## upporting Information

## A new general approach to synthesizing filled and yolk-shell structured metal oxide microspheres by applying a carbonaceous template

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Fig. S1 SEM images of the carbonaceous template microspheres (a) before and (b) after impregnation of  $Sn(Oct)_2$  at the loading rate of 0.3 mL.



**Fig. S2** (a) BJH pore size distributions of the carbon template microspheres before and after  $Sn(Oct)_2$  impregnation, (b) XRD patterns of the C-SnO<sub>2</sub> and filled and yolk-shell structured  $SnO_2$  microspheres, and (c) TG curve of the C-Sn(Oct)<sub>2</sub> composite microspheres measured under air atmospheres.



Fig. S3 Morphologies of the  $SnO_2$  microspheres obtained by post-treatment of the C-SnO<sub>2</sub> microsphere (shown in Fig. 1) in an atmosphere with high oxygen concentration and ramping rate of 10 °C min<sup>-1</sup> s.



Fig. S4 (a) BJH pore size distributions and (b)  $N_2$  adsorption and desorption isotherms of the yolk-shell and filled structured SnO<sub>2</sub> microspheres.



**Fig. S5** Morphologies of the SnO<sub>2</sub> microspheres prepared from the carbonaceous template microspheres with various loading rate of tin(II) octoate by post-treatment at 500 °C in an atmosphere with high oxygen concentration and ramping rate of 10 °C min<sup>-1</sup>: (a) 0.2 ml, (b) 0.4 ml, (c) 0.6 ml, (d) 1.0 ml, and (e) 1.5 ml.



**Fig. S6** Nitrogen adsorption and desorption isotherms and BJH pore size distributions of the  $SnO_2$  microspheres formed from the carbonaceous template microspheres with various loading rate of tin(II) octoate by post-treatment at 500 °C in an atmosphere with high oxygen concentration and ramping rate of 10 °C min<sup>-1</sup>: (a) 0.2 ml, (b) 0.4 ml, (c) 0.6 ml, (d) 1.0 ml, and (e) 1.5 ml.

![](_page_7_Figure_0.jpeg)

**Fig. S7** Morphologies and size distributions of the (a) filled and (b) yolk-shell structured  $SnO_2$  microspheres formed from the C-Sn(Oct)<sub>2</sub> microspheres with the loading rate of 0.3 mL, and (c) filled structured SnO<sub>2</sub> microspheres formed from the C-Sn(Oct)<sub>2</sub> microspheres with loading rate of 1.0 mL.

![](_page_8_Figure_0.jpeg)

Fig. S8 SEM images of the (a) Y-SnO<sub>2</sub>-LC and (b) F-SnO<sub>2</sub>-SC microspheres after 100 cycles.

![](_page_9_Figure_0.jpeg)

Fig. S9 Cycling performances of the filled structured  $SnO_2$  microspheres prepared by decomposition of the carbonaceous template with and without burning at a constant current density of 1 A g<sup>-1</sup>.

![](_page_10_Figure_0.jpeg)

Fig. S10 Cycling performances of the filled and yolk-shell structured  $SnO_2$  microspheres formed from the C-Sn(Oct)<sub>2</sub> microspheres with the same loading rate of 0.3 mL at a constant current density of 5 A g<sup>-1</sup>.

![](_page_11_Figure_0.jpeg)

Fig. S11 Rate performances of the  $SnO_2$  microspheres prepared from the carbonaceous template microspheres with various loading rate of tin(II) octoate by post-treatment at 500 °C in an atmosphere with high oxygen concentration and ramping rate of 10 °C min<sup>-1</sup>.

![](_page_12_Figure_0.jpeg)

**Fig. S12** Morphologies of the carbonaceous template microspheres with various loading rate of tin(II) octoate: (a) 0.2 ml, (b) 0.4 ml, (c) 0.6 ml, (d) 1.0 ml, and (e) 1.5 ml.

