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Anti-Pulverization Electrode Based on Low-Carbon Triple-Shelled Superstructures for Lithium-Ion Batteries

Lianhai Zu, Qingmei Su, Feng Zhu, Bingjie Chen, Huanhuan Lu, Chengxin Peng, Ting He, Gaohui Du, Pengfei He, Kai Chen, Shihe Yang, Jinhu Yang and Huisheng Peng**

Dr. L. H. Zu, B. J. Chen, C. X. Peng and Prof. J. H. Yang

School of Chemical Science and Engineering, Tongji University, Shanghai 200092, China.

E-mail: yangjinhua@tongji.edu.cn

L. H. Zu and Prof. J. H. Yang

Research Center for Translational Medicine & Key Laboratory of Arrhythmias of the Ministry of Education of China, East Hospital, Tongji University School of Medicine, No. 150 Jimo Road, Shanghai 200120, P. R. China

Dr. Q. M. Su and Prof. G. H. Du

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- 1 Institute of Physical Chemistry, Zhejiang Normal University, Jinhua 321004, P. R. China.
- 2 Dr. F. Zhu and Prof. P. F. He
- 3 School of Aerospace Engineering and Applied Mechanics, Tongji University, Shanghai
- 4 200433, China
- 5 Prof. H. S. Peng
- 6 State Key Laboratory of Molecular Engineering of Polymers, Department of Macromolecular
- 7 Science and Laboratory of Advanced Materials, Fudan University, Shanghai 200433, China.
- 8 Dr. T. He
- 9 School of Materials Science and Engineering, Tongji University, Shanghai 201804, China.
- 10 H. H. Lu and Prof. Kai Chen
- 11 Center for Advancing Materials Performance from the Nanoscale (CAMP-Nano), State Key
- 12 Laboratory for Mechanical Behavior of Materials, Xi'an Jiaotong University, Xi'an, China
- 13 Prof. S. H. Yang
- 14 Department of Chemistry, The Hong Kong University of Science and Technology, Clear
- 15 Water Bay, Kowloon, Hong Kong, China.
- 16 E-mail: penghs@fudan.edu.cn
- 17
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Abstract: The realization of anti-pulverization electrode structures, especially using low-carbon-content anode materials, is crucial for developing high-energy and long-life lithium-ion batteries (LIBs); however, this technology remains challenging. Here, we show that SnO₂ triple-shelled hollow superstructures (TSHSs) with a low carbon content (4.83%) constructed by layer-by-layer assembly of various nanostructure units can withstand a huge volume expansion of ~231.8% and deliver a high reversible capacity of 1099 mAh g⁻¹ even after 1450 cycles. These values represent the best comprehensive performance in SnO₂-based anodes to date. Mechanics simulations and *in situ* transmission electron microscopy suggest that the TSHSs enable a self-synergistic structure-preservation behavior upon lithiation/delithiation, protecting the superstructures from collapse and guaranteeing the electrode structural integrity during long-term cycling. Specifically, the outer shells during lithiation processes are fully lithiated, preventing the overlithiation and the collapse of the inner shells; in turn, in delithiation processes, the underlithiated inner shells work as robust cores to support the huge volume contraction of the outer shells; meanwhile, the middle shells with abundant pores offer sufficient space to accommodate the volume change from the outer shell during both lithiation and delithiation. This study opens a new avenue in the development of high-performance LIBs for practical energy applications.

As one of the current major energy storage technologies, lithium-ion batteries (LIBs) are widely expected to power emerging portable electronics and electric vehicles (EVs)¹⁻⁴. To meet demand, it is necessary to develop high-energy-density LIBs with both long cycling life and high power output. However, LIBs have long suffered from the severe pulverization of anode materials induced by huge volume changes upon Li ion insertion/extraction, which causes irreversible capacity loss as well as poor cycling stability and rate capability⁵⁻¹⁷. To solve this problem, in most cases, graphitic carbons with good conductivity and excellent mechanical properties were employed as flexible matrices for the anode materials to improve the cycling performance of batteries¹⁸⁻²⁹. However, the high carbon content (usually

greater than 30%) often results in a capacity decrease due to the low theoretical lithium storage capacity of graphite carbons ($\sim 372 \text{ mAh g}^{-1}$), substantially limiting their practical applications in EVs. One effective way to elevate energy density is to reduce the carbon content in composite anode materials. Nevertheless, it remains a considerable challenge to produce such composite materials with sufficiently low carbon content to ensure high capacity and, simultaneously, maintain a stable architecture for long cycling life.

