

Contents lists available at ScienceDirect

Energy Storage Materials



journal homepage: www.elsevier.com/locate/ensm

Facile synthesis and *in situ* transmission electron microscopy investigation of a highly stable Sb_2Te_3/C nanocomposite for sodium-ion batteries



Ze Yang^{a,1}, Jingying Sun^{a,1}, Yizhou Ni^a, Zhenhuan Zhao^b, Jiming Bao^b, Shuo Chen^{a,*}

^a Department of Physics and TcSUH, University of Houston, Houston, TX 77204, USA

^b Department of Electrical and Computer Engineering, University of Houston, Houston, TX 77204, USA

ARTICLE INFO

Keywords: Na-ion batteries Sb₂Te₃/C High capacity retention In situ TEM

ABSTRACT

Sb-based anode materials attract a great deal of attention recently due to their high capacity. However, large volume change during sodiation and desodiation leads to poor cyclic performance. Introduction of inactive element would improve the cyclic performance but reduce the capacity significantly. In this work, Na-active Te was introduced and Sb₂Te₃/C nanocomposite has been successfully prepared by a high energy ball mill method. The Sb₂Te₃ nanocrystals with a size of about 20 nm embedded in the carbon matrix are produced. The asobtained Sb₂Te₃/C exhibits specific capacity of 360 mA h g⁻¹ with capacity retention of 93% after 400 cycles at 1 A g⁻¹. In situ transmission electron microscopy study was carried out to investigate the origin of the high capacity retention. The synergetic effects of carbon matrix and nanosized particles can release stress efficiently during large volume change and suppress the aggregation of the pulverized nanoparticles.

1. Introduction

The global energy crisis and environmental pollution seriously threaten human sustainable development since last century [1]. Increasing desire for new energy becomes more and more urgent. Wind energy, tidal energy, solar energy, and other clean energy are restricted by time, weather, season, location or other factors which can't be employed as continuous and stable power sources [2]. As a result, batteries were introduced to store and output stable electricity [3]. Recently, rapidly growing applications of lithium-ion batteries in portable electronics, electric vehicles, and electric grid trigger the anxiety of limited of lithium resource. Despite that sodium-ion batteries are still in laboratory, the abundance of sodium in the earth's crust makes it an attractive alternative [4-6]. It has been demonstrated that carbonaceous materials, Ti-based composites, Sn-based composites, Sb-based composites, and P-based composites are potential anode materials for Na-ion batteries [7–9]. Among them, Sb-based composites manifest a great potential for the employment as anode materials due to their large reversible capacity [10-12]. However, high reversible capacity is associated with large volume change of Sb (\approx 390%) which results in rapid capacity fade during cycling [12-15]. Nanotechnology and partial substitution of Sb by other elements such as Fe, Ni, Zn, Sn, and Mo have been pursued to improve the electrochemical performances [16-26]. Most of the introduced ele-

* Corresponding author.

http://dx.doi.org/10.1016/j.ensm.2017.07.010

Received 12 April 2017; Received in revised form 13 July 2017; Accepted 13 July 2017 Available online 26 July 2017 2405-8297/ © 2017 Published by Elsevier B.V. ments are sodium-inactive which would act as backbone and buffer volume expansion. However, inactive elements would reduce the practical capacity especially when large amount of inactive components are required to improve the cyclic performance.

Recently, much attention has been paid to Sb-M (M = VI group) compounds owning to sodium-active nature of VI group elements [10,27–30]. Rhombohedral Sb₂Te₃ has been widely investigated in the areas of thermoelectric, semiconductor and topological insulator yet not been reported for Na-ion batteries [31,32]. The density of Sb₂Te₃ (6.66 g cm⁻³) is much higher than that of other Sb-M compounds, such as Sb₂O₃, Sb₂S₃, and Sb₂Se₃ [33]. Therefore, it's favorable for fabrication of a high volumetric capacity electrode (3419 mA h cm⁻³) for Na-ion batteries. To enhance the electrochemical performances, carbon incorporation is an effective approach. Various carbon materials have been composited with anode materials in Na-ion batteries due to their excellent electrical conductivity, superior chemical and electrochemical stability and low cost, such as amorphous carbon, carbon nanotubes, and reduced graphene oxide [16,27,29,34].

Herein, rhombohedral Sb₂Te₃ and Sb₂Te₃/C powders were synthesized by a high energy ball mill (HEBM) method which is easy to scale up. After introducing of graphite during ball milling, Sb₂Te₃/C electrode exhibits excellent rate and cyclic performances. Our *in situ* TEM results confirm the formation of Na₃Sb and Na₂Te at the end of discharge. They also prove that carbon can glue the Sb₂Te₃ nanopar-

E-mail address: schen34@uh.edu (S. Chen).

