Electrochimica Acta 316 (2019) 236-247

Contents lists available at ScienceDirect

Electrochimica Acta

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

# Novel amorphous CoSnO<sub>3</sub>@rGO nanocomposites highly enhancing sodium storage

Shuming Dou<sup>a</sup>, Xifei Li<sup>a, b, \*</sup>, Linlin Fan<sup>b</sup>, Dongbin Xiong<sup>b</sup>, Hirbod Maleki Kheimeh Sari<sup>b</sup>, Bo Yan<sup>b</sup>, Wen Liu<sup>b</sup>, Jianwei Li<sup>a</sup>, Jie Xu<sup>a</sup>, Dejun Li<sup>a</sup>, Xueliang Sun<sup>c, a, b</sup>

<sup>a</sup> Tianjin International Joint Research Centre of Surface Technology for Energy Storage Materials, College of Physics and Materials Science, Tianjin Normal University, Tianjin, 300387, China

<sup>b</sup> Institute of Advanced Electrochemical Energy & School of Materials Science and Engineering, Xi'an University of Technology, Xi'an, 710048, China

<sup>c</sup> Nanomaterials and Energy Lab, Department of Mechanical and Materials Engineering, Western University London, Ontario N6A 5B9, Canada

#### A R T I C L E I N F O

Article history: Received 1 February 2019 Received in revised form 24 April 2019 Accepted 13 May 2019 Available online 16 May 2019

Keywords: Mixed transition-metal oxides CoSnO<sub>3</sub> rGO Self-matrices Sodium ion batteries

#### ABSTRACT

Mixed transition-metal oxides (MTMOs) are regarded as advanced electrode materials for sodium-ion batteries (SIBs). In this study, amorphous CoSnO<sub>3</sub> nanocubes wrapped by reduced graphene oxide (marked as a-CoSnO<sub>3</sub>@rGO) are successfully designed via a facile solvothermal method accompanied by a simple calcination process. To examine this design, sodium storage behaviors of a-CoSnO<sub>3</sub>@rGO nano-composites are investigated in detail. Compared with the pristine a-CoSnO<sub>3</sub>, a-CoSnO<sub>3</sub>@rGO nano-composite with 25.1 wt% rGO exhibits enhanced electrochemical performance, for instance, it delivers a high specific capacity of 229.9 mAh g<sup>-1</sup> after 100 cycles at 50 mA g<sup>-1</sup> with a Coulombic efficiency close to 99%, and it is capable of maintaining a specific capacity of 205.7 mAh g<sup>-1</sup> even at a high current density of 800 mA g<sup>-1</sup>. Superior electrochemical performance of a-CoSnO<sub>3</sub>@rGO is primarily attributed to intrinsic "self-matrices", rGO-wrapping network, and crystalline texture engineering. Indeed, the unique 3D-rGO-wrapping architecture of a-CoSnO<sub>3</sub>@rGO manifests compelling advantages, such as developing a high conductive three-dimensional network, facilitating the ion/electron diffusion, accommodating volume change, and strengthening interaction between rGO and a-CoSnO<sub>3</sub>. It is believed that the proposed strategy may provide new insights to design hybrid anode nano-materials for advanced SIBs.

© 2019 Elsevier Ltd. All rights reserved.

# 1. Introduction

Global scarcity and high price of lithium sources have been hindering further utilization of lithium ion batteries (LIBs) in largescale energy storage systems [1-6]. In this regard, sodium ion batteries (SIBs) have presented outstanding merits for applications in smart electric grids owing to the ubiquity of sodium in nature and similarity of its properties to lithium [7-11]. Nonetheless, larger radius of Na<sup>+</sup> ions affect the phase stability and transport properties of the anode material, resulting in low utilization and inferior rate capability [12]. Hence, the major scientific hurdle of SIBs can be addressed by developing an excellent anode material with long-term cycliability and high specific capacity.

Recently, many researchers have been investigating several transition-metal oxides (TMOs) electrode materials, such as VO<sub>2</sub> [13], TiO<sub>2</sub> [14], Co<sub>3</sub>O<sub>4</sub> [15], Fe<sub>2</sub>O<sub>3</sub> [11,16] and SnO<sub>2</sub> [17,18]. Nevertheless, the main issues of TMOs lie in severe volume expansion/ shrinkage during the sodiation/desodiation processes as well as unsatisfied electrochemical reaction kinetics, leading to low rate performance and limited cycle life [19]. Superior to monometal transition-metal oxides, mixed transition-metal oxides (MTMOs) have more preferable stability due to two kinds of metal elements with different expansion coefficients, and enhance electron transfer by reducing activation energy barriers between different cations. As we previously reported, NiSnO<sub>3</sub> exhibits more preferable lithium storage performance than the mechanical mixture of SnO<sub>2</sub> and NiO [8]. The performance improvement is due that Sn and NiO could mutually act as "self-matrices" during charge/discharge processes. In addition, the smart and particular "self-matrices" suppress the aggregation of the nanosized particle and buffer the large volume change. Moreover, comparatively modified electronic structures of MTMOs can lower the kinetic energy barriers in







<sup>\*</sup> Corresponding author. Institute of Advanced Electrochemical Energy & School of Materials Science and Engineering, Xi'an University of Technology, Xi'an, 710048, China.

E-mail address: xfli2011@hotmail.com (X. Li).

electrochemical processes [19]. For example, CoSnO<sub>3</sub> is a noteworthy member of MTMOs family, in which Co and Sn act as the conductive and buffering matrix materials. Indeed, the electrochemical performance of CoSnO<sub>3</sub> is superior to that of the mixture of SnO<sub>2</sub> and CoO [20]. However, the inherent drawbacks of MTMOsbased electrodes (i.e., poor electronic conductivity and inferior structural stability), considerably hampers the cycling stability of anode materials in SIBs [19,21].

Minimizing particle size of MTMOs down to nanoscale is a common approach, which could improve the diffusion rate of ion and alleviate the mechanical strain upon intercalation/deintercalation of Na<sup>+</sup> [22]. On the other hand, combining carbon-based materials with nano-sized particles is an effective strategy to enhance sodium storage [23]. Note that novel carbonaceous materials (i.e., reduced graphene oxide (rGO) [24], CNTs [25] and porous carbon [26]) have been extensively investigated as the suitable buffering and conductive matrix for MTMOs-based anodes. For example, CoSnO<sub>3</sub>@C nanoboxes exhibit super rate capability and wonderful cycle life (i.e., over 400 cycles) in LIBs [21]. It is considered that the main benefits of combining carbonaceous materials are to improve electrical conductivity, buffer the volume changes, and enhance the electrochemical performances of the anode materials upon cycling. Simultaneously, during sodium storage process, amorphous electrode materials with intrinsically isotropic nature may reduce the degradation of electrode associated with volume change upon cycling [27]. As our group previously reported, amorphous SnO<sub>2</sub> anodes show more outstanding sodium reversible capacity (380.2 mAh  $g^{-1}$  after 100 cycles at  $50 \text{ mAg}^{-1}$ ) than that of  $\text{SnO}_2$  anodes with crystalline phases  $(138.6 \text{ mAh g}^{-1} \text{ after } 100 \text{ cycles at } 50 \text{ mA g}^{-1})$  [17]. Hence, engineering crystalline texture significantly affect cycling capability in SIBs.

In this work, amorphous CoSnO<sub>3</sub> wrapped by reduced graphene oxide (marked as a-CoSnO<sub>3</sub>@rGO) is successfully synthesized. As anodes for SIBs, they exhibit remarkable rate capacity and cycling stability due to intrinsic "self-matrices", rGO-wrapping network, and crystalline texture engineering. Therefore, the designed a-CoSnO<sub>3</sub>@rGO electrode could hold high promise for further development of advanced sodium storage devices.

