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Supplementary Information

Elaborate synthesis of black tin oxide–black titanium oxide core–shell nanotubes for ultrastable and fast lithium storage

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Experimental Details

Synthesis of SiO_2 nanorods. The SiO_2 nanorods were synthesized by a sol-gel method.[1] Typically, 0.4 g of F127 ($EO_{100}PO_{70}EO_{100}$, Sigma-Aldrich), 1 g of cetyltrimethyl ammonium bromide (CTAB, Macklin), 98 mL of deionized water, and 2 mL of 25 wt% aqueous ammonia were mixed to form a clear solution, to which 2.5 mL of tetraethylorthosilicate (TEOS, Aladdin) was added under stirring. After being stirred for 2 h, the resulting white solid was collected by centrifugation, washed with deionized water several times, and re-dispersed in 100 mL of deionized water for further use as a sacrificial template.

Synthesis of $SnO_2@SiO_2$ nanorods. The $SnO_2@SiO_2$ nanorods were synthesized by an *in situ* deposition method.[2] Briefly, 4 g of $Na_2SnO_3{\bullet}3H_2O$ (Aladdin) was dissolved in 100 mL of as-prepared SiO_2 colloid solution, to which 100 mL of absolute alcohol was added. The mixed solution was heated to 60 °C for 2 h under gentle stirring. The resulting white solid was collected by centrifugation, washed with isopropanol several times, and dried at 60 °C overnight.

Synthesis of $TiO_2@SnO_2$ nanotubes. The TiO_2 shell was synthesized by a hydrothermal method.[3] Basically, 0.2 g of $SnO_2@SiO_2$ nanorods were dispersed in 40 mL of isopropanol, followed by the addition of 0.05 mL of 99% diethylenetriamine (DETA, Alfa Aesar). After gentle stirring, 1 mL of 98% titanium isopropoxide (TIP, Adamas-Beta) was added. The mixed solution was transferred to a 100 mL Teflon-lined stainless steel autoclave, and kept at 200 °C for 24 h. The product was collected by centrifugation, washed with isopropanol several times, and dried at 60 °C overnight. It was further calcined at in air 500 °C for 2 h. The annealed product was treated with HF solution to etch away the SiO_2 template.

Synthesis of $TiO_{2-x}@SnO_{2-x}$ nanotubes. Typically, 0.6 g of $TiO_2@SnO_2$ nanotubes were ground with 0.3 g of $NaBH_4$ for 10 min, then the mixture was transferred to a corundum boat, and heated in argon at 350–400 °C for 30–60 min in argon atmosphere. After being naturally cooled down to ambient temperature, the black product was washed with diluted HCl and deionized water several times to remove reduced Sn and $NaBH_4$, and dried at 60 °C for overnight.

Electrochemical tests. A working electrode was prepared by coating a copper foil with slurry containing 70 wt% active material, 20 wt% carbon fibre, and 10 wt% binder (sodium alginate and carboxymethyl cellulose at 1:1 w/w) in deionized water. After being dried at 60 ℃ for 10 h, the working electrode was cut into disks with a diameter of 14 mm, and the mass loading of the active material was ~1 mg cm^{-1}. Li foil was used as the counter electrode. The test cell was assembled in an argon filled glove-box. The electrolyte was 1 M $LiPF_6$ in a mixture of dimethyl carbonate and ethylene carbonate (molar ratio = 1:1) with 10 vol% fluorethylene carbonate. The galvanostatic method at different charging/discharging current densities was employed to measure the electrochemical capacity using a LAND-CT2001A cycler. CV tests were carried out on the electrochemical workstation (Chi660e) between 0.01 and 3 V *vs.* Li/Li^+ at a scan rate of 0.2 mV s^{-1}. EIS measurements were performed over a frequency range from 100 kHz to 0.1 Hz.

