Growth of SnO₂ Nanoflowers on N-doped Carbon Nanofibers as Anode for Li- and Na-ion Batteries

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Highlights

• A hybrid structure of SnO₂ nanoflowers grown on N-doped carbon nanofibers (NC@SnO₂) was successfully constructed.
• N-doped carbon nanofiber accelerates the migration of Li⁺/Na⁺ ions and guides the growth of the SnO₂ nanoflowers.
• NC@SnO₂ electrode reveals excellent energy storage performance for Li- and Na-ion batteries.

Abstract It is urgent to solve the problems of the dramatic volume expansion and pulverization of SnO₂ anodes during cycling process in battery systems. To address this issue, we design a hybrid structure of N-doped carbon fibers@SnO₂ nanoflowers (NC@SnO₂) to overcome it in this work. The hybrid NC@SnO₂ is synthesized through the hydrothermal growth of SnO₂ nanoflowers on the surface of N-doped carbon fibers obtained by electrospinning. The NC is introduced not only to provide a support framework in guiding the growth of the SnO₂ nanoflowers and prevent the flower-like structures from agglomeration, but also serve as a conductive network to accelerate electronic transmission along one-dimensional structure effectively. When the hybrid NC@SnO₂ was served as anode, it exhibits a high discharge capacity of 750 mAh g⁻¹ at 1 A g⁻¹ after 100 cycles in Li-ion battery and 270 mAh g⁻¹ at 100 mA g⁻¹ for 100 cycles in Na-ion battery, respectively.

Keywords SnO₂ · Nanostructures · Anode · Li-ion battery · Na-ion battery

1 Introduction

With severe resource constraints and global environmental problems, it is necessary to develop highly efficient energy storage systems to reduce the use of fossil fuels [1–5]. Nowadays, lithium- and sodium-ion batteries (LIBs and
SIBs) have attracted widespread attention all over the world [6–8]. LIBs have been extensively applied in portable electronic equipment and electric vehicles (EVs) and intelligent power grids because of their outstanding characteristics of high energy density, no memory effect, and small self-discharge [9, 10]. Recently, owing to the lack of lithium resources and the similar chemical property of Na⁺ to Li⁺, SIBs have also received increasing attention [11, 12]. As one of the important parts for LIBs or SIBs, the high-performance electrode materials are urgently needed for next-generation battery systems.

As one of the typical transition-metal oxides (TMOs), tin dioxide (SnO₂) is widely concerned to be promising electrode materials owing to its non-toxicity, low cost, high theoretical capacity, and outstanding electrochemical performance [13–15]. Nevertheless, it is similar to the shortcomings of other oxide materials during cycling processes that SnO₂ endures the dramatic volume change. This would lead to the capacity decay and poor cycling performance [16–18]. To improve the electrochemical performance of SnO₂, nanostructured SnO₂ is employed to reduce the volume variation of SnO₂ during the charge/discharge process [19–21]. However, it is easily agglomerated for nanostructured SnO₂ to reduce the specific surface area of the active materials, leading to the attenuation of energy storage. To overcome this problem, a great deal of SnO₂/carbon composites has been designed to maintain the structural stability of electrodes and improve the electrical conductivity of composites [22–24]. In addition, the N-doped carbon composite materials are considered to enhance the electrical conductivity and accelerate the reaction speed of the SnO₂ composites, and increase defect sites for the efficient storage of lithium/sodium ions [25–27].

In this work, we synthesized a hybrid structure of N-doped carbon fibers@SnO₂ nanoflowers (NC@SnO₂) by electrospinning/hydrothermal methods. When they are used as an anode material in LIBs and SIBs, the as-prepared NC@SnO₂ hybrid material displayed excellent electrochemical properties. The high discharge capacity reached 750 mAh g⁻¹ at a current density of 1 A g⁻¹ after 100 cycles in LIBs. Meanwhile, a reversible discharge capacity of 270 mAh g⁻¹ was achieved at a current density of 100 mA g⁻¹ after 100 cycles in SIBs.