#### 2. Experimental section

#### 2.1. Materials preparation

### 2.1.1. Preparation of CoSn(OH)<sub>6</sub>@rGO nanocubes

In a typical synthesis, Na<sub>2</sub>SnO<sub>3</sub> solution (1 mmol Na<sub>2</sub>SnO<sub>3</sub>·3H<sub>2</sub>O dissolved in 20 mL deionized (DI) water) was dropped into CoSO<sub>4</sub> solution (1 mmol CoSO<sub>4</sub>·7H<sub>2</sub>O dissolved in 20 mL DI water). After dropping, the mixture was stirred for 1 h. The pink CoSn(OH)<sub>6</sub> was acquired via centrifugation method, as well as dried in air oven. Graphite oxide (GO) was synthesized according to a modifying method based on Hummer's preparation method from graphite powders [29]. Afterwards, 10 mL of GO suspension liquid  $(2.0 \text{ mg mL}^{-1})$  was added into butanol (30 mL). Then x mg (x = 235.5 mg, 50.0 mg, 29.0 mg) of CoSn(OH)<sub>6</sub> was put into the above solution with continuous stirring for 0.5 h. Then, the above mixture was put into a 50 mL Teflon container. Then, the container was encapsulated in a stainless steel autoclave followed by maintaining at 180 °C for 6 h. Finally, the black powders were obtained via suction filtration followed by freeze-drying. The final products were denoted as CoSn(OH)<sub>6</sub>@rGO-I, CoSn(OH)<sub>6</sub>@rGO-II and CoSn(OH)<sub>6</sub>@rGO-III, respectively.

#### 2.2. Preparation of a-CoSnO<sub>3</sub>@rGO nanocomposites

To obtain a-CoSnO<sub>3</sub>@rGO nanocomposites, CoSn(OH)<sub>6</sub>@rGO was thermally annealed at 300 °C (heating rate of 1 °C min<sup>-1</sup>) for 4 h in argon atmosphere. The final products are denoted as a-CoSnO<sub>3</sub>@rGO-I, a-CoSnO<sub>3</sub>@rGO-II and a-CoSnO<sub>3</sub>@rGO-III, respectively. This process is illustrated in Scheme 1. Furthermore, the pristine a-CoSnO<sub>3</sub> was prepared by the similar route, without adding GO dispersion. The pure rGO was obtained under the similar reaction conditions.

## 2.3. Materials characterization

The structural information and compositions of the as-prepared samples were carried out on X-ray diffraction (XRD, Bruker AXS D8 Advance, Cu-K<sub> $\alpha$ </sub> radiation), X-ray photoelectron spectroscopy (XPS, VG ESCALAB MK II), Raman analysis (LabRAM HR800 system, HORIBA). The amount of rGO in the a-CoSnO<sub>3</sub>@rGO nanocomposites was estimated by thermogravimetric analysis (TGA, Pyris Diamond6000, PerkinElmer Co., America) from room temperature to 600 °C (10 °C min<sup>-1</sup>) in air. Nitrogen adsorption/ desorption isotherms were conducted by using Quantachrome ASIQ2. The microstructures and morphologies of the samples were investigated by scanning electron microscopy (SEM, SU8010, Hitachi) equipped with energy dispersive spectroscopy (EDS, OXFORD 7426) mapping, and transmission electron microscopy (TEM, JEOL JEM-3000F).

#### 2.4. Electrochemical characterization

The electrochemical performances of the anode materials were studied by using CR2032-type coin half cells, and the whole assembly process was in an argon-filled glovebox. The working electrodes consisted of 80 wt% active material, 10 wt% carbon black (super P), and 10 wt% carboxymethyl cellulose (CMC) binder by weight. The well-mixed black slurry was spread on Cu foil and dried for 15 h at 80 °C. The painted electrodes were punched into 12 mm circular pieces (the average mass loading of active materials is  $0.64 \text{ mg cm}^{-2}$ ), which were used as the working electrode. The separator was glass fiber filter paper (GF/F, Whatman), and the counter electrode was Na metal foils. 1 M sodium perchlorate (NaClO<sub>4</sub>) in ethylene carbonate/propylene carbonate (EC/PC, 1:1 vol %) was employed as the electrolyte solution. The galvanostatic cycling testings and rate capability were carried out using a battery testing system with the model of Land CT2001A, fixing the potential range to 0.01–3.0 V vs Na/Na<sup>+</sup>. Cyclic voltammetry (CV, scanning rate of 0.1 mV s<sup>-1</sup>, 0.01–3.0 V vs Na/Na<sup>+</sup>) and Electrochemical impedance spectroscopy (EIS, frequency range from 0.01 Hz to 100 kHz, amplitude voltage of 5 mV) were studied by a Princeton Applied Research VersaSTAT4.

## 3. Results and discussion

Fig. 1a shows the XRD patterns of the pure  $CoSn(OH)_6$  and CoSn(OH)6@rGO nanocomposites with different rGO contents. All diffraction peaks of the bare CoSn(OH)<sub>6</sub> are assigned to the standard diffraction data of perovskite cubic Pn-3m structure of cobalt tin hydroxide (JCPDS No. 13-0356) [30], indicating its high degree of crystallinity. Simultaneously, all the three CoSn(OH)6@rGO nanocomposites exhibit strong diffraction peaks at identical positions, which is similar to XRD pattern of the pure CoSn(OH)<sub>6</sub> without noticeable signals of impurity peaks. Thus, it reflects that the phase of CoSn(OH)<sub>6</sub> reveals no distinct change during the process of rGO wrapping. After annealing in Ar, a-CoSnO<sub>3</sub> nanocubes are obtained decomposition by thermal of  $CoSn(OH)_6$ 



Scheme 1. Schematic illustration of the synthesis process of a-CoSnO3@rGO nanocomposites.



Fig. 1. (a) XRD patterns of CoSn(OH)<sub>6</sub>, CoSn(OH)<sub>6</sub>@rGO-I, CoSn(OH)<sub>6</sub>@rGO-II and CoSn(OH)<sub>6</sub>@rGO-III. (b) XRD patterns of pristine a-CoSnO<sub>3</sub>, a-CoSnO<sub>3</sub>@rGO-I, a-CoSnO<sub>3</sub>@rGO-II and a-CoSnO<sub>3</sub>@rGO-III. (c) TGA curves of a-CoSnO<sub>3</sub>@rGO-I, a-CoSnO<sub>3</sub>@rGO-II and a-CoSnO<sub>3</sub>@rGO-III. (d) Raman spectra of a-CoSnO<sub>3</sub>@rGO-I, a-CoSnO<sub>3</sub>@rGO-II and pristine rGO.

 $(CoSn(OH)_6 \rightarrow 3H_2O + CoSnO_3)$ . The XRD patterns of bare a-CoSnO<sub>3</sub> and a-CoSnO<sub>3</sub>@rGO nanocomposites with different rGO contents are depicted in Fig. 1b. Remarkably, there is a plain pattern with a broad peak at 34° in all samples, proving the formation of a $CoSnO_3$ , which is consistent with the previous literature reports [21,28,31]. Observably, with the rGO content increases, the diffraction peak of the rGO gradually emerges, especially for the  $CoSnO_3@rGO-III$  with the peak of a reflection at around 41°,

manifesting the close integration of the both in the nanocomposites. In the XRD patterns of GO and rGO (Fig. S1), it is noteworthy that the sharp diffraction peak (002) of GO at 10.8° disappears, which demonstrates that GO was translated to rGO during solvothermal and annealing treatments due to the removal of most oxygen-containing functional groups of GO [32].

