Hierarchically branched TiO$_2$@SnO$_2$ nanofibers as high performance anodes for lithium-ion batteries

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ABSTRACT

Hierarchically heterostructured TiO$_2$@SnO$_2$ core-branch nanofibers are synthesized by a facile method using electrospinning followed by a hydrothermal treatment. By carefully controlling the TiO$_2$ content in the composite, a hierarchical heterostructure featuring uniform growth of rutile SnO$_2$ nanocubes on the surface of anatase TiO$_2$ nanofibers can be obtained. The hierarchically branched TiO$_2$@SnO$_2$ nanofibers combine both advantages of SnO$_2$ with large specific capacity and TiO$_2$ with outstanding structural stability. The TiO$_2$ content plays an important role in determining both the morphology and electrochemical performance of the composite. It is found that the TiO$_2$@SnO$_2$ nanofibers with 30 wt% TiO$_2$ exhibit both large specific capacity and good cycling stability, making them promising as anodes for high performance lithium-ion batteries.

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1. Introduction

Lithium-ion batteries with high energy density, light weight, long cycle life, and environmental friendliness are the major power sources for portable electronic devices and are promising power sources for the next generation electric vehicles [1–5]. To meet the ever increasing demands for larger energy density and power density, intensive research has been invested to develop new electrode materials with improved electrochemical performance. For instance, transition metal oxides such as Fe$_2$O$_3$, SnO$_2$, Co$_3$O$_4$, and MnO$_2$ have attracted a lot of interest as anode materials for lithium-ion batteries due to their higher theoretical capacities than that of commercial graphite anode. Among these anode candidates, SnO$_2$ has attracted tremendous interest owing to its high theoretical capacity of about 782 mAh g$^{-1}$ [6,7], which is significantly higher than that of commercial graphite (372 mAh g$^{-1}$). Nevertheless, practical implementation of SnO$_2$ to lithium-ion batteries is greatly hampered by its poor cycling stability. The severe capacity fading of SnO$_2$ is caused by the large volume expansion (up to about 300%) upon lithiation, which results in electrode pulverization and loss of electrical contact [8]. Moreover, the low electrical conductivity of SnO$_2$ aggravates capacity loss especially at high charge/discharge rates. Alternatively, TiO$_2$, with a much lower theoretical capacity (~178 mAh g$^{-1}$), has also received much attention due to its outstanding cycling stability and chemical stability [9,10]. However, the low theoretical capacity of TiO$_2$ still prohibits its widespread application in lithium-ion batteries.

It has been demonstrated that the smart hybridization of SnO$_2$ and TiO$_2$ could overcome the demerits of both materials and lead to improved electrochemical performance owing to the synergetic effect [11,12]. Most of previous works employed a SnO$_2$/core-TiO$_2$ shell heterostructure for the hybrid electrode design, where the TiO$_2$ shell maintains the mechanical integrity of SnO$_2$ during the reaction with Li while SnO$_2$ core compensates the low capacity of TiO$_2$. However, such design still has limitation to maximize the electrochemical performance of the hybrid electrode. In specific, the outer TiO$_2$ encapsulation could block or retard the direct access of lithium ions to the inner SnO$_2$, which is supposed to be the main capacity contributor. The reverse core-shell structure design with SnO$_2$ as outer layer deposited on the TiO$_2$ backbone could be more beneficial as SnO$_2$ has the direct contact with lithium electrolyte. Recently, several groups have reported the synthesis of TiO$_2$@SnO$_2$ core-shell heterostructures and their application as anodes for lithium-ion batteries. Yang et al. reported SnO$_2$ nanoparticles decorated TiO$_2$(B) nanowires with promising electrochemical performance [13]. However, the synthesis of TiO$_2$(B) is tedious and the SnO$_2$ content in the composite is probably low (~30 wt%). As
SnO\textsubscript{2} is the main capacity contributor for the composite, a relatively high SnO\textsubscript{2} content is required to achieve a large specific capacity and the tunability of the TiO\textsubscript{2}/SnO\textsubscript{2} mass ratio for the composite is desirable. In another report, Fan et al. reported the synthesis of TiO\textsubscript{2} nanotube@SnO\textsubscript{2} nanoflake core-branch arrays as anodes for lithium-ion batteries [14]. Although a larger specific capacity was achieved for the hybrid arrays due to the large SnO\textsubscript{2} content, the synthesis procedure involving atomic layer deposition is complicated and difficult to be scaled up in real production. Therefore, large scale production of the desirable TiO\textsubscript{2}@SnO\textsubscript{2} core-shell heterostructures with appropriate manipulation of the TiO\textsubscript{2}/SnO\textsubscript{2} mass ratio and superior electrochemical performance remains a great challenge.