SnO_2 is an attractive anode material for LIBs due to its high theoretical lithium storage capacity ($\sim 782 \text{ mAh g}^{-1}$) and safe working potential ($\sim 0.6 \text{ V vs. Li}^+/\text{Li}$)^{17,30,31,32-35}. However, SnO_2 also suffers from a large volume change ($\sim 250\%$) and severe structural collapse that result in an unstable solid electrolyte interphase (SEI)³⁶ and an overall performance deterioration of batteries. To date, SnO_2 -based batteries capable of delivering a high reversible capacity ($> 800 \text{ mAh g}^{-1}$) over 1000 cycles have been extremely limited. In this regard, SnO_2 represents a typical class of LIB anode material facing a serious structural collapse problem that still requires resolution. Therefore, SnO_2 was selected as an example for investigation. In this work, SnO_2 triple-shelled hollow superstructures (TSHSs) with low

carbon content (4.83%) assembled hierarchically using various SnO₂-based primary nanostructure units show high lithium storage performance, including a high reversible capacity (1099 mAh g⁻¹) at 0.5 A g⁻¹ with a high capacity retention of nearly 100% after 1450 cycles and a high power output (416 mAh g⁻¹ at 4A g⁻¹) with long cycle life (1200 cycles). Further mechanics simulations coupled with *in situ* transmission electron microscopy (TEM) suggest that such a triple-shelled configuration enables a self-synergistic structure-preservation (SSSP) behavior upon lithiation/delithiation, protecting the TSHSs against collapse and guaranteeing electrode structural integrity during cycling. Therefore, the superior performance of the SnO₂ TSHS is attributed to the following two factors: the optimal structural/composition design of the TSHSs that favors the generation of high-performance LIBs and the SSSP behavior that maintains the structural integrity of the TSHSs throughout the lithiation/delithiation process. The SSSP concept provides a new strategy to construct anti-pulverization electrodes for high-performance LIBs based on low-carbon-content or carbon-free anode materials.

The synthesis of the TSHSs was realized through the layer-by-layer growth/assembly of various SnO_2 nanounits on the surface of SiO_2 nanospheres, coupled with carbonization/coating of carbon precursors. As shown in Figure 1a, the rapid hydrolysis of $\text{Na}_2\text{SnO}_3 \cdot 3\text{H}_2\text{O}$ in an ethanol-water solution leads to the dense deposition of SnO_2 nanodots on SiO_2 nanospheres, forming the first shell of SnO_2 nanodots (Figure 1a, step ①). Subsequently, the synchronous hydrolysis of the Sn-precursor and polymerization/carbonization of glucose induce the formation of organic carbon (OC)-coated SnO_2 nanodots and their loosely assembled second layer on the surface of the first dense layer (step ②). The double-shelled intermediates, when calcined under N_2 atmosphere for complete carbonization after removing the SiO_2 cores using NaOH solution, transform into the SnO_2 double-shelled hollow superstructures (DSHSs) (Figure 1a, step ③). The double-layer intermediates with exposed OH-rich groups then serve as hydrophilic interfaces for further seeded growth of SnO_2 nanorods, forming the third layer made of radially arrayed nanorods (Figure 1a, step ④). Finally, after deposition of graphenized carbon by chemical vapor deposition in C_2H_2 flow, the SnO_2 TSHSs are produced (Figure 1a, step ⑤). In the

following sections, SnO₂ DSHSs were selected and examined together with the SnO₂ TSHSs for comparison, to better understand the role of the triple-shelled configuration of the SnO₂ TSHSs in the structural stability and battery performance.