Thermogravimetric analysis (TGA) was employed to measure rGO contents in a-CoSnO<sub>3</sub>@rGO nanocomposites (Fig. 1c). The initial weight loss (up to 150 °C) is associated with the evaporation of moisture. Based on the weight loss of carbon (between 150 °C and 420 °C) [31], the contents of rGO of a-CoSnO<sub>3</sub>@rGO-I, a-CoSnO3@rGO-II and a-CoSnO3@rGO-III are calculated to be about 11.4 wt%, 25.1 wt%, and 38.1 wt%, respectively. Fig. 1d shows Raman spectra of the pristine rGO and the three a-CoSnO<sub>3</sub>@rGO nanocomposites. Notably, all samples show two peaks at 1341  $\text{cm}^{-1}$  and 1583 cm<sup>-1</sup>, which are in good agreement with D band caused by defective or disordered carbon, as well as G band originated from ordered graphitic carbon [32]. Generally, the intensity ratio of  $I_D/I_G$ is employed to measure the degree of structural disorders in carbon material [33]. Based on the fitting of Raman spectroscopy, the I<sub>D</sub>/I<sub>G</sub> ratios of a-CoSnO3@rGO-I, a-CoSnO3@rGO-II, a-CoSnO3@rGO-III and the pristine rGO are 1.59, 1.47, 1.41 and 1.35, respectively. Compared with the pristine rGO, the higher  $I_D/I_G$  ratio of a-CoSnO<sub>3</sub>@rGO indicates more disorders, which is due to the intervention of the encapsulated a-CoSnO<sub>3</sub> nanocubes in 3D-rGO networks. Furthermore, the Brunauer-Emmett-Teller (BET) specific surface area (Fig. S2a) of a-CoSnO<sub>3</sub>@rGO-II is estimated to be  $189.33 \text{ m}^2 \text{ g}^{-1}$  and larger than that of bare a-CoSnO<sub>3</sub> (135.56 m<sup>2</sup> g<sup>-1</sup>). From the corresponding pore-size distribution curves (Fig. S2b), the pore size of the bare a-CoSnO<sub>3</sub> mainly concentrate at 1.4 nm, however, the a-CoSnO<sub>3</sub>@rGO-II is possessed with the more developed mesopore peak centered around 3.8 nm. Such a large surface area with porous structure may not only provide an ample buffer space for huge volume expansion/shrinkage [34], but also accelerate Na<sup>+</sup> diffusion to achieve a high rate capability [6].

To further elucidate the chemical bonding states and elemental composition, X-ray photoelectron spectroscopy (XPS) spectra of a-CoSnO<sub>3</sub>@rGO-II were investigated. As illustrated in Fig. 2a, the survey spectrum result confirms the existence of Co, Sn, C and O atoms. Fig. 2b displays the high resolution XPS spectrum of Sn 3d where the binding energy at 495.2 eV and 486.7 eV are characteristics of  $3d_{3/2}$  and  $3d_{5/2}$ , respectively, which is in agreement with Sn<sup>4+</sup> state [31]. In the XPS spectrum of Co 2p (Fig. 2c), the two spinorbit doublet peaks at 780.9 and 796.6 eV can be related to Co  $2p_{3/2}$  and 802.8 eV. As we know, Co<sup>2+</sup> and Co<sup>3+</sup> states reveal similar binding energy peaks in the XPS spectrum of Co 2p. Correspondingly, there are two main peaks at binding energies near 780.0 and 796.0 eV, which correspond to Co  $2p_{3/2}$  and Co  $2p_{1/2}$  levels. However, for diverse valence state configurations, the values of binding



Fig. 2. XPS spectra of a-CoSnO<sub>3</sub>@rGO-II: (a) original XPS survey spectrum, (b) Sn 3d spectrum, (c) Co 2p spectrum, (d) C 1s spectrum.

energy separation are different from each other due to the spinorbit couplings configurations with  $\Delta E = 15.7 \text{ eV}$  for  $\text{Co}^{2+}$  and  $\Delta E = 15.0 \text{ eV}$  for  $\text{Co}^{3+}$ . Furthermore, the two strong peaks of Co 2p are located at 780.9 and 796.6 eV with a splitting energy of 15.7 eV, identifying the presence of  $\text{Co}^{2+}$  in a-CoSnO<sub>3</sub>@rGO-II sample [35,36]. Consequently, the existence of Sn<sup>4+</sup> and Co<sup>2+</sup> in a-CoSnO<sub>3</sub>@rGO-II nanocomposite can be reasonably concluded. Additionally, as shown in Fig. 2d, the high resolution C 1s XPS spectrum of a-CoSnO<sub>3</sub>@rGO-II can be fitted with four components: graphitized carbon bonds (sp<sup>3</sup> carbon, 285.2 eV; sp<sup>2</sup> carbon, 284.5 eV), hydroxyl and epoxy groups (C - O, 286.3 eV), carboxyl groups (O - C = O, 289.0 eV) and carbonyl groups (C = O, 287.6 eV). For the O 1s spectrum (Fig. S3), the binding energy of 531.7 eV could be related to metal-oxygen bonds and remanent oxygen-containing groups derived from rGO [33].

As shown in Fig. 3a, the bare a-CoSnO<sub>3</sub> consists of entirely uniform nanocubes with an average edge length of around 100 nm, which can be further confirmed by the low-magnification TEM image (Fig. 3b). Moreover, HRTEM image (Fig. 3c) demonstrates that the entire surface of the nanocube is rough, and no crystalline lattice fringe is observed, revealing the amorphous texture of CoSnO<sub>3</sub> nanocubes. Meanwhile, the SAED patterns of a-CoSnO<sub>3</sub> nanocubes (the inset of Fig. 3c) manifest dispersed and ambiguous halo rings with amorphous nature, which is well consistent with the XRD results [21]. For a-CoSnO<sub>3</sub>@rGO-I (Fig. 3d), a mass of aCoSnO<sub>3</sub> nanocubes are attached to the surface of rGO and formed an anti-coated structure. With the increase of rGO, a-CoSnO<sub>3</sub> nanocubes are homogeneously wrapped by wrinkled rGO in a-CoSnO<sub>3</sub>@rGO-II (Fig. 3e). Notably, the transparent gauze-like rGO is shown in Fig. S4. Remarkably, the highly crumpled rGO encapsulated a-CoSnO<sub>3</sub> forms a 3D continuous porous network structure. which may be conducive to increase the electrical conductivity and provide volume buffers for a-CoSnO<sub>3</sub> in the sodiation/desodiation processes. However, a-CoSnO3@rGO-III exhibits a scattering of a-CoSnO<sub>3</sub> nanocubes sparsely dispersed on the rGO nanosheets (Fig. 3f). As a result, introduction of a rational amount of rGO could form a continuous and conductive network texture to enhance the storage capacity and cyclic performance. Furthermore, TEM image of a-CoSnO<sub>3</sub>@rGO-II (Fig. 3g) further demonstrates the transparent interconnected gauze-like rGO evenly encapsulates a-CoSnO<sub>3</sub> nanocubes, and constitutes a high conductive 3D architecture network. The HRTEM image (the inset of Fig. 3g) reveals the amorphous structure of a-CoSnO<sub>3</sub>@rGO-II with a widespread disorder. EDS mapping of a-CoSnO<sub>3</sub>@rGO-II (Fig. 3h) proves the homogeneous distribution of Sn, O, Co and C elements originated from rGO and a-CoSnO<sub>3</sub>.

The electrochemical properties of the bare a-CoSnO<sub>3</sub>, the pristine rGO and the three a-CoSnO<sub>3</sub>@rGO nanocomposites were conducted through cyclic voltammetry (CV), as depicted in Fig. 4 and Fig. S5. For the pristine rGO anode, it can be observed from Fig. S5



Fig. 3. (a) SEM image of bare a-CoSnO<sub>3</sub>. (b) TEM and (c) HRTEM images of bare a-CoSnO<sub>3</sub> (the insert is selected-area diffraction (SAED) pattern). SEM images of (d) a-CoSnO<sub>3</sub>@rGO-I, (e) a-CoSnO<sub>3</sub>@rGO-II, and (f) a-CoSnO<sub>3</sub>@rGO-III. (g) TEM image of a-CoSnO<sub>3</sub>@rGO-II (the insert is HRTEM image). (h) EDS mapping of a-CoSnO<sub>3</sub>@rGO-II.



