Two-step oxidation of bulk Sb to one-dimensional Sb₂O₄ submicron-tubes as advanced anode materials for lithium-ion and sodium-ion batteries

Zheng Yi,^{a, b} Qigang Han,^{a, b*} Xiang Li,^{a, b} Yaoming Wu,^b Yong Cheng,^{b*} Limin Wang^b

^a State Key Laboratory of Automotive Simulation and Control, Jilin University, Changchun 130025, China;

^bState Key Laboratory of Rare Earth Resource Utilization, Changchun Institute of Applied Chemistry, CAS, Changchun 130022, China.

Corresponding Author: hanqg@jlu.edu.cn; cyong@ciac.ac.cn

Abstract: Alloying-type Sb material has been considered as an excellent anode material for lithium-ion batteries (LIBs) and sodium-ion batteries (SIBs). However, the limitation of capacity is still a challenge urging to be solved. Thus, it will be extremely meaningful to exploit novel antimony oxides (Sb₂O₄) as high-capacity anode material for both LIBs and SIBs. In this work, one-dimensional tube-like Sb₂O₄ submicron-structures are fabricated by a two-step oxidation route, and their lithium and sodium storage behaviors are investigated to be conversion-alloying-type. When evaluated as a anode material with lithium as the counter electrode, the Sb₂O₄ submicron-structures deliver a discharge capacity of 700 mAh g⁻¹ after 50 cycles at a current density of 100 mA g⁻¹, which is higher than the alloying-type Sb anode materials with a theoretical capacity of 660 mAh g⁻¹. Even at a high current density of 1000 mA g⁻¹, the substantial discharge capacity can still reach 415 mAh g⁻¹ after 100 repeated cycles. In addition, as for SIBs, the tube-like Sb₂O₄ submicron-structures can maintain a discharge capacity of 381.9 mAh g⁻¹ after 100 cycles at 100 mA g⁻¹, higher than the reported results at this field. Such excellent cycling stability and rate capability of the designed Sb₂O₄ submicron-structure can be attributed to the morphology and structure.

Keywords: lithium-ion batteries; sodium-ion batteries; anode; two-step oxidation; Sb₂O₄ submicron-tubes.

1. Introduction

Because of the high conversion efficiency, good cycling performances and without any gaseous emission, lithium-ion batteries (LIBs) have been widely used in electric vehicle and portable electronic devices with huge success[1-4]. However, due to the low theoretical specific capacity of 372 mAh g⁻¹ and safety issues derived from the dendrite formation during charging, the commercial anode material, graphite, has hindered the rising large-scale applications of the high-performance LIBs.[5-6] Therefore, a mountain of researches point to explore potential and applicable anode materials for future LIBs. In addition, the graphite is not suitable for sodium ion batteries (SIBs) due to the insufficiently large interlayer spacing, which suggested a strong requirement to develop suitable anode materials for SIBs.[7] So, in view of many previous research reports, Sb-based anode materials have been considered as one kind of alternative candidates for LIBs and SIBs because of its high theoretical specific capacity as high as 660 mAh g⁻¹. [8-9]

Alloying-type Sb anode materials have been widely studied because of their considerable superiority such as high theoretical capacity and stable voltage platform of about 0.8 V vs. Li⁺/Li and 0.5 V vs. Na⁺/Na [10-11]. Like other high-capacity anode materials (e.g. Sn, Si or metal oxides, *etc.*) [12-17], the huge volume change, derived from the mechanical stress which generated upon lithiation/delithiation or Na-intercalation–deintercalation process, has seriously hampered the improvement of electrochemical performance of the Sb-based anode materials [18]. To overcome this challenge, several strategies, such as using Sb-based alloy structure, [19-22] porous structure [18, 23] and introducing of the carbon materials, [24-28] *etc.* are developed. For example, Zn₄Sb₃ Nanotubes [19] and Mo₃Sb₇ [20] thin film are fabricated and applied as anode materials with enhanced cycling performances for LIBs or SIBs; Sb hollow nanospheres are designed by utilizing SiO₂ and Ni nanosphere as templates, respectively; [18, 23] rod-like Sb-C composite is prepared by Yitai Qian *et al.* via a synchronous reduction and carbon deposition process; [24] uniform mixture of nano-sized Sb particles and MWCNTs is achieved by using wet milling; [28] sandwiched Sb-RGO thin film is fabricated by our group, [25] *etc.* In addition, other strategy like introducing of TiO₂ is also developed to improve the cycling performance of Sb [29-30]. Above-mentioned Sb-based materials showed enhanced lithium and sodium storage performances.