¹ The authors contributed equally.



Fig. 1. (a) Schematic representation of the fabrication of the Sb₂Te₃/C nanocomposite, (b) XRD patterns and (c) Raman spectra for Sb₂Te₃, Sb₂Te₃/C and ball-milled graphite.

ticles together which would suppress the pulverization during cycling hence improve the cyclic performance.

2. Results and discussion

Sb and Te can be alloyed into layered Sb₂Te₃ by a simple HEBM method. To improve the electrochemical performances, ball milled graphite was introduced during HEBM. The fabrication process is illustrated in Fig. 1a. Fig. 1b shows X-ray diffraction (XRD) patterns for Sb₂Te₃, Sb₂Te₃/C, and ball milled graphite samples. After 48 h HEBM, the peaks corresponding to graphite become broad and weak, which suggests smaller particles and lower crystallinity. Pure rhombohedral Sb₂Te₃ (JCPDS No. 71-393) phase was formed after the first ball milling and sharp peaks can be observed. After introduction of graphite during HEBM, the peaks of Sb₂Te₃ are weaker and no other phase can be found including graphite. The weakened peaks of both graphite and Sb₂Te₃ can be ascribed to long ball milling time which leads to low crystallinity. Raman spectra of Sb₂Te₃, Sb₂Te₃/C, and ball milled graphite samples are shown in Fig. 1c. In Sb₂Te₃/C composite, the relative intensity of D band (1341 cm⁻¹) to G band (1572 cm⁻¹) decreases, and the D band (1620 cm⁻¹) becomes more obvious. It is documented that both the D band and D band are defect induced Raman vibrations, while the G band is the characteristic vibration of ordered graphite lattice. It is hence concluded that the ordered graphite lattice was destroyed during the ball milling to form defect-rich carbon. D band and G band in both spectra of graphite containing sample can be observed in Fig. 1c, indicating that a large amount of disordered carbon or defective graphitic structure exist after ball milling [35], which is in agreement with the XRD result.

TEM bright-field images of Sb₂Te₃ and Sb₂Te₃/C samples are displayed in Fig. 2a and c. The TEM image shows Sb₂Te₃ particle has irregular morphology and the high-resolution transmission electron microscopy (HRTEM) image suggests that the larger particle consists of nanocrystals. The clear crystalline lattice indicates the good crystal-linity and the distance of the lattice fringe agrees with the as-formed rhombohedral Sb₂Te₃. After introduction of graphite, many black dots

distributed on the Sb₂Te₃/C particle randomly can be observed from Fig. 2c and the contrast of pure Sb₂Te₃ is more uniform. The Sb₂Te₃ particle in Fig. 2a is larger than the Sb₂Te₃/graphite in Fig. 2c, but actually these particles are secondary particles which are composed of much smaller grains. The HRTEM images combined with fast Fourier transform (FFT) patterns shown in Fig. 2b and d confirm the formation of Sb₂Te₃. Clear orientation variation of lattice fringes can be observed in Fig. 2b which is an indicator of different nanocrystals. In Fig. 2d, an approximately 20 nm Sb₂Te₃ nanocrystal is embedded in amorphous carbon matrix. Although the carbon precursor is graphite, the defects increase greatly after ball milling and the graphite partially becomes amorphous after the long time ball milling, which is in agreement with the Raman data. The scanning electron microscopy (SEM) images in Fig. S2 show that aggregated Sb₂Te₃ and Sb₂Te₃/C particles are as large as several micrometers. Fig. 2e shows the scanning transmission electron microscopy (STEM) dark-field image of Sb₂Te₃/C samples and corresponding elemental mapping images of Sb, Te and C. The elements Sb and Te distribute uniformly inside the particle and corresponding colors fade near particle edge. As a comparison, C-rich surface and C-poor core can be observed in Fig. 2h. These elemental mappings indicate that the carbon layer coats the Sb₂Te₃ particles which is in accordance with the TEM bright-field results.

Fig. 3a displays initial five cyclic voltammetry (CV) curves of sodium half cells of Sb_2Te_3/C between 0.01-2.5 V at 0.1 mV s⁻¹. Two peaks located at 0.36 and 0.89 V vs. Na⁺/Na appear during the first negative scan. In the subsequent cycles, the intensity of the peak at 0.36 V deceases as the cycle number increases and the peak position shifts to 0.49 V. The peak at 0.89 V is assigned to activation process including formation of solid electrolyte interface (SEI) on carbon surface [36]. This process only occurred at the first cycle. The oxidization peaks at 0.59 and 0.86 V and reduction peaks at 0.49, 1.1, and 1.27 V nearly completely overlap after the second cycle, which reflects a highly reversible kinetics. *In situ* TEM results confirm the formation of Na₃Sb and Na₂Te which will be discussed later. Combined with literature, we speculate that the peak at 1.27 V may correspond to Na-ion intercalation into the Sb₂Te₃ layers as that in Sb₂S₃ and Sb₂Se₃



Fig. 2. (a) TEM and (b) HRTEM bright-field images Sb₂Te₃ sample. (c) TEM and (d) HRTEM bright-field images of Sb₂Te₃/C nanocomposite. (e-h) STEM dark-field image and corresponding elemental mappings.