Fig. 4. The cyclic voltammetry curves of (a) bare a-CoSnO<sub>3</sub>, (b) a-CoSnO<sub>3</sub>@rGO-I, (c) a-CoSnO<sub>3</sub>@rGO-II, and (d) a-CoSnO<sub>3</sub>@rGO-III at a scanning rate of 0.1 mV s<sup>-1</sup> in the voltage window of 0.01–3.0 V.

that a reduction peak shows up at 1.1 V in the first discharge curve, which is likely to be generated from the formation of the solid electrolyte interphase (SEI) film on the electrode surface. Note that there is no corresponding redox peak occurs in the succedent cycle, showing a typical characteristic of rGO. In the initial cathodic processes of all four electrodes (Fig. 4), a similar broad reduction wave from 0.03 V to 1.5 V can be observed, which might be generated from the formation of solid electrolyte interface (SEI) layer on the surface of electrode, the reductive reaction of CoSnO<sub>3</sub> with Na that forms Sn, CoO and Na<sub>2</sub>O, the further reduction of CoO into Co, as well as the transformation of Sn into Na<sub>X</sub>Sn alloys [8,28,31]. Noticeably, the reduction peaks have shifted to higher potential of 0.8 V at subsequent scans, indicating a structural reorganization. Furthermore, for CV curves of the three a-CoSnO<sub>3</sub>@rGO nanocomposites, the reductant peaks from 0.03 V to 1.5 V correspond to the conversion reaction between CoO and Na<sup>+</sup> and the alloying reaction between Sn and Na<sup>+</sup>. During the positive scans of all samples, the anodic peaks are attributed to the re-oxidation of Co to CoO and the dealloying reaction of Na<sub>x</sub>Sn [17,37,38]. All in all, the electrochemical reactions can be explicated as:

$$CoSnO_3 + Na^+ + e^- \rightarrow CoO + Sn + Na_2O$$
(1)

$$CoO + 2 Na^{+} + 2 e^{-} \leftarrow \rightarrow Co + Na_{2}O$$
(2)

$$Sn + x Na \leftarrow \rightarrow Na_x Sn$$
 (3)

Note that all redox peaks of  $a-CoSnO_3@rGO-II$  remain almost overlapped in the succedent cycles with good  $eSn + x Na \leftarrow \rightarrow Na_xSn$  lectrochemical reversibility and high stability [39].

Fig. 5a–d displays the galvanostatic discharge/charge profiles of the bare a-CoSnO<sub>3</sub>, a-CoSnO<sub>3</sub>@rGO-I, a-CoSnO<sub>3</sub>@rGO-II and a-CoSnO<sub>3</sub>@rGO-III electrodes in the 1st, 2nd, 3rd, 4th, 5th and 10th cycles at a current density of 50 mA g<sup>-1</sup>, fixing the potential range to 0.01–3.0 V vs Na/Na<sup>+</sup>. The specific capacity of the pristine rGO is 498.4 mAh g<sup>-1</sup> in the first cycle, which dramatically drops to 236.9 mAh g<sup>-1</sup> in the second cycle (Fig. S6). The initial discharge/ charge specific capacities of the bare a-CoSnO<sub>3</sub>, a-CoSnO<sub>3</sub>@rGO-I, a-CoSnO<sub>3</sub>@rGO-II and a-CoSnO<sub>3</sub>@rGO-III electrodes are 499.8/ 292.1 mAh g<sup>-1</sup>, 546.9/382.6 mAh g<sup>-1</sup>, 636.9/393.7 mAh g<sup>-1</sup> and 488.2/258.6 mAh g<sup>-1</sup>, receptively. Moreover, a-CoSnO<sub>3</sub>@rGO-II anode shows the highest reversible capacity. The initial Coulombic efficiency of a-CoSnO<sub>3</sub>@rGO-II anode is 63%, and it increases significantly to near 99% after a few cycles, which further confirms that the Na<sup>+</sup> intercalation/deintercalation of a-CoSnO<sub>3</sub>@rGO-II is highly reversible.

Fig. 6a compares the cycling performance of the as-prepared anode materials at  $50 \text{ mA g}^{-1}$  between 0.01 and 3.0 V vs Na<sup>+</sup>/Na. The pristine rGO exhibits a poor specific capacity of 143.4 mAh g<sup>-1</sup> after 100 cycles. Indeed, the pristine a-CoSnO<sub>3</sub> shows a dramatic



**Fig. 5.** The galvanostatic discharge/charge profiles of the bare a-CoSnO<sub>3</sub>, a-CoSnO<sub>3</sub>@rGO-II and a-CoSnO<sub>3</sub>@rGO-II electrodes in the 1st, 2nd, 3rd, 4th, 5th and 10th cycles in the potential range of 0.01–3.0 V versus Na/Na<sup>+</sup> at a current density of 50 mA  $g^{-1}$ .

capacity decay; its discharge specific capacity decreases to 142.7 mAh  $g^{-1}$  in the 100th cycle with inferior cycling performance, originating from the severe volumetric change and poor electrical conductivity. Favorably, all a-CoSnO<sub>3</sub>@rGO nanocomposites anodes exhibit improved cycling capabilities due to the synergistic effect between a-CoSnO<sub>3</sub> nanocubes and plicated rGO. However, a-CoSnO<sub>3</sub>@rGO-I anode with the 11.4 wt% content of rGO exhibits an unsatisfactory discharge capacity after 40 cycles, which could be ascribed to the partial aggregation of a-CoSnO3 and segmental structural damage due to the inadequate rGO wrapping. When the content of rGO increases to 25.1 wt%, a-CoSnO3@rGO-II delivers a discharge capacity of 229.9 mAh g<sup>-1</sup> after 100 cycles. Coulombic efficiencies of a-CoSnO<sub>3</sub>@rGO-II close to 99% after the 5th cycle. Moreover, the reversible specific capacity of a-CoSnO<sub>3</sub>@rGO-III with 38.1 wt% rGO is lower than that of a-CoSnO<sub>3</sub>@rGO-II. Therefore, it is of importance to employ the appropriate amount of rGO in a-CoSnO<sub>3</sub>@rGO nanocomposites for superior cycling performance.

Rate performance of the prepared electrodes was investigated at different current densities from 50 to 800 mA g<sup>-1</sup>. As presented in Fig. 6b, with the current densities increasing, the capacity of the bare a-CoSnO<sub>3</sub> decreases quickly, achieving only 39.5 mAh g<sup>-1</sup> at 800 mA g<sup>-1</sup>. By contrast, the other three a-CoSnO<sub>3</sub>@rGO nano-composites anodes show higher capacities at high rates. Conspicuously, the average specific capacities of 340.5, 302.1, 266.3, 232.4, and 205.7 mAh g<sup>-1</sup> can be obtained for a-CoSnO<sub>3</sub>@rGO-II electrode

at ascending current densities of 50, 100, 200, 400 and 800 mA  $g^{-1}$ , respectively, which exhibits much higher than those of a-CoSnO<sub>3</sub>@rGO-I and a-CoSnO<sub>3</sub>@rGO-III electrodes. Moreover, a-CoSnO<sub>3</sub>@rGO-II anode could still recover back to the discharge capacity of 273.4 mAh  $g^{-1}$  at the 80th cycle when the current density is returned back to  $50 \text{ mA g}^{-1}$ , which is even more than the obtained results of the electrode cycled in Fig. 6a. Fig. S7 compares the capacity retention values of bare a-CoSnO3, a-CoSnO3@rGO-I, a-CoSnO3@rGO-II and a-CoSnO3@rGO-III electrodes at various current densities. Based on the analysis above, a-CoSnO<sub>3</sub>@rGO-II electrode with a 3D-rGO-wrapping structure is an extremely promising anode for SIBs. To fully demonstrate the advantages of 3D-rGOwrapping architecture, the long-term cycling stabilities of the bare a-CoSnO<sub>3</sub> and a-CoSnO<sub>3</sub>@rGO-II are investigated at a high current density of 1500 mA  $g^{-1}$  (Fig. 6c). As expected, the specific capacity of a-CoSnO<sub>3</sub>@rGO-II can remain as high as 143.2 mAh  $g^{-1}$  after 250 cycles, while the bare a-CoSnO3 electrode is close to failure after 100 cycles, revealing that the stable structure derived from the interconnected rGO network is in favor of improving the transmission of the ions and electrons. This result is superior to previously reported electrochemical properties of SnO2-based and Co<sub>x</sub>O<sub>y</sub>-based materials for sodium ion batteries, which as listed in Table S1. Fig. S8 compares the morphologies of the cycled bare a-CoSnO<sub>3</sub> and a-CoSnO<sub>3</sub>@rGO-II anodes after 100 cycles. One can see from Fig. S8a and b that bare a-CoSnO<sub>3</sub> has aggregated. In contrast,