From the above, there is a considerable success in alloying-type Sb composites as anode materials for LIBs and SIBs. However, the limitation of capacity is still a challenge urging to be solved. Thus, it will be extremely meaningful to exploit novel antimony oxides (Sb_2O_4) and explore their lithium and sodium storage behaviors in view of their high theoretical specific capacity of 1227 mAh g^{-1} derived from two-step lithium and sodium insertion process including conversion and alloying reaction, as described in equation (1-4).

Hence, in this work, the lack of lithium storage data in the literature has motivated us to explore such high-capacity antimony oxide anode material for LIBs. By using bulk Sb powders as raw materials, a novel one-dimensional (1D) tube-like Sb_2O_4 submicron-structure is fabricated by a two-step oxidation route. Then, the as-prepared material is firstly applied in LIBs as an anode material with much enhanced electrochemical performance. Furthermore, their sodium storage performance is also given. The obtained enhancement suggests many promising application in LIBs and SIBs.

2. Experimental section

2.1 Synthesis of 1D solid Sb_2O_3 .

The synthesis of 1D solid Sb_2O_3 was referred to the reported references [31-33]. In a typical synthetic process, 1.16 g of polyvinyl pyrrolidone (PVP, Mw = 40000) and 1.2 mL of ethylenediamine (EA) were firstly dissolved in 80 mL deionized water under continuous ultrasonication for 0.5 h. Then, 0.3 g of commercial Sb powder was added into the mixture under vigorous stirring. After continuous stirring for 12 h at room temperature, the white products were collected. Subsequently, the samples were thoroughly washed by deionized water and absolute ethyl alcohol, and finally dried in a vacuum oven at 60°C overnight.

2.2 Synthesis of 1D hollow Sb₂O₄. To fabricate the 1D hollow Sb₂O₄, 0.1 g of the as-prepared 1D solid Sb₂O₃ was heated in a muffle furnace to 500 °C with a ramp of 3 °C min⁻¹ and maintained for 2 h under an air atmosphere. After that, the muffle furnace was allowed to cool down to room temperature naturally, and the final Sb₂O₄ was obtained.

2.3 Characterization.

The structure of the samples was characterized by a Bruker D8 Focus power X-ray diffractometer with copper target at a scan rate of 5 ° min⁻¹. The surface morphology of the products was measured by using a HITACHI S-4800 scanning electron microscope (SEM). Selected area electron diffraction (SAED) pattern and high-resolution transmission electron microscopy (HRTEM) were performed on a FEI Tecnai G2 S-Twin Transmission electron microscopy (TEM). Thermogravimetric analysis (TGA) was performed from room temperature to 900 °C with a heating rate of 10 °C min⁻¹ in air by using a STA 449 Jupiter (NETZSCH) thermogravimetry analyzer.

2.4 Electrochemical characterization.

The CR 2025 coin-type half-cells were assembled in a glove box filled with highly pure argon gas to examine the electrochemical behaviors for both LIBs and SIBs of the 1D hollow Sb₂O₄. For preparing the working electrode, active material, acetylene black and carboxymethyl cellulose (CMC, Alfa Aesar) in a weight ratio of 70:15:15 were mixed with suitable deionized water and hand-grinded for 30 min. Then, the obtained slurry was put onto Cu foil and then vacuum-dried at 80 °C for 12 h. The mass loading of the active material per electrode for testing was about 1 mg cm⁻². For LIBs, the cells were assembled with pure lithium as the counter electrode, a Celgard 2400 membrane as the separator, and 1 M LiPF₆ dissolved in ethylene carbonate and diethylene carbonate (1:1 in volume) with 5% fluoroethylene carbonate (FEC, Aladdin) additive as the electrolyte. While for SIBs, the half-cells were assembled with pure sodium foil as the counter electrode and the glass fiber (Whatman) as a separator. The electrolyte for SIBs was composed of 1 M NaClO₄ dissolved in propylene carbonate with 5% FEC additive. The charge-discharge performances were tested between 0.01 V and 2.0 V using a programmable battery testing system (LAND

CT2001A) at room temperature. The cyclic voltammogram (CV) measurements were conducted on a Bio-Logic VMP3 Electrochemical Workstation.

