

Supporting Information

Unique AAO films with adjustable hierarchical microstructures

Yi Li,* Yuyan Qin, Zhiyuan Ling, Xing Hu and Yanhua Shen

Department of Electronic Materials Science and Engineering, College of Materials Science and Engineering,

South China University of Technology, Guangzhou 510641, People's Republic of China.

E-mail: msllyi@scut.edu.cn; Fax: +86 20 8711 1224; Tel: +86 20 8711 1224

Experimental and instrumental details

High-purity (99.999 %) aluminium sheets 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 analytically pure 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 cm² exposed to the electrolyte. The first anodization were conducted in electrolyte I (0.3 M oxalic acid electrolyte) and electrolyte II (electrolyte I–ethanol = 1 : 1 v/v), respectively, with vigorous magnetic stirring and a low temperature (~3 °C). A powerful low temperature water bath, together with an electrolysis cell (1 L) was used in the anodization process, and the heat was effectively removed by using a large copper plate which was in thermal contact with the aluminium sheets. In addition, the first anodization processes were performed as follows: (1) the anodization voltage (U_a) was linearly increased at a rate of 1 V s⁻¹ until the current density (i_a) reached the setting value (500 or 600 A m⁻²), (2) a constant-current process was applied, by using which the U_a can be smoothly increased to the high target value, (3) the anodization was conducted at a designated U_a with a constant-voltage mode, and unique AAO films with aluminium substrates (AAO-Al sheets) were obtained at 180 A m⁻². For the characterization of the barrier layer surface of AAO films, a saturated CuCl₂ solution was applied to remove the residual aluminium substrate. Pre-patterned aluminium sheets were obtained by dissolving the AAO films of AAO-Al sheets in a mixture solution of CrO₃ (30 g L⁻¹) and H₃PO₄ (50 mL L⁻¹) at ~70 °C for 10 h. The second anodization was conducted in 0.3 M oxalic acid electrolyte (~3 °C) under 40 V for 8 min. The subsequent pore widening process was performed in 5wt% H₃PO₄ solution under 30 °C for 25 min. The microstructures of the samples were examined by a field-emission scanning electron microscope (FE-SEM: ZEISS Ultra 55). The anodization voltage and current were measured by multimeters (Keithley 2010 and 2410).

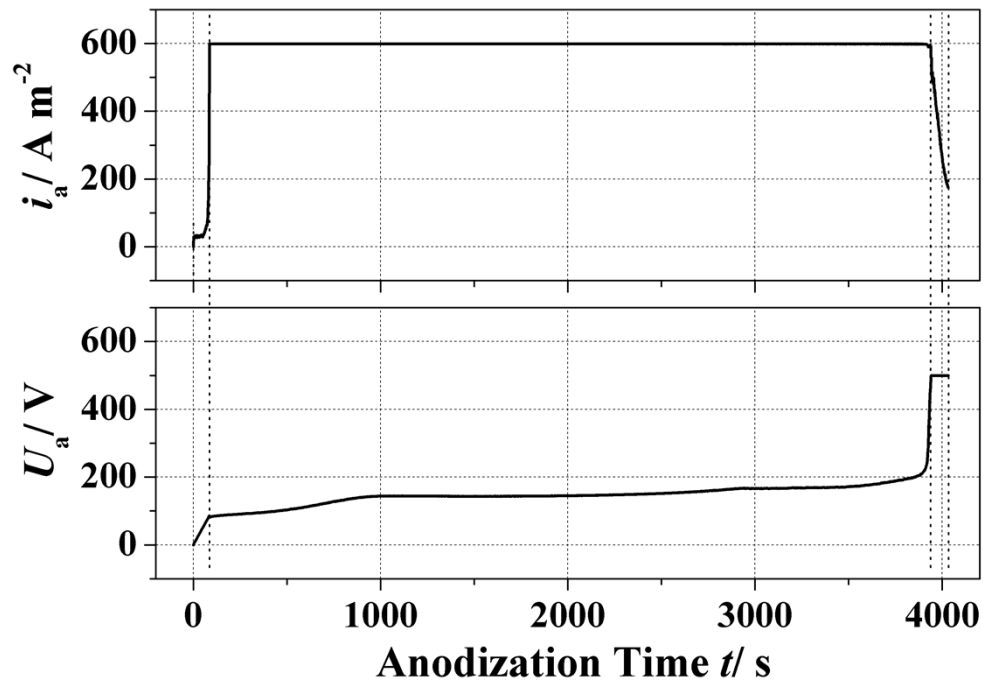


Fig. S1 The evolutions of the anodization current density (i_a) and the anodization voltage (U_a) as a function of the anodization time (t) (voltage increasing rate: 1 V s^{-1} , setting current density: 600 A m^{-2} , 0.3 M oxalic acid electrolyte), corresponding to the AAO film shown in Fig. 1.

