

Study on Hydrophilicity of Anodic Aluminum Oxide Templates with TiO₂-NTs

Yu-Wei Chang, Hsuan-Yu Ku, Jo-Shan Chiu, Shao-Fu Chang, Chien-Chon Chen

Abstract—This paper aims to discuss the hydrophilicity about the anodic aluminum oxide (AAO) template with titania nanotubes (NTs). The AAO templates with pore size diameters of 20-250 nm were generated by anodizing 6061 aluminum alloy substrates in acid solution of sulfuric acid (H₂SO₄), oxalic acid (COOH)₂, and phosphoric acid (H₃PO₄), respectively. TiO₂-NTs were grown on AAO templates by the sol-gel deposition process successfully. The water contact angle on AAO/TiO₂-NTs surface was lower compared to the water contact angle on AAO surface. So, the characteristic of hydrophilicity was significantly associated with the AAO pore size and what kinds of materials were immersed variables.

Keywords—Anodic aluminum oxide, nanotube, anodization, Sol-Gel, hydrophilicity.

I. INTRODUCTION

A recent surge of research on nanostructures has given us new opportunities and challenges. For example, titania has been described in the literature to capture its applications such as catalysis [1], sensors [2], environment [3], dielectrics [4], optoelectronics [5], and solar cells [6]-[8]. The titanium dioxide has three stable phases: anatase, brookite, and rutile [9]. The phase transformation counts on the annealing temperature at a constant oxygen pressure, as in an air furnace.

AAO has been widely used for the templates to fabricate nanostructures including nanotubes [10], nanorods [11], nanowires [12], whiskers [13] and nanospheres [14] due to its high melting point, hardness, high temperature strength, electrical or thermal insulation, high aspect ratio, and uniform pore size. Additionally, aluminum anodization is probably the most controllable self-assembly process at lower cost, thus making it a candidate material for the nanomaterials template. The structure and fabrication of AAO have been reported [15]-[17].

In this work, AAO template was made by a two-step anodizing process on a 6061 aluminum alloy substrate in acid solutions of (COOH)₂, H₂SO₄ or H₃PO₄; TiO₂ nanotubes were made by the sol-gel deposition on AAO. Our objective in this paper is to discuss the hydrophilicity of AAO surface with

TiO₂-NTs.

II. EXPERIMENTAL PROCEDURE

6061 aluminum alloy substrate was first ground to #2000 by SiC waterproof paper and was then annealed in an air furnace at 550 °C for 1 h. The sample was then put inside the electrochemical holder forming AAO through electrolyte polishing and anodization in electrochemical bath. The fabrication processes for AAO template with TiO₂ NTs consist of the following steps:

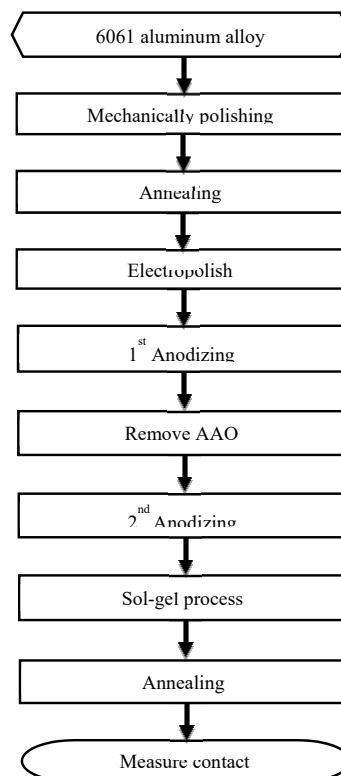


Fig. 1 Flow chart of experimental procedure

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- (i) The 6061 aluminum alloy substrate pretreatment – Polish the substrate first and then electro-polish in a electrochemical bath consisting of CH₃(CH₂)₃OCH₂CH₂OH, HClO₄, C₂H₆O with 40V DC.
- (ii) First anodization and then remove the first anodization film by soaking in a solution of 1.8 wt.% chromic acid and 6 vol.% H₃PO₄ for 30-40 minutes.
- (iii) Second anodization – Anodize the substrate with 18V DC in H₂SO₄ solution for 1-3h to form AAO templates of

different thickness.

- (iv) Adjust pH value of DI-water to 1.0–1.3; then add TiF_4 into the solution.
- (v) Immerse sample into TiF_4 solution for 10 min.
- (vi) Adjust pH value of TiF_4 solution to 3.0–3.3; then immerse sample into the solution for 120 min.
- (vii) Annealed the sample in an air furnace at 550 °C for 3h.

When the parameters (step **iii**) are changed to 40 V and 3 wt.% $\text{C}_2\text{H}_2\text{O}_4$, then 50 nm pore size of AAO can be formed. Also, when the voltage and electrolyte (step **iii**) are changed to 180V and 1 vol.% H_3PO_4 , that 250 nm pore size of AAO can be formed. After the above steps, anatase TiO_2 NTs can be obtained on the AAO template.

