

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

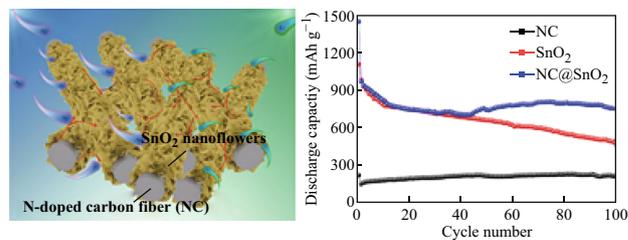
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Highlights

- 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.

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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 (SnO_2) 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 SnO_2 endures the dramatic volume change. This would lead to the capacity decay and poor cycling performance [16–18]. To improve the electrochemical performance of SnO_2 , nanostructured SnO_2 is employed to reduce the volume variation of SnO_2 during the charge/discharge process [19–21]. However, it is easily agglomerated for nanostructured SnO_2 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 SnO_2 /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 SnO_2 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@ SnO_2 nanoflowers (NC@ SnO_2) by electrospinning/hydrothermal methods. When they are used as an anode material in LIBs and SIBs, the as-prepared NC@ SnO_2 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 SnO_2 , N-doped Carbon, and NC@ SnO_2

All chemical reagents were purchased and used without further treatment. The synthesis of SnO_2 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 $600 \text{ }^\circ\text{C}$ in Ar atmosphere. To synthesize NC@ SnO_2 , 4 mmol tin(II) chloride dihydrate ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, Xilong Chemical Co., Ltd., China) and 8 mmol sodium citrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot \text{H}_2\text{O}$, 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 $180 \text{ }^\circ\text{C}$ 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@ SnO_2 samples were obtained with annealing at $500 \text{ }^\circ\text{C}$ 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 $800 \text{ }^\circ\text{C}$. Brunauer–Emmett–Teller (BET) of the sample was performed with the adsorption of N_2 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@ SnO_2 , SnO_2 , 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 $60 \text{ }^\circ\text{C}$ 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 LiPF_6 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 NaClO_4 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@SnO_2 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, SnO_2 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 SnO_2 sample is composed of agglomerated nanoflowers, which are assembled by

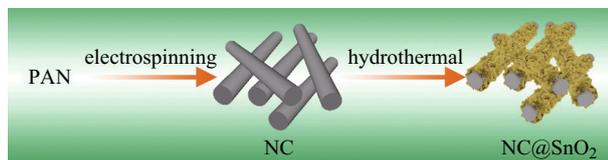


Fig. 1 Schematic diagram for synthetic process of NC@SnO_2 . (Color figure online)

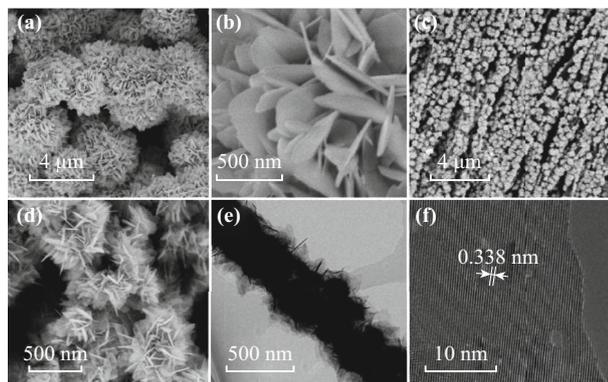


Fig. 2 a, b SEM images of SnO_2 . c, d SEM images and e, f TEM images of NC@SnO_2

nanosheets. When the NC nanofibers (Fig. S1) are introduced and used as the core for the hybrid structure, the SnO_2 nanoflowers could grow on the surface of NC nanofibers, as shown in SEM images (Fig. 2c, d). Compared to SnO_2 nanoflowers, the NC@SnO_2 composite materials are formed by thinner nanosheets and better dispersed. In addition, the TEM image (Fig. 2e) of NC@SnO_2 further indicates that one fiber is completely covered with the thin nanosheets. The high-resolution TEM image (Fig. 2f) indicates that the SnO_2 nanosheet is well crystalline and has a lattice plane (110) with a crystal lattice distance of 0.338 nm.

The crystal structures of NC@SnO_2 , SnO_2 , and NC materials were analyzed by XRD. From Fig. 3, one can observe that the diffraction peaks of NC@SnO_2 and SnO_2 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 SnO_2 (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@SnO_2 is not clearly observed. It is possible that the NC nanofibers were completely covered by the SnO_2 nanoflowers, which make the carbon peaks disappear in NC@SnO_2 . The Raman spectrum of NC@SnO_2 (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 ($I_D/I_G \approx 1.397 > 1$) indicates that there exist mass defects caused by the N-doping in NC@SnO_2 [29–31]. Additionally, the TGA curve of NC@SnO_2 (Fig. S3) indicates that the lost weight of the sample appears in the range of 400–800 °C and the weight retention of SnO_2 is confirmed to be about 67.81%.