**Fig. 6.** (a) The cycling performance of bare a- $CoSnO_3@rGO-I$ , a- $CoSnO_3@rGO-II$ , a- $CoSnO_3@rGO-II$  and pristine rGO at a current density of 50 mA g<sup>-1</sup>. (b) Rate capability of bare a- $CoSnO_3$ , a- $CoSnO_3@rGO-II$ , a- $CoSnO_3@rGO-II$  at various current densities of 50, 100, 200, 400 and 800 mA g<sup>-1</sup>. (c) Long-term cycling stabilities of bare a- $CoSnO_3$  and a- $CoSnO_3@rGO-II$  at a high current density of 1500 mA g<sup>-1</sup>. The CV curves of (d) bare a- $CoSnO_3@rGO-II$  in the potential range of 0.01–3.0 V at scanning rates of 0.1, 0.2, 0.4, 0.6, and 0.8 mV s<sup>-1</sup>. (f) The corresponding relationship between I<sub>p</sub> and v<sup>1/2</sup>.

a-CoSnO<sub>3</sub>@rGO-II nanocomposite still retains the geometric confinement of a-CoSnO<sub>3</sub> nanocubes. To sum up, the results manifest potential applicability of a-CoSnO<sub>3</sub>@rGO nanocomposite anode to advanced sodium-ion storage devices of high power density.

To investigate the electrochemical kinetics of sodium storage, the CV curves of the bare a-CoSnO<sub>3</sub> and a-CoSnO<sub>3</sub>@rGO-II was measured at different sweep rates (0.1, 0.2, 0.4, 0.6 and 0.8 mV s<sup>-1</sup>). In Fig. 6d and e, the currents of both anodic and cathodic peaks enhance with increasing the sweep rate. Simultaneously, due to the increase of sweep rate, it appears a negative-going shift of the cathodic peaks to lower values and a positive-going shift of the anodic peaks to higher potentials, which is concerned with the impacts of polarization due to the restrained kinetics of sodium diffusion across the anode materials. Meanwhile, as shown in Fig. 6f, the redox peak current (I<sub>p</sub>) exhibits a linear relationship with square root of the sweep rate ( $v^{1/2}$ ), explaining the diffusion process of the sodium ions have an enormous influenced on the electrochemical kinetics [17]. The sodium-ion diffusion coefficient of bare a-CoSnO<sub>3</sub> and a-CoSnO<sub>3</sub>@rGO-II can be calculated by the Randles-Sevcik equation (1) [40]:

$$I_p = 2.687 \times 10^5 \times n^{3/2} \times A \times D^{1/2} \times v^{1/2} \times C_0$$
 (1)

Where n is the charge-transfer number in the specific electrochemical reactions, A is the geometric area of electrode  $(A = 1.13 \text{ cm}^2)$ , v is the potential scan rate (V s<sup>-1</sup>), C<sub>0</sub> is the initial concentration of Na-ions in the solution (C<sub>0</sub> = 1 mol cm<sup>-3</sup>), and D is the diffusion coefficient of Na-ions (cm<sup>2</sup> s<sup>-1</sup>). According to Equation (4), the sodium diffusion coefficient of the bare a-CoSnO<sub>3</sub> is estimated as  $2.78 \times 10^{-16} \text{ cm}^2 \text{ s}^{-1}$ , and the corresponding values of a-CoSnO<sub>3</sub>@rGO-II increases to  $2.39 \times 10^{-15} \text{ cm}^2 \text{ s}^{-1}$ . Hence, the enhanced ion diffusivity of a-CoSnO<sub>3</sub>@rGO could be related to rGO wrapping. Furthermore, rGO wrapping can provide nanospaces between rGO nanosheets and a-CoSnO<sub>3</sub> nanocubes. The unique rGO-wrapping architecture is remarkably desirable for superior sodium storage because the existence of nanospaces can facilitate Na-ions diffusion to the encapsulated a-CoSnO<sub>3</sub> nanocubes [41].

Electrochemical impedance spectroscopy (EIS) was measured to analyze the kinetic process of half-cell upon cycling. Fig. 7a reveals the EIS spectra of bare a-CoSnO<sub>3</sub> and a-CoSnO<sub>3</sub>@rGO-II electrodes at a full-discharged state after varying cycles. The two semicircles at high and middle frequency regions are related to the interfacial film resistance and charge transfer process, while a sloping line at low frequency region is attributed to sodium-ion diffusion through electrode materials [42]. In the equivalent circuit (Fig. S9a), R<sub>s</sub> displays resistance of electrolyte solution, R<sub>sf</sub> represents resistance of SEI film, R<sub>ct</sub> is charge transfer resistance related to electrode/ electrolyte interface, and Z<sub>w</sub> is Warburg impedance originating from diffusion of Na<sup>+</sup> within the anode materials [43]. Notably, CPEsf and CPEct stand for the space charge capacitance of the SEI film and double-layer capacitance of the electrode, arising from the inhomogeneous surface of the active materials. As displayed in Fig. 7b, it is noteworthy that the R<sub>ct</sub> value of a-CoSnO<sub>3</sub>@rGO-II was lower than those of a-CoSnO<sub>3</sub>, implying that the diminution of R<sub>ct</sub> can be result of the introduction of a high conductive 3D-rGO network. The R<sub>ct</sub> value of the bare a-CoSnO<sub>3</sub> initially reduced from  $314\,\Omega$  (1st cycle) to  $194\,\Omega$  (10th cycle), and then increased to  $295\,\Omega$ (50th cycle). Strikingly, the R<sub>ct</sub> values of a-CoSnO<sub>3</sub>@rGO-II display a similar variation tendency. The abnormal change of the R<sub>ct</sub> values by increasing the number of cycles could be due to the slow activation process of the anode materials [34]. To be specific, the initial decrease of the R<sub>ct</sub> values may be relevant to the gradual permeation of the organic electrolyte, which can provide a bigger electrochemical interface between electrolyte and electrode and further improve the charge transfer kinetics [44]. In the case of R<sub>sf</sub>, compared with the bare CoSnO<sub>3</sub> anode, the a-CoSnO<sub>3</sub>@rGO-II electrode exhibits smaller impedance with the similar trend. It is



**Fig. 7.** (a) The EIS spectra of bare a-CoSnO<sub>3</sub> and a-CoSnO<sub>3</sub>@rGO-II electrodes at a full-discharged state in the frequency range from 0.01 Hz to 100 kHz after different cycles. (b) EIS parameters ( $R_{ct}$  and  $R_{sf}$ ) of bare a-CoSnO<sub>3</sub> and a-CoSnO<sub>3</sub>@rGO-II electrodes derived from the equivalent circuit. (c) The EIS spectra of a-CoSnO<sub>3</sub>@rGO-II electrode at different discharge/charge depths in the frequency range from 0.01 Hz to 100 kHz during the first one-and-a-half cycles. (d) EIS parameters ( $R_{ct}$  and  $R_{sf}$ ) of a-CoSnO<sub>3</sub>@rGO-II electrode derived from the equivalent circuit.

