Electronic Supplementary Information

SnO$_2$@TiO$_2$ double-shell nanotubes with improved high rate cyclability for lithium ion battery anode

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Experimental Details.

1. **Synthesis of SnO$_2$@TiO$_2$ double-shell nanotubes**: For electrospinning, PAN (Polyacrylonitrile, MW = 200,000 g mol$^{-1}$, Misui Chemical) was dissolved in dimethylformamide (DMF, purity = 99.5%, Daejung Chemical), and the concentration of the solution was fixed to 15 wt% to produce uniform nanofibers with an average diameter of 200–300 nm. The electrospinning conditions were optimized as follows: applied voltage: 15 kV, tip-to-collector distance: 10 cm, and flow rate of solution: 0.5 ml h$^{-1}$. The as-electrospun PAN nanofibers were directly collected on a 4-inch silicon wafer for the subsequent SnO$_2$ and TiO$_2$ coatings by ALD. The SnO$_2$ inner shell and TiO$_2$ outer shell were deposited on the as-electrospun PAN nanofibers by plasma-enhanced atomic layer deposition (PEALD). Dibutyltindiacetate (DBTDA) ($\text{(CH}_3\text{CO}_2\text{)}_2\text{Sn} \text{[(CH}_2\text{)}_3\text{–CH}_3\text{]}_2$) was used as the Sn precursor, which was evaporated at 40 $^\circ$C and transported to the deposition chamber by a 20-sccm Ar (99.99%) gas. Titanium isopropoxide (Ti(OCH(CH$_3$)$_2$)$_4$) was used as the Ti precursor, which was evaporated at room temperature and transported by 10-sccm Ar gas. The 50-sccm O$_2$ (99.99%) and Ar (99.99%) gases were used as the plasma and purge gases, respectively. The time sequence for source pulse, first purge, O$_2$ pulse, plasma pulse, and second purge was 3, 12, 8, 1, and 12 s for SnO$_2$ deposition and 1, 12, 8, 1, and 12 s for TiO$_2$ coating, respectively. The deposition was conducted with an RF power of 100 W at 240 mTorr, and the substrate temperature during deposition was maintained at 100 $^\circ$C to reduce the degradation of PAN nanofibers. The number of ALD cycles for SnO$_2$ and TiO$_2$ coatings were 300 and 600, respectively. The SnO$_2$@TiO$_2$ double-shell-coated PAN nanofibers were annealed at 700 $^\circ$C for 1 h to burn out the PAN template and to crystallize the SnO$_2$ and TiO$_2$ shells.
2. Characterization: SnO$_2$@TiO$_2$ double-shell nanotubes were characterized by field emission scanning electron microscopy (FESEM, Hitachi, S-48000) and transmission electron microscopy (TEM, FEI, Tecnai F20) equipped with energy dispersive spectroscopy (EDS). For electrochemical measurements, the test electrodes consisted of the active powder material (70 wt%), carbon black (Ketchen Black, 10 wt%) as a conducting agent and polyamide imide (PAI, 20 wt%) dissolved in N-methyl pyrrolidinone (NMP) at 60 $^\circ$C as a binder. Each component was well mixed to form slurry using a magnetic stirrer. The slurry was coated onto a copper foil substrate, pressed, and dried at 200 $^\circ$C for 4 h under a vacuum. A coin-type electrochemical cell was used with Li foil as the counter and reference electrodes, and 1 M LiPF$_6$ in ethylene carbonate (EC)/diethylene carbonate (DEC) (5:5 (v/v), PANAX) was used as the electrolyte. The cell assembly and all of the electrochemical tests were carried out in an Ar-filled glove box. The cycling experiments were galvanostatically performed using a Maccor automated tester at a constant current of 800 and 1500 mA g$^{-1}$ for the active material within the voltage range between 0.0 and 3.0 V (vs. Li/Li$^+$). During the discharging step, Li was inserted into the electrode, while Li was extracted from the electrode during the charge. After the electrochemical measurements, the coin cell was disassembled and washed completely with ethanol for SEM and TEM analyses.
**Fig. S1** Morphologies of as-electrospun PAN nanofibers on wafer.

**Fig. S2** STEM images with EDS mapping (green: Sn, red: Ti) and low-magnitude TEM images; the SnO$_2$-TiO$_2$ multishell nanotube of (a, b) 75 and (c, d) 150 ALD cycles for TiO$_2$ shell coating.
**Fig. S3** SnO$_2$ single shell nanotubes; (a) FE-SEM image, (b) STEM image and EDS line-profile (green: Sn, red: Ti), and (c) low-magnitude TEM image.
**Fig. S4** TEM images and SAED patterns at each potential in Fig. 3c: a) discharge 2.0 V (point 1), b) discharge 0.2 V (point 2), c) charge 1.5V (point 3), and d) charge 2.9 V (point 4).
**Fig. S5** Charge/discharge voltage profile of SnO$_2$ nanotube electrode between 0.01 and 3.0 V at 800 mA g$^{-1}$.

**Fig. S6** Rate capability test of SnO$_2$@TiO$_2$ double shell nanotube
Fig. S7 (a) The morphology of TiO$_2$ nanotube, (b) cycle performance and (c) charge/discharge voltage profile of TiO$_2$ nanotube electrode between 0.01 and 3.0 V at 800 and 1500 mA g$^{-1}$. 
Fig. S8 (a) STEM image of SnO$_2$ nanotube electrode after 5 cycles at 1500 mA g$^{-1}$ and (b) EDS element mapping.

Fig. S9 FESEM, STEM images, and element mapping of a, b) SnO$_2$ single-shell nanotube electrode and c, d) SnO$_2$@TiO$_2$ double-shell nanotube electrode after 50 cycles at 1500 mA g$^{-1}$. 