Various hollow SnO <sub>2</sub> materials	cycling performance	rate performance	Ref
SnO <sub>2</sub> @carbon hollow spheres	Discharge capacity of 643 mA h g <sup>-1</sup> after 300 cycles (at 0.5 A g <sup>-1</sup> , 0–3.0 V)	The discharge capacities were 520 and 210 mA h g <sup>-1</sup> at current densities of 0.2 and 3.0 A g <sup>-1</sup> , respectively. (0-3.0  V)	[57]
SnO <sub>2</sub> hollow spheres	Discharge capacity of 643 mA h g <sup>-1</sup> after 300 cycles (at 2.0 A g <sup>-1</sup> , 0.001–1.0 V)	The discharge capacities were 780 and 597 mA h g <sup>-1</sup> at current densities of 0.5 and 7.0 A g <sup>-1</sup> , respectively. $(0.001-1.0 \text{ V})$	[58]
SnO2 fiber-in-tube	Discharge capacity of 640 mA h g <sup>-1</sup> after 300 cycles (at 1.0 A g <sup>-1</sup> , 0.001–1.0 V)	The discharge capacities were 774 and 591 mA h g <sup>-1</sup> at current densities of 0.5 and 5.0 A g <sup>-1</sup> , respectively. $(0.001-1.0 \text{ V})$	[59]
Three-dimensional SnO <sub>2</sub> @TiO <sub>2</sub> double- shell nanotubes on carbon cloth	Discharge capacity of 400 mA h g <sup>-1</sup> after 100 cycles (at 1.0 A g <sup>-1</sup> , 0.01-3.0 V)	The discharge capacities were 843 and 135 mA h $g^{-1}$ at current densities of 0.16 and 7.8 A $g^{-1}$ , respectively. (0.01–3.0 V)	[60]
SnO <sub>2</sub> /C microspheres	The discharge capacity 50 and 379 mA h g <sup>-1</sup> after 800 cycles. (at 0.1 A g <sup>-1</sup> ,0-3.0 V)	The discharge capacities were 378 and 230 mA h g <sup>-1</sup> at current densities of 0.1 and 0.6 A g <sup>-1</sup> , respectively. (0 - 3.0  V)	[61]
pillar arrays of C- coated hollow SnO <sub>2</sub>	Discharge capacity of 488 mA h g <sup>-1</sup> after 50 cycles (at 1.0 A g <sup>-1</sup> , 0.005-2.0 V)	The discharge capacities were 634 and 408 mA h g <sup>-1</sup> at current densities of 0.78 and 7.8 A g <sup>-1</sup> , respectively. $(0.005 - 2.0 \text{ V})$	[62]
Carbon nanotube @SnO2-Au coaxial nanocable	Discharge capacity of 626 mA h g <sup>-1</sup> after 40cycles (at 0.18 A g <sup>-1</sup> , 0.05-1.2 V)	The discharge capacities were 660 and 392 mA h g <sup>-1</sup> at current densities of 0.18 and 7.2 A g <sup>-1</sup> , respectively. $(0.05 - 1.2 \text{ V})$	[63]

Table S1. Cycling and rate performances of various nanostructured  $SnO_2$  materials in lithium-ion batteries.

SnO <sub>2</sub> -C hollow nanostructures	Discharge capacity of 577 mA h g <sup>-1</sup> after 500 cycles (at 0.2 A g <sup>-1</sup> , 0-3.0 V)	The discharge capacities were 701 and 412 mA h g <sup>-1</sup> at current densities of 0.4 and 5.0 A g <sup>-1</sup> , respectively. (0 - 3.0  V)	[64]
Filled structured SnO2 microspheres	Discharge capacity of 450 mA h g <sup>-1</sup> after 1000 cycles (at 1 A g <sup>-1</sup> , 1.0 V)	The discharge capacities were 637 and 372 mA h g <sup>-1</sup> at current densities of <b>0.8 and 9.0 A g<sup>-1</sup></b> , respectively. (0.01 - 1.0  V)	This study