

## Electronic Supplementary Information

### Nitrogen-Doped Carbon Coated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ - $\text{TiO}_2$ /Sn Nanowire and Its Enhanced Electrochemical Property for Lithium ion Batteries

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## Experimental details

### Synthesis of $\text{Li}_4\text{Ti}_5\text{O}_{12}\text{-TiO}_2$ , $\text{Li}_4\text{Ti}_5\text{O}_{12}\text{-TiO}_2/\text{Sn}$ and $\text{Li}_4\text{Ti}_5\text{O}_{12}\text{-TiO}_2/\text{Sn}@C$

First, hydrogen titanate nanowire precursor was prepared via hydrothermal reaction between anatase  $\text{TiO}_2$  powders and concentrated NaOH solution (10 M) at 180 °C for 48 h, following the ion substitution progress of  $\text{Na}^+$  with  $\text{H}^+$  in 0.5 M  $\text{HNO}_3$  solution. Second,  $\text{Li}_{1.81}\text{H}_{0.19}\text{Ti}_2\text{O}_5 \cdot x\text{H}_2\text{O}/\text{SnO}_2$  precursor was obtained by chemical lithiation of hydrogen titanate precursor and hydrolysis process of  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$  in a 0.2 M LiOH solution heated at 180 °C for 2 h in a Teflon-lined stainless steel autoclave. Thirdly, 0.2 g  $\text{Li}_{1.81}\text{H}_{0.19}\text{Ti}_2\text{O}_5 \cdot x\text{H}_2\text{O}/\text{SnO}_2$  mixed with certain amounts of dopamine hydrochloride were added to the tris-buffer (200 mL, pH  $\approx$ 8.5) and stirred for 24 h at room temperature. Finally the precipitate was collected, and after drying it was annealed under an Ar/ $\text{H}_2$  (95%:5% Vol) atmosphere at 600 °C for 6 h. For comparison, the  $\text{Li}_4\text{Ti}_5\text{O}_{12}\text{-TiO}_2$  and  $\text{Li}_4\text{Ti}_5\text{O}_{12}\text{-TiO}_2/\text{Sn}$  samples were prepared by heating  $\text{Li}_{1.81}\text{H}_{0.19}\text{Ti}_2\text{O}_5 \cdot x\text{H}_2\text{O}$  and  $\text{Li}_{1.81}\text{H}_{0.19}\text{Ti}_2\text{O}_5 \cdot x\text{H}_2\text{O}/\text{SnO}_2$  precursors respectively, and keeping the other heating experimental variables fixed. Besides, we also synthesized the  $\text{Li}_4\text{Ti}_5\text{O}_{12}\text{-TiO}_2\text{-NWs}@C$  and  $\text{Sn}@C$  electrodes using the same hydrolysis and coating processes as contrasts shown in ESI.

