

## Facile synthesis of hierarchical fern leaf-like Sb and its application as additive-free anode for fast reversible Na-ion storage

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Hierarchical Sb was successfully fabricated *via* a very simple and cost-effective electrochemical deposition method. Morphological and structural characterizations show that the as-prepared Sb has a uniform fern leaf-like structure which is composed of well-crystallized Sb nanoparticles. The formation mechanism of the fern leaf-like Sb was also investigated. The hierarchical Sb exhibits desirable properties for sodium storage, such as high electrical conductivity and large surface area. When used as additive-free anode for Na-ion batteries, the as-obtained fern leaf-like Sb reveals excellent cycling stability and rate capability. It can afford a high reversible capacity of 589 mAh g<sup>-1</sup> over 150 cycles at 0.5 A g<sup>-1</sup> and retain a capacity of 498 mAh g<sup>-1</sup> at a high rate of 10 A g<sup>-1</sup>. Furthermore, a full cell constructed by P2-Na<sub>2/3</sub>Ni<sub>1/3</sub>Mn<sub>2/3</sub>O<sub>2</sub>/fern leaf-like Sb also displays remarkably stable and robust Na-storage performance, which includes a high capacity retention of 70 % after 100 cycles at 0.5 A g<sup>-1</sup> and a large capacity of 370 mAh g<sup>-1</sup> at 10 A g<sup>-1</sup>. The excellent electrochemical performance of fern leaf-like Sb can be attributed to its morphological and structural features that ensure the fast ion and electron transport and stable electrode structure.

### Introduction

Sodium ion batteries (SIBs) have captured increasing attention as promising alternative energy storage devices, especially for large-scale energy storage systems, owing to their low cost, environmental benignity, and abundant natural Na resources.<sup>1,2</sup> One critical bottleneck at current is to develop efficient SIBs anodes which can store large amounts of Na<sup>+</sup> robustly and durably.<sup>3</sup> Metallic Sb has attracted immense interest because of its high theoretical capacity (660 mAh g<sup>-1</sup>), which is much higher than that of graphite used for commercial LIBs anodes.<sup>4</sup> However, implementation of Sb in SIBs is challenging since it suffers from rapid capacity fading and poor rate capability caused by drastic volume expansion/contraction (390%) upon cycling.<sup>5</sup>

In order to address this issue, designing Sb with special structural features is considered to be an efficient strategy in achieving high electrochemical performance and energy density.<sup>6-9</sup> Sb anodes with various nano-structures have been fabricated to show improved Na-ion storage properties, owing to short ion and electron diffusion pathways, facile strain

relaxation, and large electrode/electrolyte contact areas.<sup>10-15</sup> However, nanomaterials are often self-aggregated due to their high surface energy, which reduces their effective contact areas among active materials, additives, and electrolyte, and thus compromise the electrochemical performance.<sup>16</sup> Therefore, it is still a challenge to keep the effective contact areas large and fully realize the advantage of active materials at nanometer scale. Recently, hierarchical structures, which possess uniform assemblies of nanoscale primary building blocks (*e.g.*, nanoparticles, nanoplates, and nanorods), have captured considerable attention on enhancing the properties of energy storage and conversion, chemical sensing, and chromatography, *etc.*<sup>17-23</sup> This multiscale texturization provides a synergistic joining of two different length scales. The nanosized subunits can guarantee their original features, while the microsized structure would provide additional benefits, such as resistance to aggregation, high porosity, and enhanced electrode stability, consequently leading to improved rate capability and cyclability over their nanostructured and bulk counterparts.<sup>17-22</sup> For instance, a hierarchical Sb anode named cypress leaf-like Sb has been successfully fabricated through chemical replacement reaction between Sb<sup>3+</sup> and commercial Mg powder.<sup>24</sup> In this hierarchical structure, the void space among the branches of cypress can relieve the volume expansion and provide active sites for sodiation. As SIB anode, it showed a high reversible capacity of 550 mAh g<sup>-1</sup> after 120 cycles. However, the rate capability is still not satisfactory, in which it only delivered a capacity of 300 mAh g<sup>-1</sup> at the current density of 3.2 A g<sup>-1</sup>.

It is reported that binder-free anode configuration could deliver better rate capability and cycling performance than the

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conventional electrode architecture.<sup>25-27</sup> Traditional paste-based electrodes (*e.g.*, cypress leaf-like Sb<sup>24</sup>) usually involve the addition of insulating organic binders to inhibit the collapse of the active materials from current collectors, and electrical conductors to maintain the electrode conductivity onto the metal current collectors.<sup>28</sup> Actually, the binders make no contribution to Na storage, and the electrical conductor only contribute to the minimal battery performance. In addition, these two components will greatly decrease the energy density of SIBs. Furthermore, the presence of binders generally results in insufficient ion permeation and blocked electron transport, due to reduced accessible contact area of the active materials and increased polarization of the electrodes.<sup>25</sup> Therefore, it is highly desirable to develop highly stable hierarchical Sb structures directly grown on current collectors without using any additives, which can not only effectively decrease the weight of the SIB system, but also enhance the energy density of SIBs.<sup>29</sup> Moreover, the direct growth of hierarchical structures on current collector can ensure convenient ion diffusion pathways and electron transport channels, and guarantee sufficient structural interspaces for accommodating the volume expansion, which can result in satisfactory rate performance.<sup>29</sup>