III. RESULTS AND DISCUSSION

In this study, we constructed an experiment equipment as shown in Fig. 2 that consists of a heater (to heat the TiF_4 solution), a stirring rod (to maintain the dispersal of the solvent), a thermometer and a beaker (to put the sample inside).

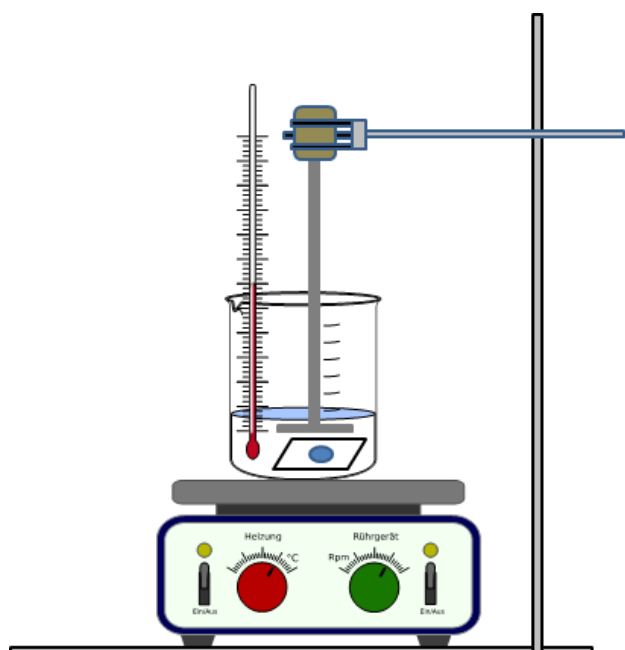


Fig. 2 Schematic diagram of AAO template with TiO_2 NTs experiment equipment

Fig. 3 shows (a) a 6061 aluminum substrate after electro-polish treatment and a 6061 aluminum substrate after the anodization and sol-gel deposition process; (b) the hydrophilicity test of an electro-polish sample. It shows that the surface after electro-polish treatment is wettable but not hydrophilic.

Fig. 4 shows the hydrophilicity test of AAO template (using H_2SO_4 solution) (a) the AAO contact angle is 44.78°; (b) the contact angle of AAO after sol-gel deposition process is 0°; (c) the contact angle of AAO after sol-gel deposition and sealing process is 4.84°; (d) SEM image of H_2SO_4 AAO pore size is 20 nm. It shows that the AAO surface is super-hydrophilic after

sol-gel or sealing process.

Fig. 5 shows the hydrophilicity test of AAO template (using $\text{C}_2\text{H}_2\text{O}_4$ solution) (a) the AAO contact angle is 27.34°; (b) the contact angle of AAO after sol-gel deposition process is 7.93°; (c) the contact angle of AAO after sol-gel deposition and sealing process is 3.58°; (d) SEM image of $\text{C}_2\text{H}_2\text{O}_4$ AAO pore size is 50 nm. It shows that the AAO surface is hydrophilic after sol-gel process and super-hydrophilic after sealing process.

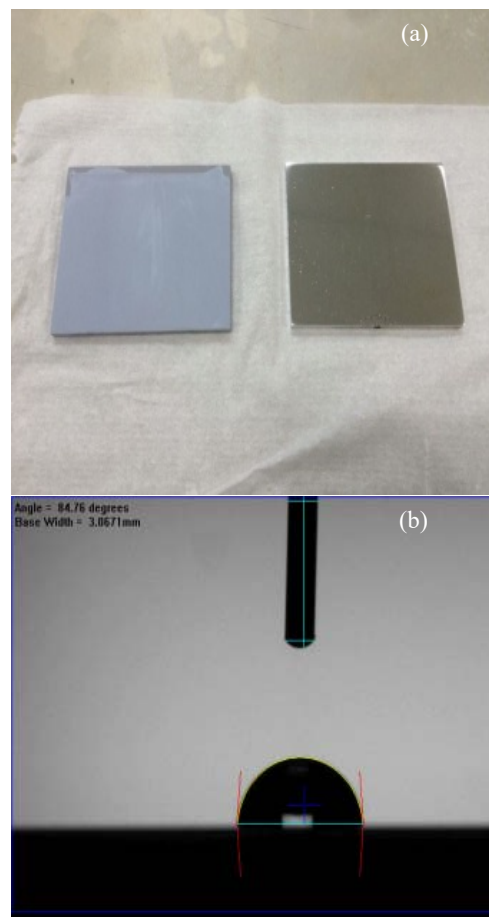


Fig. 3 Schematic diagram of (a) an electro-polish sample and a AAO template with TiO_2 NTs; (b) the electro-polish sample's contact angle is 84.76°

Fig. 6 shows the hydrophilicity test of AAO template (using H_3PO_4 solution) (a) the AAO contact angle is 37.45°; (b) the contact angle of AAO after sol-gel deposition process is 11.66 degrees; (c) the contact angle of AAO after sol-gel deposition and sealing process is 12.05°; (d) SEM image of H_3PO_4 AAO pore size 250 nm. It shows that the AAO surface is wettable but not hydrophilic after sol-gel or sealing process.

