

# Fabrication and Photocatalysis Application of Nanoporous Anodic Alumina Formed at Relatively High Temperature



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## Abstract

The nanoporous anodic aluminum oxide (AAO) is a well-known nanomaterial template that can be used for the synthesis of low-dimensional nanomaterials, as a free-standing membrane or as an etching mask for pattern transfer for various applications. Two-step potentiostatic direct-current anodization (DCA) from high-purity aluminum (Al,  $\geq 99.99\%$ ) at low temperature ( $0-10^\circ\text{C}$ ) to avoid Joule-heat enhanced dissolution effect is commonly used for fabricating the AAO template. In contrast, an hybrid pulse anodization (HPA) consisting of the normal-positive and small negative voltages is an effective method to diminish the Joule heating for synthesizing AAO even from the cheap low-purity ( $\leq 99.5\%$ ) Al foil at a relatively high temperature (HT) of  $20-25^\circ\text{C}$ . The pore structure quality of AAO using HPA is better than that using DCA at relatively high temperature due to its effective cooling. The HPA-HT AAO may also be synthesized from the Al coating on high-roughness substrate for more effective surface area to enhance  $\text{TiO}_2$  photocatalysis performance. The HPA has advantages not only in manufacturing convenience but also for enhancing pore characteristics of AAO at harsh conditions of cheap low-purity Al foils and relatively high temperature for more possibility of application.

**Keywords:** Nanoporous alumina; AAO; Anodization; Purity; Temperature; Photocatalysis

**Abbreviations:** AAO: Anodic aluminum oxide; DCA: Direct-current anodization; HPA: Hybrid pulse anodization; HT: High temperature;  $D_p$ : Pore diameter;  $D_{int}$ : Interpore distance;  $w$ : Wall thickness;  $t_b$ : Barrier thickness;  $t$ : AAO thickness;  $E$ : Potential difference;  $I$ : Corresponding current; PA: Pulse anodization

## Introduction

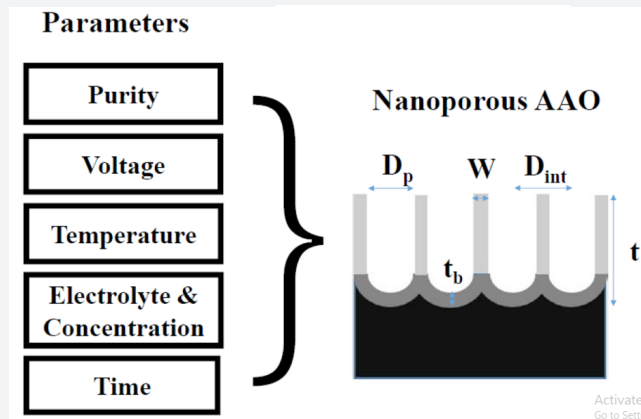
The nanostructured materials with much enhanced physical and chemical properties compared to the bulk ones have attracted much research over these decades. A popular example is the lotus effect that has self-cleaning properties due to the super-hydrophobic property of the leaf with nanostructured surface. The nanoporous anodic aluminum oxide (AAO) material is a significant template that is used for the synthesis of 1D-2D nanomaterials, as a free-standing membrane for filters or as an etching mask for pattern transfer on a desired material in different categories of application. Compared with the porous polymer template i.e., polycarbonate or polystyrene [1,2], AAO has advantages of nanoscale pores, self-organization, controllable pore size and thermal stability [3,4]. Conventional AAO templates are synthesized using two-step direct current anodization (DCA) at low temperature ( $0-10^\circ\text{C}$ ) to avoid dissolution effect. On the contrary, an effective method of hybrid pulse anodization (HPA) with normal-positive and small negative voltages is practical for AAO synthesis at a relatively high temperature of  $20-25^\circ\text{C}$  for

enhancing performance of AAO structure from the cheap low-purity ( $\leq 99.5\%$ ), costly high-purity ( $\geq 99.99\%$ ) aluminum foils and the Al coating on the desired substrates [5-7]. The schematic overview of the process parameter dependent pore geometry and morphology of AAO is shown in Figure 1. The important factors of pore geometry includes the pore diameter ( $D_p$ ), interpore distance ( $D_{int}$ ), pore wall thickness ( $w$ ), barrier thickness ( $t_b$ ) and AAO thickness ( $t$ ) those are linked to different application. The fabrication parameters like the Al purity, applied voltage, operation temperature, electrolyte content & concentration and time are related to the pore geometry and profile of AAO.