The structural and elemental analyses of the SnO₂ DSHSs and TSHSs were conducted in detail. A scanning electron microscopy (SEM) image in Figure 1b shows that the SnO₂ DSHSs are monodisperse with rougher surfaces and larger sizes (~480 nm) relative to the pristine SiO₂ nanospheres (d = 300 nm, Figure S1). From the TEM image (Figure 1c), it can be seen that the SnO₂ DSHSs are hollow with double shells, namely, a dense inner shell (the first shell) and a loose outer shell (the second shell). As shown in Figure 1d, there is a clear boundary between the two shells. The first shell is ~25 nm thick, made of densely aggregated SnO₂ nanodots, whereas the second shell possesses a larger shell thickness of ~60 nm, consisting of loosely packed SnO₂@C nanodots. A high-resolution TEM image (Figure 1d, inset) indicates that the SnO₂ nanodots are coated with a few layers of graphenized carbon. In addition, clear crystal lattices with a d-spacing of 0.335 nm were observed, corresponding to the (110) plane of the tetragonal crystal structure of SnO₂

(JCPDS no. 70-4177). The carbon coating on the SnO_2 nanodots leads to the loose packing of the $\text{SnO}_2\text{@C}$ nanodots and the formation of the thicker second shells. Compared to the SnO_2 DSHSs, the SnO_2 TSHSs exhibit much rougher surfaces and larger sizes of ~ 700 nm after the growth of the third shell of nanorod arrays, as shown in Figure 1e. The hollow characteristics and triple-shelled configuration are further revealed by the TEM image in Figure 1f. The second shells give a relatively lower contrast compared with the other two shells, caused by the lower stacking density of the $\text{SnO}_2\text{@C}$ nanodots. The triple-shelled configuration can be clearly observed in a selected-area TEM image in Figure 1g; the image shows that the third shell is made of densely assembled SnO_2 nanorods, with a shell thickness of ~ 110 nm (Figure 1g, inset at the bottom). The nanorods are estimated to be ~ 3 - 5 nm in diameter and are coated with a few layers (2-3) of graphenized carbon, as judged from the corresponding high-magnification TEM image (Figure 1g and inset on the top).

The presence of C, O and Sn elements in the SnO_2 TSHSs is evidenced by the corresponding element maps and EDS analysis (Figure S2a and 2b). Line scanning of the TSHS illustrates a shell-dependent distribution of the three elements (Figure S2c and 2d),

confirming the triple-shelled configuration of the TSHS. The XRD patterns indicate that DSHSs and TSHSs are both in tetragonal crystal structure (JCPDS no. 70-4177) (Figures S3a and S4a). The BET measurements reveal the presence of hierarchical pores, namely, micropores with diameters of ~3.5 nm and macropores of ~250 nm (hollow interiors) in the SnO₂ DSHSs and TSHSs (Figures S3b and S4b). The BET surface areas for the SnO₂ DSHSs and TSHSs are 149.3 and 65.8 m² g⁻¹, respectively. The Raman spectra in Figures S3c and S4c show typical D and G peaks for graphene materials^{37,38}, implying that the carbon contained in the samples is graphenized. It is noted that the carbon content in the SnO₂ TSHSs is relatively low (4.83%, mass ratio) compared to that of the SnO₂ DSHSs (35.1%) and other previously reported SnO₂-C composites (Table S1)^{26,27,33,39-46}. Therefore, with a set of structural/compositional advantages, such as a high content of SnO₂ active materials (95.17%), a relative high specific surface area (65.8 m² g⁻¹) and hierarchical pores, the TSHSs are expected to be a promising anode material for creating high-performance LIBs.

Figure 2 shows the electrochemical performance of the two electrodes based on the SnO₂ DSHSs and TSHSs. The long-term cycling tests measured at a current density of 0.5 A g⁻¹ over the voltage range of 0.05~2.5 V are shown in Figure 2a. It can be seen that the SnO₂ TSHS electrode displays much higher specific capacities than the DSHS electrode throughout the cycling. For example, in the first cycle, the SnO₂ TSHS electrode delivers a higher discharge capacity of 2050 mAh g⁻¹ as well as a higher initial Coulombic efficiency of 51.2% (Figure S5) relative to the SnO₂ DSHS electrode (1627 mAh g⁻¹, 44.1%). It is noted that the discharge capacities are two times the theoretical value (~782 mAh g⁻¹) of SnO₂ material, attributed to the decomposition of the electrolyte forming a solid electrolyte interface (SEI) film^{36,47}. The SnO₂ TSHS electrode shows an upward trend in capacity upon cycling accompanied by a slight fluctuation. The high capacities above 750 mAh g⁻¹ are delivered during the entire cycling process. Notably, a capacity of ~1099 mAh g⁻¹ is maintained after 1450 cycles, corresponding to a high capacity retention of ~104.7%. For the SnO₂ DSHS electrode, however, a constant capacity decrease occurred throughout the cycling process, resulting in a low capacity of 155 mAh g⁻¹ and a low capacity retention of

