

# Submicron Size of Alumina/Titania Tubes for CO<sub>2</sub>-CH<sub>4</sub> Conversion

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**Abstract**—This research provides a systematic way to study and better understand double nano-tubular structure of alumina (Al<sub>2</sub>O<sub>3</sub>) and titania (TiO<sub>2</sub>). The TiO<sub>2</sub> NT was prepared by immersing Al<sub>2</sub>O<sub>3</sub> template in 0.02 M titanium fluoride (TiF<sub>4</sub>) solution (pH=3) at 25 °C for 120 min, followed by annealing at 450 °C for 1 h to obtain anatase TiO<sub>2</sub> NT in the Al<sub>2</sub>O<sub>3</sub> template. Large-scale development of film for nanotube-based CO<sub>2</sub> capture and conversion can potentially result in more efficient energy harvesting. In addition, the production process will be relatively environmentally friendly. The knowledge generated by this research will significantly advance research in the area of Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, CaO, and Ca<sub>2</sub>O<sub>3</sub> nano-structure film fabrication and applications for CO<sub>2</sub> capture and conversion. This green energy source will potentially reduce reliance on carbon-based energy resources and increase interest in science and engineering careers.

**Keywords**—Alumina, titania, nano-tubular, film, CO<sub>2</sub>.

## I. INTRODUCTION

INCREASED energy demands and concerns about global warming compel scientists to keep looking for potential renewable energy sources unrelentingly. At the Copenhagen United Nations Climate Change Conference, these issues were not passed over, but rather extended to another more positive topic—control of greenhouse gases, especially carbon dioxide. More and more frequent human activities not only reduce supplies of fossil fuel but have also rapidly increased anthropogenic carbon dioxide to a level of great concern. Seeking alternative energy sources may allow us to retain our quality of life. Furthermore, solving the CO<sub>2</sub> issue will alleviate future problems.

In 1979, Honda and co-workers demonstrated use of photovoltaic reactions to recycle carbon dioxide via conversion into organic compounds in water [1]; much additional research on photocatalytic conversion of carbon dioxide in liquids followed [2]–[4]. This reaction involves only water and carbon dioxide to form a useful carbon cycle:



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The photocatalytic hydrocarbon-forming reaction requires photons; hence, a significant hydrocarbon reaction yield requires a photocatalyst that utilizes solar energy efficiently. Graetzel et al. [5] reported the production of methane from a mixture of carbon dioxide and hydrogen by using a nano-particle dye sensitized solar cell (NP-DSSC) system.

Because there are two double bonds between C and O (C=O), where each C=O has 745 (kJ/mol) bonding energy [6], CO<sub>2</sub> conversion always requires extremely high pressure and/or high temperature. However, CO<sub>2</sub> that is converted via a TiO<sub>2</sub> photocatalytic reduction process is relatively more manageable, allowing specific formation of compounds such as CH<sub>4</sub>, CO, CH<sub>3</sub>OH, HCHO, and HCOOH [7]. Ishitani [8] reported that platinum (Pt) dispersed on TiO<sub>2</sub> can improve the photocatalytic activity of TiO<sub>2</sub>. Slamet [9] pointed out that copper ion (Cu<sup>2+</sup>) supported on TiO<sub>2</sub> contributes significantly to improving CO<sub>2</sub> photocatalytic reduction activity. According to Varghese's [10] research, CO concentration is higher on Cu surface-loaded samples and H<sub>2</sub> concentration is higher on Pt loaded samples, indicating that Cu is more active in reducing carbon dioxide (2CO<sub>2</sub> + 4e<sup>-</sup> → 2CO + O<sub>2</sub>) while Pt prefers water reduction (H<sub>2</sub>O + h<sup>+</sup> → ·OH + H<sup>+</sup>). Also in Varghese's research, 6.8% conversion of carbon dioxide and water vapor to methane is achieved using nitrogen-doped titania nanotube arrays.