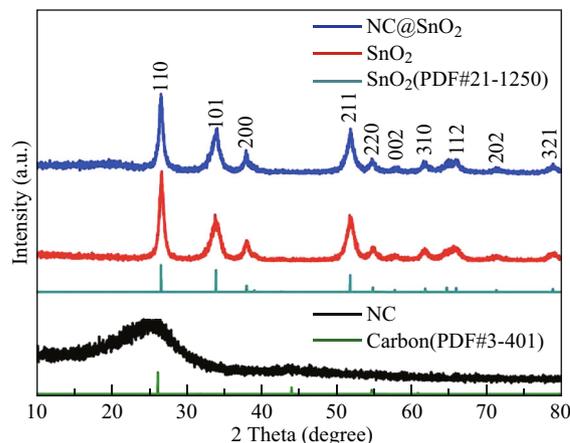


Fig. 3 XRD patterns of NC@SnO_2 , SnO_2 , and NC. (Color figure online)

The BET was utilized to confirm the surface information of the materials. Figure S4a, b shows the nitrogen adsorption–desorption isotherms of NC@SnO₂ and SnO₂ materials. The surface areas of NC@SnO₂ and SnO₂ are 45.59 and 37.01 cm³ g⁻¹, respectively. Meanwhile, the pore-size distribution curves (Figs. S4c, d) indicate that the NC@SnO₂ and SnO₂ have the average pores of 3.74 and 2.56 nm, respectively. The larger specific surface area and pore size of NC@SnO₂ are beneficial to the storage and transport of lithium/sodium ions. Moreover, the chemical component and surface electronic states of the NC@SnO₂ 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 SnO₂ [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@SnO₂. 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@SnO₂ [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@SnO₂ was investigated as anode material for LIBs. SnO₂ and NC nanofiber were also conducted for comparison. The CV curves of NC@SnO₂ 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 SnO₂ 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_xSn) 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 SnO₂ 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 Li_xSn (Eq. 3) and reversible changing reaction of Sn between SnO and SnO₂ (Eq. 4), respectively [42]. The Li⁺

