

**Supplementary Material (ESI) for Chemical Communications**  
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## **Supporting Information**

### **Novel AAO films and hollow nanostructures fabricated by ultra-high voltage hard anodization**

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## **Experimental and instrumental details.**

Highly pure aluminum sheets (99.99 %, General Research Institute for Nonferrous Metals) with a thickness of 0.3–1 mm were used as starting materials. Before anodization, the sheet was electropolished at 0–5 °C and 21 V for 5 min in a mixture solution of perchloric acid and ethanol (1:4, v/v) to diminish the roughness of the aluminum sheet surface. Then the sheet was washed in deionized water and put into a tailor-made holder with a square area of 1 cm<sup>2</sup> exposed to the electrolyte. Two kinds of electrolytes were used for anodizations under different voltages: solution (1), 0.3 M oxalic acid solution (40–215 V, 0–5 °C); solution (2), solution (1) : ethanol = 2 : 1 v/v (500–620 V, –10 °C). Anodization was conducted with vigorous magnetic stirring, a powerful low temperature bath and a large electrolysis cell (1 L) were used to maintain the low temperatures required for the anodization. For the anodization performed at 40 V, the anodization voltage is increased to the target voltage at a rate of 2 V s<sup>-1</sup>. For the anodization conducted at 140–620 V, a combined voltage increasing process was used: (1) the anodization voltage is slowly increased at a rate of 1 V s<sup>-1</sup> until the current density reaches 500 A m<sup>-2</sup>, (2) a constant-current anodization was applied at the beginning of the anodization, by which the anodization voltage can be smoothly increased to the target value, (3) then, a constant-voltage anodization was performed to obtain AAOs at designated voltages, (4) the heat was effectively removed by thermal contact of the aluminum sheet and the low temperature bath through a copper plate during anodization. All the specimens obtained were immersed into a saturated CuCl<sub>2</sub> solution to remove the residual aluminum. The acid corrosion process was performed in H<sub>3</sub>PO<sub>4</sub> solution (5 wt %) at 45 °C for 85–140 min. The morphology of the specimens was investigated by a field-emission scanning electron microscope (FESEM: LEO 1530 VP). The anodization current was measured by a Keithley 2010 multimeter.

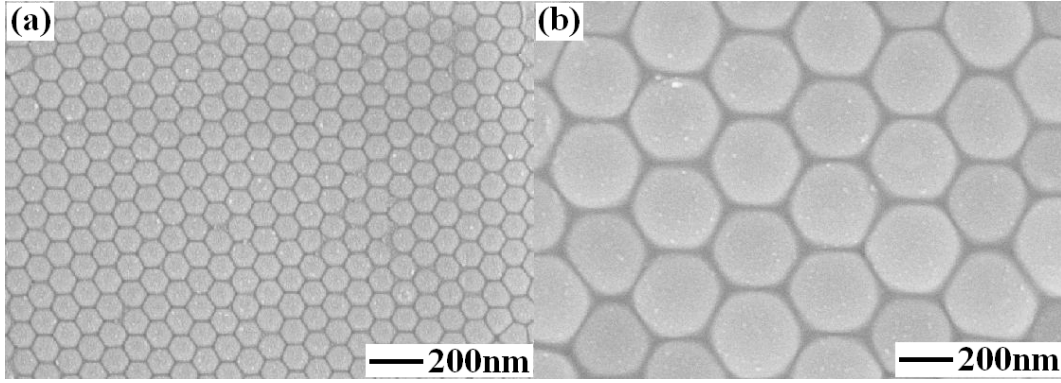


Fig. S1 SEM barrier layer images of the AAOs fabricated at (a) 40 V ( $21 \text{ A m}^{-2}$ ) and (b) 140 V ( $160 \text{ A m}^{-2}$ ) for 30 h and 4 h, respectively.

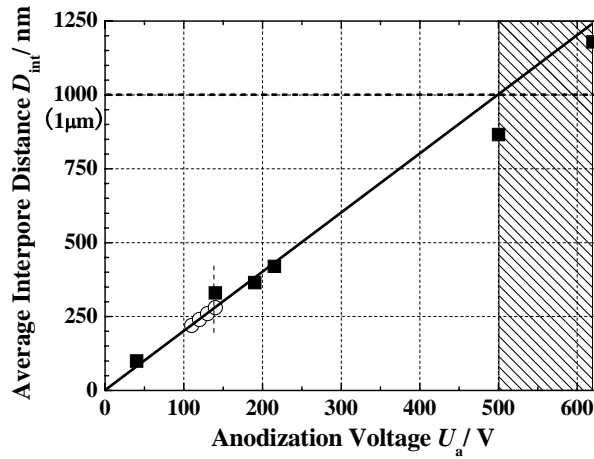
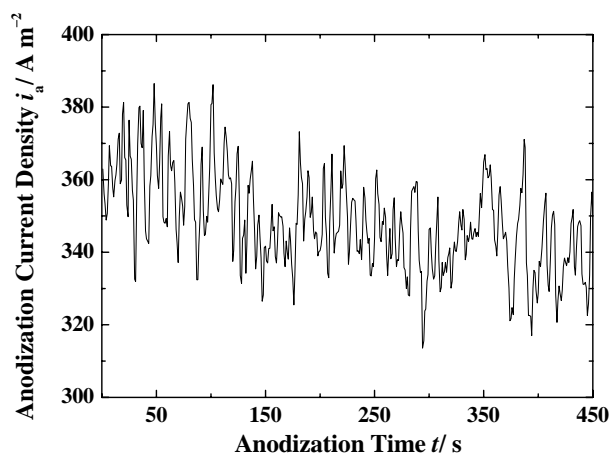


