

## Supporting Information

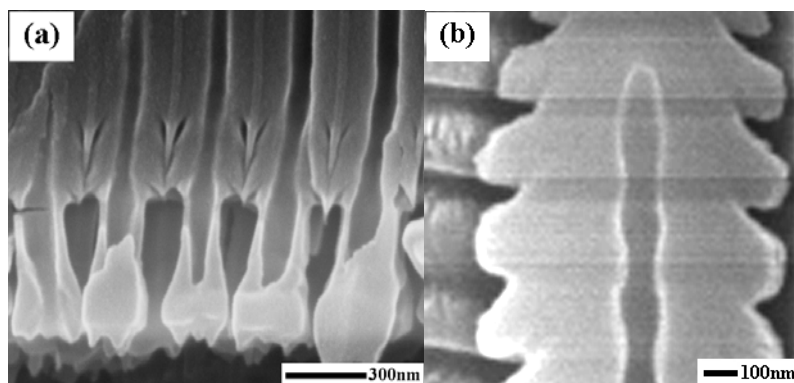
### **Unique fusiform alumina nanotubes fabricated by combined anodization**

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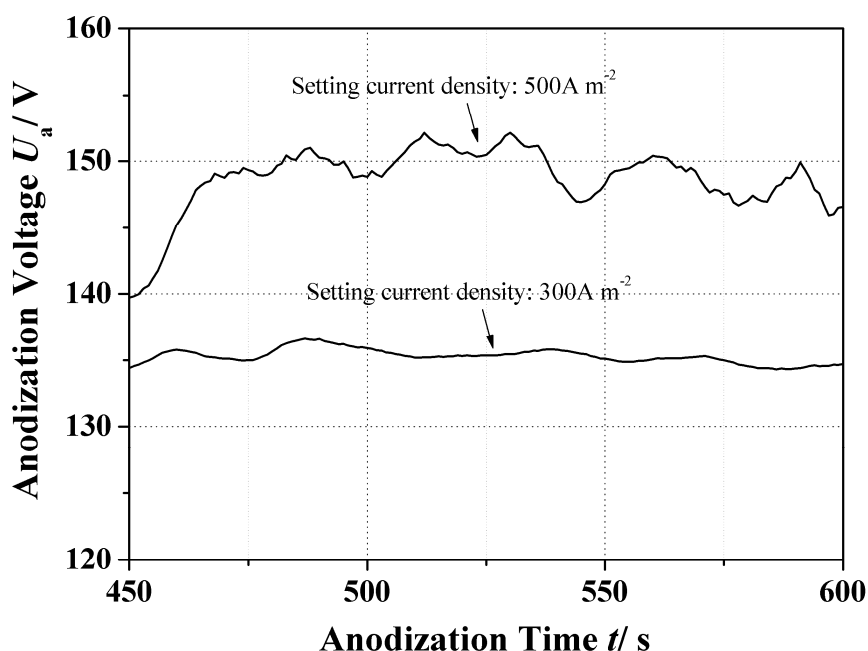
## Experimental and instrumental details.

High-purity aluminum sheets (99.99 %) with a thickness of 1 mm were used in the present experiments. Before anodization, the sheets were electropolished at 0–5 °C and 21 V for 5 min in a mixed solution of perchloric acid and ethanol (1:4, v/v) to diminish the surface roughness. Then the sheet was carefully washed with de-ionized water and put into a tailor-made holder with a square area of 1 cm<sup>2</sup> exposed to the electrolyte. Anodization were conducted in an ethanol-oxalic acid electrolyte (0.3 M oxalic acid electrolyte–ethanol = 2 : 1 v/v) at approximately –10 °C, with vigorous magnetic stirring. A powerful low temperature bath, together with an electrolysis cell (1 L) was used in the anodization process. In addition, a combined anodization process was used: (1) the anodization voltage ( $U_a$ ) was linearly increased at a rate of 20 V min<sup>-1</sup> until the current density ( $i_a$ ) reached the setting value (300 or 500 A m<sup>-2</sup>), (2) a constant current anodization process was applied for a certain time to obtain samples with diverse microstructures. Before characterization, all the obtained samples were immersed into a saturated CuCl<sub>2</sub> solution to remove the residual aluminum substrate. The microstructures of the specimens were examined by a field-emission scanning electron microscope (FE-SEM: LEO 1530 VP). The anodization voltage and current were measured by multimeters (Keithley 2010 and 2410).



**Fig. S1** (a) The partial enlarged image of “Main Text: Fig. 1(b)”; (b) the cross-sectional SEM image of the AAO fabricated at 500 V, 0.3 M oxalic acid electrolyte–ethanol = 2 : 1 v/v.