[29,37]. Then, $Na_xSb_2Te_3$ transforms into Na_2Te and Sb at 1.1 V. Finally, Sb can be alloyed with Na at 0.36 V at the first cycle or 0.49 V at other cycles. The sodiation process of Sb is a multiple step transformation of amorphous Sb into hexagonal Na_3Sb by discharging

[12,38,39]. After activation process at the first cycle, the sodiation peak of Sb shifts from 0.36 V to 0.49 V. Two oxidization peaks at 0.87 and 1.57 V can be found during positive scan while the peak at 0.87 V arises from dealloying reaction of Na_3Sb [40–42]. As a result, the other peak



Fig. 3. (a) CV curves for sodium half cells of Sb₂Te₃/C between 0.01–2.5 V at 0.1 mV s⁻¹. (b) Cyclic performance of Sb₂Te₃/C electrodes. (c) Discharging curves of Sb₂Te₃/C electrode at various current density. (d) Rate capability and (e) cyclic performances of Sb₂Te₃/C electrodes.

refers to the formation of Sb_2Te_3 . A five step electrochemical reaction mechanism is proposed as follows:

Step 1 (intercalation reaction): $Sb_2Te_3 + xNa^+ + xe^- \rightarrow Na_xSb_2Te_3$ (1)

Step 2 (conversion reaction): $Na_xSb_2Te_3 + (6 - x)Na^+ + (6 - x)e^- \rightarrow 3Na_2Te + 2Sb$ (2)

Step 3 (alloying reaction): Sb + $xNa^+ + xe^- \rightarrow Na_xSb$ (x = 1–3) (3)

Step 4 (dealloying reaction): $Na_xSb \rightarrow Sb + xNa^+ + xe^-$ (4)

Step 5 (reverse conversion reaction): $2Sb + 3Na_2Te \rightarrow Sb_2Te_3 + 6Na^+ + 6e^-$ (5)

To compare the cyclic performance of Sb₂Te₃ and Sb₂Te₃/C electrodes, the cells were activated by being cycled at 20 mA g⁻¹ for two cycles. Then, the cells were cycled at 100 mA g⁻¹ for 100 cycles as shown in Fig. 3b. The Sb₂Te₃ electrode delivers higher capacity of 491 mA h g⁻¹ at the current of 20 mA g⁻¹, but it fades quickly. After ball milled with graphite, Sb₂Te₃/C electrode delivers capacities of 418 and 400 mA h g⁻¹ at the current of 20 and 100 mA g⁻¹, respectively. To further investigate cyclic performance of Sb₂Te₃/C electrode, it was charged and discharged at the current of 1 A g⁻¹. It delivers 360 mA h g⁻¹ for the first cycle and retains as high as 93% after 400 cycles. Fluoroethylene carbonate (FEC) also plays an important role in improving its cyclic performance. The capacities of Sb₂Te₃/C electrodes are similar for the first cycle with or without FEC as an additive. However, the capacity of Sb₂Te₃/C electrode fades quickly after 120 cycles as shown in Fig. S4. FEC can form thick SEI on the surface of the active material and carbon black which can maintain the integrity of the electrode [43]. The anode shows three plateaus 1.35, 1.1, and 0.5 V during discharging process and two slopes at about 0.6 and 1.75 V at 20 mA g⁻¹ as shown in Fig. 3c, which is consistent with the CV data. The rate capability of Sb₂Te₃ and Sb₂Te₃/C electrodes are compared in Fig. 3d. The values of charge capacity are 437, 417, 398, 381, 354, 332, and 314 at the current of 20, 50, 100, 200, 500, 1000, and 2000 mA g⁻¹, respectively. After cycling at high current, the capacity can recover to 409 mA h g^{-1} when the current is set back to 20 mA g^{-1} .