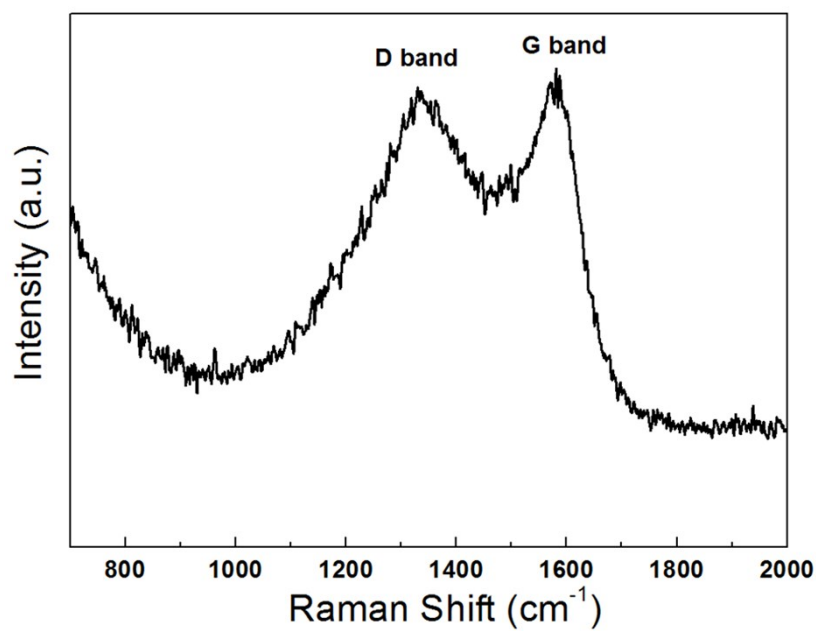
### Material Characterizations

The morphology, size and crystal structure of the as-prepared samples were characterized by MERLIN VP Compact for scanning electron microscope (SEM), Hitachi-HT7700 for TEM, and JEM-2100F for high resolution transmission electron microscopy (HRTEM), selected-area electron diffraction (SAED) and EDS mapping. X-ray diffraction (XRD) was recorded on a Rigaku D/Max-B X with Cu K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). The Raman spectrum was recorded on a HR800 Raman spectrometer (HORIBA, France) using the 488 nm line of an ArC laser as the excitation beam at a heating rate of 2 °C  $\text{min}^{-1}$ . Inductively coupled plasma mass spectroscopy (ICP-MS) analysis was carried out using iCP QC (Thermo Fisher Scientific, US) to determine the content of Sn, and elemental analyzer (CE-440) was used for nitrogen content. Thermogravimetric analysis (TGA) was carried out using thermogravimetric analyzer (NETZSCH-STA 449 F3) with a heating rate of 10 °C/min in air. Nitrogen adsorption–desorption isotherms were obtained using an Automated vapor sorption analyzer (Autosorb-iQ2-MP, Quanta Chrome) at 77.4 K under vacuum. The specific surface area was calculated by the Brunauer-Emmett-Teller (BET) method. X-ray photoelectron

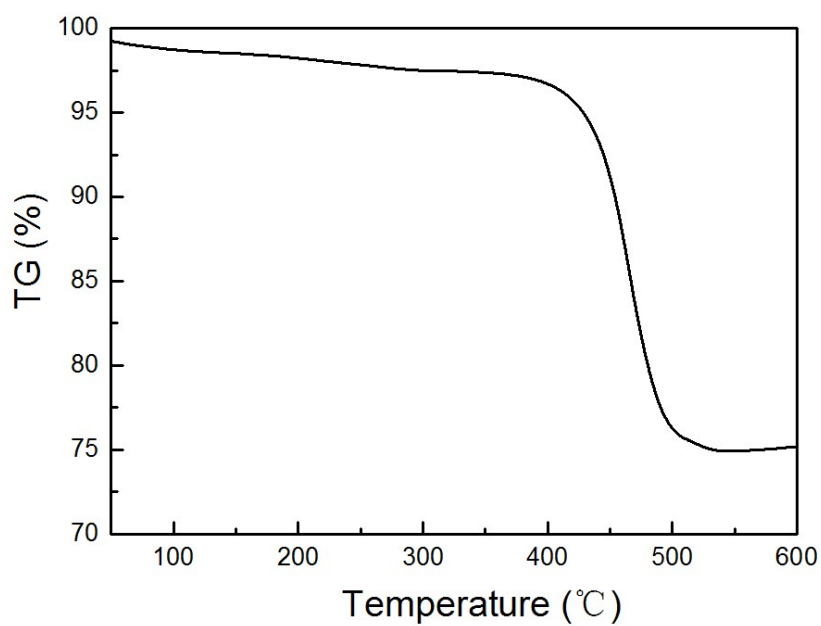
spectroscopy (XPS) spectra data were obtained using Escalab 250XI system (Thermo Fisher Scientific, US).