3. Results and discussion

The strategy for synthesizing the 1D tube-like Sb_2O_4 submicron-structures is schematically depicted in Figure 1. Firstly, according to the previous reports, the 1D solid Sb_2O_3 submicron-wires are prepared by firstly oxidation of bulk Sb powder in oxygen-dissolved water where EA acted as a catalyst and PVP presented as a surface stabilizer [31-34]. Then, the tube-like Sb_2O_4 submicron-structure is formed by secondary oxidation of the solid Sb_2O_3 in air at high temperature environment, based on the nonequilibrium interdiffusion process. Because the high temperature gradient exists between the surface and the interior, a thin layer of Sb_2O_4 is firstly transformed on the surface of the Sb_2O_3 precursor. Then, this thin layer, possessing abundant pores, can act as an interface to deliver oxygen to the inside and allow the outward diffusion of Sb_2O_3 . Thus, based on the Kirkendall effect, thorough oxidation and continuous diffusion eventually result in the formation of the Sb_2O_4 submicron-tube with a porous shell.

To confirm the morphological evolution and features of the obtained materials, the scanning electron microscopy (SEM) images are performed. As shown in Figure S1a-b (Supporting information), the bulk Sb powders are crystallized with particle sizes of several micrometers. After first oxidation, the routine particles are evolved to submicron-sized wires with a smooth surface (Figure 2a-b). The diameter of the wires is about 800 nm (Figure 2c). Furthermore, as presented in Figure 2d, the district lattice spacings of about 0.271 nm corresponds to (002) plane spacing of the submicron-sized Sb_2O_3 wire, suggesting that the submicron-sized wire grows along the [001] direction.[31-32] Moreover, after secondary oxidation of the sample, the solid submicron-sized wires can be further transformed to tube-like structures. As presented in Figure 3a-b, the 1D structure of the tube-like Sb_2O_4 inherits from the submicron-sized Sb_2O_3 wires. Some of the broken tubes are appeared (Figure 3b), suggesting the formation of the hollow structures. To further confirm this hollow structure of the tube-like Sb_2O_4 , the transmission electron microscope (TEM) is carried out (Figure 3c-d). The TEM image also shows that the shell of the Sb_2O_4 tube is nanoporous, which may be of great benefit to the enhancement of electrochemical performances of the material. In addition, the high-resolution transmission electron microscope (HRTEM) image of the tube-like Sb_2O_4 is presented in Figure

3e, in which the well-resolved lattice fringe with an inter-plane distance of 0.294 nm, indexed to the (004) plane of the Sb_2O_4 phase. As shown in Figure 3f, the selected area electron diffraction (SAED) pattern of the tube-like Sb_2O_4 taken along the [001] zone axis is a spot pattern, revealing that the submicron-wire is a single crystal, in accordance with the reported Sb_2O_3 precursor. [31-32]

The phase structures of the as-prepared samples are revealed by the X-ray diffraction (XRD) pattern. The characteristic peaks of bulk Sb powder (Figure S2a, Supporting information) can be indexed to the metallic Sb phase (JCPDS 35-0732). After first oxidation in oxygen-dissolved distilled water, the as-formed phase (Figure S2b, Supporting information) can be easily indexed to orthorhombic Sb_2O_3 phase (JCPDS 11-0689). However, it is notable that the intensities of the (110) and (200) peaks are greatly enhanced in comparison to the reference Sb_2O_3 spectrum, suggesting a strong orientation preference of wires formed along the [001] direction [31-32]. In addition, after secondary oxidation in air at 500 °C for 2h, all diffraction peaks of the final product (Figure 4) are in accordance with the characteristic peaks of the Sb_2O_4 (JCPDS 11-0694), indicating a pure phase formed in the secondary oxidation process. Similarly, the intensities of the (011) and (020) peaks are largely improved in contrast with the reference Sb_2O_4 spectrum, in agreement well with the obtained Sb_2O_3 precursor.