21.6% after cycling, only ~14.3% and ~20% of the SnO₂ TSHS electrode values, respectively. The trend in capacity change is reflected in the galvanostatic charge/discharge profiles of the SnO₂ TSHS electrode (Figure 2b). Moreover, at higher current densities of 1 and 2 A g⁻¹, the TSHS electrode can also deliver high capacities almost twice those of the DSHS electrode (Figure S6).

In addition, the SnO₂ TSHS electrode manifests a remarkable rate capability compared to the DSHS electrode. As shown in Figure 2c and Table S2, the SnO₂ TSHS electrode demonstrates high reversible capacities, from ~931 mAh g⁻¹ at 0.2 A g⁻¹ to 120 mAh g⁻¹ at 16 A g⁻¹, which is approximately 34%~344% higher than those of the SnO₂ DSHS electrode. Moreover, when the current density returns from 16 A g⁻¹ to the initial 0.2 A g⁻¹ after 120 cycles, the SnO₂ TSHS electrode still delivers a high capacity of 872 mAh g⁻¹, with a capacity retention of ~93.7%. The outstanding rate capability of the SnO₂ TSHS electrode is also confirmed by the voltage profiles tested at the corresponding current densities (Figure 2d). Moreover, to further evaluate the long-cycle high-power performance, long-term cycling tests (up to 1200 cycles) at a high current density of 4 A g⁻¹ were applied to the two electrodes. It

can be seen in Figure S7 that the SnO₂ TSHS electrode is generally stable during the cycling and displays an upward trend in capacity in the latter 1000 cycles from the 200th to the 1200th cycle. The capacity finally stabilizes at 416 mAh g⁻¹ with a capacity retention of 57.5% after 1200 cycles, which far surpasses the remaining capacity (123 mAh g⁻¹) for the SnO₂ DSHS electrode, as well as its corresponding capacity retention (25.7%). To the best of our knowledge, the superior performance of the SnO₂ TSHS electrode, such as the ultrahigh capacity (1099 mAh g⁻¹ at 0.5 A g⁻¹) remaining after long-term cycling (1450 cycles), with a capacity retention of nearly 100%, and its high power output (416 mAh g⁻¹ at 4 A g⁻¹) with long cycle life (1200 cycles), is among the best comprehensive performances for SnO₂-based anode materials reported so far. Performance comparisons between the LIBs based on the SnO₂ TSHSs and other SnO₂ anode materials are provided in Figure 2e and Table S1. In addition, it is found that the high capacity uptake of the SnO₂ TSHSs are derived from their triple-shelled configuration that enables higher reaction reversibility with a higher theoretical capacity, which is analyzed and discussed in detail based on cyclic voltammetry (CV) studies (S1, S2, Figures S8-S13)⁴⁸⁻⁵¹.

1 It is found that the TSHSs can withstand huge volume change upon lithiation/delithiation
2 after even 1450 cycles, whereas the DSHSs fail. Unlike the stable SEI film formed on the
3 TSHSs, the collapse process of the DSHSs induces repeated formation of new SEI films
4 around the surface of DSHS fragments, leading to unstable lithiation/delithiation interfaces,
5 as illustrated in Figure 3a. Figure 3b shows the TEM images of the TSHSs undergoing
6 lithiation/delithiation for 1450 cycles. It can be seen that the morphology of the TSHSs is
7 preserved well (Figure 3b, inset, and Figure S14), with a thin SEI film (~ 20 nm) covering the
8 surface of the outer shell. The existence of SEI films for the TSHSs and DSHSs are
9 confirmed by XPS analyses shown in Figure S15 and Figure S16, where some typical XPS
10 peaks correspond to LiF, PF_6^- and C=O bonds that are generally considered as the main
11 compositions of SEI film formed from the decomposition of the electrolyte of LiPF_6 . At a high
12 magnification, it is seen that the outer shells consist of uniform nanodots, indicating that the
13 nanorods in the outer shell have turned into ultrasmall nanodots after the long-term cycling.
14 Some SnO_2 nanodots with crystalline domains of $\sim 2\text{-}4$ nm are observed in the outer shell,
15 without an SEI film existing on the nanodot surfaces (Figure 3c). By contrast, the DSHS is