### **Electrochemical investigation**

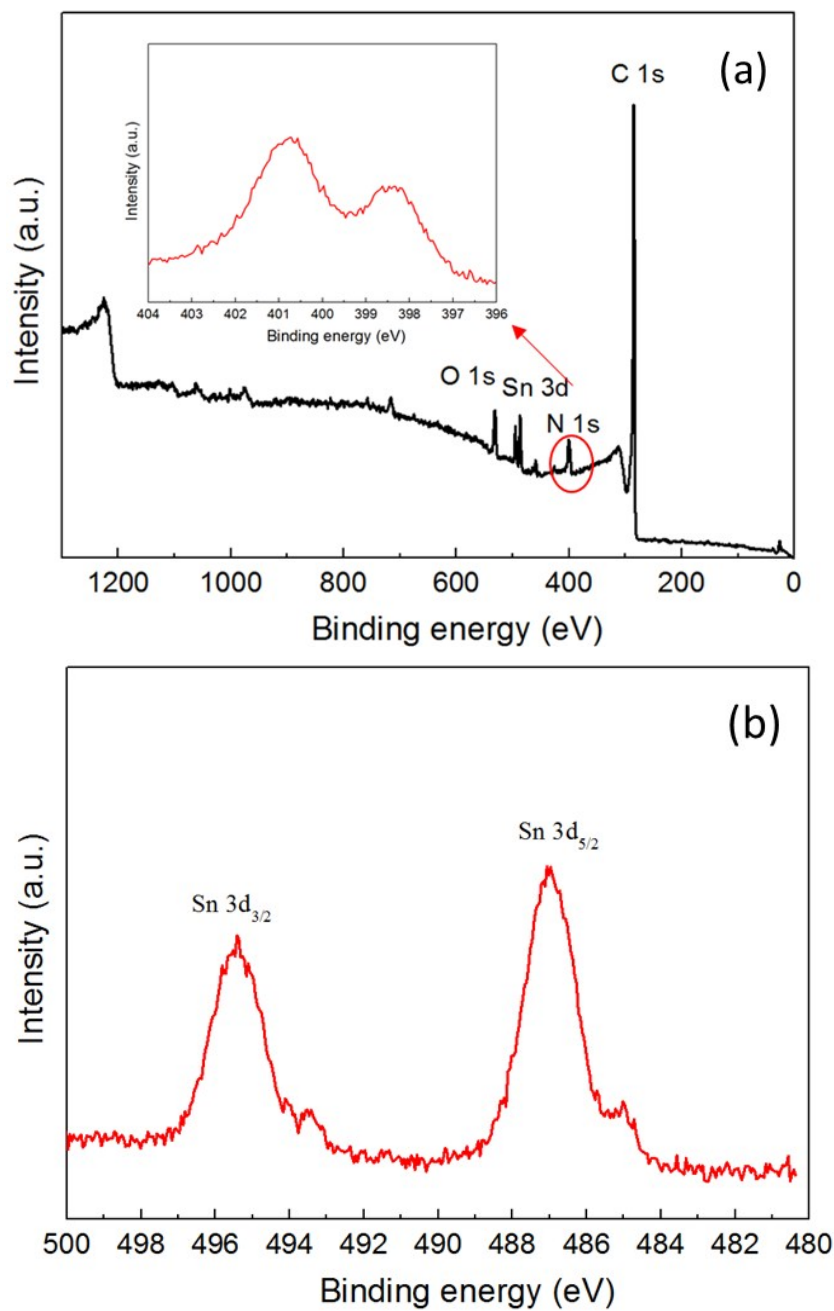
For the electrochemical measurements, the as-prepared active materials were mixed with polyvinylidene fluoride (PVDF) and Super P in a weight ratio of 80:10:10 in N-methyl-2-pyrrolidone (NMP) solution. The mixed materials were pasted on aluminum foils and dried in a vacuum oven at 100 °C for 10 h, and then were cut into discs and pressed as working electrodes (WE). The 2032-coin-type cells were assembled in an argon-filled glove-box. Pure lithium was used as the counter electrode. The electrolyte was 1 M LiPF<sub>6</sub> ethylene carbonate (EC): dimethylcarbonate (DMC) =1:1 in volume. The separator was a microporous membrane (Celguard 2400, USA). The mass loadings of all the electrodes in this work are controlled between 1.0-1.2 mg cm<sup>-2</sup>. The discharge/charge tests were carried out using a LAND Cell test 2001 A (Wuhan, China) system between 2.5 and 1.0 V. Zahner IM6 electrochemical workstation was used for cyclic voltammetry (CV) with the scan scope of 1.00-2.50 V. All the electrochemical tests were conducted at room temperature.



