Electronic Supplementary Information

Preparation of Hierarchically Structured Anodic Aluminum Oxide by Hexagonal Embedded Nanosphere Array

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1. Materials and Reagents

Ultrapure aluminium (0.3 mm, 99.999%) was purchased from Beijing Institute of Precious Metals. Polystyrene monomer was purchased from Tianjin Guangfu Fine Chemical Institute. Sodium dodecyl sulphate (SDS) was purchased from Shanghai Chemical Works. NaOH, potassium persulfate ($K_2S_2O_8$), potassium sulphate (K_2SO_4), $HClO_4$, ethanol, acetone, and phosphoric acid (85%) were purchased from Beijing Chemical Works. All reagents were analytical grade, and were used without further purification.

2. Instruments

A constant temperature tube oven with a PID-controlled thermometer was used for high-temperature annealing. Reactive ion etching (RIE) machine (Oxford Plasmalab Oxford 80 plus) was used to etch the nanospheres. A high vacuum evaporator (ZHD-300M2, Techno Technology Co. Ltd.) was used to evaporate aluminium. A DC power supply with a maximum output voltage of 110 V and output current of 7.0 A was used for the anodization. Constant temperature water bath was purchased from Bilang, Shanghai, with a controlling range of -5-95℃. Cold field emission scanning electron microscope (FESEM) from HITACHI SU8020, with an accelerating voltage of 5 kV, and the images were captured under the magnification of 20- 2000000.

3. Preparation of a built-in nanosphere template on Al sheets

Aluminium sheets were cut into 10×20 mm, and annealed under 500 ℃ for 4 hrs under N_2 ambience. Then the Al sheets were washed by acetone for degreasing, and dried in N_2. Ethanol/$HClO_4$ mixture solution with a volume ratio of 4:1 was used for electropolishing of 2.5 min, under a voltage of 17 V and 4 ℃. Then the mirror-like Al sheets were rinsed by ethanol and dried in N_2.

Next, polystyrene (PS) nanospheres with a diameter of 550 nm were prepared by emulsion polymerization method.[1] A monolayer of PS nanospheres were arranged through the air/water interface self-assembly method with the surfactant of SDS (2%).[2] Next, we slowly lifted an Al sheet at the air/water interface to transfer the PS nanosphere monolayer to the Al surface. Then the PS nanospheres were etched by O_2 plasma for 6 min under the conditions of RF power of 30 W, O_2 flow rate of 50 sccm, pressure of 10 mTorr and bias voltage of 140 V. After that, the size of PS nanospheres were reduced to 440 nm measured from the SEM image (Figure 1 G). Next, 500 nm Al was evaporated onto the etched PS nanospheres and the PS spheres built-in Al template was achieved. ,

The PS nanosphere built-in Al substrate was anodized under 110 V, 5 ℃, and the electrolyte was 0.3 M phosphoric acid. The anodization process lasted 30 min. At last, a pore-widened AAO substrate prepared by chemical etching substrate in phosphoric acid (5 wt%) at 30 ℃ for 45 min was carried out.

4. AAO obtained from a deep built-in template

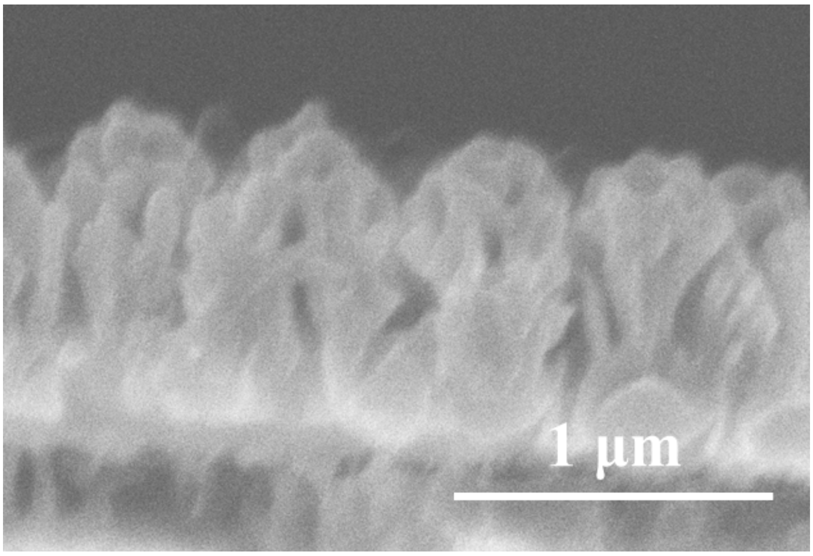

Fig. S1 Side view of the obtained by using the deep built-in template with 700 nm-thickness Al covering and the anodization time of 20 min.

The side view of the AAO substrate obtained by using the deep built-in template with 700 nm-thickness Al covering and the anodization time of 20 min. The electrolyte was 0.3 M phosphoric acid and the anodization voltage was 110 V. If PS nanoshperes were embedded deeper, for example, laying 700 nm deep from the Al surface, channel clusters can be observed with the PS nanospheres as cores. These channels forming above the PS nanospheres finally grew into "dead" channels since the PS nanospheres acted as an insulating layer and a barrier layer formed on the PS nanosphere surface.

References

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