1 collapsed into pieces with cracks during cycling (Figure 3d and Figure S14); the new
2 surfaces of the fragments generated during the collapse process are coated with abundant
3 SEI film. The collapse of the DSHSs leads to the pulverization of the DSHS electrode, which
4 inevitably induces the direct loss of active materials and an unstable SEI film repeatedly
5 being formed at newly generated interfaces, thus resulting in a capacity decrease and
6 cycling instability^{7,52}.

7 *In situ* TEM was employed to monitor the real-time structural evolution of the TSHS and
8 DSHS electrodes during a lithiation/delithiation cycle. The setup for the *in situ* TEM device is
9 illustrated in Figure 3f, where a selected TSHS or DSHS connected to the Au tip serves as a
10 working electrode and a piece of Li coated with Li₂O on W nanowire tip works as a counter
11 electrode. As shown in Figure 3g and movie S1, the TSHS expands immediately after
12 application of voltage bias. The radius of the TSHS increases gradually from the initial 360
13 nm to the maximum of 468 nm after 350 s of Li deposition and then shrinks to the minimum
14 367 nm after another 110 s of Li extraction. It is noted that the hollow interior also undergoes
15 an “expansion/contraction” process in response to lithiation/delithiation, implying a

synchronous expansion/contraction behavior of the three shells. It can also be found that some nanorods in the outer shell transform into smaller nanodots after the cycle, and the triple-shelled configuration of the TSHS is still well preserved. For the DSHS, it collapsed in 5 s during the volume shrinking process after 150 s of volume expansion with the radius increasing from 254 nm to 310 nm (Figure 3h and Movie S2). Some key values, such as volume changes as well as volume expansion ratios during lithiation for each shell of the DSHS and TSHS, were calculated (S3) and are listed in Table S3, in terms of the data obtained from *in situ* TEM observation. As can be seen, the first, second and third shells for the TSHS expanded to 145.1%, 187.9% and 242% (volume expansion ratio, r_{vv}), respectively, with a general expansion ratio (R_{vv}) of 231.8%. Relatively, the DSHS has a higher r_{vv} of 157.4% and 208.6% in the first shell and second shell, respectively, but a lower R_{vv} of 188.1%. Theoretically, the volume expansion ratio is proportional to the extent of lithiation, and a higher volume expansion ratio corresponds to a higher lithiation degree with a higher capacity. As a consequence, the TSHS can deliver higher reversible capacities (Figure 2c), due to its higher general volume expansion ratio (231.8%) than that (188.1%) of

the DSHS, which even approaches the theoretical value of 250%^{49,50}. In addition, the existence of the third shell in TSHSs can reduce the lithiation extent of both the first shell (145.1% vs 157.4%) and the second shell (187.9% vs 208.6%), thereby preventing the collapse of the two shells as well as the TSHSs. Specifically, the third shell contributes ~92.57% capacity to the total, whereas the other two shells give less than 8%, according to the calculations on the capacity contribution ratio ($R_{\Delta V/\Delta V}^i$) of individual shells for the TSHS. The calculations support quantitatively the electrochemical results that demonstrate that the TSHSs can uptake a higher capacity and are more stable against lithiation/delithiation.

It is still surprising that the triple-shelled configuration of the SnO₂ TSHSs, with a low carbon content of 4.83%, can withstand huge volume expansion of up to 242% after thousands of cycles. The test of *in situ* mechanical TEM on an individual TSHS was conducted (Figure S17). The load-displacement curve of a typical compression test on an individual TSHS shows that even with the formation of the crack, the loading force kept increasing, and the TSHS does not fracture or break into pieces as commonly observed in other cases, demonstrating an anti-pulverization structure of TSHS. To more deeply