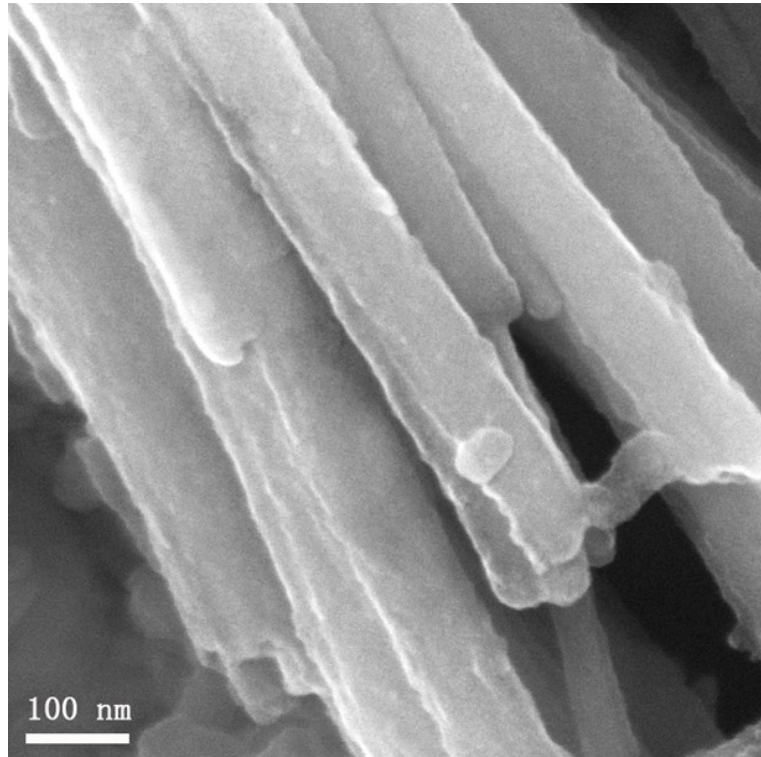
**Figure S1.** Raman spectrum of the LTO-TO-NWs/Sn@C composite.



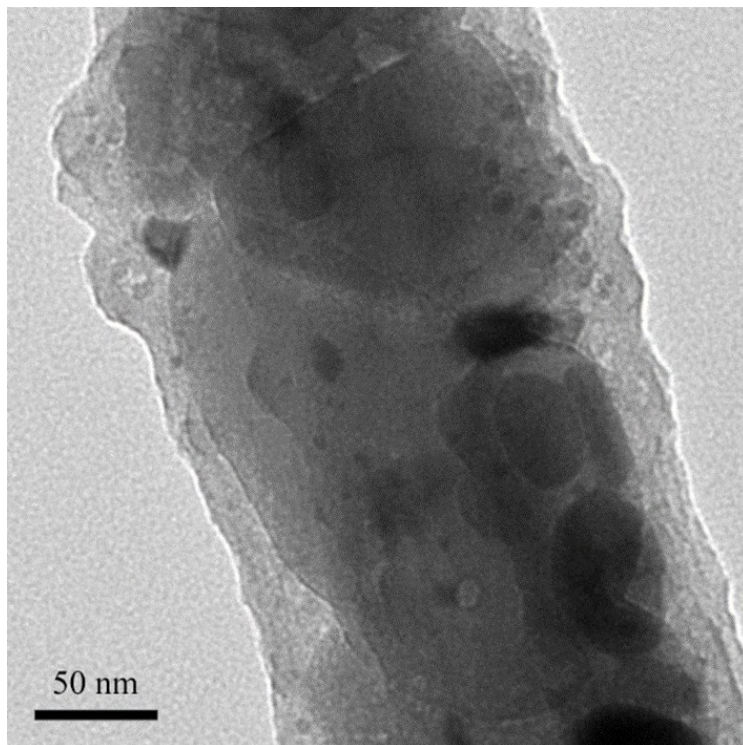
**Figure S2.** Thermogravimetric analysis (TGA) of the LTO-TO-NWs/Sn@C composite in air.