The thermogravimetric analysis (TGA) is used to explore the oxidation state of the Sb_2O_3 submicron-wires. As shown in Figure 5, the main weight increment is at the beginning of 500 °C, corresponding to the oxidation of Sb_2O_3 to Sb_2O_4 . Therefore, to obtain the tube-like Sb_2O_4 , the Sb_2O_3 submicron-wires are suitably oxidized at 500 °C in air. When increase the temperature to 600 °C, as shown in Figure S3a-b (Supporting information), the 1D structure of the obtained products almost broke. Therefore, in order to ensure that the sample is fully oxidized while the structure is well maintained, the oxidizing temperature of the Sb_2O_3 submicron-wires can be limited to about 500 °C.

In consideration of the good morphology and structure, the electrochemical performances of the as-prepared tube-like Sb_2O_4 submicron-structures are expected to be evaluated as anode materials for LIBs. Figure 6a shows the CV curves in the initial three cycles of the tube-like Sb_2O_4 submicron-structures. As shown in the first scanning, there is a huge cathodic peak around 1.1 V, which could be attributed to the reductive transformation of Sb_2O_4 to Sb and Li_2O . The cathodic peak at about 0.80 V is corresponding to

the alloying reaction of Sb to Li_3Sb . In the anodic process, the peak located at about 1.08 V may correspond to the dealloying reaction from Li_3Sb to Sb. And the peak around at 1.4 V may be ascribed to the reduction of Sb-based oxides, which is in agreement with the reported Sb_2MoO_6 and Sb_2O_3 anode materials for LIBs [35]. However, in the following cycles, the sharp cathodic peak located at 1.1 V in first cycle is replaced by a broad but weeny peak around 1.5 V, which may be due to delithiation reactions of Li_2O to Sb_2O_4 [36]. Based on the CV and some reported results, the electrochemical reaction mechanism of the Sb_2O_4 with lithium is proposed containing of conversion and alloying reaction, as described in equation (1) and (2) [37-38]. It can be seen that the alloying step is fully reversible, while the conversion reaction is not completely reversible.

Figure 6b exhibits the original two charge-discharge profiles of the tube-like Sb_2O_4 submicron-structures measured between 0.01 and 3.0 V at a current density of 100 mA g^{-1} . The first discharge curve shows a huge voltage platform located at 1.3 V, corresponding to the conversion reaction of Sb_2O_4 to Sb and Li_2O . Another recognizable voltage plateau around 0.84 V corresponds to alloying reaction of Sb to Li_3Sb . In the subsequent cycles, the first voltage plateau becomes abrupt in a broad voltage rage, while the second is almost unchanged, which is consistent with the CV results. The charge and discharge capacities in first cycle are 727.1 and $1083.8 \text{ mAh g}^{-1}$, respectively, with an initial coulombic efficiency of 66.4 %.

Figure 6c exhibits the galvanostatic charge-discharge capacity changes of as-prepared tube-like Sb_2O_4 along with the increasing of the cycle numbers at a constant current density of 100 mA g^{-1} . After the first cycle, the tube-like Sb_2O_4 submicron-structures show a relatively stable cycling performance. A reversible specific discharge capacity as high as 700 mAh g^{-1} could be retained after 50 cycles. The coulombic efficiency is close to 100%. As shown in Figure S4 (Supporting information), however, the solid Sb_2O_3 without secondary oxidation only retains a discharge capacity of 332 mAh g^{-1} , and the Sb_2O_4 with overheated oxidation at 600°C maintains a discharge capacity of 583 mAh g^{-1} after 50 cycles. The enhanced cycling performance of the tube-like Sb_2O_4 (oxidated at 500°C) can be attributed to the good morphology and special structure. The high rate discharge abilities of tube-like Sb_2O_4 submicron-structures are shown in Figure 6d measured at current densities from 100 to 2000 mA g^{-1} . It can be seen that average discharge capacities of 757.7, 613.9, 507.6 and 430.1 mAh g^{-1} are delivered at current densities of 100, 200,