## II. EXPERIMENTAL PROCEDURE

Aluminum foil (99.7%) was put inside the electrochemical holder forming AAO through electrolyte polishing and anodization in electrochemical bath. As described in Chen [11–13], AAO film can be fabricated using an anodization process. The fabrication processes for 15 nm AAO template consists of the following steps:

- (i) Polish the aluminum (Al) substrate (99.7%); then anneal in an air furnace at 550°C.
- (ii) Electro-polish the substrate in a bath consisting of HClO<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>O, and CH<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub>OCH<sub>2</sub>CH<sub>2</sub>OH with 42 V DC for 10 minutes.
- (iii) First anodization – Polish the Al substrate with 18 V DC in H<sub>2</sub>SO<sub>4</sub> solution for 20 minutes.
- (iv) Remove the first anodization film by soaking in a solution of CrO<sub>3</sub> and H<sub>3</sub>PO<sub>4</sub> for 40 minutes.
- (v) Second anodization – Repeat anodization using the solution from the first anodization, but for a longer time (several hours) to form AAO films of varying thickness.
- (vi) Remove Al substrate by soaking in a solution of CuCl<sub>2</sub> and HCl for 30 minutes.

(vii) Widen pore diameter of AAO template using 5 vol.%  $\text{H}_3\text{PO}_4$  solution for 20 minutes.

According to above steps when the voltage and electrolyte (step iii) are change to 40V and 3 wt.%  $\text{C}_2\text{H}_2\text{O}_4$ , and pore widening time is 70 min (step vii), that 60 nm pore size of AAO can be formed. As well as, when the voltage and electrolyte (step iii) are change to 195V and 1 vol.%  $\text{H}_3\text{PO}_4$ , and pore widening time is 200 min (step vii), that 300 nm pore size of AAO can be formed.

### III. RESULTS AND DISCUSSION

The fabrication of nanomaterials with controlled size and composition is of fundamental and technological interest. The template synthesis method can produce nanomaterials of uniform size easily. In using templates to produce nanostructures, one must take into account the template's chemical, mechanical, and thermal stability, its insulating properties, the minimal diameter and uniformity of the pores, and the pore density. Aluminum anodization is one of the most controllable self-assembly processes. Anodic aluminum oxide (AAO) has received much attention, because of its high aspect ratio, uniform pore size, and ordering nanopore dispersion. Additionally, it is stable in the chemical and thermal surrounding, and an inexpensive process for fabrication. Detail on the structure and preparation of alumina templates can be found elsewhere.

When anodized in an acidic electrolyte and controlled in the suitable conditions, aluminum forms a porous oxide with very uniform and parallel cell pores. Each cell contains an elongated cylindrical sub-micron or nanopore normal to the aluminum surface, extending from the surface of the oxide to the oxide/metal interface, where it is sealed by a thin barrier oxide layer with approximately hemispherical geometry.

Honeycomb structures with high aspect ratios on the nanometer scale have received interest for various applications. To obtain a nanochannel array as a template, nanoporous alumina formed by anodization has widely been studied for several decades. Aluminum in the presence of air or aqueous electrolytes is always covered with a thin natural layer of alumina. When a positive voltage is applied to an aluminum substrate in a suitable electrolyte, pores form on the surface at almost random positions. However, under specific conditions, almost perfect hexagonally ordered pores in anodic alumina can be obtained.

The anodizing oxide film of AAO consists of two layers: the porous thick outer layer (porous type) that grows on an inner layer (barrier type), which is thin, dense and dielectrically compact, and called the barrier layer, the active layer or the dielectric layer. The barrier layer is very thin, typically with a thickness of between 0.1 and 2% of that of the entire film. Depending on the various electrolytes, anodizing time, and anodizing voltage, AAO could be formed to compact alumina, thick porous alumina, or etching types. Compact alumina (no pores) was formed in a very weak acid or neutral solution, and thickness was determined by applied voltage. Thick porous

alumina formed in a medium acid solution, and thickness was determined by anodizing time. Pore density increased when anodizing time increased, but decreased when anodizing voltage increased. For example, Fig. 1 showed the bottom images of AAO. (a) A dense barrier layer presents on the AAO bottom, (b) barrier layer was dissolved by  $\text{H}_3\text{PO}_4$  solution and honeycomb structure of bottom AAO was presented. (c) AAO pores were enlarged after pore widening process by  $\text{H}_3\text{PO}_4$  solution.