worth noting that the abrupt change of  $R_{sf}$  (2nd cycle) is observed clearly, which could be related to the growth of the SEI film on the material surface. After 2 cycles, the Rsf value of the a-CoSnO3@rGO-II remains a relatively stable state, explicating the stability of the SEI film [43,46]. Fig. 7c shows the EIS spectra of a-CoSnO<sub>3</sub>@rGO-II electrode at different charge/discharge depths during the first oneand-a-half cycles, fixing the frequency range to 0.01–100000 Hz. According to the equivalent circuit, the kinetic parameters are illustrated in Fig. 7d. Initially, the value of R<sub>ct</sub> exhibits a sudden drop from the first point to the second point, and then it increases with the increase of discharge depth in the first discharge process. Following the first charge process,  $R_{ct}$  reaches a maximum of 353  $\Omega$ , and slowly decreases with the increase of charge depth. The value of  $R_{ct}$  drops to a minimum (209  $\Omega$ ) when the charge depth is 1.3 V. Afterwards, the values of R<sub>ct</sub> reach to a relatively stable state. The values of R<sub>ct</sub> are the main contribution to total resistance upon cycling, which could directly reflect the potential polarization degree [34]. The increasing R<sub>ct</sub> observed at the starting of the 1st discharge process may be related to the polarization phenomenon, while the similar variation of R<sub>ct</sub> is not detected during the 2nd discharge process [45]. In the 1st charge process, such a gradual decrease of  $R_{ct}\xspace$  value indicates that the electrochemical reaction becomes easier in the voltage range of 0.4-1.3 V. The variation tendency in R<sub>ct</sub> could be primarily ascribed to the enlarged surface area of the anode owing to conversion reactions in the 1st discharge process. The enhanced contact between electrolyte and the active material not only improves electrode activity, but also reduces the impedance of R<sub>ct</sub> [46]. Interestingly, the change tendency of the R<sub>sf</sub> value can almost resemble that of the R<sub>ct</sub> value in the first one-and-a-half cycles. Firstly, the value of R<sub>sf</sub> gradually increases until the charge potential of 0.9 V in the 1st cycle. This phenomenon can reflect the forming process of the SEI layer. After that, the fall of R<sub>sf</sub> value could be attributed to the partial decomposition of the SEI film in the 1st change process [34,47]. Notably, during the 2nd discharge-charge cycle, the R<sub>sf</sub> value arrives at a relatively stable level. Therefore, it is significant for the value of R<sub>ct</sub> and R<sub>sf</sub> to return to the relatively stable state in the initial cycling process, which can be advantageous to the excellent cycling stability of the a-CoSnO<sub>3</sub>@rGO-II [43]. Fig. S9b and c exhibit the Nyquist plots of a-CoSnO<sub>3</sub>@rGO-II at different charge/discharge potentials in the 2nd and 10th cycles, respectively. However, the diameters of all semicircles during the 2nd cycle are smaller than those of 10th, suggesting reduced charge-transfer resistances.

To determine the sodiation/desodiation mechanism of the



Fig. 8. HRTEM images and corresponding SAED patterns of the a-CoSnO<sub>3</sub>@rGO-II electrode at different potentials state in 5th discharge/charge process: (a and b) fully discharged to 0.01 V, (c and d) charged to 3.0 V.

CoSnO<sub>3</sub>@rGO nanocomposite, the fully charged and discharged states of the electrode are conducted through the ex-situ HRTEM and SAED measurements, and the results are presented in Fig. 8. When the a-CoSnO<sub>3</sub>@rGO-II anode is discharged to 0.01 V (Fig. 8a), the *d*-spacings of 0.203, 0.213, and 0.191 nm could be assigned to the (541) and (611) crystal plane of the Na<sub>15</sub>Sn<sub>4</sub> phase (JCPDS No. 31-1327) and the (101) crystal plane of the Co phase (JCPDS No. 05-0727), respectively. In addition, the corresponding SAED image (Fig. 8b) elucidates the appearance of the above two phase. Fig. 8c and d are the HRTEM and SAED images of the electrode after fully charged. The *d*-spacings of 0.262 and 0.227 nm could be characteristic of the (110) crystal plane of Sn phase (JCPDS No. 19-1365) and the (200) crystal plane of the CoO phase (JCPDS No. 42-1300), respectively, as exhibited in Fig. 8c. Furthermore, the CoO and Sn phase can be observed in SAED pattern of Fig. 8d. These results reveal the re-oxidation of Co to CoO and the dealloying reaction of Na<sub>X</sub>Sn during the desodiation process.

To further confirm the sodiation and desodiation process, the ex-situ XPS analysis of the fully charged and discharged a-CoS- $nO_3@rGO$ -II electrode are performed. Fig. S10a and b display the Co 2p and Sn 3d spectra of a-CoSnO<sub>3</sub>@rGO-II discharged to 0.01 V in the 5th cycle. In the XPS spectrum of Co 2p, the two new peaks at 778.3 eV and 793.2 eV are in agreement with  $2p_{3/2}$  and  $2p_{1/2}$  of  $Co^0$ , respectively [38]. Compared with the high-resolution XPS spectrum of Sn 3d of the initial state (Fig. 2b), one can observe from Fig. S10b that the binding energies of Sn  $3d_{3/2}$  and Sn  $3d_{5/2}$  have reduced to 493.5 eV and 485.0 eV, respectively, which can be correlated with the reduction process of Sn<sup>4+</sup> to Sn<sup>0</sup> [48,49]. The result certifies that CoSnO<sub>3</sub> can be able to transform into the Sn-based and Co metallic specimen at the full discharged state. When charging back to 3.0 V (Fig. S10c), the corresponding peaks of

Co<sup>0</sup> 2p have disappeared; meanwhile, the Sn 3d XPS spectrum in Fig. S10d indicates the Sn can maintain the valence state of 0 during fully desodiation. Apparently, the ex-situ XPS result coincides with the ex-situ HRTEM and SAED data. Hence, the ex-situ XPS analysis combined with the ex-situ HRTEM and SAED technique can convincingly support the proposed electrochemical mechanisms (reactions 1-3) and the discussions on Scheme 2.

The extraordinary electrochemical performance of a-CoSnO<sub>3</sub>@rGO nanocomposites can be on account of the following points: (i) as demonstrated in Scheme 2, the reductive reaction of CoSnO<sub>3</sub> with Na can convert to Na<sub>2</sub>O, Sn and CoO in the 1st discharge process. Clearly, the formed Na<sub>2</sub>O can serve on the matrix. Notably, when alloying between Sn with Na, CoO can serve on a "matrix". Meanwhile, Sn can serve on a "matrix" when converting between CoO and Na<sup>+</sup>. With increased cycling number, CoO and Sn can serve on "self-matrices" for each other. The intrinsic "self-matrix" is beneficial to superior electrochemical properties of MTMOsbased anodes; (ii) high conductive rGO nanosheets could provide efficient pathways for electron (graphene current collector) and shorten the sodium-ion diffusion pathways (electrolyte filled in the pores), enhancing charger transport kinetics, effectively; (iii) rGO nanosheets can provide a number of disordered sites, which can provide adequate interspaces and superficial areas to load nanomaterials, increasing the loading content of a-CoSnO<sub>3</sub> nanocubes, efficiently. Moreover, it can be used as electrical conductor to interconnect the separated a-CoSnO<sub>3</sub> nanoparticles, forming a high conductive 3D-rGO network; (iv) the unique rGO-wrapping architecture can prevent rGO from aggregation and inhibit the a-CoSnO<sub>3</sub> restacking issue, which can easily provide necessary void space to buffer the stress induced by the volume change during discharge/ charge processes, contributing to superior structural stability in the



**Scheme 2.** The mechanism of a-CoSnO<sub>3</sub>@rGO-II anode as "self-matrices" upon cycling: in the first discharge process, a-CoSnO<sub>3</sub>@rGO-II anode can be electrochemically decomposed into Sn, CoO and Na<sub>2</sub>O (I), but the CoO and Sn have totally different working voltages. CoO is first reduced to Co particles (II). After that, Sn particles react with Na to form Na<sub>x</sub>Sn (III). The re-oxidation of Co to CoO and the dealloying reaction of Na<sub>x</sub>Sn can happen during the charge process (IV).

electrode material; (v) intrinsic isotropic nature of amorphous  $CoSnO_3$  significantly relieves the internal stress to adapt the volume change during sodiation/desodiation. The loose dense structure makes for improving the ionic/atomic mobility within the active materials.

