

Tip-like anodic alumina

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Abstract

Porous anodic alumina membranes and various nanotips have been demonstrating individually their unique usefulness in current nanotechnology. We present a one-step electrochemical approach to fabricate nanoscale alumina tips (tip-like anodic alumina, TAA) in order to combine the benefits of porous anodic alumina and a nanoscale tip array. The realized TAA has an ordered tip surface with controllable aspect ratio and high sheet density of $\sim 10^{11} \text{ cm}^{-2}$. The formation of alumina nanotips is due to the heat-driven dissolution of the nanopore surface. We have further shown that the surface nanostructure in TAA leads to the wettability reversal, and preferred nucleation and growth during material deposition. The easy and large-scale fabrication of TAA makes it possible for novel nanodevice applications.

(Some figures in this article are in colour only in the electronic version)

The anodic technique of aluminium has a long history, and so far there are two kinds of anodic alumina reported [1, 2]. One is a non-porous barrier-type anodic alumina with its most important commercial use in the field of dielectric capacitors [1]. The other is porous anodic alumina (PAA), which has highly ordered hexagonal cells and circular nanopores with high porosity, and this porous-type thin film possesses excellent corrosion and abrasion resistance, as well as being a good base for paints and dyes. In nanotechnology, PAA films have been employed as filters, sensors and templates for nanostructured materials [3]. Due to its capability of synthesizing nanodots, nanorods, nanowires, nanotubes and nanopores of various materials, PAA has become the focus of current nanostructure fabrication [4]. Here we will report a new kind of anodic alumina, i.e. tip-like anodic alumina (TAA). It has a porous base with tip-like surface, and its difference from PAA can be easily seen in the schematic diagram of figure 1.

Nanoscaled tips have been demonstrating their unique usefulness in different applications such as atomic force microscopy, scanning tunnelling microscopy, chemical force microscopy, imaging sensors, field emission equipment, anti-refraction coatings and nanoindentation [5]. For these practical applications, the controllable aspect ratio, high density and regulation of nanotips are the most important factors required.

Semiconductor, oxide and metal nanotips have been widely reported. There are also many approaches to fabricate these nanotips. Nevertheless, in order to realize ordered and as-desired nanotips, complicated facilities and special methods are always needed. Our present nanotip fabrication of TAA is very simple, low-cost and easy to use to manufacture large-scale samples. TAA combines the benefits of PAA and a nanoscale tip array. It not only enriches the category but also widens the application of anodic alumina. Novel tip effects have also been realized in this new kind of anodic alumina through examining the wettability and depositing In_2O_3 and Au.

We have reported self-organized well-ordered PAA fabricated by anodization of aluminium in oxalic and phosphoric acids [6]. Figures 2(a) and (b) display field emission scanning electron microscopy (FESEM) images of PAA formed at 195 V in 0.4 M phosphoric acid at -10°C . The low temperature is helpful to both the anodizing stabilization and the improvement of the PAA's regulation [6b]. PAA spontaneously organizes into closely packed hexagonal cells with an ordered circular nanopore array. The diameter and interval of pores are $\sim 100 \text{ nm}$ and 320 nm , respectively. From the cross-sectional view of the membrane, straight parallel holes perpendicular to the surface were confirmed.

To obtain TAA, cleaned and electropolished high-purity (99.999%) Al sheets were directly anodized in a mixed

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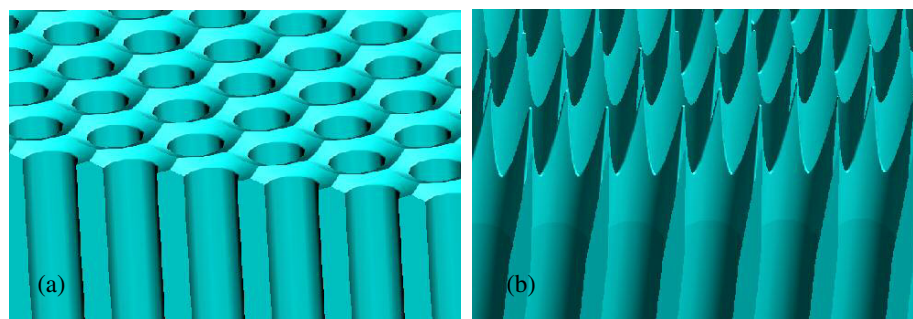


Figure 1. Schematic diagram of (a) porous anodic alumina and (b) tip-like anodic alumina.