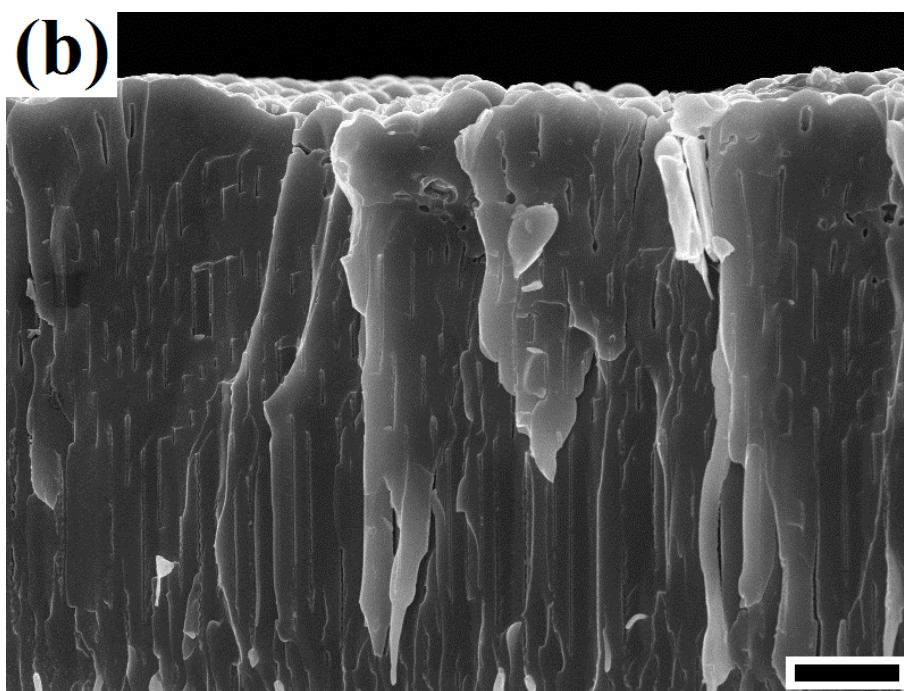
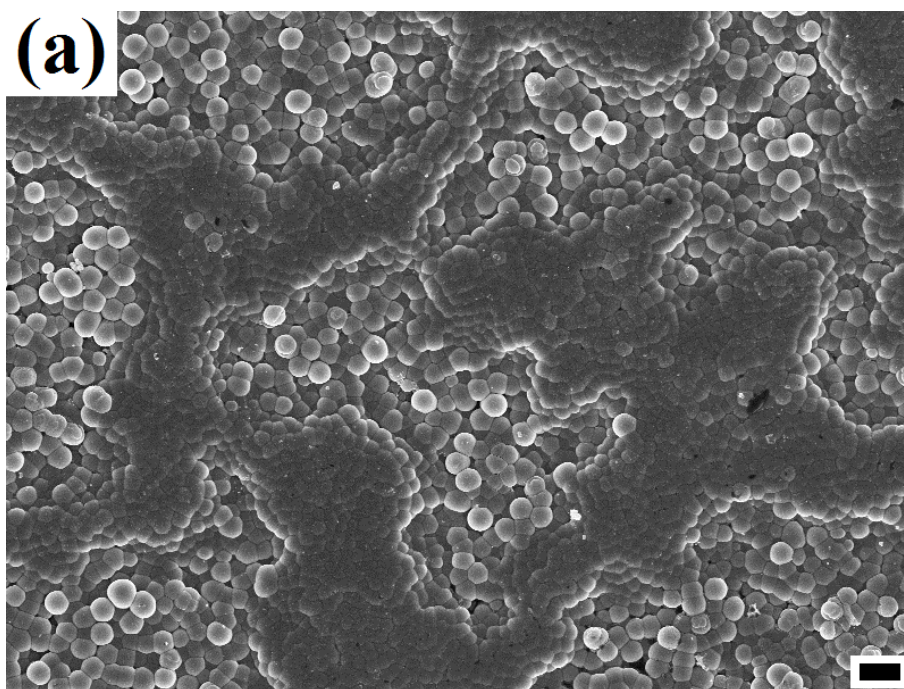


Fig. S2 Corresponding to the images in Fig. 1, enlarged SEM images of the AAO film (voltage increasing rate: 1 V s^{-1} , setting current density: 600 A m^{-2} , 0.3 M oxalic acid electrolyte), scale bars = $2 \text{ }\mu\text{m}$, (a) the barrier layer surface, (b) the cross-section.