In this work, we prepared hierarchically structured TiO\textsubscript{2}@SnO\textsubscript{2} composites by a combination of electrospinning and subsequent hydrothermal treatment. The hydrothermally grown SnO\textsubscript{2} nanocubes have solid contact with the TiO\textsubscript{2} nanofibers, resembling the morphology of a string of beads. Therefore, the SnO\textsubscript{2} nanocubes on the surface of the TiO\textsubscript{2} nanofibers can directly provide larger surface area for lithium insertion/extraction which could lead to large reversible capacity, while the backbone of TiO\textsubscript{2} nanofibers can sustain the structure stability during the cycling. Benefiting from the above features, the as-prepared TiO\textsubscript{2}@SnO\textsubscript{2} core-branch composite electrodes exhibit improved cycling stability and excellent rate capability, making them promising as advanced anodes for lithium-ion batteries.

2. Experimental

2.1. Synthesis of TiO\textsubscript{2} nanofibers

The synthesis procedure is illustrated in Fig. 1. TiO\textsubscript{2} nanofibers were prepared by an electrospinning method [15]. In detail, 4 g polyvinyl pyrrolidone (PVP), 20 mL acetic acid, and 10 mL titanium (IV) isopropoxide (TTIP) were mixed in ethanol with stirring for 1 h at room temperature condition to obtain a viscous TiO\textsubscript{2} sol. Subsequently, the as-obtained TiO\textsubscript{2} sol was loaded in a plastic syringe equipped with a 24-gauge stainless steel needle with applied voltage of 20 KV. The fluid rate was dominated by 1 mL h\textsuperscript{-1} using a syringe pump and the working distance was fixed at 10 cm to collect the TiO\textsubscript{2}/PVP composite nanofibers. Afterwards, the TiO\textsubscript{2} nanofibers was obtained by annealing at 500 °C for 2 h in air to remove the PVP.

2.2. Synthesis of TiO\textsubscript{2}@SnO\textsubscript{2} (ST) hierarchical structures

The different amounts of SnCl\textsubscript{4} and electrospun TiO\textsubscript{2} nanofibers were dispersed in 30 mL deionized water for preparing ST composites with different TiO\textsubscript{2}/SnO\textsubscript{2} mass ratios. The NaOH aqueous solution was used to adjust the pH value of above solution to be 9. Then, the solution was transferred into a 50 mL Teflon-lined stainless steel autoclave. The autoclave was heated and maintained at 220 °C for 3 h. After cooling down to ambient temperature condition, the as-synthesized products were washed with ethanol and deionized water in sequence, and dried at 80 °C for 12 h under a vacuum oven. The as-obtained ST composites with 10, 20, and 30 wt% TiO\textsubscript{2} were denoted as ST1, ST2, and ST3, respectively.

2.3. Materials characterization

The crystal structure of the as-obtained ST composites materials were characterized by X-ray diffraction (XRD, Bruker-AXS D8 Advance) with Cu K\textalpha radiation and Raman spectroscopy (Jobin-Yvon T6400 Micro-Raman system). The morphologies and microstructures of the ST composites materials were investigated by using field emission scanning electron microscopy (FE-SEM, Quant 250FEG), transmission electron microscopy (TEM, JEOL-2010), and high-resolution transmission electron microscopy (HRTEM, FEI Tecnai 20). The elemental compositions of the ST composites materials were analyzed by using energy-dispersive X-ray spectroscopy (EDS) attached to the TEM and X-ray photoelectron spectroscopy (XPS) by a PHI 5000 XPS system with a monochromatic Al anode X-ray source.