2 Experimental Section

2.1 Synthesis of SnO₂, N-doped Carbon, and NC@SnO₂

All chemical reagents were purchased and used without further treatment. The synthesis of SnO₂ nanoflowers was carried out according to the previous literature [28]. The N-doped carbon (NC) nanofibers were synthesized by electrospinning as follows: 0.6 g polyacrylonitrile (PAN, Sigma-Aldrich Co., Ltd. USA) was firstly added into 7 g N, N-dimethylformamide (DMF, Sinopharm Chemical Reagent Co., Ltd., China). Then, the above solution was poured into 10 mL plastic syringe and followed by electrospinning. The NC nanofibers were finally obtained via annealing the precursor at 600 °C in Ar atmosphere. To synthesize NC@SnO₂, 4 mmol tin(II) chloride dihydrate (SnCl₂·2H₂O, Xilong Chemical Co., Ltd., China) and 8 mmol sodium citrate (Na₃C₆H₅O₇·2H₂O, Tianjin Hengxing Chemical Reagent Manufacturing Co., Ltd., China) were firstly dissolved into the mixed solvent of 15 mL ethanol and 15 mL water. After stirring for 30 min, 80 mg NC nanofibers were introduced into the above blend solution. Subsequently, the mixture solution was put into a Teflon-lined stainless steel autoclave at 180 °C for 12 h after continuous ultrasound for 30 min. The precursor samples were taken out the autoclave after the end of the reaction and ultrasonic cleaning with deionized water and ethanol. Finally, the NC@SnO₂ samples were obtained with annealing at 500 °C for 3 h in Ar gas.

2.2 Material Characterizations

The X-ray diffraction (XRD) of the samples was conducted with a Shimadzu XRD-6000 instrument, and the morphologies and structural features of the samples were characterized by scanning electron microscopy (SEM, Hitachi S4800) and transmission electron microscopy (TEM; JEOL 2010 with an accelerating voltage of 200 kV). The thermogravimetric analysis (TGA) of the powder sample was surveyed with a WCT-1D instrument (BOIF, China) in air atmosphere from 30 to 800 °C. Brunauer–Emmett–Teller (BET) of the sample was performed with the adsorption of N₂ with a nova 2000 e volumetric adsorption analyzer (Kangta, USA). The element composition and chemical bonds of the sample were detected by X-ray photoelectron spectroscopy (XPS, Thermo Scientific Escalab 250Xi, USA). Raman spectra of the samples were conducted by utilizing micro-Raman spectrometer (LabRAM HR Evolution, HORIBA).

2.3 Electrochemical Measurements

The working electrodes of LIBs and SIBs were fabricated by using 80 wt% of active materials (NC@SnO₂, SnO₂, and NC), 10 wt% of acetylene black, and 10 wt% of carboxymethylcellulose sodium (CMC). The mixture was uniformly distributed in the deionized water and ethanol and coated on the copper foil which dried at 60 °C in a vacuum drying oven for a day. CR2025-type coin half-batteries of as-prepared electrodes were assembled in the
glove box with water and oxygen content of less than 0.5 ppm. The microporous polypropylene (Celgard 2400) and glass microfiber filter membranes (Whatman, Grade GF/A) were utilized as a separator of LIBs and SIBs, respectively. And corresponding metal plates were used as the counter electrodes of batteries. The electrolyte of LIBs was composed of 1.0 M of LiPF₆ solution which mixed ethylene carbonate (EC) and dimethyl carbonate (DMC) with 1:1 in volume, and the electrolyte of SIBs was constituted by 1.0 M of NaClO₄ solution which mixed EC with DMC (1:1 in volume), accompanied with 5% fluoroethylene carbonate (FEC) of additive agent. The electrochemical property and cyclic voltammetry measurement of LIBs and SIBs were performed with Neware Battery Testing System and CHI 660C Electrochemical Workstation, respectively.

3 Results and Discussion

The synthetic process of NC@SnO₂ is schematically shown in Fig. 1. Firstly, NC nanofibers were synthesized by the electrospinning method using PAN as the precursor, followed by heat treatment. Subsequently, SnO₂ nanoflowers were grown on the NC nanofibers by hydrothermal method. The morphology and structures of the samples were characterized by SEM and TEM, as displayed in Fig. 2. Figure 2a, b displays that SnO₂ sample is composed of agglomerated nanoflowers, which are assembled by nanosheets. When the NC nanofibers (Fig. S1) are introduced and used as the core for the hybrid structure, the SnO₂ nanoflowers could grow on the surface of NC nanofibers, as shown in SEM images (Fig. 2c, d). Compared to SnO₂ nanoflowers, the NC@SnO₂ composite materials are formed by thinner nanosheets and better dispersed. In addition, the TEM image (Fig. 2e) of NC@SnO₂ further indicates that one fiber is completely covered with the thin nanosheets. The high-resolution TEM image (Fig. 2f) indicates that the SnO₂ nanosheet is well crystalline and has a lattice plane (110) with a crystal lattice distance of 0.338 nm.