### 4. Conclusion

In this study, a handy and smart strategy to design a-CoSnO<sub>3</sub> nanocubes encapsulated by crumpled rGO was successfully developed. The designed a-CoSnO<sub>3</sub>@rGO nanocomposites used as SIBs anodes have been studied in detail. Notably, a-CoSnO3@rGO-II nanocomposite with 3D-wrapping network texture exhibits more remarkable sodium storage capability than those of a-CoSnO<sub>3</sub>@rGO-I with anti-coated architecture and a-CoSnO<sub>3</sub>@rGO-III with separate encapsulated structure, demonstrating that different rGO-based hybrid structures could vastly affect the performance of the nanocomposite anodes in SIBs. Therefore, a-CoSnO<sub>3</sub>@rGO with optimized rGO content (25.1 wt%) delivers a high specific capacity of 229.9 mAh  $g^{-1}$  after 100 cycles at 50 mA  $g^{-1}$ , and it is capable of maintaining a specific capacity of 205.7 mAh  $g^{-1}$  even at a high current density of 800 mA  $g^{-1}$ . It is believed that the introduction of rGO, accompanied by synergistic effects of the components, is a significant strategy to enhance the electrochemical capabilities by improving electronic conductivity and preventing active particles from aggregation. Furthermore, the 3D-wrapping network texture plays a key role in enhancing rate capacity by strengthening charger transport kinetics and accommodating structural variation during the sodiation/desodiation processes. Besides, the sodium storage mechanism of the CoSnO3@rGO nanocomposite is systematically investigated by the ex-situ HRTEM and SAED technique as well as the ex-situ XPS analysis. Accordingly, our study could provide crucial direction to create more compelling rGO-based functional materials, which is significant for studying advanced electrode materials in SIBs.

## Acknowledgements

This research was supported by the National Natural Science Foundation of China (51572194 and 51672189), the National Key Research and Development Program of China (2018YFB0105900), the Tianjin Major Program of New Materials Science and Technology (16ZXCLGX00070), and Tianjin Science and Technology Project (18PTZWHZ00020).

# Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.electacta.2019.05.068.

## References

- [1] J.Y. Hwang, S.T. Myung, Y.K. Sun, Sodium-ion batteries: present and future, Chem. Soc. Rev. 46 (2017) 3529–3614.
- [2] H. Kang, Y. Liu, K. Cao, Y. Zhao, L. Jiao, Y. Wang, H. Yuan, Update on anode materials for Na-ion batteries, J. Mater. Chem. A 3 (2015) 17899–17913.
- [3] T. Wang, D. Su, D. Shanmukaraj, T. Rojo, M. Armand, G. Wang, Electrode materials for sodium-ion batteries: considerations on crystal structures and sodium storage mechanisms, Electrochem. Energy Rev. 1 (2018) 200–237.
- [4] X. Guo, S. Zheng, G. Zhang, X. Xiao, X. Li, Y. Xu, H. Xue, H. Pang, Nanostructured graphene-based materials for flexible energy storage, Energy Storage Mater 9 (2017) 150–169.
- [5] Y. Fang, L. Xiao, Z. Chen, X. Ai, Y. Cao, H. Yang, Recent advances in sodium-ion battery materials, Electrochem. Energy Rev. 1 (2018) 294–323.
  [6] C. Wu, Y. Jiang, P. Kopold, P.A. van Aken, J. Maier, Y. Yu, Peapod-like carbon-
- [6] C. Wu, Y. Jiang, P. Kopold, P.A. van Aken, J. Maier, Y. Yu, Peapod-like carbonencapsulated cobalt chalcogenide nanowires as cycle-stable and high-rate materials for sodium-ion anodes, Adv. Mater. 28 (2016) 7276–7283.
- [7] N. Yabuuchi, K. Kubota, M. Dahbi, S. Komaba, Research development on sodium-ion batteries, Chem. Rev. 114 (2014) 11636–11682.
- [8] X. Li, C. Wang, Significantly increased cycling performance of novel "selfmatrix" NiSnO3 anode in lithium ion battery application, RSC Adv. 2 (2012) 6150–6154.
- [9] Y. Yan, Y.X. Yin, Y.G. Guo, L.J. Wan, A sandwich-like hierarchically porous carbon/graphene composite as a high-performance anode material for sodium-ion batteries, Adv. Energy Mater. 4 (2014) 1301584.
- [10] C. Wu, L. Shen, S. Chen, Y. Jiang, P. Kopold, P.A. van Aken, J. Maier, Y. Yu, Topdown synthesis of interconnected two-dimensional carbon/antimony hybrids as advanced anodes for sodium storage, Energy Storage Mater 10 (2018) 122–129.

- [11] Z. Jian, B. Zhao, P. Liu, F. Li, M. Zheng, M. Chen, Y. Shi, H. Zhou, Fe<sub>2</sub>O<sub>3</sub> nanocrystals anchored onto graphene nanosheets as the anode material for lowcost sodium-ion batteries, Chem. Commun. 50 (2014) 1215–1217.
- [12] J. Song, Z. Yu, M.L. Gordin, S. Hu, R. Yi, D. Tang, T. Walter, M. Regula, D. Choi, X. Li, A. Manivannan, D. Wang, Chemically bonded phosphorus/graphene hybrid as a high performance anode for sodium-ion batteries, Nano Lett. 14 (2014) 6329–6335.
- [13] D. Chao, C. Zhu, X. Xia, J. Liu, X. Zhang, J. Wang, P. Liang, J. Lin, H. Zhang, Z.X. Shen, H.J. Fan, Graphene quantum dots coated VO<sub>2</sub> arrays for highly durable electrodes for Li and Na ion batteries, Nano Lett. 15 (2015) 565–573.
- [14] Y. Zhang, C.W. Foster, C.E. Banks, L. Shao, H. Hou, G. Zou, J. Chen, Z. Huang, X. Ji, Graphene-rich wrapped petal-like rutile TiO<sub>2</sub> tuned by carbon dots for high-performance sodium storage, Adv. Mater. 28 (2016) 9391–9399.
- [15] G. Longoni, M. Fiore, J.H. Kim, Y.H. Jung, D.K. Kim, C.M. Mari, R. Ruffo, Co<sub>3</sub>O<sub>4</sub> negative electrode material for rechargeable sodium ion batteries: an investigation of conversion reaction mechanism and morphology-performances correlations, J. Power Sources 332 (2016) 42–50.
- [16] D. Kong, C. Cheng, Y. Wang, B. Liu, Z. Huang, H.Y. Yang, Seed-assisted growth of α-Fe2O3 nanorod arrays on reduced graphene oxide: a superior anode for high-performance Li-ion and Na-ion batteries, J. Mater. Chem. A 4 (2016) 11800–11811.
- [17] L. Fan, X. Li, B. Yan, J. Feng, D. Xiong, D. Li, L. Gu, Y. Wen, S. Lawes, X. Sun, Controlled SnO<sub>2</sub> crystallinity effectively dominating sodium storage performance, Adv. Energy Mater. 6 (2016) 1502057.
- [18] J. Patra, H.C. Chen, C.H. Yang, C.T. Hsieh, C.Y. Su, J.K. Chang, High dispersion of 1-nm SnO<sub>2</sub> particles between graphene nanosheets constructed using supercritical CO<sub>2</sub> fluid for sodium-ion battery anodes, Nano Energy 28 (2016) 124–134.
- [19] Y. Zhao, X. Li, B. Yan, D. Xiong, D. Li, S. Lawes, X. Sun, Recent developments and understanding of novel mixed transition-metal oxides as anodes in lithium ion batteries, Adv. Energy Mater. 6 (2016) 1502175.
- [20] F. Huang, Z.Y. Yuan, H. Zhan, Y.H. Zhou, J.T. Sun, A novel tin-based nanocomposite oxide as negative-electrode materials for Li-ion batteries, Mater. Lett. 57 (2003) 3341–3345.
- [21] Z. Wang, Z. Wang, W. Liu, W. Xiao, X.W. Lou, Amorphous CoSnO<sub>3</sub>@C nanoboxes with superior lithium storage capability, Energy Environ. Sci. 6 (2013) 87–91.
- [22] J. Chen, S. Li, V. Kumar, P.S. Lee, Carbon coated bimetallic sulfide hollow nanocubes as advanced sodium ion battery anode, Adv. Energy Mater. 7 (2017) 1700180.
- [23] X. Gao, J. Wang, D. Zhang, K. Adair, K. Feng, N. Sun, H. Zheng, H. Shao, J. Zhong, Y. Ma, X. Sun, X. Sun, Carbon coated bimetallic sulfide nanodots/carbon nanorod heterostructure enabling long-life lithium-ion batteries, J. Mater. Chem. A 5 (2017) 25625–25631.
- [24] S. Wu, R. Ge, M. Lu, R. Xu, Z. Zhang, Graphene-based nano-materials for lithium-sulfur battery and sodium-ion battery, Nano Energy 15 (2015) 379–405.
- [25] Y.S. Hu, X. Liu, J.O. Muller, R. Schlogl, J. Maier, D.S. Su, Synthesis and electrode performance of nanostructured V<sub>2</sub>O<sub>5</sub> by using a carbon tube-in-tube as a nanoreactor and an efficient mixed-conducting network, Angew. Chem. Int. Ed. 48 (2009) 210–214.
- [26] S. Dong, C. Li, X. Ge, Z. Li, X. Miao, L. Yin, ZnS-Sb<sub>2</sub>S<sub>3</sub>@C core-double shell polyhedron structure derived from metal-organic framework as anodes for high performance sodium ion batteries, ACS Nano 11 (2017) 6474–6482.
- [27] H. Ye, L. Wang, S. Deng, X. Zeng, K. Nie, P.N. Duchesne, B. Wang, S. Liu, J. Zhou, F. Zhao, N. Han, P. Zhang, J. Zhong, X. Sun, Y. Li, Y. Li, J. Lu, Amorphous MoS<sub>3</sub> infiltrated with carbon nanotubes as an advanced anode material of sodiumion batteries with large gravimetric, areal, and volumetric capacities, Adv. Energy Mater. 7 (2017) 1601602.
- [28] F. Fan, G. Fang, R. Zhang, Y. Xu, J. Zheng, D. Li, Influences of carbon content and coating carbon thickness on properties of amorphous CoSnO<sub>3</sub>@C composites as anode materials for lithium-ion batteries, Appl. Surf. Sci. 311 (2014) 484–489.
- [29] X. Li, Y. Hu, J. Liu, A. Lushington, R. Li, X. Sun, Structurally tailored graphene nanosheets as lithium ion battery anodes: an insight to yield exceptionally