understand why the TSHS is stable during the lithiation process, an elastic-plastic model coupled to Li diffusion was adopted to evaluate the lithiation-induced deformation and stress states (S4). In the simulations, we are more attentive to tensile stress as it is the key factor for the collapse of the electrode structures. Figure 4a shows the morphology evolution of TSHSs during the lithiation process, where colors from blue to red correspond to different lithiation extents (or Li-ion concentrations) from low lithiation to high lithiation, respectively. Initially, the Li-ion concentration in the TSHS structure is ~ 0 (0 s). Afterwards, partial lithiation of the TSHS occurs, leading to some structural deformation on the side contacting the electrode (120 s). This deformation continues until the TSHS is fully lithiated at 350 s. The stress simulation after the lithiation in Figure 4b shows that the third shell experiences very low tensile stress, despite a huge compressive stress (up to ~ 230 MPa) in the region adjacent to the second shell. The second shell is almost in a stress-free state due to the existence of sufficient inter-nanodot space to effectively relieve both tensile and compressive stress. For the first shell, a tensile stress (~ 150 MPa) generates dramatically near the region between the first and the second shells. Figure 4c presents the stress state for the TSHS at

different lithiation extents and times during the lithiation process. It can be found that a tensile stress exists in the first shell throughout the lithiation, with the corresponding peak values increasing monotonically with lithiation proceeding (Figure 4d). For the DSHS, a similar structural deformation occurred during lithiation, as shown in Figure S18a. However, the tensile stress behavior in the first shell during lithiation is different from that of the TSHS (Figure S18 b-d). As shown in Figure S18d, the peak values of the tensile stress decrease continuously through the lithiation process from ~185 MPa to ~110 MPa, which indicates that the DSHS may collapse at the very beginning of the lithiation process. It is noted that the DSHS undergoes a higher maximum tensile stress (~185 MPa) in the first shell than that (~165 MPa) of the TSHS, demonstrating that the TSHS possesses better structural stability due to the triple-shelled configuration.

It is noteworthy that the DSHS collapsed during volume shrinking, instead of volume expanding, in the delithiation process (Figure 3h, *in situ* TEM observation). This result implies that a high tensile stress should be produced during the delithiation process and lead to the collapse of the DSHS. The stress states for the sample, however, are challenging to

simulate due to the difficulty of modeling delithiation processes. For the TSHS, a huge tensile stress during the delithiation process is also considered to be generated, especially in the third shell, which is the most lithiated and expanded. As seen in Figure 3g, compared with the initial state before cycling, the space of the second shell of the TSHS after delithiation is clearly compressed, whereas the position of the first shell is almost unchanged (R_1 , from initial 180 nm to final 181 nm). This finding demonstrates that the third shell has experienced tremendous volume shrinkage and huge tensile stress that may transfer to the first shell via the second shell. The first shell is underlithiated in the lithiation process, observed from *in situ* high-resolution TEM images of the TSHS in Figure S19. The first shell with a low lithiation extent and a low volume change may serve as a robust and stable inner core to support the shrunken third shell and alleviate the stress in the third shell, protecting the third shell as well as the TSHS from collapse. Certainly, the second shell with abundant pores may also be crucial for buffering the volume shrinkage from the third shell. Consequently, the TSHS can effectively resist the huge volume contraction.

1 Taking both lithiation and delithiation into consideration, it can be deduced that a self-
2 synergistic structure-preservation behavior occurs in the TSHSs during cycling: as illustrated
3 in Figure S20a, during the lithiation process, the third shells that contribute to the major
4 capacity prevent the overlithiation and the breaking of the first shells; in turn, in the
5 delithiation process, the underlithiated first shells work as a robust core to support the huge
6 volume contraction of the third shells; and the second shells with abundant pores offer
7 sufficient space to accommodate the volume change from the third shell during both lithiation
8 and delithiation⁵⁵. By contrast, for the DSHS, without the third shells that consume most of
9 the lithium ions released from the cathode, the first inner shells are fully lithiated with more
10 volume expansion in the lithiation process, and subsequently undergo tremendous volume
11 shrinkage and huge tensile stress during delithiation, which leads to the collapse of the first
12 shells as well as the DSHSs (Figure S20b).