The crystal structures of NC@SnO₂, SnO₂, and NC materials were analyzed by XRD. From Fig. 3, one can observe that the diffraction peaks of NC@SnO₂ and SnO₂ are well consistent with the standard card (JCPDS card No. 21-1250), and the 2θ values of main peaks centered at 26.58, 33.88, 37.95, 51.75, and 54.76 are corresponded to the lattice planes of tetragonal SnO₂ (110), (101), (200), (211), and (220), respectively. The diffraction peaks of NC are in accordance with the standard card (JCPDS card No. 3-401), and the 2θ values 26.60 and 54.79 are corresponded to the lattice planes of hexagonal carbon (006) and (0012), respectively. Nevertheless, the peak of carbon for the NC@SnO₂ is not clearly observed. It is possible that the NC nanofibers were completely covered by the SnO₂ nanoflowers, which make the carbon peaks disappear in NC@SnO₂. The Raman spectrum of NC@SnO₂ (Fig. S2) indicates that the two peaks at ~1350 and 1580 cm⁻¹ are corresponded to the D peak of disorder carbon and the G peak of graphitic carbon. The relative intensity (I_D/I_G ≈ 1.397 > 1) indicates that there exist mass defects caused by the N-doping in NC@SnO₂ [29–31]. Additionally, the TGA curve of NC@SnO₂ (Fig. S3) indicates that the lost weight of the sample appears in the range of 400–800 °C and the weight retention of SnO₂ is confirmed to be about 67.81%.
The BET was utilized to confirm the surface information of the materials. Figure S4a, b shows the nitrogen adsorption–desorption isotherms of NC@SnO\(_2\) and SnO\(_2\) materials. The surface areas of NC@SnO\(_2\) and SnO\(_2\) are 45.59 and 37.01 cm\(^3\) g\(^{-1}\), respectively. Meanwhile, the pore-size distribution curves (Figs. S4c, d) indicate that the NC@SnO\(_2\) and SnO\(_2\) have the average pores of 3.74 and 2.56 nm, respectively. The larger specific surface area and pore size of NC@SnO\(_2\) are beneficial to the storage and transport of lithium/sodium ions. Moreover, the chemical component and surface electronic states of the NC@SnO\(_2\) material were further surveyed by XPS, and all peaks of these elements Sn, O, N, and C are observed as shown in Fig. S5 [32]. The high-resolution spectra of Sn 3d, O 1s, N 1s, and C 1s were recorded as shown in Fig. 4. The peaks of the Sn 1s (Fig. 4a) could be resolved into 486.78 and 495.12 eV, which are assigned to the binding energies of Sn 3d\(_{5/2}\) and Sn 3d\(_{3/2}\) of SnO\(_2\) [33]. The peaks of the O 1s (Fig. 4b) can be divided into two peaks of 530.61 and 531.36 eV and corresponded to Sn–O and C=O, respectively [34, 35]. The signal of N 1s could be obviously divided into two peaks of 398.00 and 399.76 eV (Fig. 4c), which well accorded with the binding energies of pyridinic N and pyrrolic N [36], it is verified the existence of nitrogen in NC@SnO\(_2\). Additionally, the peaks of the C 1s (Fig. 4d) could be resolved into three binding energies. The peak located at 285.89 eV corresponding to C–N bond can further confirm the presence of nitrogen in NC@SnO\(_2\) [37], and the other peaks of 284.42 and 288.54 eV are accorded with the binding energies of C–C and C=O, respectively [38].