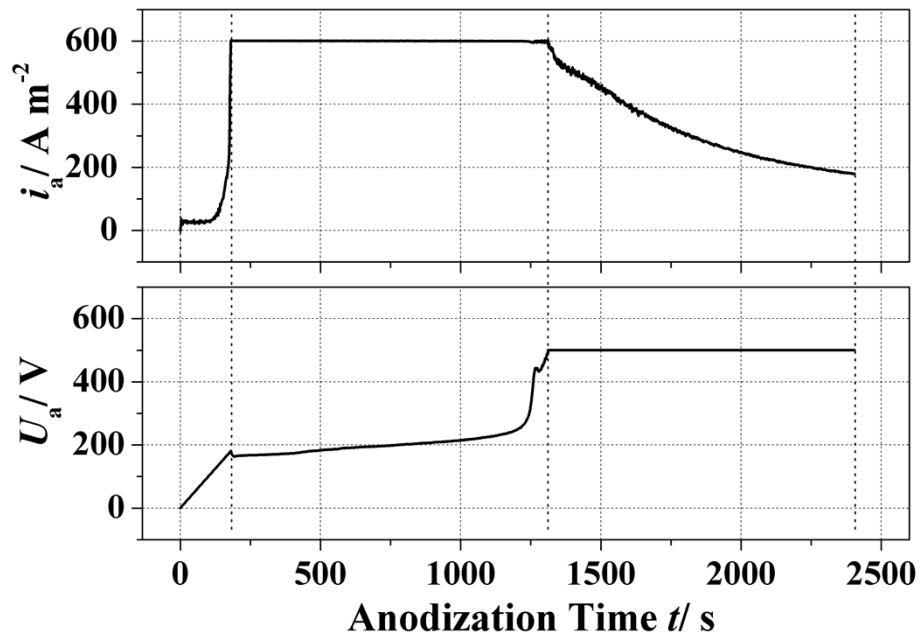


Fig. S3 The evolutions of the anodization current density (i_a) and the anodization voltage (U_a) as a function of the anodization time (t), (b) SEM images of the AAO film (voltage increasing rate: 1 V s^{-1} , setting current density: 600 A m^{-2} , 0.3 M oxalic acid electrolyte–ethanol = $1 : 1 \text{ v/v}$), corresponding to the AAO film shown in Fig. 2.