AAO film with different pore size and thickness can be made by altering parameter values such as solution, time of anodization, applied voltage, electrolyte temperature, etc. For instance, AAO with 40 nm to 80 nm pore diameter can be produced by anodization of 3 wt.% $(\text{COOH})_2$ solution; AAO with 8 nm to 25 nm pore diameter can be produced by

anodization of 10 vol.% H_2SO_4 solution; AAO with 180 nm to 350 nm pore diameter can be produced by anodization of 1 vol.% H_3PO_4 solution.

The results revealed that the kinds of acidic solution and applied voltages appear to be important variables in the pore size and pore density of AAO templates. Generally, there is a suitable range of applied voltage in each concentration of acidic

solution. Clearly, the findings indicate that AAO template possesses the wettability itself. It can be reasoned that the structure of AAO template is porous, and then, the capillarity action will be occurred. Furthermore, the contact angles reduced after immersing titanium in AAO templates by sol-gel and sealing process.

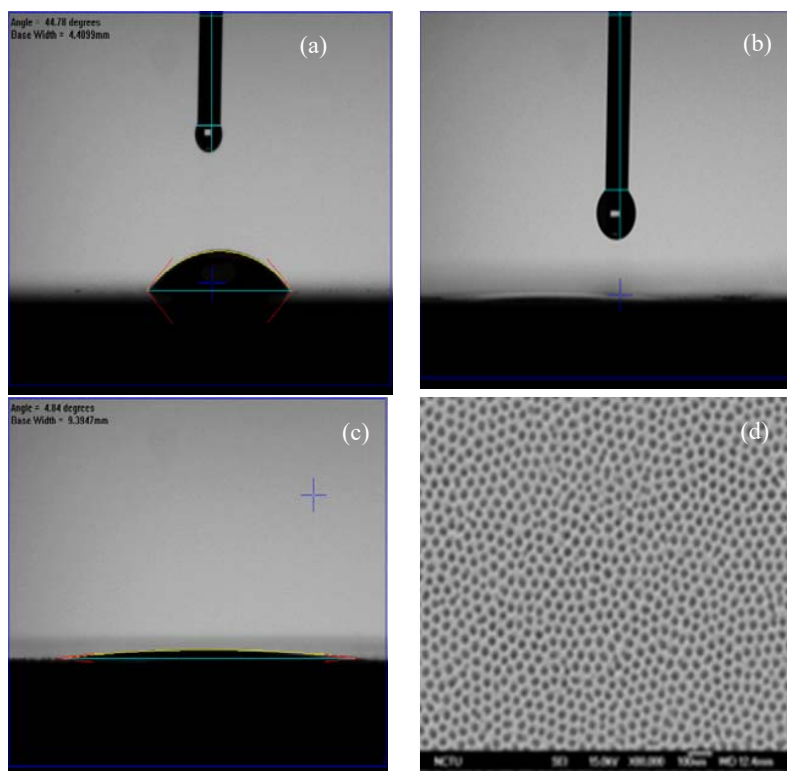
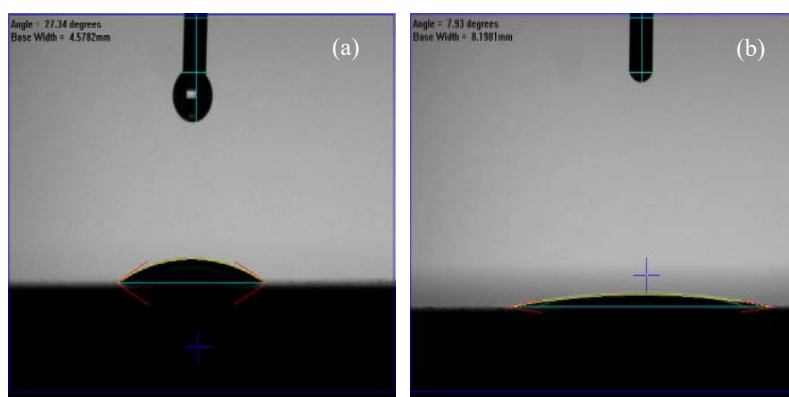