The CV curves of Sb₂Te₃/C electrode after the first cycle at various scan rates are shown in Fig. 4. Similar shapes at various scan rates exhibit broad peaks during both positive and negative scans. Considering the small size of the crystals, capacitive behavior may have a great effect on the rate capability. The relationship between the measured peak current (i) and the sweep rate (v) can be described as: i= av^b [44,45]. The *b*-value qualitatively exhibits the degree of capacitive effect, which can be determined by the slope of the log(v)log(i) plots. A capacitive process will be presented when the *b*-value approaches 1, while diffusion dominated behavior when b is close to 0.5. The $\log(v)$ -log(i) plots for peak 1, 1[,] 2, 2[,] and 2[,] of Sb₂Te₃/C electrode are depicted in Fig. 4c and d. The b-values are 0.82, 0.90, 0.83, 0.77, and 0.97, respectively. It indicates more favorable capacitive behaviors for all these peaks especially peak 2``, which explains the excellent rate capability. The b-value of peak 2`` is as high as 0.97, suggesting this capacitive process is independent of sweep rate. The $\log(v) - \log(i)$ plots of Sb₂Te₃ electrode are not compared here due to the fast capacity fade after several scans.

To further understand the mechanism of the sodiation process, *in* situ TEM experiments were carried out. Fig. 5a schematically illustrates the experimental setup of *in situ* TEM device. Briefly, *in situ* TEM device consists of an individual Sb₂Te₃ or Sb₂Te₃/C electrode, a layer of Na₂O solid electrolyte, and a bulk Na counter electrode. The morphological evolution of Sb₂Te₃ is shown in Fig. 5b and c. A main Sb₂Te₃ particle is about 764 nm in size and a smaller particle attached to the main particle. After sodiation, a lateral expansion from 764 to 863 nm corresponds to ~ 13% size expansion. Some cracks nucleate and grow on the boundary between the main and the attached particle

as shown in Fig. 5b and c and Movie S1, as indicated by the circle. Moreover, some bulges grow from the pure Sb_2Te_3 particle, as indicated by the arrows. Similar morphological evolutions have also been found during electrochemical lithiation of Si and CoS_2 [46,47].

For the individual Sb₂Te₃/C electrode, a small main particle attached to a main particle was chosen to demonstrate the advantage of the ball-milled graphite as shown in Fig. 5d-g. Selected-area electron diffraction (SAED) patterns confirmed the existence of Sb₂Te₃ and ball-milled graphite. After sodiation, Sb₂Te₃ is converted to Na₂Te and Na₃Sb. In Fig. 5f and g and Movie S2, no cracks or fractures can be found at the boundary between the main and attached particle. The main particle laterally expended from 364 to 454 nm. corresponding to $\sim 25\%$ size expansion. It's surprising to observe that individual Sb₂Te₃/C expands larger than Sb₂Te₃ electrode because the latter shows the higher capacity for Na-ion batteries as shown in Fig. 3b. Note that in Na-batteries, a large amount of conductive black carbon (10 wt%) were mixed with Sb₂Te₃. We speculate that the less conductive nature of Sb₂Te₃ compared with Sb₂Te₃/C and formation of cracks is responsible for the smaller expansion. However, it is carbon free for pure Sb₂Te₃ electrode in the TEM device. Considering the agglomerated nanocrystals of Sb₂Te₃, the cracks and fractures inside the main particle may lead to contact loss which will block the electron transfer. Similar morphologies of Sb₂Te₃/C electrodes before and after 100 cycles can be observed in Fig. S5 which is in agreement with in situ TEM results.

Fig. 6 schematically illustrates the morphology evolution of the Sb₂Te₃ and Sb₂Te₃/C electrodes during cycling. Sb₂Te₃ nanocrystals connect with each other directly and agglomerate into larger particles. The cracks and fractures form at the boundary between nanocrystals when sodiation. Some nanocrystals may lose contact which will lead to capacity fade after several times of expansion and shrink. After comilled with graphite, Sb₂Te₃ nanocrystals no longer connect with each other directly. The carbon matrix not only provides a high electron transfer way, but also acts as backbone to suppress whole particle falling apart and bridge Sb₂Te₃ nanograins. In addition, crystal size plays an important role in cyclic life of sodium-ion batteries, such as Sb and Bi anode materials [6,48,49]. The size dependent formation of fracture would lead to various degrees of contact loss during cycling. Smaller crystal size of Sb₂Te₃ in Sb₂Te₃/C nanocomposite than that in pure Sb₂Te₃ is more efficient to release stress during large volume change, hence the cyclic performance [6,47].

3. Conclusions

In summary, Sb₂Te₃ and Sb₂Te₃/C samples have been successfully fabricated by a facile HEBM method. Sb₂Te₃ nanograins agglomerate into larger particles for pure Sb₂Te₃ sample while Sb₂Te₃ nanoparticles embedded in carbon matrix for Sb₂Te₃/C sample. The Sb₂Te₃/C electrode shows a high capacity of 360 mA h g⁻¹ and capacity retention of 93% after 400 cycles at the current of 1 A g⁻¹. Moreover, it delivers 437 mA h g⁻¹ at the current of 20 mA g⁻¹ and retains 314 mA h g⁻¹ at 2000 mA g⁻¹. *In situ* TEM results show cracks which grow at the boundary between the main and attached particle for pure Sb₂Te₃ particle should be responsible for the severe capacity fade. The excellent electrochemical performances of Sb₂Te₃/C can be attributed to the synergistic effects of the carbon matrix and nanosized particles which can release stress efficiently during large volume change and suppress the aggregation of the pulverized nanoparticles.