Characterizations. Transmission electron microscopy (TEM) was performed by a Hitachi HT7700 microscope operated at an accelerating voltage of 100 kV. Scanning transmission electron microscopy (STEM) was performed by a JEOL JEM-2100F microscope operated at an accelerating voltage of 120 kV. Scanning electron microscopy (SEM) was performed by a Hitachi SU8010 microscope operated at an accelerating voltage of 10 kV. X-ray photoelectron spectroscopy (XPS) was performed by a Thermo Scientific Escalab 250Xi spectrometer. X-ray diffraction (XRD) was performed by a Bruker D8 Advanced X-ray diffractometer with Cu Kα radiation (λ = 0.154 nm). X-ray fluorescence (XRF) was performed by a Shimadzu EDX-7000 with the powder-oxide mode. To determine the conductivity, the powders were pressed into pellets for the I-V measurements, whose thickness was ~0.06 mm, and cross-sectional area was ~0.35 mm^2. The room temperature I-V curves were obtained in a voltage range of (–0.2)–(+0.2) V at a scanning rate of 0.1 V s^{-1}.

Supplementary Figures

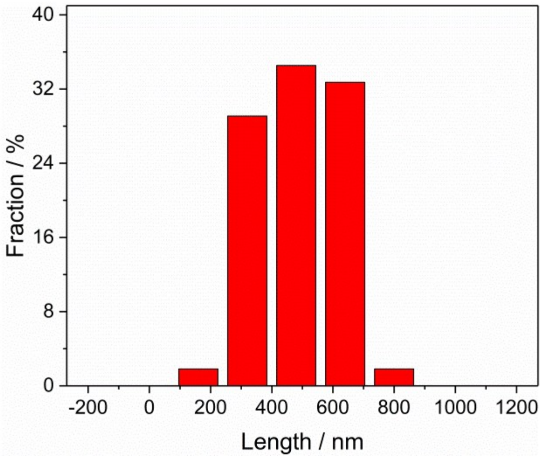

Figure S1. Length distribution of SiO_2 nanorods.

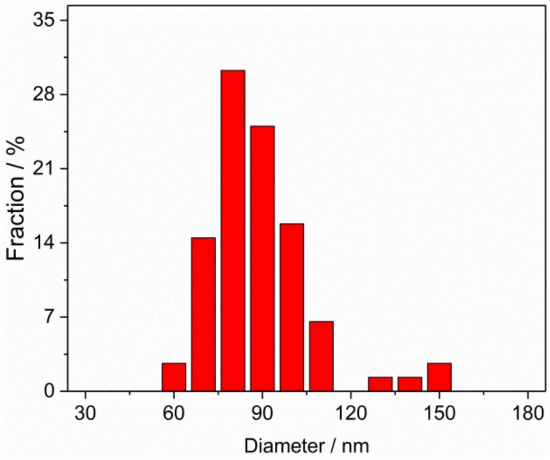

Figure S2. Diameter distribution of SiO_2 nanorods.

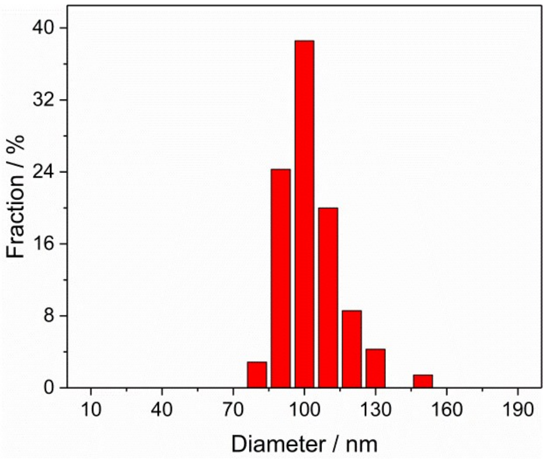

Figure S3. Diameter distribution of $SnO_2@SiO_2$ nanorods.