500 and 1000 mA g⁻¹, separately. Furthermore, even at a high current density of 2000 mA g⁻¹, the average discharge capacity can also reach to as high as 370.9 mAh g⁻¹. Importantly, the discharge specific capacity can resume when the current density is returned to a lower value. After 70 cycles at 100 mA g⁻¹, the capacity could also maintain at a value of 675 mAh g⁻¹. For further confirming the excellent cycling performance and rate capacity of the tube-like Sb₂O₄, the cells are also measured at a galvanostatic current density of 1 A g⁻¹ for 100 repeated cycles. As presented in Figure 6e, a high discharge capacity of 415 mA h g⁻¹ is delivered even after 100 charge/discharge cycles at this harsh condition.

To detect the morphology and structure variation of the cycled tube-like Sb₂O₄ submicron-structure, SEM and TEM images of the cycled tube-like Sb₂O₄ electrode material are carried out. As revealed in Figure 7, the structure of the tube-like Sb₂O₄ after 50 repeated cycles is nearly maintained, suggesting the excellent electrochemical performance of this sample.

Based on the good lithium storage performance, it is extremely significant to take an attempt to extend the sodium storage properties of the tube-like Sb₂O₄ submicron-structure. Therefore, a half cell is assembled with the pure sodium as the counter electrode. Figure 8a shows the initial two charge/discharge profiles of the tube-like Sb₂O₄ submicron-structure electrode at a current density of 100 mA g⁻¹. It can be seen that for the discharging profiles, there are one slope from 0.9 V to 0.5 V and two plateaus around 0.5 V and from 0.2 V to 0.01 V. In charging voltage profiles, two slopes from 0.6 to 0.8 V and 1.2 to 1.6 V are also presented. As claimed in the reported electrochemical sodium storage mechanism of Sb₂O₄ film, the electrochemical reactions of tube-like Sb₂O₄ submicron-structure is perhaps two-step, as described in equation (3) and (4). The first step at 0.9 V to 0.5 V involves the conversion reaction of Sb₂O₄ into Sb and Na₂O; and then follows the alloy reaction of Sb into Na₃Sb at 0.2 V to 0.01 V [38].

The sodium storage performance of the tube-like Sb₂O₄ submicron-structure is also investigated by the cycling capability as shown in Figure 8b. It can be seen that a half cell can deliver a first discharge capacity of about 622.8 mAh g⁻¹ at 100 mA g⁻¹. When the cell is discharged at 100 mA g⁻¹ for 100 cycles, a capacity of 381.9 mAh g⁻¹ can be maintained. This capacity is not high, however, which is encouraging in comparison with the reported Sb₂O₄ film cycled only 20 cycles at 0.1C [38].

Combined with the above results, it can be seen that the tube-like Sb_2O_4 submicron-structure exhibits splendid electrochemical performances for both in LIBs and SIBs. Although the conversion reaction step is not completely reversible, the reversible capacity of the tube-like Sb_2O_4 can also reach as high as 700 mAh g^{-1} after 50 cycles for LIBs, which is larger than that of the theoretical capacity (660 mAh g^{-1}) of the alloying-type Sb anode materials. Furthermore, their sodium storage capacity is also encouraging. Therefore, the development of high-capacity antimony oxides is significant in this work.

4. Conclusions

In summary, by using the bulk Sb powders as the raw materials, the tube-like Sb_2O_4 micron-structure has been successfully fabricated via a facile two-step oxidation route. This obtained tube-like Sb_2O_4 micron-structure is used as an anode material for LIBs, which exhibits improved lithium storage performance in comparison with the solid Sb_2O_3 and overheated Sb_2O_4 . Furthermore, its sodium storage performance is also confirmed. In consideration of the low cost of the raw materials, simple synthetic process and the good electrochemical performances of the obtained materials, we believe our method may shed some light on a scalable fabrication of Sb-based materials and other tube-like structures.

Acknowledgement

This work is supported by the Creative Research Groups of the National Natural Science Foundation of China (Grant No. 21521092), and the China Postdoctoral Science Foundation (Grant No. 2015m580253).