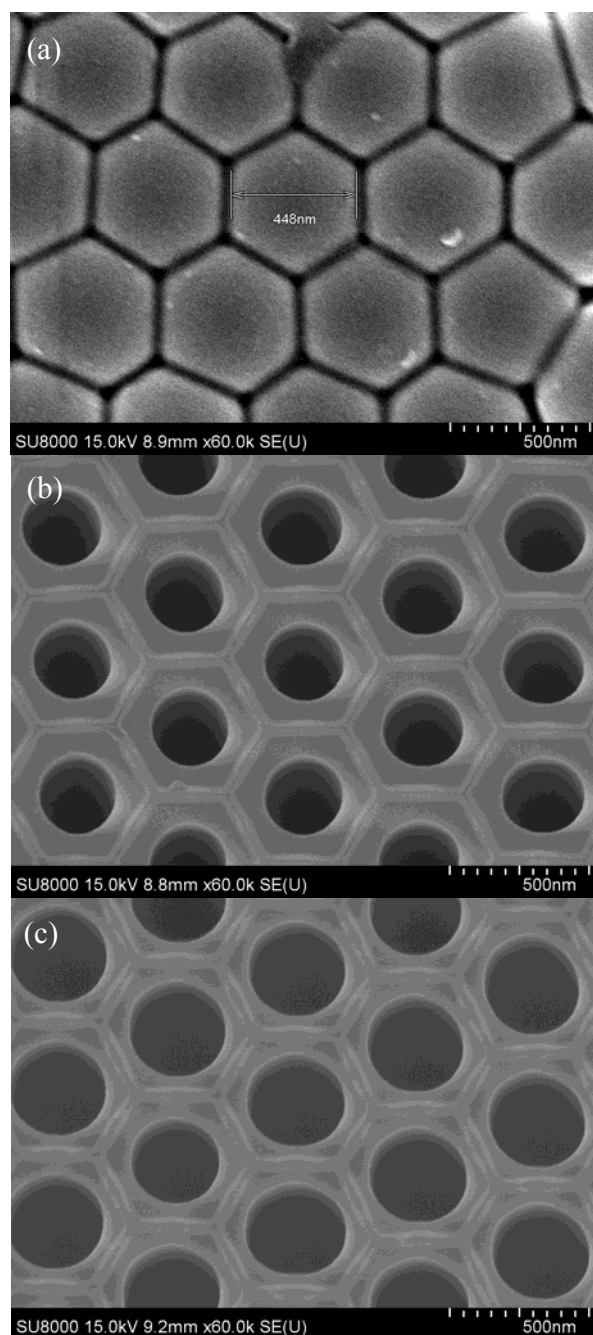


Fig. 1 Bottom images of AAO; (a) barrier layer, (b) honeycomb pores, enlarged pores

It is proposed that the mechanical stress at the metal/oxide

interface causes repulsive force between the neighboring pores which promotes the formation of an ordered hexagonal pore array. The voltage determines the barrier layer thickness and AAO cell size of the film. As two experience formulas can estimate the pore size and the pore distance of AAO. The pore size with voltage is:  $C=mV$ , where  $C$  is cell size (nm),  $V$  is anodizing voltage (V), and  $m$  is a constant (2~2.5). The pore distance with voltage is  $V=(2R-10)/2$ , where  $2R$  is spacing distance (5~1000 nm).

The thick outer porous layer has morphology of an array of self-organized hexagonal nanopores under suitable conditions of voltage, temperature, current density and electrolytic composition. The films formed in acid solutions below approximately 100 V are generally believed to be completely amorphous. At higher voltages, crystalline forms of  $\gamma$ -alumina are thought to be generated as local islands within the amorphous film.

Fig. 2 showed the top images of AAO. (a) Disordering pores presented after 200 V anodization and the pore sizes are between 300 ~500 nm. (b) Ordering pores present after pore widening process by  $H_3PO_4$  solution, the pore size is 450 nm. (c) AAO film thickness is 256 $\mu m$ , and (d) AAO has straight tube structure. The melting point of the barrier oxide is near 1000  $^{\circ}C$ , also the AAO template is stable around 800  $^{\circ}C$  which is lower than that of bulk alumina (2017  $^{\circ}C$  for  $Al_2O_3(\gamma)$ ).

