

Three-Dimensional Ni/TiO₂ Nanowire Network for High Areal Capacity Lithium-Ion Microbattery Applications

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Section 1: Fabrication of the three-dimensional (3-D) Ni/TiO₂ nanowire network

1.1 Fabrication of 3-D porous anodic alumina (PAA) templates

The 3-D PAA template used in this study was prepared via a one-step anodization process.^{1,2} Prior to the anodization process, the aluminum foil (1000 series Al with 99.5% purity, McMaster 9060K16) was cleaned using acetone and water. The backside of the cleaned Al foil was protected by plastic film with glue. Then, the Al foil was placed in an electrolytic tank containing 30 ml 85 wt% H₃PO₄, 400 ml 100 wt% ethanol and 1600 ml water with another Al foil as counter electrode. The anodization took place at -3 °C with a constant DC voltage of 160 V under a continuous stirring. After anodizing for 3 days, the residual aluminum on the backside of the sample was removed in a 1 M CuCl₂ solution. The backside of as-obtained 3-D PAA template was immersed in 3 wt% H₃PO₄ at 45 °C for 3 hours to remove the dense Al₂O₃ barrier on bottom and enlarge the size of nanochannels and side-holes.

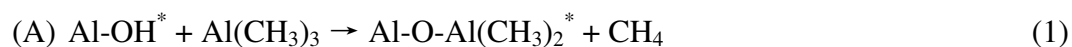
1.2 Fabrication of 3-D Ni nanowire conducting network

A 50 nm thin gold layer was sputtered on the backside of the PAA templates serving as the conducting seed layer for electroplating Ni nanowires. The electrodeposition was carried out in a three-electrode electrochemical cell (CHI 760c) at room temperature, where a piece of Ni foil was used as the counter electrode. The electrolyte consisted of 270 g L⁻¹ NiSO₄·6H₂O, 40 g L⁻¹ NiCl₂·6H₂O and 40 g L⁻¹ H₃BO₃.³ An Ag/AgCl electrode was used as reference electrode. A constant voltage of -1 V vs Ag/AgCl was applied between gold seed layer and counter electrode. After the electrodeposition with desirable time, the sample was immersed in 5 M NaOH solution to remove the PAA template. Then the sample was cleaned by water and dried in vacuum oven.

1.3 Atomic layer deposition of TiO₂ active material

The deposition of active material TiO₂ on the conducting Ni network was carried out in a viscous-flow, hot-wall type ALD reactor described in detail elsewhere.⁴ Deposition was performed in static mode in order to conformably coat the high surface area Ni nanostructures. Ultra high purity (UHP) grade N₂ was used as the carrier gas during the deposition. Base pressure of the reactor was kept at one Torr. Prior to TiO₂ deposition, about 60 Å thick ALD Al₂O₃ (alumina) was pre-deposited as a seed layer. This layer is needed to insure proper TiO₂ nucleation.⁵ The sequential dosing of trimethylaluminum (TMA) and water were used for ALD Al₂O₃ where titanium tetrachloride (TiCl₄) and water were used for ALD TiO₂. The chemistries of ALD Al₂O₃ and TiO₂ were well studied and understood and has been shown to result in high quality films.^{6,7} The coating process was performed at a reaction temperature of 120 °C. At this deposition temperature, both Al₂O₃ and TiO₂ are in amorphous state.^{8,9}

The surface chemistry of the binary reaction sequence during Al₂O₃ ALD can be described as the following two reactions:¹⁰



Similarly, the TiO₂ ALD process can be described as follows:¹¹



Section 2: Structural and Electrochemical Characterization

2.1 Structural Characterization of ALD films

Figure S1a shows the X-ray diffraction (XRD) pattern of the 32 μm -long 3-D Ni nanowire network before and after applying 50 cycles ALD Al_2O_3 and 50 cycles ALD Al_2O_3 / 320 cycles ALD TiO_2 coatings. The three peaks in all three samples can be indexed to (111), (200), (220) as a cubic Ni phase (JCPDS 04-0850). No additional XRD peaks can be observed after applying Al_2O_3 and $\text{Al}_2\text{O}_3/\text{TiO}_2$ coatings, which indicates that ALD Al_2O_3 and TiO_2 coatings are amorphous. The X-ray photoelectron spectroscopy (XPS) study on TiO_2 coating in Figure S1b shows that the film is nearly stoichiometric 1/2 Ti/O ratio with about 3 at.% of chlorine impurities. The carbon signal originates from the absorption of organics when the sample was taken out from the ALD chamber.