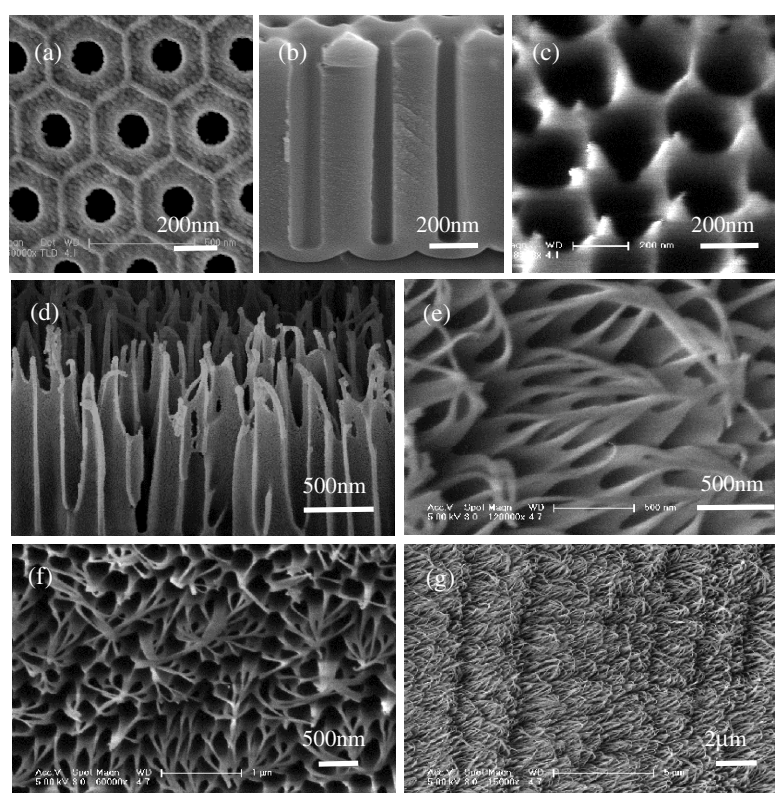


Figure 2. (a) Bottom view and (b) cross-sectional FESEM images of PAA. (c)–(e) FESEM images of TAAs with different tip lengths. (f) Top view and (g) large-scale FESEM images of TAA.

acid (phosphoric acid, citric acid, ethanol and Al ions) under an appropriate anodizing voltage of ~ 180 V with a high electrolyte temperature of 20°C for various anodizing durations. It should be noted that the current density is as high as 500 A m^{-2} , which is between the high-field [4a, 4b] and moderate [2] anodizations. The tip lengths of TAAs are adjustable through the anodizing time, as seen from ~ 50 , 200 and 500 nm in figures 2(c)–(e) with times of ~ 25 min, 40 min and 50 min, respectively, indicating the controllable aspect ratio due to the similar tip width of these ordered TAAs. The growth rate is not constant. It is slow at the beginning since we find that there are no tips if the anodizing time is less than 15 min, and it becomes faster as time goes on. However, when its length is about 500 nm, it does not grow any more, which may be caused by the balance of growth and dissolution of the tips. Although the surface of TAA is full of tips, its bottom

is still porous alumina with much higher porosity than that of common PAA.

When the tips are short, as shown in figures 2(c) and (d), they are independently standing on PAA bases. When the tips are long enough, they are not upright anymore, as shown in figures 2(e) and (f). The tips bend and connect each other, leading to the formation of kinks at some points. We could realize large-scale (over 10 cm^2) tip-like porous alumina films, and figure 2(g) shows ordered TAA with an area of over $55\ \mu\text{m}^2$. The sheet density of nanotips (near 10^{11} cm^{-2}) is twice that of nanopores in PAA, which can be easily observed from figures 2(c) and (d) due to six tips standing on a single nanopore. The shape of these alumina nanotips is adjustable by not only different anodizing conditions, but also chemical erosion processes in dilute acids according to [7a]. Both our x-ray diffraction (XRD) and energy dispersive spectra results