The defects in low-purity Al may increase the dissolution for irregular pore structure. The anodization voltage is proportional to the  $D_{int}$  and generally has a positive relation to  $D_p$ . Also, the electrolyte type has its proper anodization voltage to AAO formation. The Titanium dioxide ( $\text{TiO}_2$ ) is widely used for photocatalyst after the discovered Honda-Fujishima effect in 1972 [8]. A great number of publications show the research on the microstructure

of  $\text{TiO}_2$  for enhancing performance of photocatalyst. The AAO was studied to assist synthesis of high-order  $\text{TiO}_2$  nanowire arrays via sputtering and atomic layer deposition for comparison to explore the potential catalysis, and energy applications in the future [9]. Using optoelectronically engineered nanoporous photonic crystals for visible light-enhanced photocatalysis is proposed recently

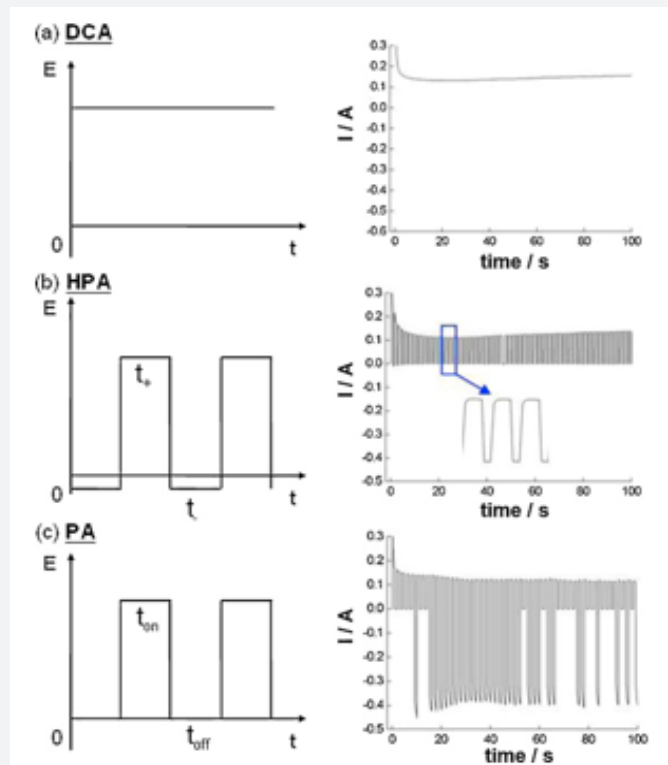
[10]. In addition, the HPA at a relatively high temperature is useful for anodizing the high-roughness Al film with hillocks or spheres morphology to form the modified 3D AAO that is advantageous for the following  $\text{TiO}_2$  film or nanoparticles coating for enhancing the photocatalysis enhancement owing to the increased contact surface area [7,11].



**Figure 1:** The overview of fabrication parameters and the pore geometry and morphology of AAO including pore diameter ( $D_p$ ), inter-pore distance ( $D_{int}$ ), pore wall thickness ( $w$ ), barrier thickness ( $t_b$ ) and thickness ( $t$ ).