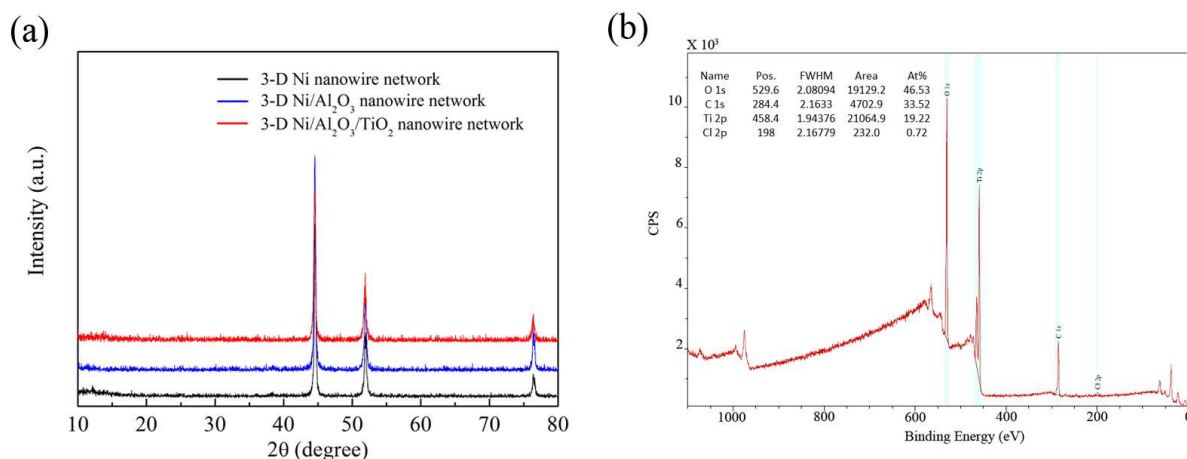


Figure S1: a) XRD pattern on 3-D Ni nanowire network without coating and with Al_2O_3 or $\text{Al}_2\text{O}_3/\text{TiO}_2$ coatings. b) XPS result of as-deposited ALD TiO_2 film.

2.2 Resistivity of ALD Al₂O₃-coated Ni substrate

Figure S2 presents the standard I-V curve of 50 cycles ALD Al₂O₃ coated plain Ni substrate using four-point electrical measurement. The linear I-V curve demonstrates ohmic contact between ALD Al₂O₃-coated Ni substrate and electrode. The resistivity is measured to be $1.13 \times 10^{-5} \text{ ohm.cm}^{-1}$, which is 1.6 times as much as that of pure Ni but is still very conductive. This measurement demonstrates that the ALD 50 cycles of Al₂O₃ coating does not block the electron transport.

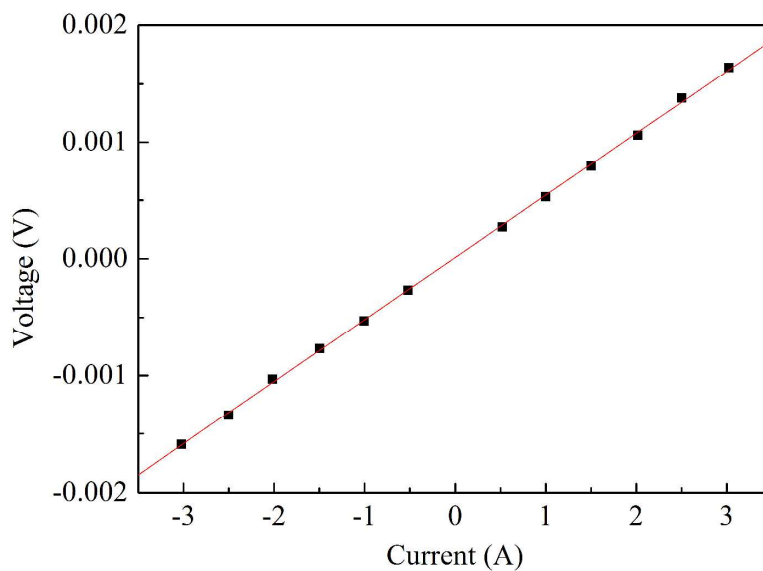


Figure S2. Current-voltage curve of ALD Al₂O₃-coated plain Ni foil.

2.3 Cross-sectional SEM images of the straight Ni/TiO₂ nanowire arrays

Figure S3 shows the surface and the cross-sectional SEM images of the straight Ni/TiO₂ nanowire arrays with different nanowire lengths. It shows that the nanowire arrays agglomerate as clustered nanowires. The size of nanowire clusters becomes larger from hundreds of nanometers to tens of micrometers when the length of the nanowires increases from 5 μm to 28 μm .