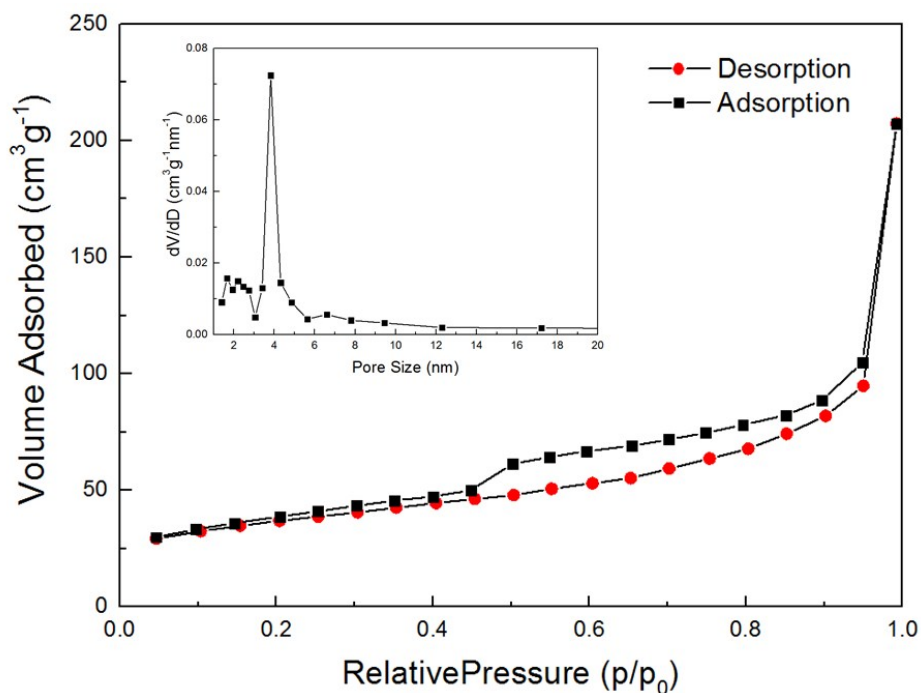
**Figure S3.** (a) The full XPS spectrum of LTO-TO-NWs/Sn@C composite. The inset shows the N1s spectrum of LTO-TO-NWs/Sn@C composite. (b) Sn 3d XPS spectra of as-prepared LTO-TO-NWs/Sn@C composite. Note that Sn<sup>4+</sup> signal in Fig. S3(b) is that some Sn NPs near the surface of the carbon layer were oxidized to SnO<sub>2</sub>.



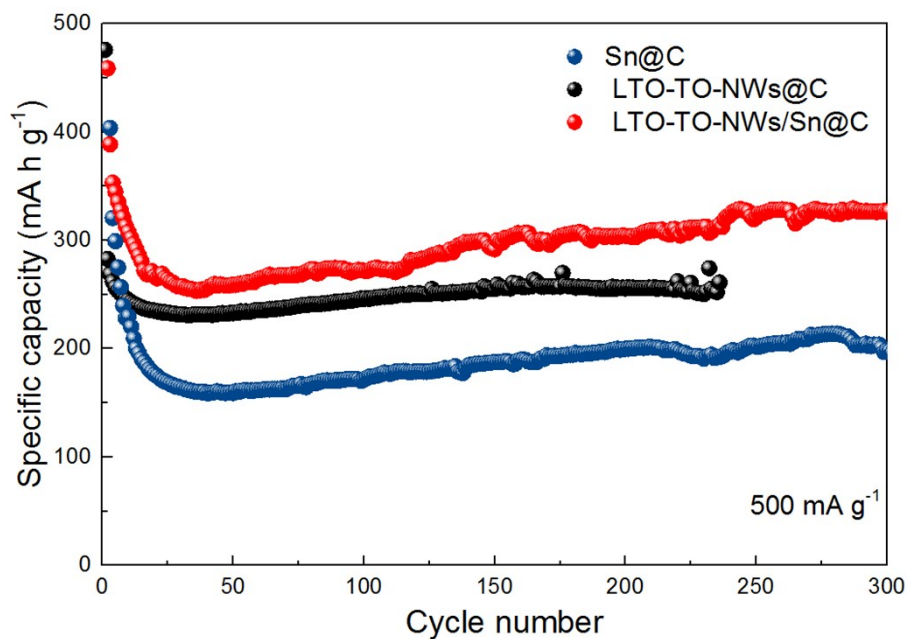
**Figure S4.** SEM image of LTO-TO-NWs/Sn@C composite.



**Figure S5.** TEM image of LTO-TO-NWs/Sn@C composite.



**Figure S6.** N<sub>2</sub> sorption isotherms of LTO-TO-NWs/Sn@C composite.



**Figure S7.** Cycling performance of Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>-TiO<sub>2</sub>-NWs@C (LTO-TO-NWs@C), Sn@C and LTO-TO-NWs/Sn@C electrode materials at 500 mA g<sup>-1</sup>. Note that the cycling performance of the three electrodes at 500 mA g<sup>-1</sup> demonstrates that LTO-TO-NWs/Sn@C possesses much higher capacity and better stability than LTO-TO-NWs@C and Sn@C electrodes.