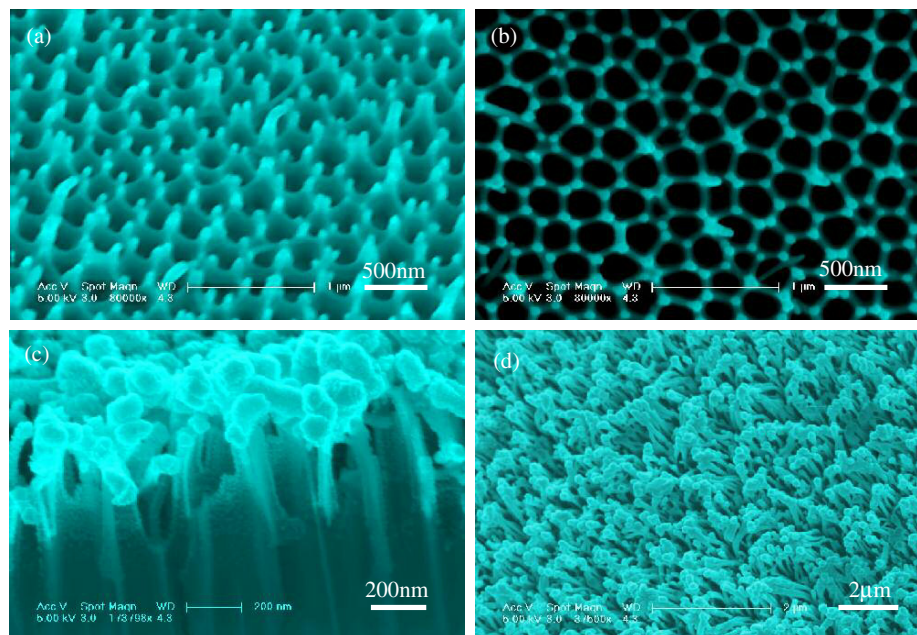


Figure 3. (a) Oblique and (b) top view SEM images of In_2O_3 sputtered on short TAA tips. (c) Oblique and (d) top view SEM images of Au deposited on long TAA tips.

confirm that the TAA present is really composed of alumina. XRD results further confirm that both PAA (fabricated in phosphoric acid, -10°C , 195 V) and TAA are polycrystalline. We believe that the high electric field on the thin barrier layer is the key factor to determine the crystallinity of PAA and TAA, since PAAs fabricated in sulfuric acid (15–25 V) and oxalic acid (40 V) are all amorphous.

The growth mechanism of TAA is different from that of hard [4a, 4b] (high-field) and moderate [2] anodizations of PAAs, which are always conducted at low temperature (0°C). Higher anodizing temperatures of 20°C employed during TAA fabrication will inevitably and significantly increase specimen surface temperature, resulting in the alumina dissolution. Six nanotips will therefore come into being from the remains at six corners of each PAA hexagonal cell due to uneven dissolution of the cell walls if nanopores are ordered enough, as shown in figures 2(c) and (d). The tip formation process is similar to that of alumina nanowires by immersing PAA into corrosive solutions such as NaOH [7b] and phosphoric acid [7a]. This TAA formation process can be further confirmed by its higher porosity (figures 2(c) and (d)) as compared with that of PAA (figures 2(a) and (b)). The proper operational temperature is between 15 and 25°C . No tips form at lower temperature, while the specimen burns at higher temperature. Beside the important factor of electrolyte temperature, the electrolyte composition also plays a key role in the TAA formation. Phosphoric acid is the basic and primary composition of electrolyte, and it is crucial for the formation of porous alumina. A buffering agent of citric acid is added into electrolyte to stabilize the anodic process and avoid burning [8] since its erosion ability is less than that of phosphoric acid. Both ethanol and Al ions are mainly used to make the anodization easy-going at high electrolyte temperature and anodizing voltage. At the same time, they are also helpful for anodizing stabilization. Through adjusting electrolyte

composition and temperature, we can control the dissolving rate and realize TAA in one step without pretreatment or two-step anodization.

In order to reveal the special properties/advantages of TAA, we studied its wettability, and found that the TAA surface is hydrophobic with contact angles (CAs) over 90° although CAs are different on different nanotips due to the sensitivity of CAs to surface nanostructures, in contrast to the hydrophilic characteristic with CAs $\sim 60^\circ$ in PAAs. The ordered nanoscale tip array contributes to the wettability reverse from PAA's hydrophilicity to TAA's hydrophobic property [9]. We further investigated the deposition of In_2O_3 and Au on TAAs with different tip lengths. Interestingly, both the oblique (figure 3(a)) and top view (figure 3(b)) FESEM images confirm that sputtered In_2O_3 deposited and grew along the short nanotips of TAA, and that about six In_2O_3 nanorods stand on top of a hexagonal TAA. It was also found that almost all Au particles deposited on the extended alumina tips, as shown in figures 3(c) and (d). The deposition of In_2O_3 nanorods and Au particles on TAA is totally different from that on PAA since the latter always leads to nanodot arrays at the bottom of nanopores and clogging of nanopores [3a]. These nanoscale tips on the TAA contribute to the wettability reversal, and preferred nucleation and growth during the material deposition.

In conclusion, we demonstrated a new kind of anodic alumina, i.e. TAA, in a one-step electrochemical method. It has ordered tip surface with a controllable aspect ratio and high sheet density of $\sim 10^{11} \text{ cm}^{-2}$. The heat-driven dissolution of nanopore surface contributes to the formation of nanotips. We have further shown that TAA has quite different wettabilities and deposition characteristics. TAA may find novel applications, especially in sensors, due to its unique and ordered surface, as well as easy and large-scale fabrication.

Acknowledgments

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