The NC@SnO\(_2\) was investigated as anode material for LIBs. SnO\(_2\) and NC nanofiber were also conducted for comparison. The CV curves of NC@SnO\(_2\) between 0.001 and 3.0 V vs Li\(^+\)/Li at scan rate of 0.1 mV s\(^{-1}\) are shown in Fig. 5a, and it can be observed that there exists a subtle distinction in the first three cycles. The reduction peaks are found at the scope of 1.5–1.8 and 0.5–1.0 V at the first curve. They are attributed to the conversion process from SnO\(_2\) to Sn (Eq. 1) and the formation of SEI films, respectively [39, 40]. The peak below 0.5 V is associated with the lithiation (Li\(_x\)Sn) of Sn (Eq. 2) [41]. In the following two CV curves, the reduction peaks at about 1.2, 0.8, and 0.3 V are associated with the reversible conversion reaction of SnO\(_2\) and alloy–dealloy reaction of Sn [42]. The oxidation peaks of about 0.8, 1.2 V and the small oxidation peak of 2.1 V are derived from the delithiation reaction of LixSn (Eq. 3) and reversible changing reaction of Sn between SnO and SnO\(_2\) (Eq. 4), respectively [42].

![Fig. 4 XPS spectra of the NC@SnO\(_2\): a Sn 3d, b O 1s, c N 1s, and d C 1s. (Color figure online)](image-url)
de/intercalation of conversion process is described as follows,

$$\text{SnO}_2 + 4\text{Li}^+ + 4\text{e}^- \rightarrow \text{Sn} + 2\text{Li}_2\text{O}, \quad (1)$$

$$\text{Sn} + x\text{Li}^+ + x\text{e}^- \rightarrow \text{Li}_x\text{Sn} \quad (0 < x < 4.4), \quad (2)$$

$$\text{Li}_x\text{Sn} \rightarrow \text{Sn} + x\text{Li}^+ + x\text{e}^- \quad (0 < x < 4.4), \quad (3)$$

$$\text{Sn}/\text{SnO} + \text{Li}_2\text{O} \rightarrow \text{SnO}/\text{SnO}_2 + 2\text{Li}^+ + 2\text{e}^- \quad (4)$$

The charge/discharge profiles of NC@SnO$_2$ at the 1st, 2nd, 3rd, and 5th cycle were displayed at in Fig. 5b. The voltage platforms of charge–discharge can be observed to be consistent with the oxidation–reduction peaks of above CV curves. The initial discharge–charge capacities of NC@SnO$_2$ are 1463.6 and 1009.8 mAh g$^{-1}$, respectively. And the low initial coulombic efficiency of 67.0% may be associated with the formation of SEI film and the irreversible reactions of SnO$_2$ material in the first cycle [32, 43]. The cycling performance of NC@SnO$_2$, SnO$_2$, and NC is shown in Fig. 5c. The discharge capacity of NC@SnO$_2$ is about 750 mAh g$^{-1}$ at 1 A g$^{-1}$ after 100 cycles, while the discharge capacities of SnO$_2$ and NC only remain 480 and 220 mAh g$^{-1}$, respectively. In Fig. 5d, one can see that the average capacities of NC@SnO$_2$ are about 1100, 850, 763, 684, 615, 568, and 905 mAh g$^{-1}$ at different current densities of 0.2, 0.5, 1, 2, 4, 6, and 0.2 A g$^{-1}$, respectively. However, the average capacities of SnO$_2$ are only about 966, 842, 765, 685, 525, 370, and 770 mAh g$^{-1}$ at 0.2, 0.5, 1, 2, 4, 6, and 0.2 A g$^{-1}$, respectively. And the NC electrode exhibits the capacities less than 550 mAh g$^{-1}$ at various current densities.

The electrochemical property of NC@SnO$_2$ was further investigated in SIBs. Figure 6a displays the CV curves of NC@SnO$_2$ in the voltage range from 0.001 to 3.0 V vs Na$^{+}$/Na at scan rate of 0.1 mV s$^{-1}$. The obvious slope of 0.5–1.0 V is ascribed to the generation of the SEI film and the irreversible reactions between SnO$_2$ with sodium ions to generate Na$_x$Sn alloys in the first cycle [22]. In the initial three cycles, the two reduction peaks at about 1.0 and 0.3 V correspond to the insertion of sodium ions with the formation of Sn and Na$_x$Sn, respectively. And the oxidation peak at 1.25 V corresponds to the de-intercalation of sodium ions [44, 45]. The reversible reaction of SnO$_2$ with sodium ions to the production of Na$_2$O and Na$_x$Sn in the charge–discharge process can be represented as follows [44].
SnO$_2$ + 4Na$^+$ + 4e$^-$ $\rightarrow$ Sn + 2Na$_2$O,  
Sn + xNa$^+$ + xe$^-$ $\rightarrow$ Na$_x$Sn ($0 < x < 4$).