high lithium storage performance, Nanoscale 5 (2013) 12607-12615.

- [30] S.J. Richard Prabakar, S.C. Han, J. Jeong, K.-S. Sohn, M. Pyo, CoSn(OH)<sub>6</sub> hybridized with anionic and cationic graphenes as a new high-capacity anode for lithium ion batteries, Mater. Des. 118 (2017) 294–303.
- [31] Y. Cao, L. Zhang, D. Tao, D. Huo, K. Su, Facile synthesis of CoSnO<sub>3</sub>/Graphene nanohybrid with superior lithium storage capability, Electrochim. Acta 132 (2014) 483–489.
- [32] D. Xiong, X. Li, H. Shan, B. Yan, L. Dong, Y. Cao, D. Li, Controllable oxygenic functional groups of metal-free cathodes for high performance lithium ion batteries, J. Mater. Chem. A 3 (2015) 11376–11386.
- [33] W. Yao, Y. Dai, K. Ge, J. Luo, Q. Shi, J. Xu, Strongly coupled hybrid ZnCo<sub>2</sub>O<sub>4</sub> quantum dots/reduced graphene oxide with high-performance lithium storage capability, Electrochim. Acta 210 (2016) 783–791.
- [34] B. Yan, X. Li, Z. Bai, L. Lin, G. Chen, X. Song, D. Xiong, D. Li, X. Sun, Superior sodium storage of novel VO<sub>2</sub> nano-microspheres encapsulated into crumpled reduced graphene oxide, J. Mater. Chem. A 5 (2017) 4850–4860.
- [35] M.B. Ali, A. Barras, A. Addad, B. Sieber, H. Elhouichet, M. Ferid, S. Szunerits, R. Boukherroub, Co<sub>2</sub>SnO<sub>4</sub> nanoparticles as a high performance catalyst for oxidative degradation of rhodamine B dye and pentachlorophenol by activation of peroxymonosulfate, Phys. Chem. Chem. Phys. 19 (2017) 6569–6578.
- [36] S. Thota, V. Narang, S. Nayak, S. Sambasivam, B.C. Choi, T. Sarkar, M.S. Andersson, R. Mathieu, M.S. Seehra, On the nature of magnetic state in the spinel Co(2)SnO(4), J. phys.: Condens. Matter 27 (2015) 166001.
- [37] L. Chang, K. Wang, L. Huang, Z. He, H. Shao, J. Wang, Hierarchically porous CoO microsphere films with enhanced lithium/sodium storage properties, J. Alloy. Comp. 725 (2017) 824–834.
- [38] L. Chang, K. Wang, L-a. Huang, Z. He, S. Zhu, M. Chen, H. Shao, J. Wang, Hierarchical CoO microflower film with excellent electrochemical lithium/sodium storage performance, J. Mater. Chem. A 5 (2017) 20892–20902.
  [39] Y. Fang, L. Xiao, J. Qian, Y. Cao, X. Ai, Y. Huang, H. Yang, 3D graphene decorated
- [39] Y. Fang, L. Xiao, J. Qian, Y. Cao, X. Ai, Y. Huang, H. Yang, 3D graphene decorated NaTi<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> microspheres as a superior high-rate and ultracycle-stable anode material for sodium ion batteries, Adv. Energy Mater. 6 (2016) 1502197.
- [40] W. Liu, X. Li, D. Xiong, Y. Hao, J. Li, H. Kou, B. Yan, D. Li, S. Lu, A. Koo, K. Adair, X. Sun, Significantly improving cycling performance of cathodes in lithium ion batteries: the effect of Al<sub>2</sub>O<sub>3</sub> and LiAlO<sub>2</sub> coatings on LiNi<sub>0.6</sub>Co<sub>0.2</sub>Mn<sub>0.2</sub>O<sub>2</sub>, Nano Energy 44 (2018) 111–120.
- [41] X. Zhou, Y.X. Yin, L.J. Wan, Y.G. Guo, Self-assembled nanocomposite of silicon nanoparticles encapsulated in graphene through electrostatic attraction for lithium-ion batteries, Adv. Energy Mater. 2 (2012) 1086–1090.
- [42] X. Ge, Z. Li, L. Yin, Metal-organic frameworks derived porous core/shellCoP@C polyhedrons anchored on 3D reduced graphene oxide networks as anode for sodium-ion battery, Nano Energy 32 (2017) 117–124.
- [43] Z. Li, L. Yuan, Z. Yi, Y. Liu, Y. Huang, Confined selenium within porous carbon nanospheres as cathode for advanced Li-Se batteries, Nano Energy 9 (2014) 229–236.
- [44] Z. Li, L. Zhang, X. Ge, C. Li, S. Dong, C. Wang, L. Yin, Core-shell structured CoP/ FeP porous microcubes interconnected by reduced graphene oxide as high performance anodes for sodium ion batteries, Nano Energy 32 (2017) 494–502.
- [45] D. Xie, X. Xia, Y. Zhong, Y. Wang, D. Wang, X. Wang, J. Tu, Exploring advanced sandwiched arrays by vertical graphene and N-doped carbon for enhanced sodium storage, Adv. Energy Mater. 7 (2017) 1601804.
- [46] B. Yan, M. Li, X. Li, Z. Bai, L. Dong, D. Li, Electrochemical impedance spectroscopy illuminating performance evolution of porous core-shell structured nickel/nickel oxide anode materials, Electrochim. Acta 164 (2015) 55–61.
- [47] J.B. Goodenough, Y. Kim, Challenges for rechargeable Li batteries, Chem. Mater. 22 (2010) 587–603.
- [48] J.-K. Meng, W.-W. Wang, Q.-C. Wang, M.-H. Cao, Z.-W. Fu, X.-J. Wu, Y.-N. Zhou, Graphene supported ultrafine tin oxide nanoparticles enable conversion reaction dominated mechanism for sodium-ion batteries, Electrochim. Acta 303 (2019) 32–39.
- [49] J. Ding, Z. Li, H. Wang, K. Cui, A. Kohandehghan, X. Tan, D. Karpuzov, D. Mitlin, Sodiation vs. lithiation phase transformations in a high rate-high stability SnO<sub>2</sub> in carbon nanocomposite, J. Mater. Chem. A 3 (2015) 7100–7111.