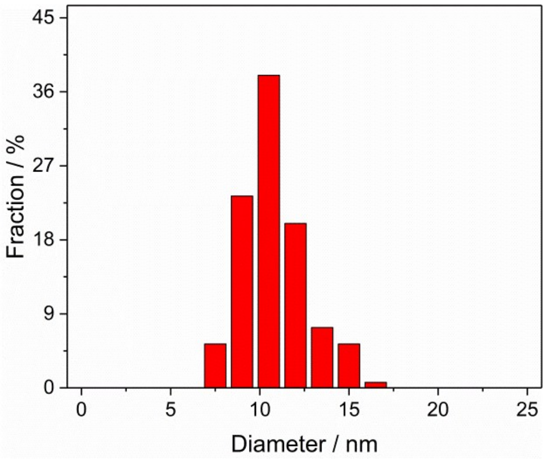

Figure S4. Thickness distribution of TiO_2 layer.

Figure S5. Photograph of TiO_2@SnO_2 nanotubes (left) *vs.* TiO_{2-x}@SnO_{2-x} nanotubes (right).

Table S1. Elemental ratios of TiO_2@SnO_2 and TiO_{2-x}@SnO_{2-x} nanotubes as determined by XRF, in which the lower Sn content in the latter is attributed to the removal of the reduced Sn by HCl.

TiO_2@SnO_2 nanotubes	Sn	Ti	Si	Total
Weight ratio (%)	72.0	26.9	1.1	100
TiO_{2-x}@SnO_{2-x} nanotubes	Sn	Ti	Si	Total
Weight ratio (%)	60.2	39.5	0.3	100

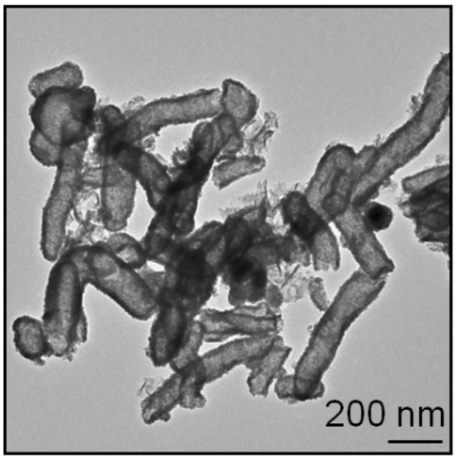

Figure S6. TEM image of SnO_{2-x} nanotubes (without the TiO_{2-x} shell).

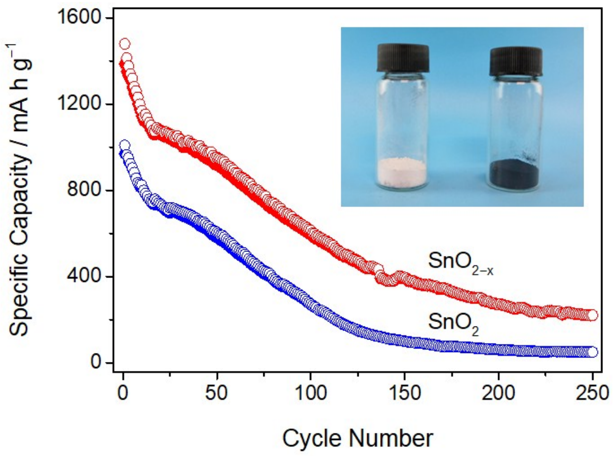

Figure S7. Cycle behaviors of SnO_2 and SnO_{2-x} nanotubes, respectively. The inset shows a photograph of SnO_2 nanotubes (left) *vs.* SnO_{2-x} nanotubes (right).