Figure 6b displays the discharge/charge capacities of 555.7/212.5 mAh g$^{-1}$ in the first charge/discharge cycle, respectively, with a coulombic efficiency of 38.2%. The low coulombic efficiency can be attributed to the formation of SEI film, and the irreversible reaction of SnO$_2$ with sodium ion to form Na$_x$Sn alloys in the first discharge process [46, 47]. In this work, the SnO$_2$ and NC electrodes are used as a reference. In Fig. 6c, one can see that the discharge capacity of NC@SnO$_2$ is about 270 mAh g$^{-1}$, compared with 55 and 220 mAh g$^{-1}$ of SnO$_2$ and NC at 100 mA g$^{-1}$ after 100 cycles. The rate performances for the three electrodes were also studied as shown in Fig. 6d. When the current densities were set at 0.05, 0.1, 0.2, 0.4, 0.8, 1, and 0.1 A g$^{-1}$, the NC@SnO$_2$ electrode exhibits the discharge capacities of about 295, 300, 280, 247, 202, 193, and 300 mAh g$^{-1}$, respectively. These results are better than those of SnO$_2$ and NC electrodes.

To further demonstrate the structural stability of hybrid NC@SnO$_2$, the SEM images of electrodes after about 75 cycles are given in Figs. 7 and S6. The SEM images of NC@SnO$_2$ and SnO$_2$ electrodes as anode for LIBs after cycling are shown in Fig. 7. Compared to the SEM images of the SnO$_2$ electrodes (Fig. 7c, d), we can observe the obvious NC could be retained, and the SnO$_2$ nanoflowers are not completely collapsed as shown in Fig. 7a, b. It demonstrates that the hybrid NC@SnO$_2$ electrodes have the better cycle performance and rate capability than those of SnO$_2$ electrodes in the LIBs due to the more stable structure of hybrid NC@SnO$_2$ material. We also investigated the structural change of both NC@SnO$_2$ and SnO$_2$ electrodes for SIBs. As shown in the SEM images of NC@SnO$_2$ electrode after cycling (Fig. S6a), the network structure of the NC could still be observed and no obvious reunion in comparison with the SnO$_2$ electrode (Fig. S6c). However, SnO$_2$ nanoflowers are completely collapsed in both NC@SnO$_2$ and SnO$_2$ electrodes, as shown in the high-magnification SEM images (Fig. S6b, d). This is because that the formation of Na–Sn alloy with enormous volume changes makes the pulverization of SnO$_2$ material upon repetitive cycling [20]. These results indicated that NC nanofibers of the NC@SnO$_2$ electrode can not only provide
a conductive network, but also prevent the aggregation and pulverization of the SnO2 nanoflowers during the charge and discharge process.

## 4 Conclusion

In summary, we have successfully prepared a hybrid structure of NC@SnO2 by electrospinning/hydrothermal methods. The NC nanofibers of the hybrid NC@SnO2 can prevent the agglomeration of SnO2 nanoflowers and effectively accelerate the transition of Li\textsuperscript+\textsuperscript+\textsuperscript+\textsuperscript+\textsuperscript+\textsuperscript+ to promote the rate capability. Moreover, the structure can make more surface of the nanoparticle exposed and buffer the volume expansion of SnO2 to enhance discharge capacity and cycling performance during cycling process. In addition, the hybrid NC@SnO2 could deliver a discharge capacity of 750 mAh g\textsuperscript–1 after 100 cycles at 1 A g\textsuperscript–1 for Li-ion battery and 270 mAh g\textsuperscript–1 after 100 cycles at 100 mA g\textsuperscript–1 for Na-ion battery.