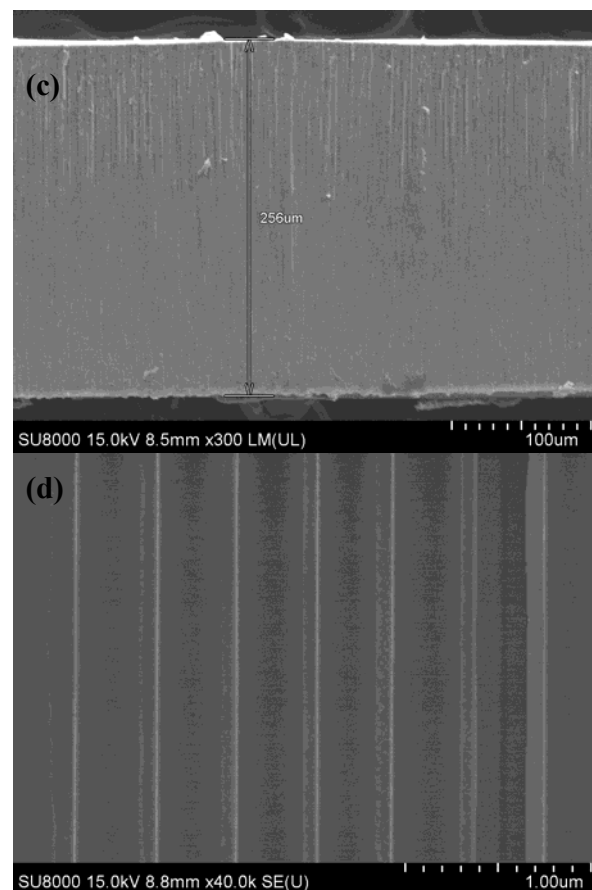
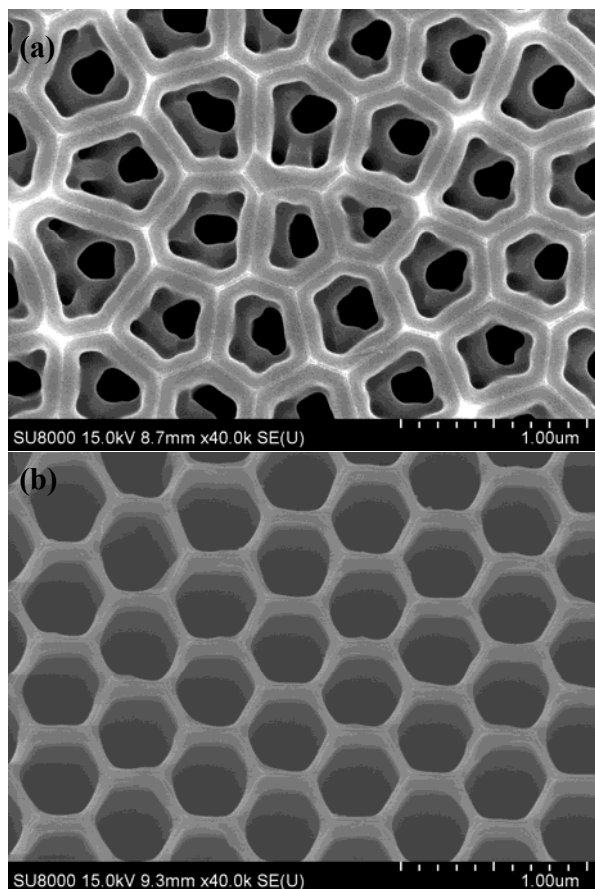


Fig. 2 AAO images; (a) disordering pores, (b) ordering pores, 256  $\mu m$  film thickness, (d) straight tube structure

Samples of 10 cm  $\times$  10 cm size AAO/ $TiO_2$  NT films were loaded into a glass chamber with valves for evacuation and gas feeding. After the samples were loaded, the chamber was evacuated to about 10 mTorr using a mechanical pump and then sealed. The valves were switched to make  $CO_2$  flow first through de-ionized water in a conical flask, and then flow into the reactor. The amount of  $H_2O$  vapor in the feed stream ( $H_2O/CO_2$  molar ratio) was regulated by the temperature of the water in the conical flask. Carbon dioxide (99.99% pure), via a mass flow controller (MKS instruments), was passed through a bubbler containing de-ionized water before entering the reaction chamber. Both inlet and outlet valves were kept open with the chamber flushed for more than 10 min and then closed, maintaining a nominal excess pressure of less than 1.0 psi. All photocatalytic carbon dioxide conversion experiments were done under AM 1.5 (300 W, 91160-Oriel Solar Simulator, 100  $mw\ cm^{-2}$ ). Reaction products were analyzed using a gas chromatograph equipped with flame ionization (FI) and thermal conductivity (TC) detectors. The FI detector enabled detection of most hydrocarbons, and the TC detector was used for other products. A schematic diagram of the experimental setting is shown in Fig. 3.