2.4. Electrochemical measurements

The slurry was mixed with the as-obtained ST composite, carbon black (Super P) and poly (vinylidene difluoride) (PVDF) by weight ratios of 8:1:1 in N-methylpyrrolidone (NMP), casted onto a copper foil and dried at 120 °C for 12 h under a vacuum oven. The mass loading of the as-obtained ST composites was in the range of 2–5 mg cm\textsuperscript{-2}. 1 M LiPF\textsubscript{6} in ethylene carbonate and diethyl carbonate (v/v = 1:1) solution was used as electrolyte solution, and Celgard 2400 was used as a separator. Typical coin cells were assembled by using lithium metal as counter electrodes and ST composites electrodes in an Ar filled-glove box at ambient temperature. The electrochemical properties of ST composites electrodes were assessed by cyclic voltammetry (CV)

![Fig. 1. Schematic diagram of the synthesis process of hierarchically heterostructured TiO\textsubscript{2}@SnO\textsubscript{2} core-branch nanofibers.](image)

![Fig. 2. XRD patterns of the hierarchically structured ST1 (a), ST2 (b), and ST3 (c) composite nanofibers.](image)
measurements using a CHI660D electrochemical workstation and galvanostatic charge/discharge measurements on a LAND CT2001A battery tester.

3. Results and discussions

Fig. 2 shows the XRD patterns of the ST composites with different TiO2 contents. As shown in Fig. 2a, except for a small hump at about 25°, all other diffraction peaks can be assigned to rutile SnO2 (JCPDS Card No. 41-1445), suggesting a high degree of crystallinity of the SnO2 nanocubes [16]. The small hump at 25° can be assigned to the (101) reflection of anatase TiO2 (JCPDS Card No. 21-1272) [17], which is probably due to the small content of TiO2 in ST1 sample. With the increasing of the TiO2 content in the composites, the (101) peak and another newly emerged (200) (located at 48°) peak for anatase TiO2 become more and more distinct. It is obvious that the adopted synthesis method is effective to prepare TiO2@SnO2 composites without trace of impurity phase.

Raman measurements were further applied to provide complementary structural information to the ST composites. Fig. 3 shows the Raman spectra of the ST composites with various TiO2 contents. As shown in Fig. 3a, the Raman bands located at 626, 461, and 778 cm⁻¹ correspond to the A1g, Eg, and B2g vibrational modes of tetragonal SnO2 [18]. A1g and B2g are related to the expansion and contraction of vibrational modes of Sn—O bonds, while Eg is related to the vibration of oxygen in the oxygen plane. Another four bands located at 146, 400, 518, and 638 cm⁻¹ can be attributed to anatase TiO2 [19]. The two bands at 638 and 146 cm⁻¹ are assigned to the Eg modes, the band at 400 cm⁻¹ corresponds to the B1g mode, and the band at 518 cm⁻¹ is assigned to the A1g mode. The Raman results, agreeing well with the XRD results, indicate the successful synthesis of anatase TiO2 and rutile SnO2 composites.

The electronic structures of the samples were investigated by XPS measurements. The survey-scan XPS spectrum of the ST3 sample in Fig. 4a demonstrates the co-existence of Ti, Sn, and O elements in the composite. The O 1s core-level XPS spectrum of ST3 is shown in Fig. 4b, where a peak at 530.0 eV is attributed to the lattice oxygen in TiO2 and SnO2 [20]. Fig. 4c shows the Ti 2p core-level XPS spectrum, revealing two distinct peaks at 458.2 and 464.2 eV for Ti 2p3/2 and the Ti 2p1/2, respectively. The splitting energy between Ti 2p3/2 and Ti 2p1/2 peaks is about 5.8 eV, indicating a normal state of Ti⁴⁺ in the as-prepared TiO2@SnO2 composites [21]. Moreover, the splitting of energy between Sn 3d5/2 (486.0 eV) and Sn 3d3/2 (494.5 eV) peaks is 8.5 eV in Fig. 4d, indicating the oxidation state of Sn is 4⁺ in the composite [16,21].