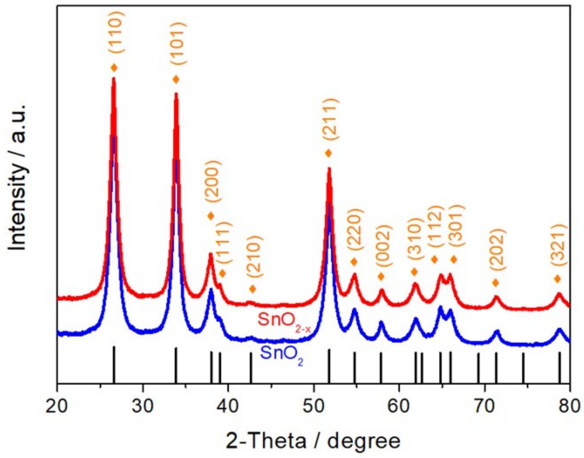

Figure S8. XRD patterns of SnO_2 and SnO_{2-x} nanotubes. The black lines correspond to rutile SnO_2 (JCPDS card No. 41–1445).

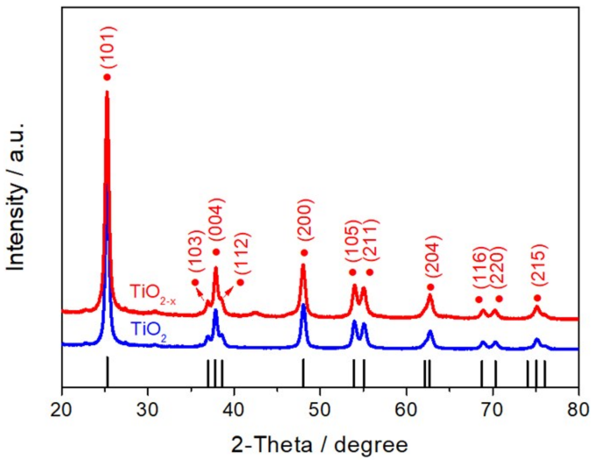

Figure S9. XRD patterns of TiO_2 and TiO_{2-x} nanoplatelets. The black lines correspond to anatase TiO_2 (JCPDS card No. 21–1272).

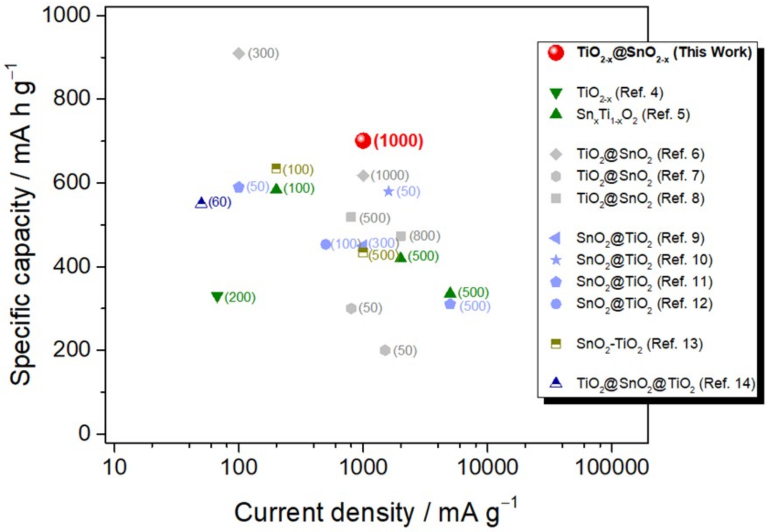

Figure S10. Comparison of capacities of our $TiO_{2-x}@SnO_{2-x}$ nanotubes and other reports (each bracket shows the corresponding cycle number).