13 In summary, SnO₂ TSHSs were fabricated via the layer-by-layer assembly of various SnO₂
14 structure units. SnO₂ TSHSs exhibit outstanding lithium-storage performance as an LIB
15 anode, such as high capacity, long cycling life and high rate capability. The superior

comprehensive performance is ascribed to the unique structural design of the TSHSs and the SSSP mechanism that maintains the structural integrity of the TSHSs during the lithiation/delithiation process. The SSSP behavior is derived from the triple-shelled configuration of the TSHSs, which is demonstrated by *in situ* TEM and mechanics simulations. This study establishes a prototypical model to recognize the specific working mechanism involved in the hollow or multi-shelled structure anodes that have been widely employed for LIBs. This novel SSSP concept provides a new strategy to construct anti-pulverization electrodes, using carbon-free anode materials or those containing less carbon, for the development of high-performance LIBs with high energy, long cycle life and high power.

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Supporting Information

Additional characterizations, and performances tests.

Supporting Information is available from the Wiley Online Library or from the author.

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Figures and captions

Figure 1. Synthetic route, and morphology and structure characterization for the TSHSs and DSHSs. a) Synthetic route for SnO₂ double-shelled hollow superstructure (DSHS) and Triple-shelled hollow superstructures (TSHS). b-d) SEM (b) and TEM (c-d) images of SnO₂ DSHSs. Inset in (d) is the high-resolution TEM image for an arbitrarily selected SnO₂@C nanodot. e-g) SEM (e) and TEM (f-g) images of SnO₂ TSHSs. TEM image in (g) corresponds to the rectangle area in (f). Insets in (g) are magnified (right bottom) and high-resolution (upper right) TEM images showing the third shell assembled by SnO₂ nanorod arrays and single nanorod coated with few-layer graphene, respectively.

1

2 Figure 2. Battery performance of the TSHSs and the DSHSs. a) Cycling performance of the
 3 SnO_2 DSHS and TSHS electrodes at 0.5 A g^{-1} between 2.5 and 0.05 V in coin-type half cells
 4 at room temperature. b) Galvanostatic charge-discharge profiles of SnO_2 TSHS electrode at
 5 the 10th, 100th, 400th, 1000th, and 1450th cycle at 0.5 A g^{-1} . c) Rate capability of the SnO_2
 6 DSHS and TSHS electrodes at current densities between 0.2 and 16 A g^{-1} , respectively. d)
 7 Galvanostatic charge-discharge profiles of the SnO_2 TSHS electrode at current densities

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1 between 0.2 and 16 A g⁻¹. e) Comprehensive performance comparison (specific capacity vs
 2 cycle vs current density) of SnO₂ TSHS-based LIB with other SnO₂ anode-based LIBs.

3
 4 Figure 3. Structure stability study of the TSHS and DSHS. a) Schematic illustration of final
 5 architecture state of SnO₂ TSHS and DSHS upon lithiation/delithiation up to 1450 cycles. b-
 6 c) Low- (b) and high-resolution (c) TEM images of a SnO₂ TSHS after 1450 cycles. d-e)
 7 Low- (d) and high-resolution (e) TEM images of a SnO₂ DSHS after 1450 cycles. f)

1 Schematic of the dry cells based on a SnO₂ TSHS and a DSHS for *in situ* TEM study. g-h)
2 Time-lapse TEM images for a SnO₂ TSHS (g) and a DSHS (h) during a full lithiation-
3 delithiation process with an applied voltage of ± 3 V between W and Au electrodes. Scale
4 bars in g and h are 200 nm and 150 nm, respectively.

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1

2 Figure 4. Mechanics simulations for the TSHS during lithiation process. a) Maximum
 3 principal stress contours on deformed shapes of TSHS during lithiation at 0, 120 and 350 s.
 4 Normalized Li concentration, c_{Li} , defined as the actual Li concentration divided by the Li
 5 concentration in the fully lithiated state. The lithiation reaction front is located at the interface
 6 between pristine (blue) and lithiated (red) phases. b) Evolution of stress in the three shells of
 7 a TSHS after lithiation. The shell thickness, from the first shell to the third shell, is normalized

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as 0 to 1. c) hoop stress evolution of the first, second and third shell of the TSHS during lithiation. d) the peak value of tensile stress in first shell as function of time.

Table of contents

SnO₂ triple-shelled hollow superstructures with a low carbon content (4.83%) can withstand a huge volume expansion of ~231.8% and deliver a high reversible capacity of 1099 mAh g⁻¹ even after 1450 cycles, due to their self-synergistic structure-preservation behavior that protects the superstructures from collapse and guarantees the electrode structural integrity during long-term cycling.

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Author/s:

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