Novel Three-Dimensional Nanoporous Alumina as a Template for Hierarchical TiO$_2$ Nanotube Arrays

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Porous anodic aluminium oxide (AAO), made by electrochemical anodization of aluminium, has been extensively investigated in the past two decades for its widespread applications in the field of nanoscience and nanotechnology. Besides its use as photonic crystals,[12] sensors[3] bio-separators[4] and superhydrophobic supports,[5,6] porous AAO is very likely the most commonly used hard template, which allows fabrication of a broad spectrum of 1D nanostructures.[7–20] In general, the anodization of aluminium has to be carried out under relatively mild conditions with a chemically or electrochemically polished mirror-finished Al surface. Any harsh conditions, e.g., an elevated temperature and/or an increased concentration of electrolyte, a high voltage or a rough Al surface, could cause a very high local current flow, eventually leading to a catastrophic ‘breakdown’ of the substrate.[21–23] So far, a few attempts have been made in order to avoid a breakdown during an anodization.[24–29] For instance, Chu et al. found that aged sulfuric acid helps to improve the critical anodizing potential for a breakdown.[24] Lee et al. demonstrated that a pre-anodized oxide layer (>400 nm) is able to provide uniform pore nucleation sites and therefore effectively suppresses the breakdown during hard or mild anodization in phosphoric acid (H$_3$PO$_4$) at a high voltage (e.g., 195 V).[26,27] Nevertheless, a very smooth, mirror-finished aluminium surface as well as a low anodizing temperature are still needed in order to avoid failure of anodization under harsh conditions. Particularly, anodization of Al in H$_3$PO$_4$ at a high voltage still remains challenging. Any surface pits or defects will likely result in a burnt Al foil.

We recently found that anodizing Al in phosphoric acid (H$_3$PO$_4$) can be accomplished at a high voltage (195 V) using an extremely rough, chemically etched microstructured aluminium foil. Even under conditions as harsh as 10 wt% H$_3$PO$_4$ and room temperature (~22 °C), we did not observe any signs of breakdown during the entire anodization process. The as-anodized Al exhibits a hierarchical micro-/nano-structured surface with 3D distributed nanopores. Moreover, the dimensions of the microstructures and nanopores can be independently tuned by the chemical etching process and the anodization conditions, respectively. The resulting hierarchical 3D AAO can be used as template to fabricate a number of micro-/nano-structures with controllable morphology, offering a generic route for the preparation of hierarchical architectures. Furthermore, the micrometer-sized Al terraces on the surface of the microstructured Al foils show very interesting phenomena upon anodization. For instance, it allowed observation of the evolution of nanopores at the edges of an Al micro-terrace during anodization.

Microstructuring Al surface was achieved by chemically etching the as-received Al foils (99.999%, Goodfellow) in a mixed solution of CuCl$_2$ and HCl at room temperature. Figure 1 shows representative scanning electron micrographs (SEM, JEOL 6701F) of the microstructured Al surface etched in different solutions for the same etching duration (5 min). It is evident that the etching exclusively results in the formation of numerous interconnected and hierarchically arranged micrometer-sized terraces on the Al surface. The average size of these terraces can be well tuned from several micrometers to a few tens of nanometers by adjusting the ratio of HCl to CuCl$_2$. Obviously, the etching treatment greatly increases the effective anodizing area as compared to planar Al.

Figures 2 reveals the top-view and cross-sectional view SEM micrographs of the 3D hierarchical nanopore structure obtained by anodizing microstructured Al foils in 10 wt% H$_3$PO$_4$ at 10 °C. More information about the sample appearance and morphology as well as the anodizing current-time transients is presented in Figures S1 and S2 in the Supporting Information. Upon anodization, a hierarchical 3D nanoporous architecture that combines both micrometer-sized terraces and nanometer-sized channels on each terrace is obtained. Interestingly, the microstructured Al provides a unique platform to explore the 3D evolution of oxide nanopores during anodization.[30–32] In the traditional
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Additionally, two differing nanopore growth modes were observed near the edges of the terraces: (i) Near the concave edges, where two adjacent terraces connect, branched nanopores are observed, as visibly enhanced with black lines in Figure 2d. (ii) Around the convex edges, the nanopores initially grow perpendicularly to the terrace faces but subsequently bend, as shown in Figure 2e. This bending is a result of the interaction of the electric fields at the anodization front when the bottoms of nanopores evolving from two neighboring facets are approaching each other. We believe that the unusual growth modes of the nanopores are closely related to the electric field distribution near the edges and the buildup of internal stress of the micro-cubes. It is inferred that the growth of nanopores near the vertexes of micro-terraces should be more complex. However, it is practically difficult to examine the overview morphology of this region.