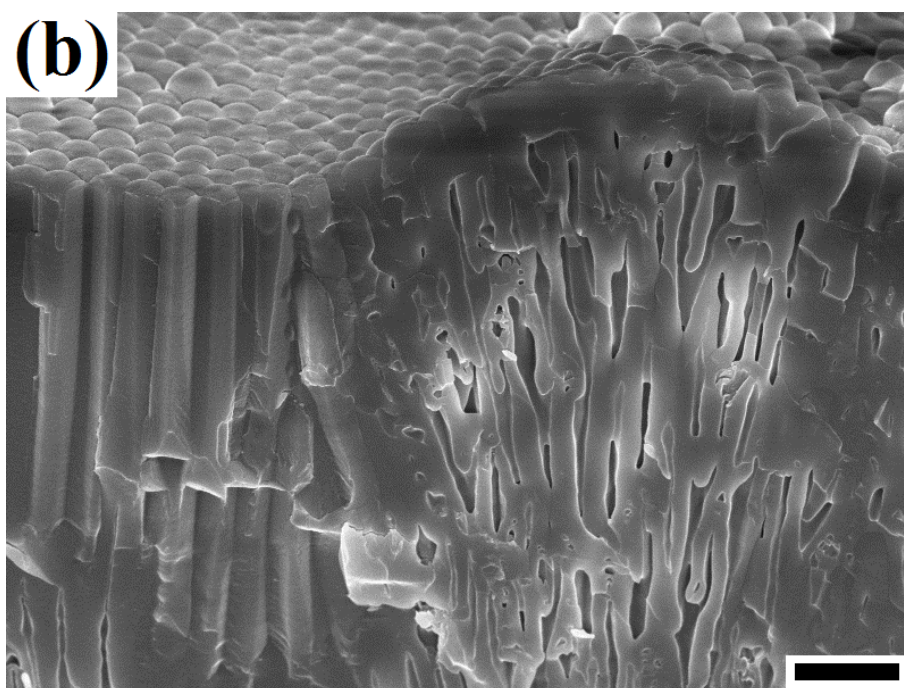
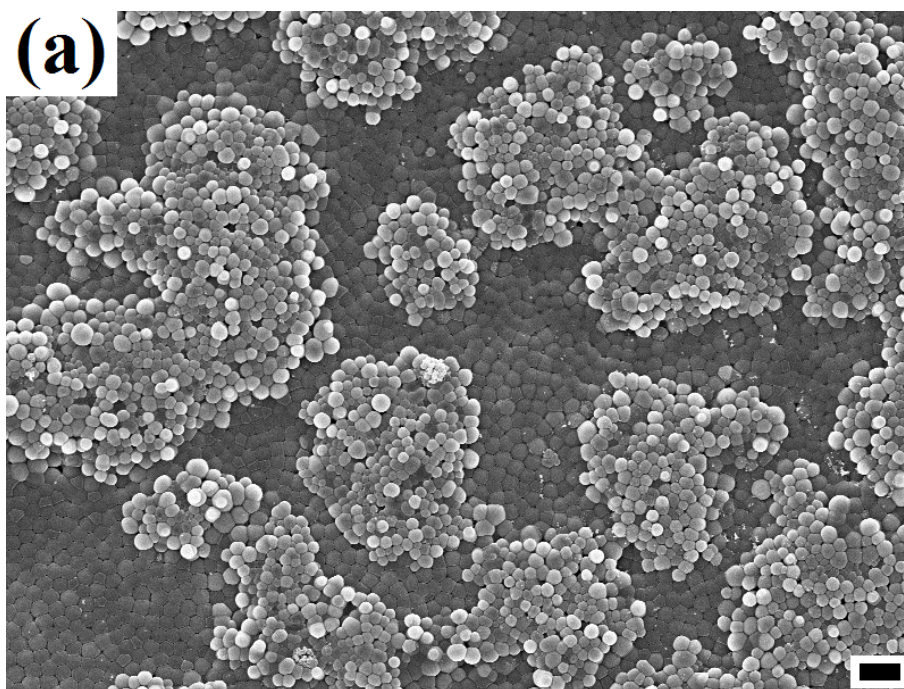


Fig. S4 Corresponding to the images in Fig. 2, enlarged SEM images of the AAO film (voltage increasing rate: 1 V s^{-1} , setting current density: 600 A m^{-2} , 0.3 M oxalic acid electrolyte–ethanol = 1 : 1 v/v), scale bars = $2 \mu\text{m}$, (a) the barrier layer surface, (b) the cross-section.

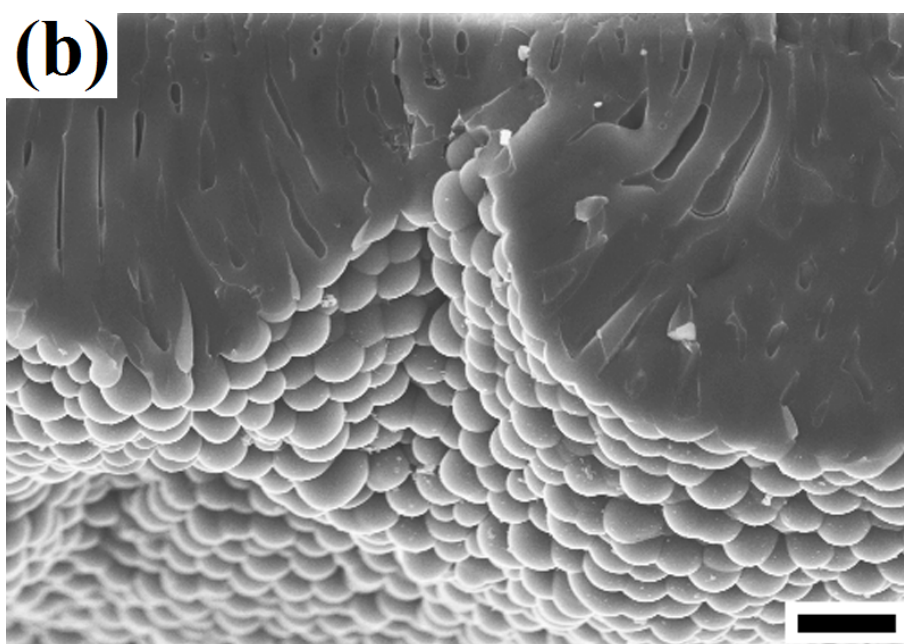
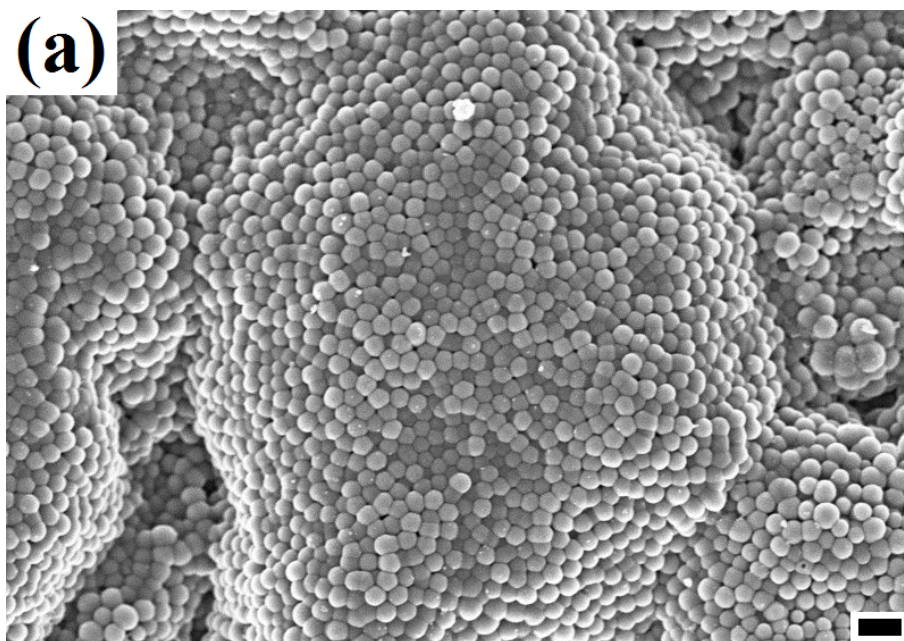