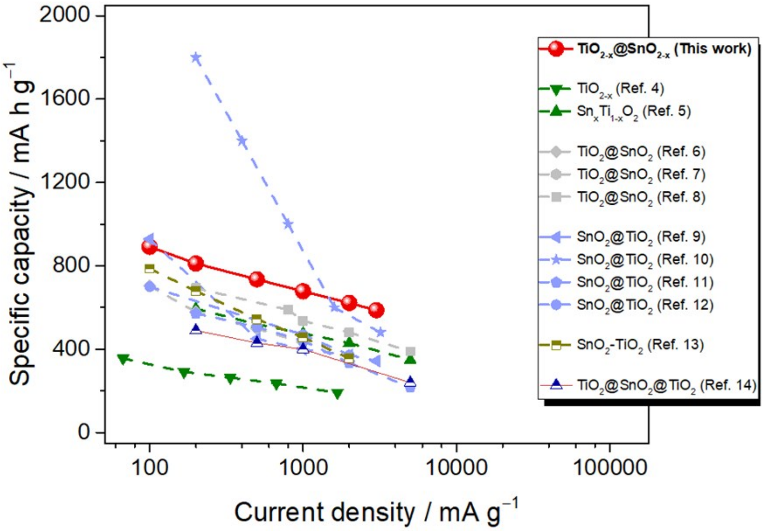

Figure S11. Comparison of rate capabilities of our TiO_{2-x}@SnO_{2-x} nanotubes and other reports.

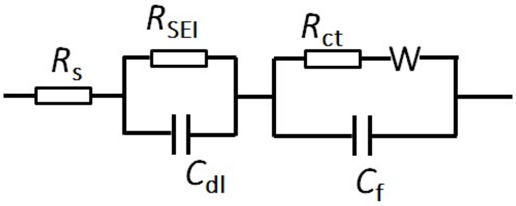

Figure S12. Equivalent circuit for the EIS measurements.

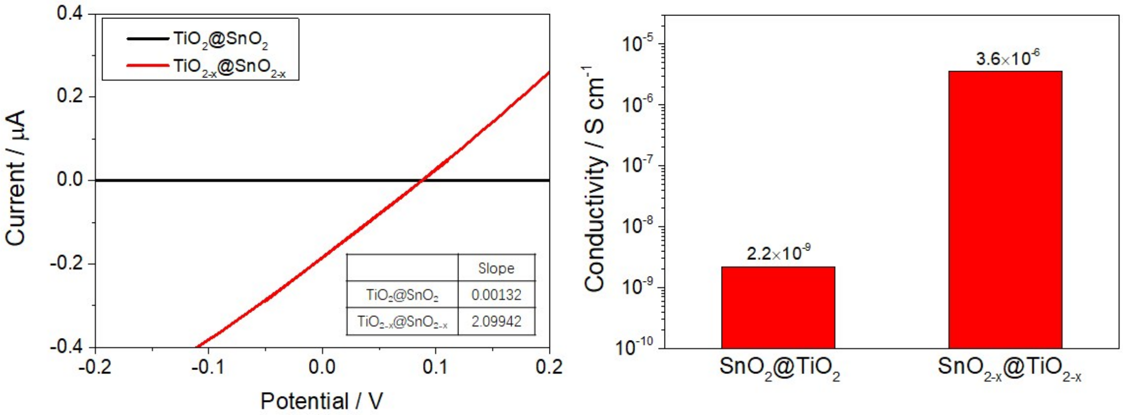

Figure S13. Comparison of conductivities of TiO_2@SnO_2 and TiO_{2-x}@SnO_{2-x} nanotubes.

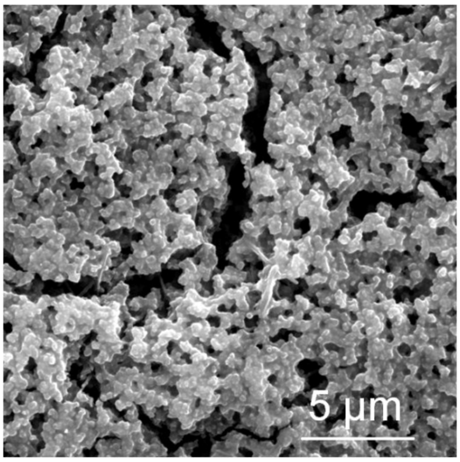

Figure S14. SEM image of electrode consisting of TiO_{2-x}@SnO_{2-x} nanotubes after being cycled at 1 A g^{-1} for 1000 cycles.

Supplementary References

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