Fig. 4 shows (a) top-view and (b) side-view SEM images of  $Al_2O_3$  template made by 1%  $H_3PO_4$  solution and pore widening for 180 min with a tube diameter of 500 nm, and  $TiO_2$  NT

deposited inside  $\text{Al}_2\text{O}_3$  template. The thickness of the  $\text{TiO}_2$  NT pore wall depends on the deposition time. A longer deposition time causes a smaller  $\text{TiO}_2$  NT pore size, and a  $\text{TiO}_2$  rod presents after a long deposition time. However, the  $\text{TiO}_2$  NT surface area is reduced, with increased NT walls [14].

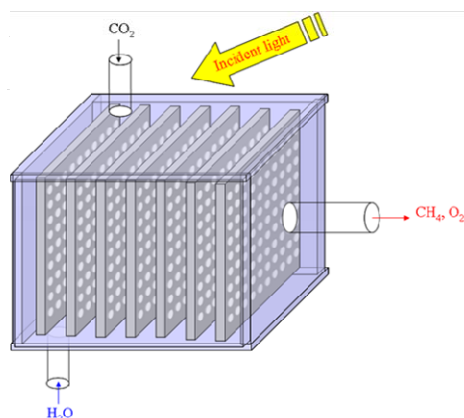


Fig. 3 Schematic diagram of a simple apparatus to measure insulator efficiency and heat transfer coefficient

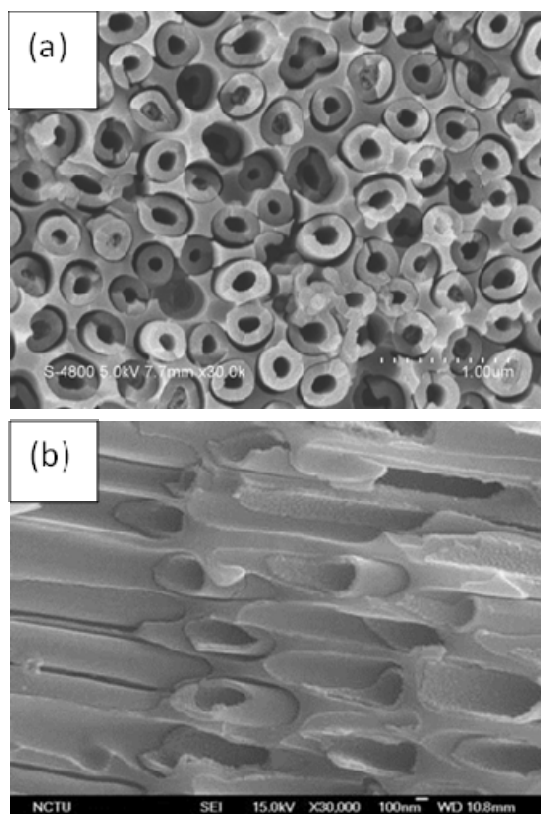


Fig. 4 SEM images of  $\text{TiO}_2$  NT in AAO template; (a) top view of  $\text{TiO}_2$  NT with 300 nm pore size on AAO template with 500 nm, (b) side view of  $\text{TiO}_2$  NTs inside AAO template

#### IV. CONCLUSIONS

Since the  $\text{Al}_2\text{O}_3$  template process is sensitive to the operation conditions, defects will appear in  $\text{Al}_2\text{O}_3$  template when

unsuitable conditions are used. The conditions include electrolyte temperature, applied voltage, electrolyte composition, electrolyte stirring, and current density distribution. In an anodization process, the working electrode presents an exothermic reaction. Control of electrochemical parameters when preparing small-scale samples for academic research is not difficult. In mass production environments, however, maintenance of constant current density and temperature becomes a critical issue. In this paper we have success made a large size of nano-structure tubular film which is a potential material for green energy application.

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