Fig. 4 Schematic diagram of (a) the AAO contact angle is 44.78°; (b) the contact angle of AAO after sol-gel deposition process is 0°; (c) the contact angle of AAO after sol-gel deposition and sealing process is 4.84°; (d) SEM image of H_2SO_4 AAO pore size is 20 nm



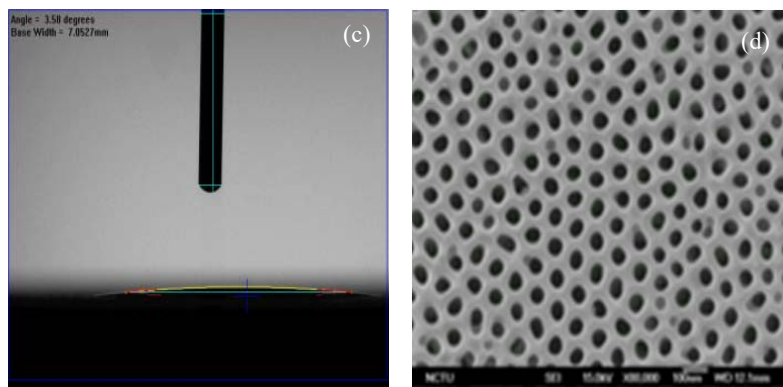


Fig. 5 Schematic diagram of (a) the AAO contact angle is 27.34°; (b) the contact angle of AAO after sol-gel deposition process is 7.93°; (c) the contact angle of AAO after sol-gel deposition and sealing process is 3.58°; (d) SEM image of $C_2H_2O_4$ AAO pore size 50 nm

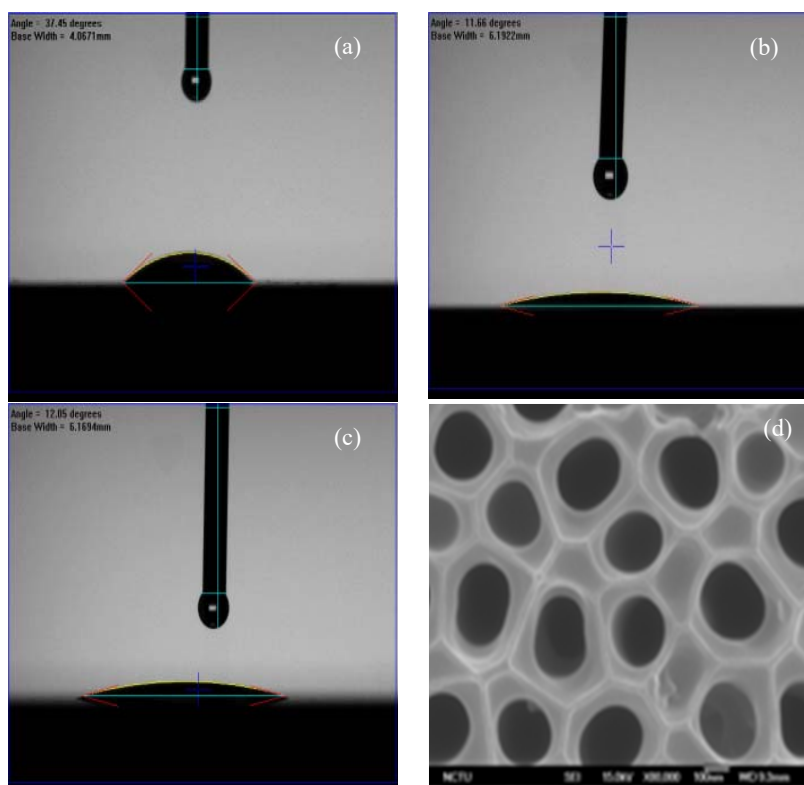


Fig. 6 Schematic diagram of (a) the AAO contact angle is 37.45 °; (b) the contact angle of AAO after sol-gel deposition process is 11.66 °; (c) the contact angle of AAO after sol-gel deposition and sealing process is 12.05°; (d) SEM image of H_3PO_4 AAO pore size 250 nm

IV. CONCLUSIONS

To conclude, the present study is preliminary research on evaluating the hydrophilicity property about the AAO with TiO_2 NTs, but its relevance to the pore size research of AAO can also be seen. The ordered array Al_2O_3 NT films with different pore diameters were varied with kinds of acid solution, applied voltage, and electrolyte temperature principally. Moreover, titanium was immersed in the AAO templates by sol-gel process. The results revealed that pore size of AAO templates appears to be an important variable in wettability. Furthermore, a major finding is that the contact

angle reduced after immersing titanium in AAO templates. But, it remains unclear why the values of AAO contact angle could not have a tendency toward the AAO pore size. This kind of TiO_2 nanostructure is still very much in the experimental stage and much more has yet to be done. There is a continuing need for an adequate theoretical basis for the practical application of AAO templates with TiO_2 NTs.

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