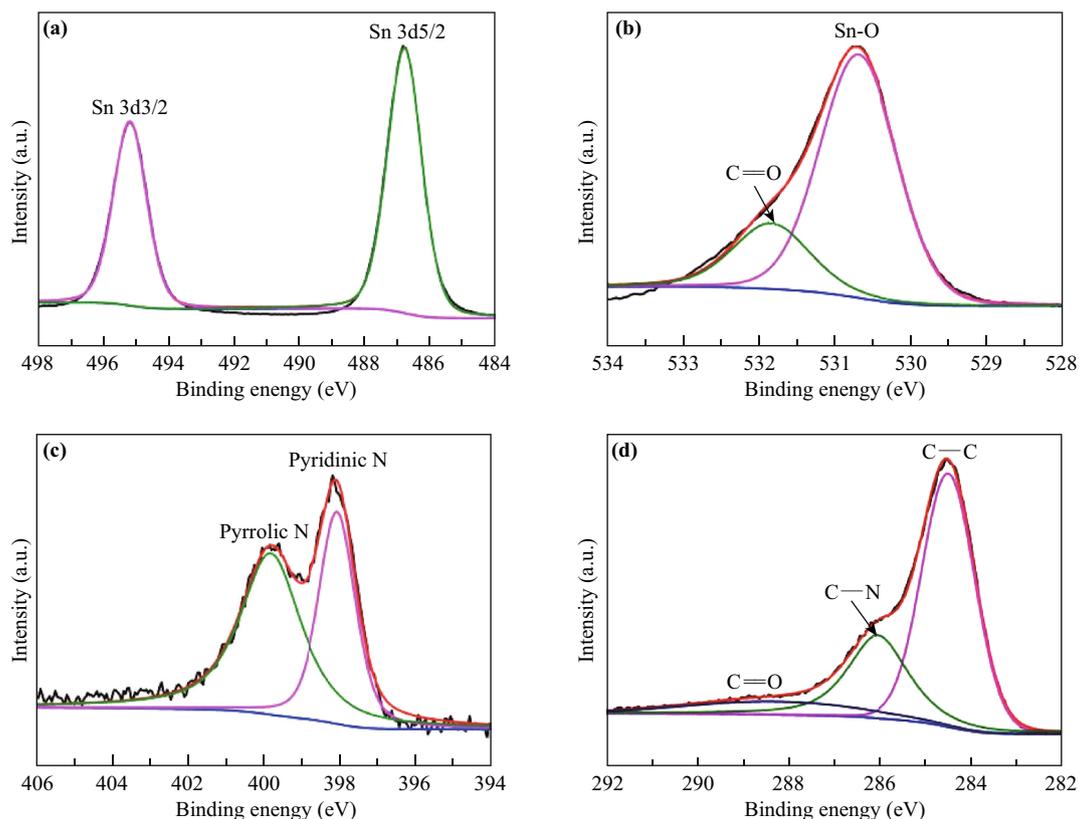


Fig. 4 XPS spectra of the NC@SnO₂: **a** Sn 3d, **b** O 1s, **c** N 1s, and **d** C 1s. (Color figure online)

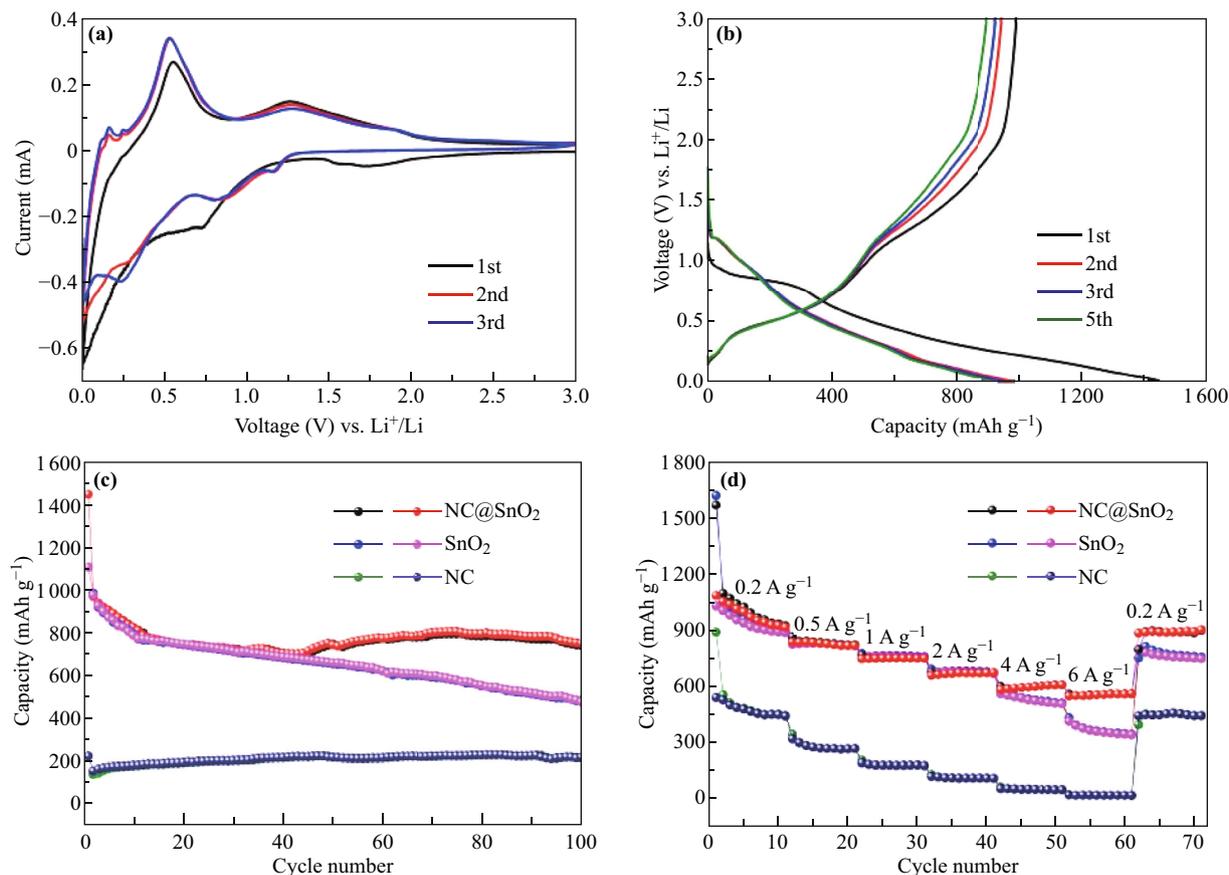
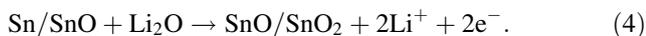
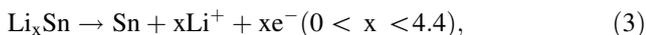
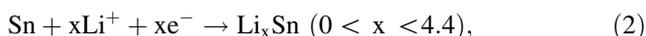
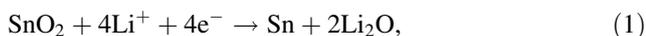