It is worth mentioning that according to our experience, the probability of failure (i.e., breakdown) in anodizing Al in phosphoric acid is as high as 20–30%. This applies even under optimal conditions with a pre-anodization treatment,[26,27] namely, using an electropolished mirror-finished Al surface at 195 V in 1 wt% H3PO4 at 1 °C. In stark contrast, we never suffered from breakdown during anodizing microstructured Al, even under harsh conditions. Obviously, the microstructured Al has a much higher tolerance against the critical conditions. In fact, we found that the microstructured Al was also able to sustain without breakdown upon anodization in 0.3 M sulfuric acid at an anodic voltage as high as 190 V (Figure S3, Supporting Information). The high breakdown resistance can be ascribed to the following virtues of microstructured Al: (i) As revealed by exponentially decreasing current profiles in I-t curves (Figure S1), 3D hierarchical micrometer-scale features on the Al surface are highly effective for accumulating stress in anodic oxide. The stress-driven retardation of oxidation kinetics may positively contribute to suppressing the breakdown of anodic oxide. The present stress relevance of oxidation kinetics may also explain the effective suppression of breakdown during hard anodization of Al with an oxide layer.[26,34] (ii) Microstructured Al has a much larger surface area in comparison to a flat Al foil. The effective anodizing current density of microstructured Al samples, even if a high anodic voltage is applied, is not as high as it’s supposed to be for the flat Al foil, and most likely is lower than the threshold current density that may cause a breakdown. This also indicates that it is the current density (i.e., the effective electric field strength across the barrier oxide), but not the anodic voltage that governs way to prepare porous alumina, the nucleation and growth of nanopores usually occur two-dimensionally on an extended flat Al surface. As a result, the nanopores grow vertically to the Al surface, giving rise to a close-packed array of straight and parallel nanochannels. For the microstructured Al, it is obvious that the distribution of the electric field governing the growth of nanopores must be rather complicated. However, extensive SEM examinations demonstrated that the vertical growth mode of nanopores still applies to all exposed Al facets regardless of their orientations (Figure 2c). It is also noteworthy that in some places the Al residing in the interior of micro-cubes was not completely oxidized. An example is shown in Figure 2c as an area marked with a black line. This observation is consistent with the anodization behavior of Al in a confined micrometer-sized trench,[33] and implies that the accumulation of compressive stress during anodization plays an important role in governing the oxidation kinetics. Previously, Lee et al. observed long Al nanopillars at the irregular cell junctions of porous alumina formed by malonic acid-based hard anodization.[34] We believe that the formation of Al nanopillars is also associated with stress-induced retardation of anodic oxidation under high electric field.

Figure 1. SEM micrographs of microstructured Al surfaces obtained by etching. The etching was conducted at room temperature in a mixed solution containing 0.2 M CuCl2 and HCl with varying concentrations (a) 0 M, (b) 0.5 M, (c) 1 M, (d) 2 M, (e) 4 M, and (f) 6 M. The etching time was 5 min in all cases.
Templated Hierarchical TiO$_2$ Nanotube Arrays

The anodization behavior,[35] These merits may reasonably explain why the microstructured Al can be sustained during anodization in H$_3$PO$_4$ under such harsh conditions.

Analogous to traditional porous AAO membranes, the as-prepared hierarchical 3D porous alumina can also be used as template to fabricate hierarchical micro-/nano-architectures that cannot be easily realized by conventional physical and chemical routes. As a proof-of-concept, we demonstrate in this communication the fabrication of hierarchical 3D titania (TiO$_2$) nanotube arrays. Figure 3 displays a magnified SEM micrograph showing the morphology of the convex edge of the terrace, from which many branched nanotubes are observed. These branched nanotubes should be the replica of the branched nanopores formed near the concave edges of the Al terraces during anodization (Figure 2d). Obviously, the TiO$_2$-ALD process reproduced the structure of the parent template with a high fidelity. In Figure 3d, a broken section of the sample is shown, in which the tubular structure is apparent. Furthermore, transmission electron microscopy (TEM, JEOL-1010) investigations also confirmed the tubular nature of the fabricated nanostructures. Both straight and branched nanotubes can be observed by TEM, as shown in Figure 3e,f. The measured thickness of the tube walls is approximately 20 nm. The inset of Figure 3f exhibits an electron diffraction (ED) pattern of the annealed TiO$_2$ nanotubes, indicating that the nanotubes are polycrystalline after thermal annealing. Besides TiO$_2$ nanotubes, we also demonstrated that hierarchical 3D polystyrene nanorod arrays can be fabricated by polymer wetting using the as-obtained 3D AAO as templates (Supporting Information, Figure S5).