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### References

1. J. Xu, J. Ma, Q. Fan, S. Guo, S. Dou, Recent progress in the design of advanced cathode materials and battery models for high-performance lithium-X (X=O2, S, Se, Te, I2, Br 2) batteries. Adv. Mater. 29, 16066454 (2017). https://doi.org/10.1002/adma.201606454

2. C. Cui, J. Xu, L. Wang, D. Guo, M. Mao, J. Ma, T. Wang, Growth of NiCo2O4@MnMoO4 nanocolom arrays with superior pseudocapacitor properties. ACS Appl. Mater. Interfaces 8(13), 8568–8575 (2016). https://doi.org/10.1021/acsami.6b02962

3. D. Guo, L. Lai, A. Cao, H. Liu, S. Dou, J. Ma, Nanoarrays: design, preparation and supercapacitor applications. RSC Adv. 5(69), 55856–55869 (2015). https://doi.org/10.1039/C5RA09453D

4. F. Mao, W. Guo, J. Ma, Research progress on design strategies, synthesis and performance of LiMn2O4-based cathodes. RSC Adv. 5(127), 105248–105258 (2015). https://doi.org/10.1039/C5RA17777F

5. J. Xu, Y. Dou, Z. Wei, J. Ma, Y. Deng, Y. Li, H. Liu, S. Dou, Recent progress in graphite intercalation compounds for rechargeable metal (Li, Na, K, Al)-ion batteries. Adv. Sci. 4(10), 1700146 (2017). https://doi.org/10.1002/advs.201700146

6. L. Wang, B. Ruan, J. Xu, H.K. Liu, J. Ma, Amorphous carbon layer contributing Li storage capacity to Nb2O5@C nanosheets. RSC Adv. 5(45), 36104–36107 (2015). https://doi.org/10.1039/C5RA05935F

7. Y. Cai, J. Ma, T. Wang, Hydrothermal synthesis of x-Ni(OH)2 and its conversion to NiO with electrochemical properties. J. Alloys Compd. 582, 328–333 (2014). https://doi.org/10.1016/j.jallcom.2013.07.206

8. C. Cui, X. Li, Z. Hu, J. Xu, H. Liu, J. Ma, Growth of MoS2@C nanobowls as a lithium-ion battery anode material. RSC Adv. 5(112), 92506–92514 (2015). https://doi.org/10.1039/C5RA17992K

9. V. Etacheri, R. Marom, R. Elazari, G. Salitria, D. Aurbach, Challenges in the development of advanced Li-ion batteries: a review. Energy Environ. Sci. 4(9), 3243–3262 (2011). https://doi.org/10.1039/c1ee01598b

10. P. Roy, S.K. Srivastava, Nanostructured anode materials for lithium-ion batteries. J. Mater. Chem. A 3(6), 2454–2484 (2015). https://doi.org/10.1039/C4TA04980B

11. L. Wang, Y.-G. Sun, L.-L. Hu, J.-Y. Piao, J. Guo, A. Manthiram, J. Ma, A.-M. Cao, Copper-substituted Na0.65Ni0.3CuMn0.5O2 cathode materials for sodium-ion batteries with suppressed P2–O2 phase transition. J. Mater. Chem. A 5(18), 8752–8761 (2017). https://doi.org/10.1039/C7TA00880E

12. V. Palomares, P. Serras, I. Villaluenga, K.B. Hueso, J. Carretero-Gonzalez, T. Rojo, Na-ion batteries, recent advances and present challenges to become low cost energy storage systems. Energy Environ. Sci. 5(3), 5884–5901 (2012). https://doi.org/10.1039/c2ee02781j

13. Y. Chen, J. Ma, Q. Li, T. Wang, Gram-scale synthesis of ultra-small SnO2 nanocrystals with an excellent electrochemical performance. Nanoscale 5(8), 3262–3265 (2013). https://doi.org/10.1039/c3nr00356f

14. S.J.R. Prabakar, Y.-H. Hwang, E.-G. Bae, S. Shim, D. Kim, M.S. Lah, K.-S. Sohn, M. Pyo, SnO2-graphene composites with self-assembled alternating oxide and amine layers for high Li-storage and excellent stability. Adv. Mater. 25(24), 3307–3312 (2013). https://doi.org/10.1002/adma.201301264

15. J. Deng, Y. Chen, J. Ma, E. Zhang, T. Wang, Solvothermal synthesis of hollow urchin-like SnO2 nanospheres with superior lithium storage behavior. J. Nanosci. Nanotechnol. 13(6), 4297–4301 (2013). https://doi.org/10.1166/jnn.2013.7181