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Fig. 5a–i show the FESEM images of the as-prepared core-branch TiO$_2$@SnO$_2$ nanofibers with different TiO$_2$ contents at various magnifications. It is clear that the diameter of the nanofibers becomes larger and larger as the TiO$_2$ content decreases, indicating thicker SnO$_2$ shells are coated on the TiO$_2$ nanofiber surface. Inset in Fig. 5a shows the FESEM image of the bare TiO$_2$ nanofibers and the diameter of the TiO$_2$ nanofibers is estimated to be in the range between 100 and 200 nm. As shown in the enlarged FESEM images, it can be seen that SnO$_2$ nanocubes of 100 to 200 nm are uniformly branched on the TiO$_2$ nanofibers, demonstrating the hierarchical core-branch architecture. Fig. 5j–l show the EDS spectra of the various ST nanofibers, presenting that the as-prepared ST1, ST2, and ST3 composites consist of 8 wt%, 18 wt%, and 33 wt% of TiO$_2$.

TEM measurements were further carried out to investigate the microstructure of the ST composite. Fig. 6a shows the TEM image of the ST3 sample, displaying the core-branch hierarchical nanoarchitecture with SnO$_2$ cubes vertically aligned on the TiO$_2$ nanofiber. The average size of the SnO$_2$ nanocubes is about 100 nm, agreeing well with the FESEM results. Fig. 6b shows a TEM image at the interface area between TiO$_2$ nanofiber and one SnO$_2$ nanocube. It can be seen that the TiO$_2$ nanofiber is composed of numerous nanoparticles and the SnO$_2$ nanocube has close contact with the TiO$_2$ nanofiber. The HRTEM images taken from the red squares of S1 and S2 in Fig. 6b are shown in Fig. 6c and d, respectively. Fig. 6c shows well-defined lattice fringes with two interplanar spacings of 0.21 and 0.17 nm, corresponding to the (210) and (211) planes of anatase TiO$_2$, respectively. Simultaneously, the HRTEM image in Fig. 6d also shows well-defined lattice fringes with an interplanar spacing of 0.26 nm, corresponding to the (101) planes of rutile SnO$_2$. Further, a scanning transmission electron microscopy (STEM) image with corresponding EDS mapping images of Ti, Sn, and O elements for the ST3 sample are shown in Fig. 7. The distributions of Sn and O elements are uniform and clearly broader compared to the Ti distribution, validating the core-branch structure with uniform growth of SnO$_2$ nanocubes on the surface of TiO$_2$ nanofibers.

The electrochemical performances of various ST composites were investigated by testing half cells. Fig. 8a–c show the CV curves of the ST1, ST2, and ST3 electrodes in the voltage range of 0.05–3.0 V at a scan rate of 0.1 mV s$^{-1}$ at room temperature. As can be seen, the CV behaviors of the ST composite electrodes are generally consistent with those of other reported TiO$_2$/SnO$_2$ composites [17,20]. Obviously, all the first cycle CV curves are different from the second and third ones, which can be partially ascribed to the electrolyte decomposition for the solid-electrolyte interface (SEI) layer formation at low potential [22]. As shown in the three CV curves (Fig. 8a–c), the first reduction peak at around 0.75 V corresponds to the reduction of SnO$_2$ to Sn by Li$^+$ insertion as described in Eq. (1) [23]. This reaction is not fully reversible and
such peaks become very weak and shifts to higher potential for the 2nd and 3rd cycles. Another reduction peaks located at around 0.20 V can be attributed to Li-Sn alloying reactions according to Eq. (2) [24]. Meanwhile, the sharp oxidation peak at about 0.5 V can be attributed to the reversible dealloying reactions of the Li-Sn system, and another oxidation peak at about 1.0 V corresponds to the partial oxidation from Sn to SnO2 [21]. For the ST2 and ST3 electrodes, the CV curves exhibit another pair of redox peaks between 1.7 and 2.1 V, which can be assigned to Li ion insertion/extraction into/from TiO2 as described in Eq. (3) [25]. No obvious redox peaks for TiO2 can be found in the CV curve of ST1 in Fig. 8a, which is probably due to the rather low TiO2 content in the composite.

