Electronic Supplementary Material (EIS) for

Atomically Precise Growth of Sodium Titanates as Anode Materials for High-Rate and Ultralong Cycle-Life Sodium-Ion Batteries

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Fig. S1. Low-magnification SEM images of sodium titanate thin films deposited on (a) nitrogen-doped CNTs using 200 cycles, (b) Si (100) wafer using 400 cycles, and (c,d) AAO template using 200 cycles (top and cross-section views). The deposition was performed at 250 °C using ALD recipe of \((\text{NaO}^{\text{tBu}}\text{H}_2\text{O}) + (\text{TTIP-H}_2\text{O})\).

Fig. S2. FTIR spectra of (a) bare double-side polished Si wafer, (b) anatase TiO$_2$ deposited by ALD at 225 °C, and (c) sodium titanate deposited by ALD at 225 °C on double-side polished Si wafer. The sharp peak located at 1460 cm$^{-1}$ in (c) is attributable to the formation of Na-O bonds in the sodium titanate films [1]. The peak centered at 439 cm$^{-1}$ in (b) is ascribed to Ti-O-Ti bonds typically observed in anatase TiO$_2$ [2]. Disappearance of 439 cm$^{-1}$ peak in (c) indicates the breaking of Ti-O-Ti bonds and formation of Na-O-Ti bonds in the sodium titanate films. Peaks from 605 cm$^{-1}$ to 1105 cm$^{-1}$ result from double-side polished Si wafer.
**Fig. S3.** Selected-area electron diffraction (SAED) patterns of (a) sodium titanates as-deposited on CNTs at 225 °C, and (b) sodium titanates/CNTs annealed at 500 °C in air.

**Fig. S4.** Crystal structure of anatase TiO$_2$ (top) and Na$_{0.23}$TiO$_2$ (bottom) viewed along the $b$-axis. Red spheres represent oxygen, blue spheres represents titanium ions, yellow spheres represent sodium ions, and blue polyhedrons represent the Ti – O octahedra.
Fig. S5. SEM images of sodium titanates (a,b) as-deposited at 225 °C, after annealing in air at (c,d) 500 °C, (e,f) 700 °C, and (g,h) 900 °C, respectively.

Fig. S6. Cross-section SEM image of sodium titanates deposited on Si wafer at 275 °C using 400 ALD cycles.
Fig. S7. Raman spectra of A-NaTiO and Na$_{0.23}$TiO$_2$. Raman bands below 278 cm$^{-1}$ can be assigned to lattice modes and Na-O-Ti stretching vibration modes [3]; Raman bands between 370 and 484 cm$^{-1}$ can be assigned to framework of Ti-O-Ti vibrations [4]; Raman bands between 632 and 683 cm$^{-1}$ are due to the Ti-O-Ti stretch in edge-shared TiO$_6$ [1, 3-5]; Raman band at 873 cm$^{-1}$ can be assigned to the symmetric stretch of short Ti-O bonds involving non-bridging oxygen atoms associated with sodium ions [1,4,5].

Fig. S8. XRD pattern of Na$_{0.23}$TiO$_2$/CNT composite prepared by annealing amorphous sodium titanates in argon gas for 10h.
**Fig. S9.** (a) CV curve of pristine CNTs measured between 0.1 to 2.5V at a scanning rate of 0.1 mV s\(^{-1}\); and (b) cycling performance of pristine CNTs at a current rate of 10 mA g\(^{-1}\).

**Fig. S10.** Discharge capacity of A-NaTiO/CNT and C-NaTiO/CNT composites at a current rate of 10 mA g\(^{-1}\).
Fig. S11. TG results of A-NaTiO and C-NaTiO on CNTs as measured in air atmosphere at a heating rate of 30 ° min⁻¹.

Fig. S12. Rate capability of A-NaTiO in this work in comparison with other types of sodium titanates reported in reference [1, 6-10]. At each current density, the discharge capacity of each sample was taken at the second cycle for comparison.
**Fig. S13.** Cycling stability of A-NaTiO/CNT electrodes prepared with acetylene black (AB) (A-NaTiO/CNTs:PVDF:AB = 8:1:1) and without AB (NaTiO/CNTs:PVDF = 9:1) at a current density of 10 mA g$^{-1}$.

**References**