4. Methods

4.1. Sample preparation

 Sb_2Te_3 and Sb_2Te_3/C powders were prepared by HEBM. The mixture of Sb (Afla Aesar, 99.5%) and Te (Afla Aesar, 99.5%) powders with the atomic ratio of 2:3 were added into a stainless steel jar and



Fig. 4. (a) and (b) CV curves for sodium half cells of Sb₂Te₃/C between 0.01–2.5 V at various scan rate. Relationship between logarithm peak current and logarithm scan rates for (c) peak 1, 1` and (d) peak 2, 2` and 2``.

sealed in a glove box under argon protection. After being ball-milled for eight hours at a speed of 1200 rpm (Spex 8000M), Sb₂Te₃ powder was obtained. Graphite powder was ball milled for 48 h before use. Then the graphite powder was mixed with Sb₂Te₃ and ball milled for 48 h to produce the Sb₂Te₃/C composite powder.

4.2. Characterizations

Powder XRD (Rigaku, SmartLab, Cu K α radiation) was used to characterize the phase and structure of the Sb₂Te₃ and Sb₂Te₃/C samples.

The SEM observation was carried out using a field emission scanning microscope (LEO, 1525). The Raman spectra was recorded on a Horiba Triax550 and a T64000 spectrometer with an excitation wavelength of 532 nm. The (S)TEM and HRTEM observation were performed on a JEOL 2010F microscope. *In situ* TEM experiments were performed with a Hummingbird nano-manipulator TEM holder. The powders were attached to a half copper grid which was used as the working electrode. Na metal attached to a tungsten wire served as the counter electrode. The naturally formed Na₂O on Na metal during the holder loading process acts as a solid electrolyte allowing Na⁺ transport.



Fig. 5. (a) Illustration of the experiment setup of *in situ* TEM device. TEM images of Sb₂Te₃ (b) before and (c) after sodiation. SAED images and TEM images of Sb₂Te₃/C (d, f) before and (e, g) after sodiation.



Movie S1. In situ TEM sodiation process of Sb₂Te₃ electrode. A video clip is available online. Supplementary material related to this article can be found online at doi:10.1016/j.ensm.2017.07.010.



Movie S2. In situ TEM sodiation process of Sb₂Te₃/C electrode.Supplementary material related to this article can be found online at doi:10.1016/j.ensm.2017.07.010.



Fig. 6. Schematic illustration of the morphology evolution of the Sb₂Te₃ and Sb₂Te₃/C electrodes during cycling.

4.3. Electrochemical characterization

Electrochemical performances were investigated with CR2032 coin cells. The coin cells were fabricated with the Sb₂Te₃ or Sb₂Te₃/C as the working electrode, metallic sodium as both the counter and reference electrode, 1 mol L⁻¹ NaClO₄ in mixed propylene carbonate (PC)/ ethylene carbonate (EC) (1:1 in volume) solution with an addition of 5% FEC as the electrolyte, and glass fibre as the separator. The working electrode was fabricated on Cu foil by coating mixed slurry of 80 wt% active material, 10 wt% conductive black carbon and 10 wt% polyvinylidene fluoride (PVDF) binder in N-methylpyrrolidone (NMP) solvent. The cells were charged and discharged on a battery testing system (Land CT2001A, China) between 0.01 and 2.5 V versus Na⁺/Na at room temperature. CV was measured by an electrochemistry work-station (BioLogic, SP-200).

Conflict of interest

The authors declare no competing financial interest.

Acknowledgements

The authors would like to acknowledge the support from the

Defense University Research Instrumentation Program (FA2386-14-1-3007) for TEM hardware purchase and TcSUH as the TcSUH Robert A. Welch Professorships on High Temperature Superconducting (HTSg) and Chemical Materials (E-0001).

Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.ensm.2017.07.010.