### Discussion

#### Fabrication of AAO at Relatively High Temperature



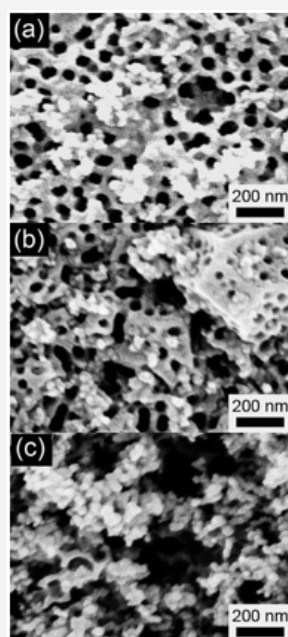
**Figure 2:** 13 Real-time monitoring current-time diagram. Comparison of the relationship between the applied potential difference ( $V$ ) and the corresponding current ( $I$ ) as a function of time ( $t$ ) in (a) DCA (b) HPA and (c) PA process.

The traditional two-step direct-current anodization (DCA) on Al foils at a constant voltage may lead to the well-ordered AAO configuration compared to the one-step anodization. However, the stern process conditions are usually required at low temperatures of 0-10°C from high-purity (>99.99%) Al foils. The low electrolyte temperature is to reduce the Joule-heat induced dissolution rate of alumina during anodization but corresponds to the decreased growth rate. On the other hand, Chung et al. [5,6] demonstrated the feasibility of AAO fabrication from low-purity Al foil ( $\leq 99.5\%$ ) at relatively high temperature (HT) of 20-25°C using the hybrid pulse anodization (HPA) method consisting of the normal-positive and small negative voltages that could overcome the limitation of conventional low-temperature AAO process to form nanopores by diminishing Joule heat during anodization, even from the cheap low-purity Al material. Figure 2 shows the real-time monitoring current-time diagram of the relationship between the applied potential difference (E) and the corresponding current (I) as a function of time (t) in (a) DCA (b) HPA and (c) PA (pulse anodization) process at 25°C, respectively. The continuous I-t diagram in DCA (Figure 2a) leads to heat accumulation for the thermally enhanced Joule heat dissolution to break the pore structure formed at 25°C. In contrast, the pore structure formed by HPA at 25°C can be kept due to the effective cooling of tiny current during t- duration to diminish the Joule-heat dissolution (Figure 2b). Regarding the I-t relation by conventional pulse anodization (PA) with alternate positive and zero potential differences (Figure 2c), we can see the clear negative current during PA compared to the nearly zero current during HPA. In the toff duration of PA with 0 V, it is like a discharging capacitor to randomly release the charges accumulated in ton duration for the cathodic current that is attributed to the impurities of Al and the quick change of

polarization between two electrodes in a very short time. For the t- duration of HPA with a small value, it can reduce the discharging effect and have insufficient potential to overcome the energy barrier height of cathodic reduction reaction. Therefore, nearly zero cathodic current occur accordingly.

### Application of AAO for enhancement of TiO<sub>2</sub> photocatalysis

The case study of nanoporous AAO template applied for enhancing TiO<sub>2</sub> photocatalysis is that using the commercial P25-TiO<sub>2</sub> nanoparticles (21±5 nm) coating by sol-gel method on the various HPA AAO films on the Si substrates. The formation of HPA AAO pores on the smooth (2D) and extremely rough (3D) Al films can produce the 2D planar and 3D AAO nanostructures, respectively. The 3D AAO is also over-etched in the 5 wt% phosphoric acid at 25°C during pore widening and called as the over-etched 3D nanoporous AAO film. Figure 3a-c shows the SEM micrographs of the commercial P25-TiO<sub>2</sub> nanoparticles coating on the 2D AAO, 3D AAO and over-etched 3D AAO films, respectively. It is seen that the TiO<sub>2</sub> nanoparticles are partly adsorbed on the cell walls of each pore in the planar AAO due to the van der Waals force. Also, less P25-TiO<sub>2</sub> nanoparticles diffuse into the pore channels (Figure 3a). The nanoparticles in the solution are considered as Brownian motion for coating on the AAO film. The random motion results in difficulty of P25-TiO<sub>2</sub> nanoparticles to move into the single-aspect pore channel of planar AAO. On the other hand, the 3D porous AAO exists more TiO<sub>2</sub> nanoparticles adsorption not only on the surface but also in pore channels (Figure 3b). The hillocks in rough surface containing a great number of non-perpendicular pores for more probability of introducing P25-TiO<sub>2</sub> nanoparticles in Brownian motion.



