## **Electronic Supplementary Information**

## Sandwiched C@SnO<sub>2</sub>@C Hollow Nanostructures as an Ultralong-Lifespan High-Rate Anode Material for Lithium-Ion and Sodium-Ion Batteries

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Fig. S1. (a) A typical SEM image of the 3D interconnected NaCl cubes coated with uniform thin film of  $SnCl_4-C_6H_8O_7$  complex after freeze-drying process. (b)-(c) SEM and (d)-(e) TEM images of 3D porous carbon networks homogeneously anchored with numerous ultrasmall  $SnO_2$  nanocrystals of 2~5 nm (denoted with C@SnO<sub>2</sub> composites) after removing NaCl but before the CVD carbon coating process. Note

that the C@SnO<sub>2</sub> composite does not display perfectly pore structure because of some defects and fractures resulting from structural collapses of the NaCl template during the carbonization or template removal process. (g) A typical SEM image of 3D interconnected NaCl particles coated with C@SnO<sub>2</sub>@C (NaCl@C@SnO<sub>2</sub>@C) before eliminating the NaCl template.



Fig. S2. (a) XRD patterns and (b) TGA profile of C@SnO<sub>2</sub>@C HNSs and C@SnO<sub>2</sub> composite. It can be seen that the diffraction peaks of C@SnO<sub>2</sub> composites can be well indexed to the tetragonal SnO<sub>2</sub> phase (JCPDS 41-1445) and the C@SnO<sub>2</sub> composites contains 43.5 wt.% carbon without the CVD carbon coating process.



Fig. S3. (a) TEM image and SEAD pattern, (b, c) HRTEM images, (d) elemental line scanning image of the C@SnO<sub>2</sub>@C HNSs composite, in which a definite composition order of the shells is confirmed. The outer carbon shell, which derived from the CVD of  $C_2H_2$ , shows a clear profile both in HRTEM and elemental line scanning images and its thickness is about 5 nm. The interbedded SnO<sub>2</sub> layer with a thickness of about 6 nm is composed of numerous ultrasmall SnO<sub>2</sub> nanocrystals. The inner hollow carbon core, which derived from the pyrolysis of solid carbon source (citric acid), can be recognized from the C element line scanning image in Fig. S3d and its thickness is about 4 nm.



Fig. S4. (a) XPS spectra of Sn3d peaks and (b) Raman spectrum of C@SnO<sub>2</sub>@C



HNSs.

Fig. S5. Nitrogen adsorption-desorption isotherms of C@SnO<sub>2</sub> composites.



Fig. S6. (a) Galvanostatic charge–discharge voltage profiles plotted for the first, second and 10th cycles of the C@SnO<sub>2</sub>@C HNS electrode for SIB anode at a current density of 0.1 A  $g^{-1}$ . (b) Cycling performance of the C@SnO<sub>2</sub>@C HNS electrode for SIB anode at a current density of 0.1 A  $g^{-1}$ .



Fig. S7. (a) TEM and (b) HRTEM image of C@SnO<sub>2</sub>@C HNSs as a LIB anode after

1000 cycles at 10 A g<sup>-1</sup>.



Fig. S8. Schematic illustration of a C@SnO<sub>2</sub>@C HNS for lithium storage processes. Sodium storage processes of the nanostructures like the case of lithium storage processes.



Fig. S9. (a) Comparison of rate capacity of C@SnO<sub>2</sub>@C HNS electrode for LIB anode with those of representative SnO<sub>2</sub>/C composite anodes previously reported. (b) (a) Comparison of rate capacity of C@SnO<sub>2</sub>@C HNS electrode for SIB anode with those of representative SnO<sub>2</sub>/C composite anodes previously reported.

Table S1. Comparison of specific lithium storage capacity and capacity retention at different current densities for C@SnO<sub>2</sub>@C HNS electrode with those of the representative previously reported  $SnO_2/C$  composite anodes.

Materials	Current density (A g <sup>-1</sup> )	Cycle number	Specific capacity (mAh g <sup>-1</sup> )	Capacity retention (%)
C@SnO2@C HNSs         0.1           [this work]         5           10	0.1	50	933	92
	5	1000	550	95
	10	1000	285	92
Carbon-coated SnO <sub>2</sub> submicroboxes <sup>[S1]</sup>	0.5	100	491	50
Carbon-coated SnO <sub>2</sub> nanoplates <sup>[S2]</sup>	0.2	50	700	80
Carbon-coated hierarchical	0.1	50	920	75

SnO <sub>2</sub> hollow spheres <sup>[S3]</sup>				
2D graphene/ SnO <sub>2</sub> @C <sup>[S4]</sup>	0.2	100	800	90
Carbon-encapsulated porous SnO <sub>2</sub> <sup>[S5]</sup>	0.5	200	516	81
SnOx/carbon nanohybrids [S6]	0.5	200	608	86
Ultrasmall SnO <sub>2</sub> confined in micro/mesoporous carbon <sup>[S7]</sup>	1.4	2000	443	75
SnO <sub>2</sub> /graphene composites <sup>[S8]</sup>	0.1	200	872	85
Reduced GO/SnO <sub>2</sub>	0.1	200	718	72
nanocomposites [S9]	0.5	200	514	70
Graphene-based mesoporous SnO <sub>2</sub> composite <sup>[S10]</sup>	0.782	50	847.5	78
Graphene/SnO <sub>2</sub> composite [S11]	0.08	120	591.9	60
SnO <sub>2</sub> @C nanocomposites [S12]	0.1	200	880	86
SnO <sub>2</sub> /carbon nanotubes [S13]	0.5	200	602	64

Table S2. Comparison of specific sodium storage capacity and capacity retention at different current densities for C@SnO<sub>2</sub>@C HNSs electrode with those of representative  $SnO_2$ /carbon composite anodes reported previously.

Materials	Current density	Cycle	Specific capacity	Capacity
	(A g <sup>-1</sup> )	number	(mAh g <sup>-1</sup> )	retention (%)
C@SnO <sub>2</sub> @C HNSs	0.1	30	405	97%
[this work]		3000	200	90
SnO <sub>2</sub> /graphene composites [S14]	0.05	70	297	79

SnO <sub>2</sub> particles dispersed between graphene nanosheets [S15]	0.5	100	260	82
SnO <sub>2</sub> nanoparticles embedded in 3D graphene <sup>[S16]</sup>	0.1	200	432	85.7
SnO <sub>2</sub> @N-doped carbon@SnO <sub>2</sub> nanotubes <sup>[S17]</sup>	0.025	50	492	72
SnO <sub>2</sub> @void@C porous nanowires <sup>[S18]</sup>	0.2	100	308	83
Sn/SnO <sub>2</sub> /C composites [S19]	0.02	100	245	78
Carbon encapsulated SnO <sub>2</sub> nanocomposites <sup>[S20]</sup>	0.152	200	360	80

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