Supporting Information

Controlled synthesis of aligned Ni−NiO core−shell nanowire arrays on glass substrates as a new supercapacitor electrode

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Experimental

Synthesis of AAO templates: A series of metallic thin films (Ti, W, and Al) were deposited on fluorine-doped SnO_2 conducting glass (FTO, Pilkington TEC15) substrates by RF-magnetron sputtering with 3 cathodes using Ti, W, and Al targets on each cathode at room temperatures and 200 W under Ar flow (20 sccm) with a working pressure of 5 mTorr. The deposition time for Ti, W, and Al layers was 1, 4, and 270 minutes, respectively, and the deposition was done without breaking the vacuum between each layer. The thicknesses of Ti, W, and Al layer were approximately 5 nm, 70 nm, and 1.8 μm, respectively. The AAO templates were produced by electrochemically anodizing the Al films at 70 V (ramping rate 5 V sec^{-1}) and 3 °C in a two-electrode cell, which contained a Pt counter electrode and 0.3 M aqueous oxalic acid solution. A computer-controlled source meter was used for the electrochemical anodization. After anodizing for 4 minutes, the samples were rinsed with water, followed by ethanol and then dried under a stream of nitrogen. The partially anodized oxide layer was selectively etched using a mixture of phosphoric acid and chromic acid (6 wt% H_3PO_4 and 1.8 wt% H_3CrO_4 in H_2O) at room temperatures for 6 hours. Then, the samples were anodized again using the same condition until the sample becomes transparent (normally for 18 minutes). The anodization process is self limiting owing to the formation of WO_3 in the bottom of the vertical pores.[1]. After rinsing the anodized samples using the same condition as described above, the barrier layers in the bottom of the pores was perforated by selectively etching the WO_3 using a pH 7 buffer solution (BECKMAN, phosphate buffer) at room temperatures for 10 minutes.[1] The samples were rinsed again before being used as a template for electrochemical deposition of Ni NWs.

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Synthesis of NW Arrays: Ni NWs were electrochemically deposited from a Watts solution (containing 300 g L^{-1} $NiSO_4 \cdot 6H_2O$, 45 g L^{-1} $NiCl_2 \cdot 6H_2O$, 45 g L^{-1} H_3BO_3) using a potentiostat/galvanostat (VMC−4, Princeton Applied Research) in a three-electrode cell with a platinum counter electrode and Ag/AgCl reference electrode. A constant potential of −1 V (vs. Ag/AgCl) was applied at 55 °C until the deposition charge reaches 0.6 C cm^{-2} so as not to form overlayers. Then, the AAO templates were dissolved by soaking the sample in 1 M aqueous NaOH solution at room temperatures for 30 minutes. The core−shell NW arrays were prepared by electrochemically depositing $Ni(OH)_2$ layers on the surface of the freestanding Ni NWs using the same three-electrode system with 0.1 M aqueous $Ni(NO_3)_2$ solution. A constant current (1.5 mA cm^{-2}) was maintained for 100 seconds for thinner shell samples (150 mC cm^{-2}) and 300 seconds for thicker shell samples (450 mC cm^{-2}). The $Ni(OH)_2$ layer was converted to NiO by annealing the samples at 300 °C for 1 hour.

Characterization: The morphological properties of the samples were characterized by field emission scanning electron microscopy (FE-SEM, JEOL JSM−7000F) and high-resolution transmission electron microscopy (HR-TEM, FEI Tecnai F20 UT, operating at 200 kV) with energy dispersive X-ray spectroscopy (EDS). Electrochemical measurements were performed with a three-electrode glass cell set-up, consisting of a Ni–NiO core−shell NW working electrode, a platinum counter electrode, and an Ag/AgCl reference electrode. Galvanostatic charge/discharge cycling and cyclic voltammetry were carried out using the potentiostat/galvanostat from −0.1 to 0.4 V in 1 M KOH solution at room temperatures.

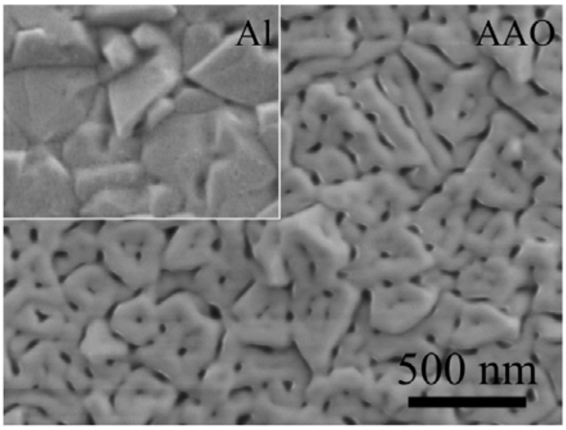

Figure S1. Top view of SEM image of the AAO template prepared using a single-step anodization. The inset shows the top view of the morphology of the starting Al thin film with the same scale.

Figure S1 shows that the pore ordering is much worse when the AAO template is prepared using a single-step anodization compared to that prepared using a two-step anodization (Figure 2a). The surface morphology of the starting Al thin film (inset of Figure S1) is relatively unchanged even after anodization, presumably due to the negligible chemical etching of Al_2O_3 in the anodization solution.

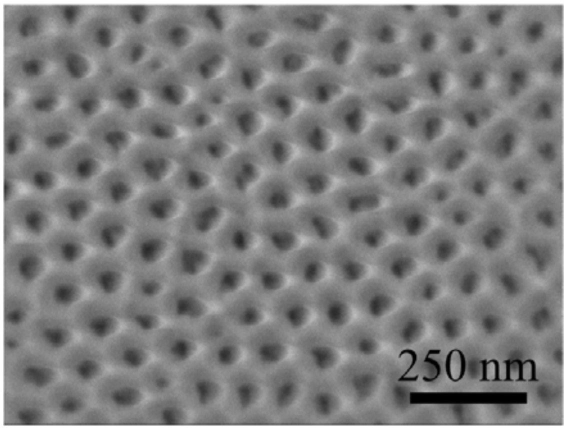

Figure S2. Top view of SEM image of the AAO template prepared using a two-step anodization with 10-minute anodization of first sacrificial AAO layer.

Figure S2 shows that the pore ordering is further improved when a thicker first sacrificial AAO layer (10 min of first step anodization) is prepared during the two-step anodization compared to the thinner counterpart presented in Figure 2a (4 min of first step anodization).

References

(1) Oh, J.; Thompson, C. V. *Adv. Mater.* **2008**, *20*, 1368.