Figure 3 shows the degradation profile of the MB solution as a function of time upon UV illumination. The results show that among the prepared samples the 3D TiO$_2$ nanotube arrays exhibit the best photocatalytic performance towards degradation of MB owing to their large surface area and the enhanced light-harvesting capability possibly resulting from their hierarchical structure.

In summary, we report a new strategy to fabricate porous alumina with a hierarchical micro-/nano-porous morphology without suffering from breakdown. The surprisingly high tolerance of microstructured aluminium to critical anodization conditions is ascribed on the one hand, to the accumulated stress in the anodic oxide which retards the anodization kinetics and thereby suppresses breakdown, and on the other hand, to the large surface area of microstructured aluminium that helps to reduce the effective anodizing current density: a governing factor of breakdown. These 3D AAO membranes can be utilized as templates to fabricate hierarchical 3D TiO$_2$...
nanotube arrays and polystyrene nanorod arrays by using atomic layer deposition and polymer wetting, respectively. Given the fact that a general method for preparing hierarchical micro-/nano-structures is presently still absent, our approach reported here represents an important advance in this regard and will have a great impact on the development of many applications such as solar cells, batteries and photo-/electro-catalysts, where the use of hierarchical structures is preferred.

Experimental Section

Preparation of AAO membranes: The conventional AAO membranes were prepared by a two-step anodization process, as reported previously.\(^\text{[37]}\) In order to obtain hierarchical 3D porous AAO membranes, the highly pure Al foils were first chemically etched in a mixture of CuCl\(_2\) (0.2 M) and HCl (0.5–2 M) at room temperature for 5 min. Afterwards, the micro-structured Al substrates were directly anodized at 195 V in 1–10 wt% H\(_3\)PO\(_4\) solution for 3 h at various temperatures ranging from 1 °C to room temperature. The free-standing hierarchical 3D porous AAO was obtained by selectively etching the remaining Al substrate away in a mixed aqueous solution of CuCl\(_2\) (0.2 M) and HCl (4 M).

Atomic Layer Deposition (ALD) of TiO\(_2\): The deposition of TiO\(_2\) was carried out in a commercial ALD chamber (Savannah 100, Cambridge Nanotechnology Inc.) utilizing Ar both as precursor carrier and purge gas at a pressure of 0.2 Torr. Titanium tetra-isopropoxide (TIP) and deionized H\(_2\)O were used as precursors. The pulse durations for TIP and H\(_2\)O were 1 s and 1.3 s, respectively, and the purge time for both precursors was 60 s. The deposition was performed at 150 °C for 800 cycles, which resulted in film thickness of 20 nm. Three different substrates, namely, a bare Si wafer, a conventional porous AAO membrane and a hierarchical 3D porous AAO membrane, were used in order to obtain a compact TiO\(_2\) film, a 2D TiO\(_2\) nanotube array and a 3D TiO\(_2\) nanotube array, respectively. For photocatalytic studies, all as-deposited samples were annealed at 450 °C in air for 2 h to obtain crystalline anatase TiO\(_2\).

Characterization: The morphology and structure of the samples were examined by a field emission scanning electron microscope (JEOL, JSM-6701F) and a transmission electron microscope (JEOL, JEM-1010). The photocatalytic activity of the samples was evaluated by degrading \(5 \times 10^{-5}\) M methylene blue aqueous solution under the irradiation of a UV light (9 W). All the samples were installed into a home-made cell where only 1 cm\(^2\) area was exposed to the analyte solution and UV light for investigation. The concentration of MB in the analyte solution was monitored by measuring the maximum absorption of the methylene blue at 668 nm with a micro-UV-Vis spectrometer (NanoDrop 1000, Thermo Scientific).

Figure 3. (a–d) SEM micrographs of the hierarchical 3D TiO\(_2\) nanotube arrays fabricated by ALD of TiO\(_2\) using 3D porous AAO as a template. (e,f) Typical TEM images of the TiO\(_2\) nanotubes annealed at 450 °C in air for 2 h. Inset of (f): electron diffraction pattern.

Figure 4. Photocatalytic performance of the hierarchical 3D TiO\(_2\) nanotube arrays, 2D TiO\(_2\) nanotube arrays and a compact TiO\(_2\) film towards the degradation of methylene blue under UV illumination. The TiO\(_2\) was deposited using ALD, followed by a thermal treatment in air at 450 °C for 2 h. The deposited TiO\(_2\) was 20 nm thick for all samples (with an empirical deposition rate of 0.25 Å/cycle for 800 cycles).
Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.


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