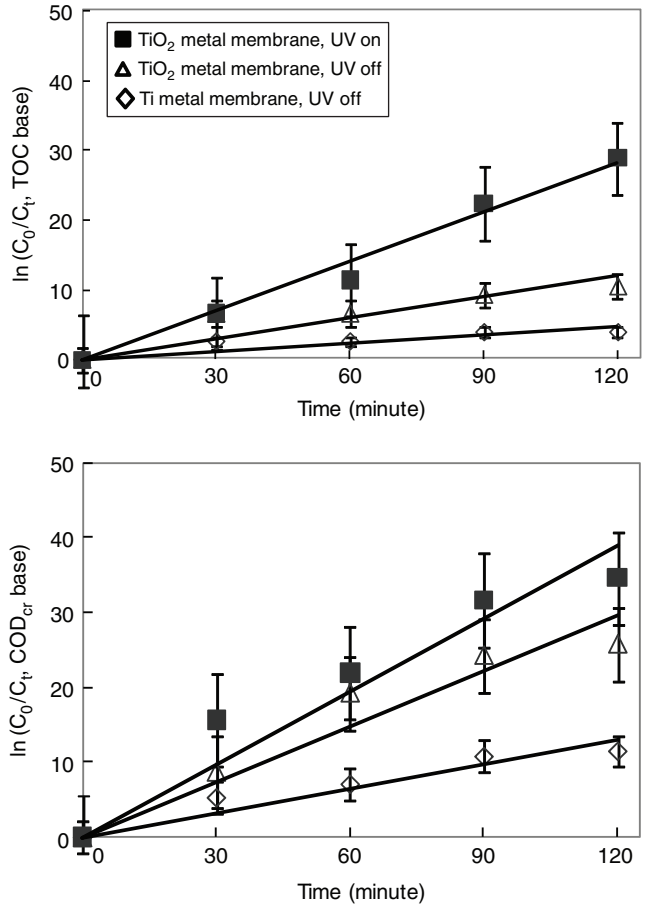

Fig. 6. The variation of *Ln (C_0/C_t)* as a function of reaction time on organics.

It is completely different from just conventional TiO_2 particles deposition methods such as sol-gel method. Through anodization, Ti membrane becomes to have permanent immobilized TiO_2 nano tube on membrane surface. It is able to provide enough contact time between organic contaminants and generated Reactive Oxygen Species (ROS) by UV illumination. This may be effective for fouling reduction and is easy for membrane cleaning.

4. Conclusions

Anodization technique was applied to fabricate a self-organized, nano-structured TiO_2 metal membrane on micro-porous Ti membrane substrate for water and wastewater treatment. Regular nanotubular arrays were obtained on micro porous membrane surface and inside under the condition of KH_2PO_4 electrolyte with 0.35 wt.% NH_4F and 25 V of applied potential by anodization. The results of SEM and XRD explained the surface characteristics and the reactivity; the SEM images proved better various structural properties such as very large surface area, controlled nanotube pore size and growth distribution. By the XRD patterns, the anodized TiO_2 membrane showed the enhanced photocatalytic properties of anatase phase and small crystal size. From the results of photocatalytic activity, the anodized nano-structured TiO_2 membrane annealing at 500°C had effective organics decomposition capacity. This anodization method enabled the fabricated nano-structured TiO_2 membrane to have high photocatalytic activity and desired pore structure.

Acknowledgements

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