References

- [1] M. Armand, J.-M. Tarascon, Building better batteries, *Nature*, 451 (2008) 652-657.
- [2] A. Pramanik, S. Maiti, S. Mahanty, Superior lithium storage properties of $\text{Fe}_2(\text{MoO}_4)_3/\text{MWCNT}$ composite with a nanoparticle (0D)–nanorod (1D) hetero-dimensional morphology, *Chemical Engineering Journal*, 307 (2017) 239–248.

- [3] G. Q. Jia, Z. N. Deng, X. Liu, H. Jiang, C. Z. Li, Building radially oriented architecture by tailorable V₂O₅ nanoribbons toward enhanced lithium storage, *Chemical Engineering Journal* 304 (2016) 194–200.
- [4] H. Jiang, H. X. Zhang, Y. Fu, S. J. Guo, Y. J. Hu, L. Zhang, Y. Liu, H. L. Liu, and C. Z. Li, Self-Volatilization Approach to Mesoporous Carbon Nanotube/Silver Nanoparticle Hybrids: The Role of Silver in Boosting Li Ion Storage, *ACS Nano*, 10 (2016) 1648–1654.
- [5] M.X. Liu, X.M. Ma, L.H. Gan, Z.J. Xu, D.Z. Zhu, L.W. Chen, A facile synthesis of a novel mesoporous Ge@C sphere anode with stable and high capacity for Lithium ion batteries, *Journal of Materials Chemistry A*, 2 (2014) 17107-17114.
- [6] W. Li, D. Yoon, J. Hwang, W. Chang, J. Kim, One-pot route to synthesize SnO₂-Reduced graphene oxide composites and their enhanced electrochemical performance as anodes in lithium-ion batteries, *Journal of Power Sources*, 293 (2015) 1024-1031.
- [7] D. Yoon, D. H. Kim, K. Y. Chung, W. Chang, S. M. Kim, J. Kim, Hydrogen-enriched porous carbon nanosheets with high sodium storage capacity, *Carbon*, 98 (2016) 213-220.
- [8] H.S. Hou, M.J. Jing, Z.D. Huang, Y.C. Yang, Y. Zhang, J. Chen, Z.B. Wu, X.B. Ji, One-Dimensional Rod-Like Sb₂S₃-Based Anode for High-Performance Sodium-Ion Batteries, *Acs Applied Materials & Interfaces*, 7 (2015) 19362-19369.
- [9]. S. Zhou, X. Liu, Y. Xu, Y. X. Liu, Z. H. Dai, and J. C. Bao, An SbOx/Reduced Graphene Oxide Composite as a High-Rate Anode Material for Sodium-Ion Batteries, *J. Phys. Chem. C*, 118 (2014), 23527–23534.
- [10] H.L. Lv, S. Qiu, G.X. Lu, Y. Fu, X.Y. Li, C.X. Hu, J.R. Liu, Nanostructured Antimony/carbon Composite Fibers as Anode Material for Lithium-ion Battery, *Electrochimica Acta*, 151 (2015) 214-221.
- [11] M. He, K. Kraychyk, M. Walter, M.V. Kovalenko, Monodisperse Antimony Nanocrystals for High-Rate Li-ion and Na-ion Battery Anodes: Nano versus Bulk, *Nano letters*, 14 (2014) 1255-1262.
- [12] Y.J. Zhang, L. Jiang, C.R. Wang, Preparation of a porous Sn@C nanocomposite as a high-performance anode material for lithium-ion batteries, *Nanoscale*, 7 (2015) 11940-11944.
- [13] H. Zhao, W. Yuan, G. Liu, Hierarchical electrode design of high-capacity alloy nanomaterials for lithium-ion batteries, *Nano Today*, 10 (2015) 193-212.
- [14] S. L. Jing, H. Jiang, Y. J. Hu, J. H. Shen, and C. Z. Li, Face-to-Face Contact and Open-Void Coinvolved Si/C Nanohybrids Lithium-Ion Battery Anodes with Extremely Long Cycle Life, *Adv. Funct. Mater.*, 25 (2015) 5395–5401.
- [15] X. M. Ma, M. X. Liu, L. H. Gan, P. K. Tripathi, Y. H. Zhao, D. Z. Zhu, Z. J. Xu and L. W. Chen, Novel mesoporous Si@C microspheres as anodes for lithium-ion batteries, *Phys. Chem. Chem. Phys.*, 16 (2014) 4135-4142.