References

- G.L. Li, Z. Yang, Y. Jiang, C.H. Jin, W. Huang, X.L. Ding, Y.H. Huang, Towards polyvalent ion batteries: a zinc-ion battery based on NASICON structured Na₃V₂(PO₄)₃, Nano Energy (25) (2016) 211–217.
- [2] Z.G. Yang, J.L. Zhang, M.C. Kintner-Meyer, X.H. Lu, D. Choi, J.P. Lemmon, J. Liu, Electrochemical energy storage for green grid, Chem. Rev. (111) (2011) 3577–3613.
- [3] X. Zhao, S.A. Vail, Y. Lu, J. Song, W. Pan, D.R. Evans, J.J. Lee, Antimony/graphitic carbon composite anode for high-performance sodium-ion batteries, ACS Appl. Mater. Interfaces (8) (2016) 13871–13878.
- [4] C. Fang, Y.H. Huang, W.X. Zhang, J.T. Han, Z. Deng, Y.L. Cao, H.X. Yang, Routes to high energy cathodes of sodium-ion batteries, Adv. Energy Mater. (6) (2015) 1501727.
- [5] L.W. Ji, W.D. Zhou, V. Chabot, A.P. Yu, X.C. Xiao, Reduced graphene oxide/tinantimony nanocomposites as anode materials for advanced sodium-ion batteries, ACS Appl. Mater. Interfaces (7) (2015) 24895–24901.

- [6] T. Ramireddy, N. Sharma, T. Xing, Y. Chen, J. Leforestier, A.M. Glushenkov, Size and composition effects in Sb-carbon nanocomposites for sodium-ion batteries, ACS Appl. Mater. Interfaces (8) (2016) 30152–30164.
- [7] H. Kim, H. Kim, Z. Ding, M.H. Lee, K. Lim, G. Yoon, K. Kang, Recent progress in electrode materials for sodium-ion batteries, Adv. Energy Mater. (6) (2016) 1600943.
- [8] M. Wang, Z.Z. Yang, J.Q. Wang, W.H. Li, L. Gu, Y. Yu, Sb nanoparticles encapsulated in a reticular amorphous carbon network for enhanced sodium storage, Small (11) (2015) 5381–5387.
- [9] D.P. Kundu, E. Talaie, V. Duffort, L.F. Nazar, The emerging chemistry of sodium ion batteries for electrochemical energy storage, Angew. Chem. Int. Ed. (54) (2015) 3431–3448.
- [10] X.H. Xiong, G.H. Wang, Y.W. Lin, Y. Wang, X. Ou, F.H. Zheng, C.H. Yang, J.H. Wang, M.L. Liu, Enhancing sodium ion battery performance by strongly binding nanostructured Sb₂S₃ on sulfur-doped graphene sheets, ACS Nano (10) (2016) 10953–10959.
- [11] N.N. Wang, Z.C. Bai, Y.T. Qian, J. Yang, One-dimensional yolk-shell Sb@Ti-O-P nanostructures as a high-capacity and high-rate anode material for sodium ion batteries, ACS Appl. Mater. Interfaces (9) (2017) 447–454.
- [12] Y.N. Ko, Y.C. Kang, Electrochemical properties of ultrafine Sb nanocrystals embedded in carbon microspheres for use as Na-ion battery anode materials, Chem. Commun. (50) (2014) 12322–12324.
- [13] S. Liu, J.K. Feng, X.F. Bian, J. Liu, H. Xu, Morphology-controlled synthesis of nanoporous-antimony anode for high-performance sodium-ion batteries, Energy Environ. Sci. (9) (2016) 1229–1236.
- [14] Y. Zhao, A. Manthiram, High-capacity, high-rate Bi–Sb alloy anodes for lithium-ion and sodium-ion batteries, Chem. Mater. (27) (2015) (3196-3130).