16. F. Yan, X. Tang, Y. Wei, L. Chen, G. Cao, M. Zhang, T. Wang, Stannous ions reducing graphene oxide at room temperature to produce SnO2-porous, carbon-nanofiber flexible mats as binder-free anodes for lithium-ion batteries. J. Mater. Chem. A 3(24), 12672–12679 (2015). https://doi.org/10.1039/C5TA02107C
17. Y. Zhao, C. Wei, S. Sun, L.P. Wang, Z.J. Xu, Reserving interior void space for volume change accommodation: an example of cable-like mwwnts@SnO2@C composite for superior lithium and sodium storage. Adv. Sci. 2(6), 1500097 (2015). https://doi.org/10.1002/advs.201500097

18. C. Guan, X. Wang, Q. Zhang, Z. Fan, H. Zhang, H.J. Fan, Highly stable and reversible lithium storage in SnO2 nanowires surface coated with a uniform hollow shell by atomic layer deposition. Nano Lett. 14(8), 4852–4858 (2014). https://doi.org/10.1021/nl502192p

19. X.M. Yin, C.C. Li, M. Zhang, Q.Y. Hao, S. Liu, L.B. Chen, T.H. Wang, One-step synthesis of hierarchical SnO2 hollow nanostructures via self-assembly for high power lithium-ion batteries. J. Phys. Chem. C 114(17), 8084–8088 (2010). https://doi.org/10.1021/jp100224x

20. L. Chen, X. Yin, L. Mei, C. Li, D. Lei et al., Mesoporous SnO2@carbon core-shell nanostructures with superior electrochemical performance for lithium ion batteries. Nanotechnology 23(3), 035402 (2011). https://doi.org/10.1088/0957-4484/23/3/035402

21. L. Fan, X. Li, B. Yan, J. Feng, D. Xiong et al., Controlled SnO2 crystallinity effectively dominating sodium storage performance. Adv. Energy Mater. 6(10), 1502057 (2016). https://doi.org/10.1002/aenm.201502057

22. M. Dirican, Y. Lu, Y. Ge, O. Yildiz, X. Zhang, Carbon-confined SnO2-electrodeposited porous carbon nanofiber composite as high-capacity sodium-ion battery anode material. ACS Appl. Mater. Interfaces. 7(33), 18387–18396 (2015). https://doi.org/10.1021/acsami.5b04338

23. B. Huang, X. Li, Y. Pei, S. Li, X. Cao, R.C. Massé, G. Cao, Novel carbon-encapsulated porous SnO2 anode for lithium-ion batteries with much improved cyclic stability. Small 12(14), 1945–1955 (2016). https://doi.org/10.1002/smll.201503419

24. J. Xu, G. Jia, W. Mai, H.J. Fan, Energy storage performance enhancement by surface engineering of electrode materials. Adv. Mater. Interfaces 3(20), 1600430 (2016). https://doi.org/10.1002/admi.201600430

25. X. Zhou, L.J. Wan, Y.G. Guo, Binding SnO2 nanocrystals in nanotube@SnO2 nanoflake core-branch arrays for lithium-ion battery anode. Nano Energy 4, 105–112 (2014). https://doi.org/10.1016/j.nanoen.2013.12.018

26. B. He, W.-C. Li, A.-H. Lu, High nitrogen-content carbon nanosheets formed using the Schiff-base reaction in a molten salt medium as efficient anode materials for lithium-ion batteries. J. Mater. Chem. A 3(2), 579–585 (2015). https://doi.org/10.1039/C4TA05056H

27. J. Ou, Y. Zhang, L. Chen, Q. Zhao, Y. Meng, Y. Guo, D. Xiao, Nitrogen-rich porous carbon derived from biomass as a high performance anode material for lithium ion batteries. J. Mater. Chem. A 3(12), 6534–6541 (2015). https://doi.org/10.1039/C4TA06614F

28. R. Li, B. Wang, S. Ji, P. Jin, Facile synthesis of ultrasmall stannic oxide nanoparticles as anode materials with superior cyclability for lithium-ion batteries. RSC Adv. 6, 8084–8088 (2016). https://doi.org/10.1039/C5RA07599H