- [16] R. Z. Hu, D. Z. Chen, G. Waller, Y. P. Ouyang, Y. Chen, B. T. Zhao, B. Rainwater, C. H. Yang, M. Zhu and M. L. Liu, Dramatically enhanced reversibility of Li₂O in SnO₂-based electrodes: the effect of nanostructure on high initial reversible capacity, *Energy Environ. Sci.*, 9 (2016) 595-603.
- [17] X. Liu, Y. J. Hu, G. Q. Jia, H. X. Zhang, H. Jiang and C. Z. Li, Homologous V₂O₃/C box-in-box and V₂O₅ box for lithium-ion full cells, *J. Mater. Chem. A*, 4 (2016) 12030–12035.
- [18] H.S. Hou, M.J. Jing, Y.C. Yang, Y.R. Zhu, L.B. Fang, W.X. Song, C.C. Pan, X.M. Yang, X.B. Ji, Sodium/Lithium Storage Behavior of Antimony Hollow Nanospheres for Rechargeable Batteries, *Acs Applied Materials & Interfaces*, 6 (2014) 16189-16196.
- [19] J.J. Xu, H.Y. Wu, F. Wang, Y.Y. Xia, G.F. Zheng, Zn₄Sb₃ Nanotubes as Lithium Ion Battery Anodes with High Capacity and Cycling Stability, *Adv Energy Mater*, 3 (2013) 286-289.
- [20] L. Baggetto, E. Allcorn, R.R. Unocic, A. Manthiram, G.M. Veith, Mo₃Sb₇ as a very fast anode material for lithium-ion and sodium-ion batteries, *J Mater Chem A*, 1 (2013) 11163-11169.
- [21] S. Liao, Y. Sun, J. Wang, H. Cui, C. Wang, Three dimensional self-assembly ZnSb nanowire balls with good performance as sodium ions battery anode, *Electrochimica Acta*, 211 (2016) 11-17.
- [22] L. Baggetto, H.-Y. Hah, C.E. Johnson, C.A. Bridges, J.A. Johnson, G.M. Veith, The reaction mechanism of FeSb₂ as anode for sodium-ion batteries, *Physical Chemistry Chemical Physics*, 16 (2014) 9538-9545.
- [23] H. Kim, J. Cho, Template synthesis of hollow Sb nanoparticles as a high-performance lithium battery anode material, *Chem Mater*, 20 (2008) 1679-1681.
- [24] L. Fan, J.J. Zhang, J.H. Cui, Y.C. Zhu, J.W. Liang, L.L. Wang, Y.T. Qian, Electrochemical performance of rod-like Sb-C composite as anodes for Li-ion and Na-ion batteries, *J Mater Chem A*, 3 (2015) 3276-3280.
- [25] Z. Yi, Q.G. Han, Y. Cheng, F.X. Wang, Y.M. Wu, L.M. Wang, A novel strategy to prepare Sb thin film sandwiched between the reduced graphene oxide and Ni foam as binder-free anode material for lithium-ion batteries, *Electrochimica Acta*, 190 (2016) 804-810.
- [26] L. Hu, X. Zhu, Y. Du, Y. Li, X. Zhou, J. Bao, A Chemically Coupled Antimony/Multilayer Graphene Hybrid as a High-Performance Anode for Sodium-Ion Batteries, *Chem Mater*, 27 (2015) 8138-8145.
- [27] X. Liu, Y. Du, X. Xu, X. Zhou, Z. Dai, J. Bao, Enhancing the Anode Performance of Antimony through Nitrogen-Doped Carbon and Carbon Nanotubes, *The Journal of Physical Chemistry C*, 120 (2016) 3214-3220.
- [28] X. S. Zhou, Z. H. Dai, J. C. Bao and Y. G. Guo, Wet milled synthesis of an Sb/MWCNT nanocomposite for improved sodium storage, *J. Mater. Chem. A*, 1 (2013) 13727–13731.