- [15] L. Wu, H.Y. Lu, L.F. Xiao, X.P. Ai, H.X. Yang, Y.L. Cao, Electrochemical properties and morphological evolution of pitaya-like Sb@C microspheres as high-performance anode for sodium ion batteries, J. Mater. Chem. A (3) (2015) 5708–5713.
- [16] Y.J. Zhu, X.G. Han, Y.H. Xu, Y.H. Liu, S.Y. Zheng, K. Xu, L.B. Hu, C.S. Wang, Electrospun Sb/C fibers for a stable and fast sodium-ion battery anode, ACS Nano (7) (2013) 6378-6386.
- [17] S. Liao, Y. Sun, J. Wang, H. Cui, C.X. Wang, Three dimensional self-assembly ZnSb nanowire balls with good performance as sodium ions battery anode, Electrochim. Acta (211) (2016) 11–17.
- [18] C.C.H. Tran, C. Autret, C. Damas, B. Claude-Montigny, J. Santos-Peña, An electrochemical study of Fe_{1.18}Sb_{1.82} as negative electrode for sodium ion batteries, Electrochim. Acta (182) (2015) 11–19.
- [19] Z.M. Liu, X.Y. Yu, X.W.D. Lou, U. Paik, Sb@C coaxial nanotubes as a superior longlife and high-rate anode for sodium ion batteries, Energy Environ. Sci. (9) (2016) 2314–2318.
- [20] J. Duan, W. Zhang, C. Wu, Q.J. Fan, W.X. Zhang, X.L. Hu, Y.H. Huang, Selfwrapped Sb/C nanocomposite as anode material for high-performance sodium-ion batteries, Nano Energy (16) (2015) 479–487.
- [21] C.W. Lee, J.C. Kim, S. Park, H.J. Song, D.W. Kim, Highly stable sodium storage in 3-D gradational Sb–NiSb–Ni heterostructures, Nano Energy (15) (2015) 479–489.
- [22] W. Li, C. Hu, M. Zhou, H.W. Tao, K.L. Wang, S.J. Cheng, K. Jiang, Carbon-coated Mo₃Sb₇ composite as anode material for sodium ion batteries with long cycle life, J. Power Sources (307) (2016) 173–180.
- [23] M. Walter, S. Doswald, M.V. Kovalenko, Inexpensive colloidal SnSb nanoalloys as efficient anode materials for lithium- and sodium-ion batteries, J. Mater. Chem. A (4) (2016) 7053–7059.
- [24] L. Li, K.H. Seng, D. Li, Y. Xia, H.K. Liu, Z. Guo, SnSb@carbon nanocable anchored on graphene sheets for sodium ion batteries, Nano Res. (7) (2014) 1466–1476.
- [25] J.U. Seo, C.M. Park, Nanostructured SnSb/MO_x (M = Al or Mg)/C composites: hybrid mechanochemical synthesis and excellent Li storage performances, J. Mater. Chem. A (1) (2013) 15316–15322.
- [26] H.S. Hou, X.Y. Cao, Y.C. Yang, L.B. Fang, C.C. Pan, X.M. Yang, W.X. Song, X.B. Ji, NiSb alloy hollow nanospheres as anode materials for rechargeable lithium ion batteries, Chem. Commun. (50) (2014) 8201–8203.
- [27] D.Y. Yu, P.V. Prikhodchenko, C.W. Mason, S.K. Batabyal, J. Gun, S. Sladkevich, A.G. Medvedev, O. Lev, High-capacity antimony sulphide nanoparticle-decorated graphene composite as anode for sodium-ion batteries, Nat. Commun. (4) (2013) 2922.
- [28] W. Li, M. Zhou, H.M. Li, K.L. Wang, S.J. Cheng, K. Jiang, Carbon-coated Sb₂Se₃ composite as anode material for sodium ion batteries, Electrochem. Commun. (60) (2015) 74–77.
- [29] S.S. Yao, J. Cui, Z.H. Lu, Z.L. Xu, L. Qin, J.Q. Huang, Z. Sadighi, F. Ciucci, J.K. Kim, Unveiling the unique phase transformation behavior and sodiation kinetics of 1D van