Fig. 5 Electrochemical performance for LIBs: **a** Cyclic voltammograms of NC@SnO₂ at 0.1 mV s⁻¹. **b** Charge-discharge voltage profiles of NC@SnO₂. **c** Cycling performances of NC@SnO₂, SnO₂, and NC at 1 A g⁻¹. **d** Rate capabilities of NC@SnO₂, SnO₂, and NC. (Color figure online)

de/intercalation of conversion process is described as follows,



The charge/discharge profiles of NC@SnO₂ 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@SnO₂ 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 SnO₂ material in the first cycle [32, 43]. The cycling performance of NC@SnO₂, SnO₂, and NC is shown in Fig. 5c. The discharge capacity of NC@SnO₂ is about 750 mAh g⁻¹ at 1 A g⁻¹ after 100 cycles, while the discharge capacities of SnO₂ and NC only remain 480 and 220 mAh g⁻¹, respectively. In Fig. 5d, one

can see that the average capacities of NC@SnO₂ 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 SnO₂ 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@SnO₂ was further investigated in SIBs. Figure 6a displays the CV curves of NC@SnO₂ 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 SnO₂ with sodium ions to generate Na_xSn 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_xSn, respectively. And the oxidation peak at 1.25 V corresponds to the de-intercalation of sodium ions [44, 45]. The reversible reaction of SnO₂ with sodium ions to the production of Na₂O and Na_xSn in the charge-discharge process can be represented as follows [44],