- [29] N. Wang, Z. Bai, Y. Qian, J. Yang, Double - Walled Sb@ TiO₂- x Nanotubes as a Superior High - Rate and Ultralong - Lifespan Anode Material for Na - Ion and Li - Ion Batteries, *Advanced materials*, (2016).
- [30] Z. Yi, Q. Han, S. Ju, Y. Wu, Y. Cheng, L. Wang, Fabrication of One-Dimensional Sb@ TiO₂ Composites as Anode Materials for Lithium-Ion Batteries, *Journal of The Electrochemical Society*, 163 (2016) A2641-A2646.
- [31] Z.T. Deng, F.Q. Tang, D. Chen, X.W. Meng, L. Cao, B.S. Zou, A simple solution route to single-crystalline Sb₂O₃ nanowires with rectangular cross sections, *J Phys Chem B*, 110 (2006) 18225-18230.
- [32] Z.T. Deng, D. Chen, F.Q. Tang, X.W. Meng, J. Ren, L. Zhang, Orientated attachment assisted self-assembly of Sb₂O₃ nanorods and nanowires: End-to-end versus side-by-side, *J Phys Chem C*, 111 (2007) 5325-5330.
- [33] Z. Yi, Q. Han; Y. Cheng; Y. Wu; L. Wang, Facile synthesis of symmetric bundle-like Sb₂S₃ micron-structures and their application in lithium-ion battery anodes. *Chemical communications*, 52 (2016) 7691-7694.
- [34] W. Luo, S. Lorgier, B. Wang, C. Bommier, X.L. Ji, Facile synthesis of one-dimensional peapod-like Sb@C submicron-structures, *Chemical communications*, 50 (2014) 5435-5437.
- [35] X. Lu, Z. Y. Wang, L. Lu, G. Yang, C. M. Niu, and H. K. Wang, Synthesis of Hierarchical Sb₂MoO₆ Architectures and Their Electrochemical Behaviors as Anode Materials for Li-Ion Batteries, *Inorg. Chem.*, 55 (2016) 7012–7019.
- [36] D. Larcher, A.S. Prakash, L. Laffont, M. Womes, J.C. Jumas, J. Olivier-Fourcade, M.S. Hedge, J.M. Tarascon, Reactivity of antimony oxides and MSb₂O₆ (M=Cu,Ni,Co), trirutile-type phases with metallic lithium, *Journal of the Electrochemical Society*, 153 (2006) A1778-A1787.
- [37] M.Z. Xue, Z.W. Fu, Electrochemical reaction of lithium with nanostructured thin film of antimony trioxide, *Electrochem Commun*, 8 (2006) 1250-1256.
- [38] Q. Sun, Q.Q. Ren, H. Li, Z.W. Fu, High capacity Sb₂O₄ thin film electrodes for rechargeable sodium battery, *Electrochem Commun*, 13 (2011) 1462-1464.

Figure 1. Schematic illustration for the formation of tube-like Sb_2O_4 micron-structures by a two-step oxidation route.

Figure 2. (a) SEM image, (b-c) TEM images and (d) HRTEM image of the solid Sb_2O_3 submicron-wires.

Figure 3. (a-b) SEM images, (c-d) TEM images, (e) HRTEM image and (f) the corresponding SAED pattern of the tube-like Sb_2O_4 submicron-structures.

Figure 4. XRD pattern of the tube-like Sb_2O_4 submicron-structures.

Figure 5. The TG curves of the Sb_2O_3 submicron-wire.

Figure 6. Electrochemical lithium storage performance of the tube-like Sb_2O_4 submicron-structures; (a) CV curves, (b) galvanostatic charge–discharge curves, (c) cycle performances and (d) rate performance, and (e) galvanostatic charge/discharge cycle performances at a current density of 1000 mA g^{-1} .

Figure 7. (a-b) The SEM images and (c) TEM image of the tube-like Sb_2O_4 electrode materials for LIBs after 50 repeated cycles.

Figure 8. Electrochemical sodium storage performance of the tube-like Sb_2O_4 submicron-structures; (a) galvanostatic charge–discharge curves and (b) cycle performances at a current density of 100 mA g^{-1} .

Graphic abstract