Fig. S5 Corresponding to the image in Fig. 3(a), SEM images of the AAO film (voltage increasing rate: 1 V s^{-1} , setting current density: 500 A m^{-2} , 0.3 M oxalic acid electrolyte), scale bars = $2 \text{ }\mu\text{m}$, (a) the barrier layer surface, (b) the cross-section.

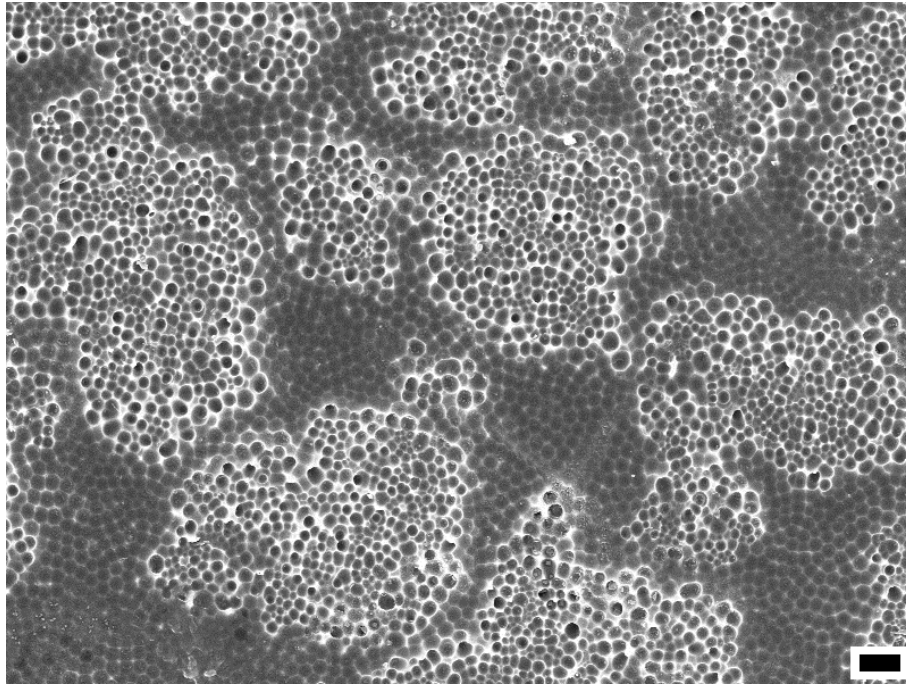


Fig. S6 The enlarged SEM image of the patterned aluminium substrate which can be obtained by removing the as-prepared AAO film, corresponding to the sample shown in Fig. 2 and Fig. S4, scale bar = 2 μm .