**Table S1.** Comparison of this work with previously reported Ti-based high-capability composites.

Materials	Content of high capacity materials (wt %)	Capacity after cycles (mAh g <sup>-1</sup> )
<b>N-doped carbon coated Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>-TiO<sub>2</sub>/Sn nanowires (this work)</b>	<b>18 (Sn)</b>	<b>360, 600 cycles (1,000 mA g<sup>-1</sup>)</b>
Li <sub>4</sub> Ti <sub>5</sub> O <sub>12</sub> -TiO <sub>2</sub> nanowires (comparison)	0	150, 400 cycles (500 mA g <sup>-1</sup> )
Li <sub>4</sub> Ti <sub>5</sub> O <sub>12</sub> -TiO <sub>2</sub> /Sn nanowires (comparison)	26 (Sn)	166, 400 cycles (500 mA g <sup>-1</sup> )
N-doped carbon coated Li <sub>4</sub> Ti <sub>5</sub> O <sub>12</sub> -TiO <sub>2</sub> (comparison)	0	230, 240 cycles (500 mA g <sup>-1</sup> )
N-doped carbon coated Sn NPs (comparison)	70 (Sn)	190, 300 cycles (500 mA g <sup>-1</sup> )
Li <sub>4</sub> Ti <sub>5</sub> O <sub>12</sub> /Sn nano-composite <sup>S1</sup>	10 (Sn)	200, 30 cycles (0.02 C)
Li <sub>4</sub> Ti <sub>5</sub> O <sub>12</sub> /tin phase composite <sup>S2</sup>	~10 (Sn & SnO <sub>2</sub> )	224, 50 cycles (100 mA g <sup>-1</sup> )
Li <sub>4</sub> Ti <sub>5</sub> O <sub>12</sub> 2D nanosheets and SnO <sub>2</sub> 0D nanocrystals <sup>S3</sup>	25 (SnO <sub>2</sub> )	150, 30 cycles (0.1 mA cm <sup>-2</sup> )
Core-shell SnO <sub>2</sub> @Li <sub>4</sub> Ti <sub>5</sub> O <sub>12</sub> <sup>S4</sup>	60 (SnO <sub>2</sub> )	457, 30 cycles (100 mA g <sup>-1</sup> )
Core-shell α-Fe <sub>2</sub> O <sub>3</sub> @ Li <sub>4</sub> Ti <sub>5</sub> O <sub>12</sub> <sup>S5</sup>	~30 (α-Fe <sub>2</sub> O <sub>3</sub> )	249.3, 30 cycles (100 mA g <sup>-1</sup> )
Li <sub>4</sub> Ti <sub>5</sub> O <sub>12</sub> /NiO nanocomposite <sup>S6</sup>	5 (NiO)	176, 100 cycles (1 C)
Li <sub>4</sub> Ti <sub>5</sub> O <sub>12</sub> /Co <sub>3</sub> O <sub>4</sub> composite <sup>S7</sup>	12.5 (Co <sub>3</sub> O <sub>4</sub> )	~300, 50 cycles (160 mA g <sup>-1</sup> )
TiO <sub>2</sub> -Sn/C core-shell nanowires arrays <sup>S8</sup>	24.8 (Sn)	459, 160 cycles (335 mA g <sup>-1</sup> )
TiO <sub>2</sub> -Sn@C core-shell microspheres <sup>S9</sup>	37.5 (Sn)	206, 2,000 cycles (500 mA g <sup>-1</sup> )
TiO <sub>2</sub> (B)@SnO <sub>2</sub> / carbon nanowires <sup>S10</sup>	15 (SnO <sub>2</sub> )	669, 67 cycles (60 mA g <sup>-1</sup> )
SnO <sub>2</sub> @TiO <sub>2</sub> @reduced graphene oxide nanotubes <sup>S11</sup>	--(SnO <sub>2</sub> )	~700, 70 cycles (500 mA g <sup>-1</sup> )
SnO <sub>2</sub> /TiO <sub>2</sub> nanocomposite <sup>S12</sup>	65 (SnO <sub>2</sub> )	~600, 100 cycles (0.2C)
SnO <sub>2</sub> @TiO <sub>2</sub> double-shell nanotubes <sup>S13</sup>	~45 (SnO <sub>2</sub> )	200, 50 cycles (1,500 mA g <sup>-1</sup> )



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