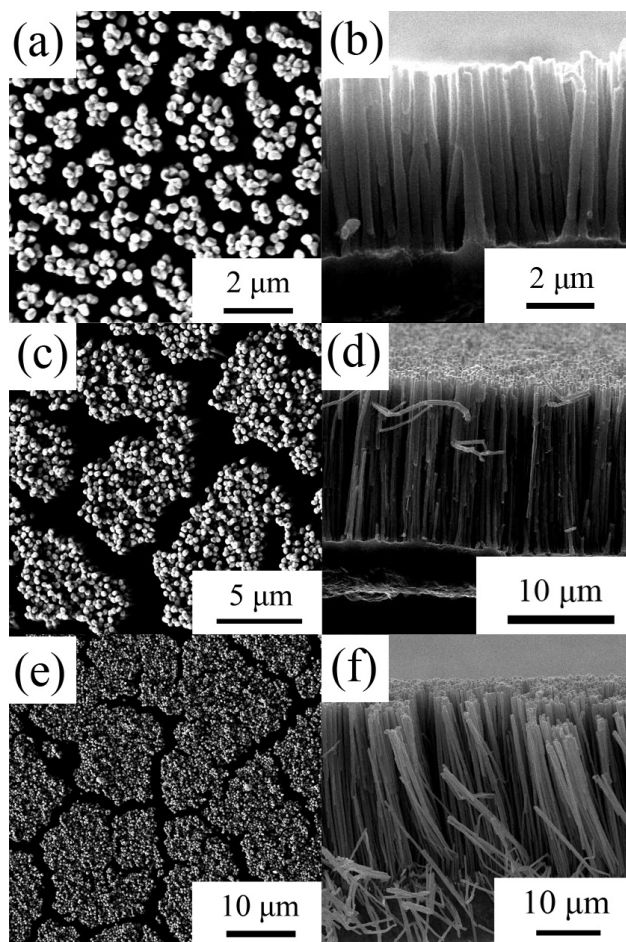


Figure S3. SEM images of the surface morphology and the cross-section of nanowire arrays with different lengths: a) and b) 5 μm , c) and d) 15 μm , and e) and f) 28 μm .

2.4 Electrochemical performance of ALD Al_2O_3 -coated 3-D Ni nanowire network

Considering that the native oxide of Ni is hard to be completely avoided, we have characterized the electrochemical performance of a control sample, i.e., ALD 50 cycles Al_2O_3 -coated 32 μm -long 3-D Ni nanowire network without TiO_2 coating, as shown in Figure S4. It shows an irreversible discharging capacity of 0.012 $\text{mAh}\cdot\text{cm}^{-2}$ at the first cycle, and a stable discharging capacity of around 0.001 $\text{mAh}\cdot\text{cm}^{-2}$ after first cycle, which is less than 1% of the capacity of 3-D Ni/ Al_2O_3 / TiO_2 nanowire network (0.16 $\text{mAh}\cdot\text{cm}^{-2}$).

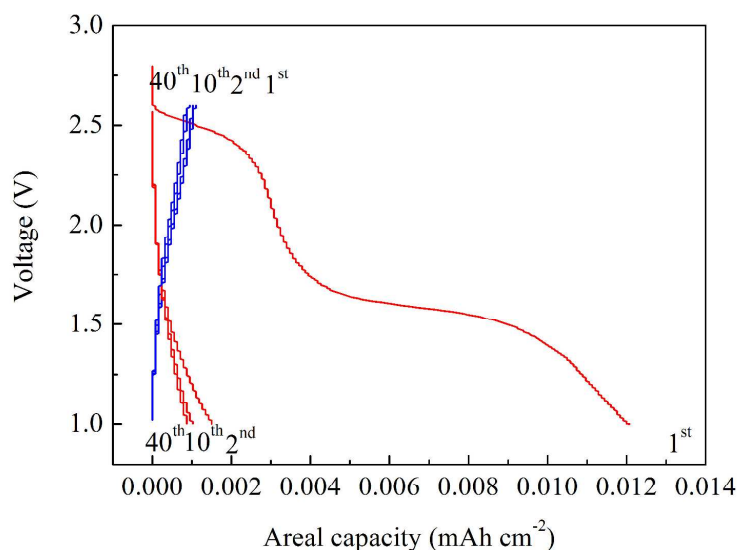


Figure S4: Galvanostatic discharging/charging curves of a control sample of 32- μm long 3-D Ni/ Al_2O_3 nanowire network at a current density of 0.0016 $\text{mAh}\cdot\text{cm}^{-2}$.

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