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

\[
\text{Sn} + x\text{Li}^+ + xe^- \rightarrow \text{Li}_x\text{Sn} (0 \leq x \leq 4.4) \quad (2)
\]

\[
\text{TiO}_2 + x\text{Li}^+ + xe^- \rightarrow \text{Li}_x\text{TiO}_2 (x \leq 1) \quad (3)
\]

**Fig. 6.** (a) TEM image of the ST3 nanofibers. (b) Magnified TEM image at the interface between TiO2 and SnO2. (c) HRTEM image of the rectangular area S1. (d) HRTEM image of the rectangular area S2.

**Fig. 8d–f** show the galvanostatic charge/discharge curves of hierarchically heterostructured ST1, ST2, and ST3 electrodes in a potential window of 0.05–3.0 V at a current density of 100 mA g\(^{-1}\), respectively. The initial discharge and charge capacities of the different electrodes are 2002.3 and 1025.1 mAh g\(^{-1}\) for ST1, 1755.4 and 866.1 mAh g\(^{-1}\) for ST2, and 1439.1 and 754.3 mAh g\(^{-1}\) for ST3, respectively. The initial irreversible capacity loss for the ST electrodes could be attributed to the SEI layer formation and partial reversibility of the reaction between SnO2 and Sn [Eq. (1)] [26–28]. It is obvious that the reversible capacity of the ST electrodes can be increased by increasing the TiO2 content in the composite.

Cycling performances of the three hierarchically structured ST electrodes were investigated at the same current density of 500 mA g\(^{-1}\) for 100 cycles in **Fig. 9a**. For the ST1 electrode, although the initial capacity is large, it drops quickly and only retains 150 mA g\(^{-1}\) after 100 cycles. Importantly, the ST2 and ST3 electrodes exhibit greatly improved cycling stability with much smaller capacity loss during cycling. The major reason of the poor cycling stability is the drastic volume change of the SnO2, which results in electrode pulverization and loss of electrical contact [17,21]. For the ST composites, when the SnO2 content is increased, the stain and volume change of the electrode during lithiation and delithiation will also be increased. As the TiO2 content decreases, the size of SnO2 nanocubes becomes larger (**Fig. 5**), which could further decrease the structural stability of the composites. Therefore, the hierarchically structured ST3 electrode displays excellent capacity retention with 453.3 mAh g\(^{-1}\) retained after 100 cycles. The rate capabilities of the three ST electrodes were compared in **Fig. 9b**. Although the ST3 electrode exhibits a lower specific capacity than the other two electrodes at low current
Fig. 7. (a) STEM image of the ST3 nanofiber and the corresponding EDS elemental mapping images for Sn (b), Ti (c), and O (d) elements.

Fig. 8. CV curves of the ST1(a), ST2(b), and ST3(c) electrodes at a scan rate of 0.1 mV s$^{-1}$ between 0.05 V and 3.0 V. Charge/discharge voltage profiles of the ST1 (d), ST2 (e), and ST3 (f) electrodes at 100 mA g$^{-1}$ between 0.05 V and 3.0 V.