**Figure 3:** The SEM micrographs of the commercial P25-TiO<sub>2</sub> nanoparticles coating on the: (a) 2D planar AAO, (b) 3D AAO (c) over-etched 3D AAO films.

Moreover, the valleys in the 3D AAO structure are helpful to aggregate more  $\text{TiO}_2$  nanoparticles comparing to the planar structure. Figure 3c shows the  $\text{P25-TiO}_2$  nanoparticles deposited on over-etched porous AAO by longer pore widening. It reveals the most  $\text{TiO}_2$  nanoparticles appear in the very rough substrate. Comparing with the 3D AAO structure, the over-etched porous AAO has much larger pore size and surface area to accommodate and adsorbed more  $\text{P25-TiO}_2$  nanoparticles. In addition, the  $\text{P25-TiO}_2$  nanoparticles adhesion in the pore channels are much stable than on the surface that benefits for photocatalysis. The photocatalytic performance of  $\text{P25-TiO}_2$  on various supporting materials including Si wafer, 2D AAO, 3D AAO, and over-etched 3D AAO after water flushing is further studied. For the as-deposition samples, the photocatalysis data show similar decomposition trend either in the pure Si wafer or AAO (over-etched 3D). Each sample exhibits good photocatalytic performance by completely decomposing MB after 12 h UV irradiation. However, the  $\text{P25-TiO}_2$  on the pure Si behaves greatly decrease in photocatalysis after water flushing. After 20 h UV irradiation, the concentration of MB maintains in 82.3%. It reveals that desorption of  $\text{P25-TiO}_2$  from the supporting Si wafer happens due to the poor adhesion. In contrast, the MB concentration decreases to 22.6% for the over-etched 3D AAO sample after 20 h UV irradiation. It evidences the good adhesion of  $\text{P25-TiO}_2$  on the AAO. The over-etched 3D AAO has the best photocatalytic performance towards degradation of MB due to the largest surface area for photocatalysis reaction and adsorption of  $\text{TiO}_2$ . It is noted that the 2D AAO and 3D AAO have in-between photocatalysis performance with 55.7% and 48.8% MB concentration after 20 h photo-degradation. This implies that the  $\text{P25-TiO}_2$  which adsorbed on 2D AAO and 3D AAO surface slightly desorbed after to water flushing. However, the porous structure can keep most of  $\text{P25-TiO}_2$  in pores comparing to the flat surface of Si wafer.

## Conclusion

The HPA with normal-positive and small negative voltages is an effective method for AAO fabrication from low-purity Al at relatively high temperatures of 20-25°C for promoting AAO structure in comparison with conventional AAO synthesized from high-purity Al using two-step DCA at low temperature (0-10 °C) to avoid dissolution effect. Comparing the I-t curves of DCA and HPA from bulk Al, the HPA at the negative period with nearly zero cathodic current can exhibit effective cooling to diminish Joule heating for promoting AAO quality. In addition, the HPA AAO can be synthesized at 25°C from the Al coating on high-roughness substrate for more effective surface area and good adhesion to enhance  $\text{TiO}_2$  photocatalysis performance after water flushing. The best photocatalysis performance can be obtained by depositing

commercial  $\text{P25-TiO}_2$  nanoparticles on the over-etched 3D AAO. After water flushing, the over-etched 3D AAO maintains the ~77% photocatalysis performance of as-deposited sample. Moreover, the over-etched 3D AAO exhibits the largest surface area for catalytic reaction and adsorption of  $\text{P25-TiO}_2$  compared with the intact 2D and 3D AAO.

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