It can be seen from Fig. S1(a) that the internal pore diameter is not constant, but continuously changed under constant current anodization with a fluctuating  $U_a$ . Moreover, it was found that a continuously changed internal pore diameter can also be realized under constant voltage anodization with a fluctuating  $i_a$  (Fig. S1(b)).<sup>1</sup> Therefore, it can be concluded that both the fluctuations of  $U_a$  and  $i_a$  can change the internal pore diameter. These results agree well with the results reported by Su *et al.*<sup>2,3</sup>



**Fig. S2** The evolutions of the anodization voltage ( $U_a$ ) as a function of the anodization time ( $t$ ) with setting current densities of 300 and 500 A m<sup>-2</sup>, respectively. (0.3 M oxalic acid electrolyte–ethanol = 2 : 1 v/v)

It can be seen that the fluctuation amplitude of the  $U_a$  with a current density of 500 A m<sup>-2</sup> is apparently larger than that obtained under 300 A m<sup>-2</sup>. Considering that there is a relationship between  $i_e$  and  $U_a$ , and fluctuations of the  $i_e$  and  $U_a$  have inverse

variation trends (see the main text), it is expected that the  $i_e$  transients during constant current anodization can be investigated by analyzing the  $U_a$  transients which can be easily measured. Moreover, it should be noted that although the as-prepared ANTs are relatively uniform, their growth may not be completely synchronous, thus resulting in relatively irregular fluctuations of the  $i_e$  and  $U_a$  shown in Fig. S2 and Fig. 5 (see the main text).

In addition, measurement results show that the maximum  $U_a$  that can be applied before the constant current mode (Main Text: the dotted line in Fig. 5) and its corresponding cell size ( $D_{\text{cell}}$ ) (Main Text: Fig. 1(b)) are 147 V and 313 nm, respectively, and a proportionality constant ( $\zeta$ ) between  $D_{\text{cell}}$  and  $U_a$  of 2.1 nm V<sup>-1</sup> can be obtained. This value agrees well with the previously proposed value ( $\sim 2.0$  nm V<sup>-1</sup>) for hard anodization when a continuous nanoporous AAO film is obtained.<sup>4</sup> However, it is found that the maximum  $U_a$  difference (Main Text: Fig. 5) and external diameter difference (Main Text: Fig. 1 and 2) under the constant current mode (500 A m<sup>-2</sup>) are approximately 13.5 V and 152 nm, respectively, and a proportionality constant of 11.3 nm V<sup>-1</sup> can be obtained. This value is quite different from that reported before for mild or hard anodization,<sup>4-10</sup> which further means that the intrinsic formation mechanism of continuous nanoporous AAO films and separated fusiform ANTs are different. Considering that the anodization is performed under the constant current mode and apparent variations of the ANT's external diameters can also be observed during constant voltage anodization,<sup>1</sup> the fluctuation of the electronic current density during the anodization process is considered to be the main reason for the formation of such unique fusiform ANTs.

## References

- 1 Y. Li, Z. Y. Ling, S. S. Chen, X. Hu and X. H. He, *Chem. Commun.*, 2010, **46**, 309.
- 2 Z. X. Su, G. Hähner and W. Z. Zhou, *J. Mater. Chem.*, 2008, **18**, 5787.
- 3 Z. X. Su and W. Z. Zhou, *J. Mater. Chem.*, DOI: 10.1039/c0jm02521f.
- 4 W. Lee, R. Ji, U. Gösele and K. Nielsch, *Nat. Mater.*, 2006, **5**, 741.
- 5 Y. Li, Z. Y. Ling, J. C. Wang, S. S. Chen, X. Hu and X. H. He, *Chin. Sci. Bull.*, 2008, **53**, 1608.
- 6 S. Z. Chu, K. Wada, S. Inoue, M. Isogai and A. Yasumori, *Adv. Mater.*, 2005, **17**, 2115.
- 7 Y. Li, Z. Y. Ling, S. S. Chen and J. C. Wang, *Nanotechnology*, 2008, **19**, 225604.
- 8 A. P. Li, F. Müller, A. Birner, K. Nielsch and U. Gösele, *J. Appl. Phys.*, 1998, **84**, 6023.
- 9 K. Nielsch, J. Choi, K. Schwirn, R. B. Wehrspohn and U. Gösele, *Nano Lett.*, 2002, **2**, 677.
- 10 W. Lee, R. Scholz and U. Gösele, *Nano Lett.*, 2008, **8**, 2155.