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at constant current densities, it retains evidently better reversibility by providing higher capacities at high rates. At a current density of 2.0 A g⁻¹, the ST3 electrode can still show a higher capacity of 373.8 mAh g⁻¹, which are much larger than 128.4 mAh g⁻¹ for ST1 and 232.1 mAh g⁻¹ for ST2 electrodes, respectively. The promising electrochemical performance of the ST3 electrode can be attributed to the synergistic effect of the hierarchical architecture, where the TiO₂ nanoanode core provides good structural stability while the SnO₂ shell affords large reversible capacity. Moreover, the cycling performance and rate performance of the present ST3 electrode are compared with those of reported SnO₂/TiO₂ composites in literature (Table 1) [17,21,23,29–31]. It is noted that the present ST3 composite electrode exhibits superior rate performance and cycling performance compared to previously reported works, indicating its potential application as anode in lithium-ion batteries.

4. Conclusions

In summary, the hierarchically branched TiO₂@SnO₂ nanofibers with tunable TiO₂/SnO₂ mass ratios have been successfully synthesized via electrosprinning followed by hydrothermal treatment. The hydrothermal process promotes the uniform distribution of rutile SnO₂ nanocubes on the surface of the electrosprinning anatase TiO₂ nanofibers. The TiO₂ nanofibers not only provide a stable skeleton to grow the SnO₂ branch and build the hierarchical architecture but also function as strain buffer to improve the structural stability of the composite nanofiber. Results show the TiO₂@SnO₂ core-branch nanofibers with 30 wt% TiO₂ exhibit both excellent cycling stability (453.3 mAh g⁻¹ after 100 cycles at a current density of 500 mA g⁻¹) and good rate capacity (378.3 mAh g⁻¹ at a current density of 2.0 A g⁻¹), suggesting they can be promising anodes for the next-generation high performance lithium-ion batteries.

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References


Table 1

<table>
<thead>
<tr>
<th>Composite electrodes</th>
<th>Potential range/V</th>
<th>Rate performance</th>
<th>Capacity retention</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>G(TiO₂)SnO₂</td>
<td>0.01–3.0</td>
<td>250 mAh g⁻¹ at 1.0 A g⁻¹</td>
<td>462 mAh g⁻¹ after 50 cycles at 50 mA g⁻¹</td>
<td>[17]</td>
</tr>
<tr>
<td>TiO₂@SnO₂@CN</td>
<td>0–3.0</td>
<td>400 mAh g⁻¹ at 1.6 A g⁻¹</td>
<td>600 mAh g⁻¹ after 300 cycles at 160 mA g⁻¹</td>
<td>[21]</td>
</tr>
<tr>
<td>SnO₂/TiO₂</td>
<td>0.01–3.0</td>
<td>200 mAh g⁻¹ at 1.5 A g⁻¹</td>
<td>300 mAh g⁻¹ after 50 cycles at 800 mA g⁻¹</td>
<td>[29]</td>
</tr>
<tr>
<td>SnO₂-NPs/TiO₂ NFs</td>
<td>0.01–2.5</td>
<td>160 mAh g⁻¹ at 1.6 A g⁻¹</td>
<td>100 mAh g⁻¹ after 75 cycles at 100 mA g⁻¹</td>
<td>[23]</td>
</tr>
<tr>
<td>SnO₂@TiO₂ nanowires</td>
<td>0–3.0</td>
<td>204 mAh g⁻¹ at 2.0 A g⁻¹</td>
<td>201 mAh g⁻¹ after 500 cycles at 2.0 A g⁻¹</td>
<td>[30]</td>
</tr>
<tr>
<td>SnO₂@TiO₂</td>
<td>0.05–3.0</td>
<td>100 mAh g⁻¹ at 1.6 A g⁻¹</td>
<td>369 mAh g⁻¹ after 100 cycle at 100 mA g⁻¹</td>
<td>[31]</td>
</tr>
<tr>
<td>ST3 composite</td>
<td>0.05–3.0</td>
<td>378.3 mAh g⁻¹ at 2.0 A g⁻¹</td>
<td>453.3 mAh g⁻¹ after 100 cycles at 500 mA g⁻¹</td>
<td>this work</td>
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