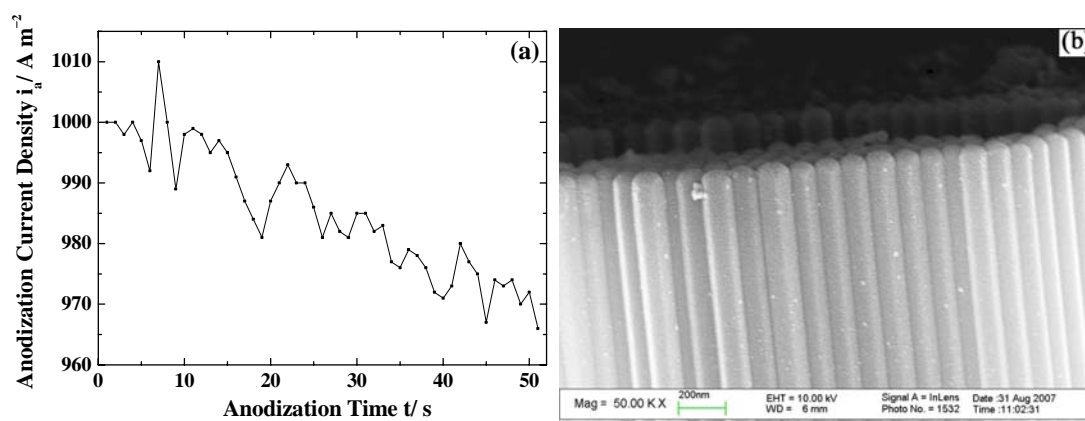
Fig. S2 The evolution of the inter-pore distance ( $D_{\text{int}}$ ) as a function of anodization voltage ( $U_a$ ): the data marked by filled black squares were obtained in our experiment; the data marked by open black circles represent the data in reference 1; the black solid line represents the linear relationship of the data with a proportionality constant  $\zeta_{\text{HA}} = 2.0 \text{ nm V}^{-1}$ . The shadow background for  $U_a > 500 \text{ V}$  represents the self-organized regime unexplored until now.

It can be seen that the  $D_{\text{int}}$  of the AAO prepared at 140 V ( $160 \text{ A m}^{-2}$ ) is 330 nm, which is apparently larger than that (280 nm,  $230 \text{ A m}^{-2}$ ) reported by Lee et al<sup>1</sup>. This result agrees well with the previous conclusion that: (1) the  $D_{\text{int}}$  is not solely dependent on the  $U_a$ , but also influenced by the current density ( $i_a$ ), and increases with the decrease of  $i_a$ ; (2) the linear relationship between  $D_{\text{int}}$  and  $U_a$  is only a special case under the condition that  $i_a$  is little changed<sup>1-3</sup>.



**Fig. S3** The evolution of anodization current density ( $i_a$ ) as a function of anodization time ( $t$ ): the last 450 s of the whole anodization process conducted at 500 V.

It can be seen that current density oscillations occur in the anodization. It should be noted that although the cell current density oscillations are relatively regular, the oscillations of all the AAO cells may not be simultaneous, thus result in relatively irregular anodization current density oscillations.



**Fig. S4** The current density oscillations (a) and SEM image (b) of the AAO fabricated in sulfuric acid electrolyte. Anodization was performed in a  $\text{H}_2\text{SO}_4\text{-Al}_2(\text{SO}_4)_3\text{-H}_2\text{O}$  mixture solution ( $\text{H}_2\text{SO}_4$ :  $0.75 \text{ mol l}^{-1}$  and  $\text{Al}_2(\text{SO}_4)_3$ :  $0.15 \text{ mol l}^{-1}$ ) at  $0\text{-}5^\circ\text{C}$  and 50 V, with vigorous magnetic stirring.

1 W. Lee, R. Ji, U. Gösele and K. Nielsch, *Nat. Mater.*, 2006, **5**, 741.

2 Y. Li, Z. Y. Ling, S. S. Chen and J. C. Wang, *Nanotechnology*, 2008, **19**, 225604.

3 Y. B. Li, M. J. Zheng, L. Ma and W. Z. Shen, *Nanotechnology*, 2006, **17**, 5101.