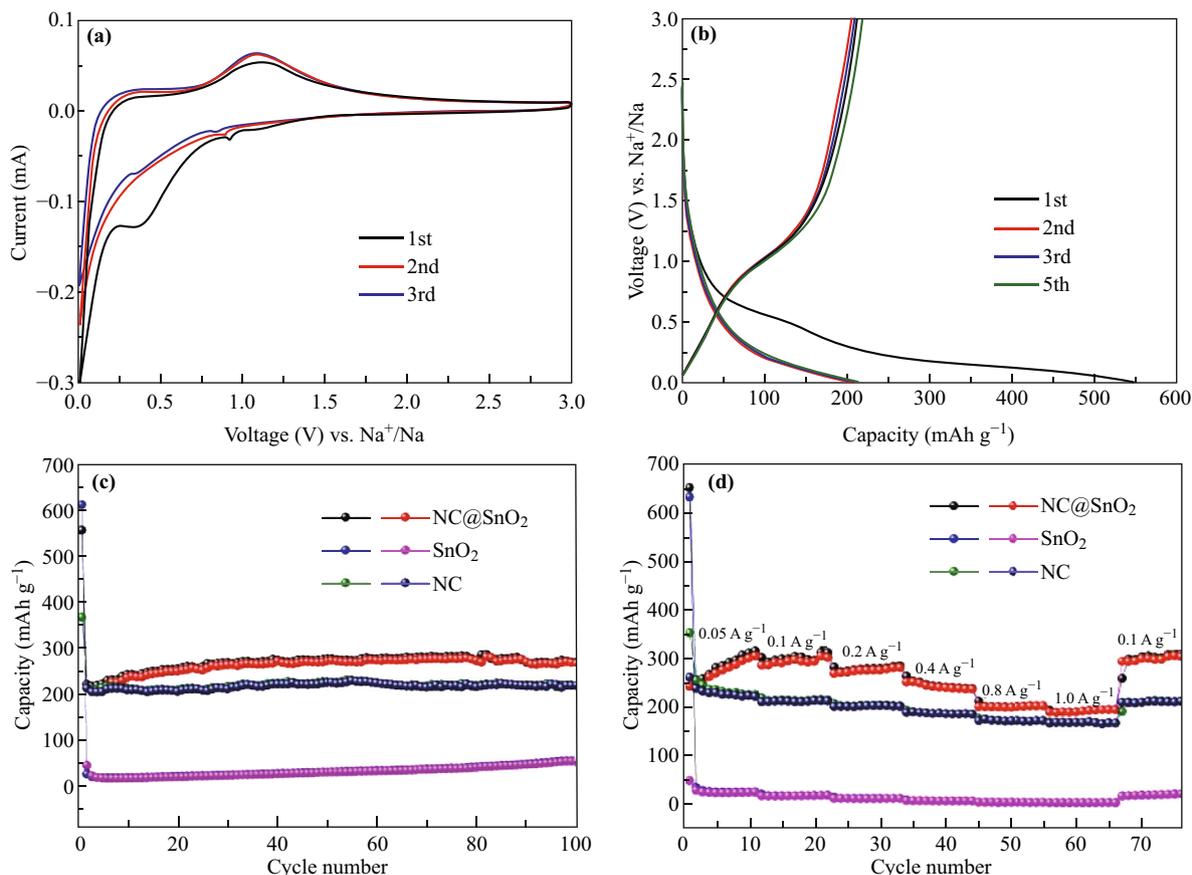


Fig. 6 Electrochemical performance for SIBs: **a** Cyclic voltammetry curves of NC@SnO₂ at 0.1 mV s⁻¹. **b** Charge–discharge voltage profiles of NC@SnO₂. **c** Cycling performances of NC@SnO₂, SnO₂, and NC at 100 mA g⁻¹. **d** Rate capabilities of NC@SnO₂, SnO₂, and NC. (Color figure online)

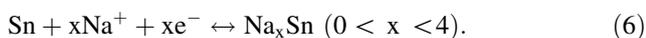
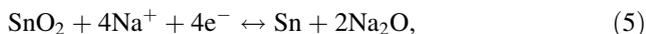


Figure 6b displays the discharge/charge capacities of 555.7/212.5 mAh g⁻¹ in the first charge/discharge cycle, respectively, with a coulombic efficiency of 38.2%. The low coulombic efficiency can be attributed to the formation of SEI film, and the irreversible reaction of SnO₂ with sodium ion to form Na_xSn alloys in the first discharge process [46, 47]. In this work, the SnO₂ and NC electrodes are used as a reference. In Fig. 6c, one can see that the discharge capacity of NC@SnO₂ is about 270 mAh g⁻¹, compared with 55 and 220 mAh g⁻¹ of SnO₂ 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@SnO₂ 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 SnO₂ and NC electrodes.

To further demonstrate the structural stability of hybrid NC@SnO₂, the SEM images of electrodes after about 75

cycles are given in Figs. 7 and S6. The SEM images of NC@SnO₂ and SnO₂ electrodes as anode for LIBs after cycling are shown in Fig. 7. Compared to the SEM images of the SnO₂ electrodes (Fig. 7c, d), we can observe the obvious NC could be retained, and the SnO₂ nanoflowers are not completely collapsed as shown in Fig. 7a, b. It demonstrates that the hybrid NC@SnO₂ electrodes have the better cycle performance and rate capability than those of SnO₂ electrodes in the LIBs due to the more stable structure of hybrid NC@SnO₂ material. We also investigated the structural change of both NC@SnO₂ and SnO₂ electrodes for SIBs. As shown in the SEM images of NC@SnO₂ electrode after cycling (Fig. S6a), the network structure of the NC could still be observed and no obvious reunion in comparison with the SnO₂ electrode (Fig. S6c). However, SnO₂ nanoflowers are completely collapsed in both NC@SnO₂ and SnO₂ 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 SnO₂ material upon repetitive cycling [20]. These results indicated that NC nanofibers of the NC@SnO₂ electrode can not only provide

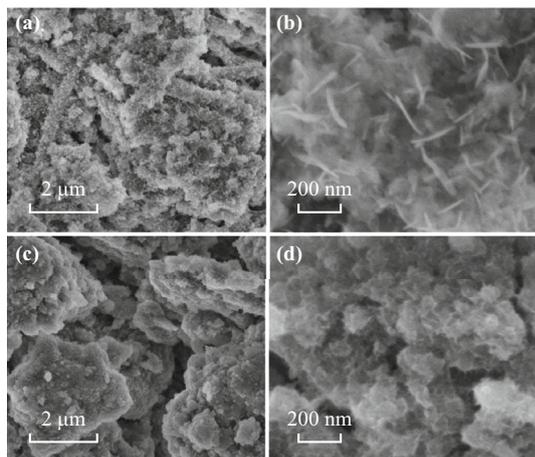


Fig. 7 SEM images of the electrodes after cycles for the Li-ion batteries: **a, b** NC@SnO₂ and **c, d** SnO₂

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⁺/Na⁺ ion to promote the rate capability. Moreover, the structure can make more surface of the nanoflower 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⁻¹ after 100 cycles at 1 A g⁻¹ for Li-ion battery and 270 mAh g⁻¹ after 100 cycles at 100 mA g⁻¹ for Na-ion battery.

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