29. J. Li, C. Zhang, L. Shao, Z. Tian, Z. Deng, C. Gao, A mini review on nanocarbon-based 1D macroscopic fibers: assembly strategies and mechanical properties. Nano-Micro Lett. 9, 51 (2017). https://doi.org/10.1007/s40820-017-0151-7

30. Y. Liu, Y. Zhao, Z. Zhang, F. Qu, A. Umar, X. Wu, Hierarchical SnO2 nanostructures made of intermingled ultrathin nanoshells for environmental remediation, smart gas sensor, and supercapacitor applications. ACS Appl. Mater. Interfaces. 6(3), 2174–2184 (2014). https://doi.org/10.1021/am405301v

31. Z. Lin, X. Xiong, J. Zheng, G. Wang, C. Yang, Three-dimensional N-doped graphene as anode material with superior cycle stability for sodium ion batteries. Mater. Lett. 202, 123–126 (2017). https://doi.org/10.1016/j.matlet.2017.05.046

32. Y. Luo, X. Zhou, Y. Zhong, M. Yang, J. Wei, Z. Zhou, Preparation of core-shell porous magnetite@carbon nanospheres through chemical vapor deposition as anode materials for lithium-ion batteries. Electrochim. Acta 154, 136–141 (2015). https://doi.org/10.1016/j.electacta.2014.12.038

33. H. Wang, S. Dou, S. Wang, L. Wang, T. Wang, J. Ma, J. Zhang, Y. Yu, Synthesis of electrocatalytically functional carbon honeycombs through cooking with molecule precursors. Int. J. Hydrogen Energy 42(10), 6472–6481 (2017). https://doi.org/10.1016/j.ijhydene.2017.01.187

34. H. Wang, S. Dou, S. Wang, L. Wang, T. Wang, J. Ma, J. Zhang, Y. Yu, Synthesis of electrocatalytically functional carbon honeycombs through cooking with molecule precursors. Int. J. Hydrogen Energy 42(10), 6472–6481 (2017). https://doi.org/10.1016/j.ijhydene.2017.01.187

35. M. Zhang, Z. Sun, T. Zhang, D. Sui, Y. Ma, Y. Chen, Excellent cycling stability with high SnO2 loading on a three-dimensional graphene network for lithium ion batteries. Carbon 102, 32–38 (2016). https://doi.org/10.1016/j.carbon.2016.02.032

36. R. Li, B. Wang, S. Ji, P. Jin, Facile synthesis of ultrasmall stannic oxide nanoparticles as anode materials with superior cyclability and rate capability for lithium-ion batteries. RSC Adv. 6(59), 54179–54184 (2016). https://doi.org/10.1039/C6RA00964F

37. R. Hu, Y. Ouyang, T. Liang, H. Wang, J. Liu, J. Chen, C. Yang, L. Yang, M. Zhu, Stabilizing the nanostructure of SnO2 anodes by transition metals: a route to achieve high initial coulombic efficiency and stable capacities for lithium storage. Adv. Mater. 29(13), 1605006 (2017). https://doi.org/10.1002/adma.201602006

38. W. Chen, K. Song, L. Mi, X. Feng, J. Zhang, S. Cui, C. Liu, Synergistic effect induced ultrafine SnO2/graphene nanocomposite as an advanced lithium/sodium-ion batteries anode. J. Mater. Chem. A 5(20), 10027–10038 (2017). https://doi.org/10.1039/C7TA01634D

39. M. Yang, X. Li, B. Yan, L. Fan, Z. Yu, D. Li, Reduced graphene oxide decorated porous SnO2 nanotubes with enhanced sodium...
46. R.S. Kalubarme, J.-Y. Lee, C.-J. Park, Carbon encapsulated tin oxide nanocomposites: an efficient anode for high performance sodium-ion batteries. ACS Appl. Mater. Interfaces. 7(31), 17226–17237 (2015). https://doi.org/10.1021/acsami.5b04178

47. S. Li, Y. Wang, J. Qiu, M. Ling, H. Wang, W. Martens, S. Zhang, SnO₂ decorated graphene nanocomposite anode materials prepared via an up-scalable wet-mechanochemical process for sodium ion batteries. RSC Adv. 4(91), 50148–50152 (2014). https://doi.org/10.1039/C4RA09699A