der Waals $\mathrm{Sb}_2\mathrm{S}_3$ anodes for sodium ion batteries, Adv. Energy Mater. (2016) 1602149.

- [30] X.S. Zhou, X. Liu, Y. Xu, Y.X. Liu, Z.H. Dai, J.C. Bao, An SbO_x/reduced graphene oxide composite as a high-rate anode material for sodium-ion batteries, J. Phys. Chem. C (118) (2014) 23527–23534.
- [31] H.J. Zhang, C.X. Liu, X.L. Qi, X. Dai, Z. Fang, S.C. Zhang, Topological insulators in Bi₂Se₃, Bi₂Te₃ and Sb₂Te₃ with a single Dirac cone on the surface, Nat. Phys. (5) (2009) 438–442.
- [32] C. Schumacher, K.G. Reinsberg, L. Akinsinde, S. Zastrow, S. Heiderich, W. Toellner, G. Rampelberg, C. Detavernier, J.A.C. Broekaert, K. Nielsch, J. Bachmann, Optimization of electrodeposited p-doped Sb₂Te₃ thermoelectric films by millisecond potentiostatic pulses, Adv. Energy Mater. (2) (2012) 345–352.
- [33] K.H. Nam, C.M. Park, Layered Sb₂Te₃ and its nanocomposite: a new and outstanding electrode material for superior rechargeable Li-ion batteries, J. Mater. Chem. A (4) (2016) 8562–8565.
- [34] Y. Zhu, Y. Wen, X. Fan, T. Gao, F. Han, C. Luo, S.C. Liou, C. Wang, Red phosphorus-single-walled carbon nanotube composite as a superior anode for sodium ion batteries, ACS Nano (9) (2015) 3254–3264.
- [35] G.L. Li, Z. Yang, Y. Jiang, W.X. Zhang, Y.H. Huang, Hybrid aqueous battery based on Na₃V₂(PO₄)₃/C cathode and zinc anode for potential large-scale energy storage, J. Power Sources (308) (2016) 52–57.
- [36] S.Q. Wang, L. Xia, L. Yu, L. Zhang, H.H. Wang, X.W. Lou, Free-standing nitrogendoped carbon nanofiber films: integrated electrodes for sodium-ion batteries with ultralong cycle life and superior rate capability, Adv. Energy Mater. (6) (2016) 1502217.
- [37] X. Ou, C.H. Yang, X.H. Xiong, F.H. Zheng, Q.C. Pan, C. Jin, M.L. Liu, K. Huang, A new rGO-overcoated Sb₂Se₃ nanorods anode for Na⁺ battery: *in situ* X-ray diffraction study on a live sodiation/desodiation process, Adv. Funct. Mater. (27) (2017) 1606242.
- [38] A. Darwiche, C. Marino, M.T. Sougrati, B. Fraisse, L. Stievano, L. Monconduit, Better cycling performances of bulk Sb in Na-ion batteries compared to Li-ion systems: an unexpected electrochemical mechanism, J. Am. Chem. Soc. (134) (2012) 20805–235211.
- [39] M. He, K. Kravchyk, M. Walter, M.V. Kovalenko, Monodisperse antimony nanocrystals for high-rate Li-ion and Na-ion battery anodes: nano versus bulk, Nano Lett. (14) (2014) 1255–1262.
- [40] S. Qiu, X.Y. Wu, L.F. Xiao, X.P. Ai, H.X. Yang, Y.L. Cao, Antimony nanocrystals encapsulated in carbon microspheres synthesized by a facile self-catalyzing solvothermal method for high-performance sodium-ion battery anodes, ACS Appl. Mater. Interfaces (8) (2016) 1337–1343.
- [41] F. Wan, J.Z. Guo, X.H. Zhang, J.P. Zhang, H.Z. Sun, Q. Yan, D.X. Han, L. Niu, X.L. Wu, *In situ* binding Sb nanospheres on graphene via oxygen bonds as superior anode for ultrafast sodium-ion batteries, ACS Appl. Mater. Interfaces (8) (2016) 7790–7799.
- [42] L.Y. Hu, X.S. Zhu, Y.C. Du, Y.F. Li, X.S. Zhou, J.C. Bao, A chemically coupled antimony/multilayer graphene hybrid as a high-performance anode for sodium-ion batteries, Chem. Mater. (27) (2015) 8138–8145.
- [43] W.J. Li, S.L. Chou, J.Z. Wang, J.H. Kim, H.K. Liu, S.X. Dou, Sn_{4+x}P₃ @ amorphous Sn-P composites as anodes for sodium-ion batteries with low cost, high capacity, long life, and superior rate capability, Adv. Mater. (26) (2014) 4037–4042.
- [44] C. Chen, Y.W. Wen, X.L. Hu, X.L. Ji, M.Y. Yan, L.Q. Mai, P.P. Hu, B. Shan, Y.H. Huang, Na+ intercalation pseudocapacitance in graphene-coupled titanium oxide enabling ultra-fast sodium storage and long-term cycling, Nat. Commun. (6) (2015) 6929.
- [45] D. Chao, P. Liang, Z. Chen, L. Bai, H. Shen, X. Liu, X. Xia, Y. Zhao, S.V. Savilov, J. Lin, Z.X. Shen, Pseudocapacitive Na-ion storage boosts high-rate and areal capacity of self-branched 2D layered metal chalcogenide nanoarrays, ACS Nano (10) (2016) 10211–10219.
- [46] Q.M. Su, J. Xie, J. Zhang, Y.J. Zhong, G.H. Du, B.S. Xu, *In situ* transmission electron microscopy observation of electrochemical behavior of CoS₂ in lithium-ion battery, ACS Appl. Mater. Interfaces (6) (2014) 3016–3022.
- [47] X.H. Liu, L. Zhong, S. Huang, S.X. Mao, T. Zhu, J.Y. Huang, Size-dependent fracture of silicon nanoparticles during lithiation, ACS Nano (6) (2012) 1522–1531.
- [48] J. Sottmann, M. Herrmann, P. Vajeeston, Y. Hu, A. Ruud, C. Drathen, H. Emerich, H. Fjellvåg, D.S. Wragg, How crystallite size controls the reaction path in nonaqueous metal ion batteries: the example of sodium bismuth alloying, Chem. Mater. (28) (2016) 2750–2756.
- [49] N. Zhang, Y. Liu, Y. Lu, X. Han, F. Cheng, J. Chen, Spherical nano-Sb@C composite as a high-rate and ultra-stable anode material for sodium-ion batteries, Nano Res. (8) (2015) 3384–3393.