Electrochemical deposition is one of the best methods to prepare additive-free electrodes.<sup>30-32</sup> This method offers many advantages, including simple and low-cost equipment, possible operation at room temperature, easily scale up from atomic dimensions to large areas, fast growth rates, high efficiency, rigid control of film thickness, uniformity and deposition rate.<sup>33</sup> Moreover, the most distinctive advantage of electrodeposition is to fabricate the additive-free electrodes with various complicated shapes. Building upon the above points, in this paper, we synthesized a hierarchical Sb structure directly grown on Ti substrate using one-step electrochemical deposition, which possesses the morphology of fern leaf. The as-prepared fern leaf-like Sb is composed of well-crystallized Sb nanoparticles. Further investigation of the growth mechanism of fern leaf-like Sb was also carried out. The fern leaf-like Sb exhibits desirable properties for sodium storage, such as high electrical conductivity and large surface area. It was applied as the additive-free Sb anode for SIB, showing excellent cyclability and rate capability for both Na-ion half and full cells, which can be attributed to its morphological and structural features that can ensure the fast ion and electron transport, and stable electrode structure. We believe that the excellent performance of Sb gained here shall arouse increasing attention on synthesizing more interesting and efficient hierarchical Sb electrodes without any additives for energy storage devices.

## Experimental

### Materials synthesis

#### 1. Synthesis of fern leaf-like Sb

0.0036 mol SbCl<sub>3</sub> was dissolved into 100 mL ethylene glycol under vigorous magnetic stirring for 30 min. The fern leaf-like Sb was prepared using an electrodeposition method. The electrodeposition was conducted in a two-electrode cell with Ti foil as the working electrode and Pt foil as the counter electrode at a constant current density of 1.0 mA cm<sup>-2</sup>. The product was washed with ethanol and deionized water, and dried at 80 °C under vacuum.

#### 2. Synthesis of layered P2-Na<sub>2/3</sub>Ni<sub>1/3</sub>Mn<sub>2/3</sub>O<sub>2</sub>

The P2-Na<sub>2/3</sub>Ni<sub>1/3</sub>Mn<sub>2/3</sub>O<sub>2</sub> was prepared by a co-precipitation method with nickel and manganese nitrates in a stoichiometric amount with sodium hydroxide. Na<sub>2</sub>CO<sub>3</sub> was added afterwards as the sodium source. The calcinations were taken at 600 °C for 4 h and 900 °C for 10 h in air.

#### 3. Synthesis of Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>/C

Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>/C was prepared by using a typical sol-gel method. Citric acid (0.2627 g), NaOH (0.515 g), NH<sub>4</sub>VO<sub>3</sub> (0.9746 g), and NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> (1.4375 g) were added into 200 mL deionized water under constant stirring at 80 °C. After several hours, most of water was evaporated. Then, the solution was dried at 80 °C for 12 h under vacuum. The mixture were then preheated at 300 °C for 4 h and heated at 850 °C for 8 h under N<sub>2</sub> atmosphere to obtain Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>/C sample.

### Materials characterizations

The morphology and structure were characterized by using scanning electron microscope (SEM, Hitachi S4800), high-resolution transmission electron microscope (HRTEM, FEI Titan 80-300) and X-ray diffraction (XRD, Bruker-axs Discover D8 applying Cu Kα (1.54056 Å)).

### Electrochemical measurements

The cells were assembled using CR2032 coin-type cells in a glove filled with nitrogen with a glass fiber separator (Whatman, GFB/55) and the electrolyte solution of 1.0 M NaClO<sub>4</sub> in EC: PC (1:1 by volume) with the addition of 5% fluoroethylene carbonate (FEC). The half cells were composed of Na metal as both counter and reference electrode and fern leaf-like Sb as working electrode. The mass loading of fern leaf-like Sb is about 0.6 mg cm<sup>-2</sup>. The full cells were constructed by the fern leaf-like Sb as negative electrode and P2-Na<sub>2/3</sub>Ni<sub>1/3</sub>Mn<sub>2/3</sub>O<sub>2</sub> and Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>/C as the positive electrodes, respectively. The galvanostatic charge-discharge tests were performed at various current densities on LAND-CT2001A test system (Wuhan, China). Cyclic voltammogram (CV) was tested on a BioLogic VSP potentiostat. Electrochemical impedance spectroscopy (EIS) was also taken on a BioLogic VSP potentiostat with frequency of 1 MHz to 10 mHz at the charge state (2.0 V). All of these experiments were conducted at room temperature.

P2-Na<sub>2/3</sub>Ni<sub>1/3</sub>Mn<sub>2/3</sub>O<sub>2</sub> was prepared by mixing 80% P2-Na<sub>2/3</sub>Ni<sub>1/3</sub>Mn<sub>2/3</sub>O<sub>2</sub>, 10% acetylene black, and 10% poly(vinylidene fluoride) (PVDF) by weight with an appropriate

amount of 1-methyl-2-pyrrolidinone (NMP). The above mixture was pressed onto an aluminum foil which served as a current collector. The cathode was dried at 120 °C in vacuum for 12 h.  $\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{C}$  positive electrode was also prepared using the above steps and mass ratios. These two different full cells are excessive positive electrode mass.

## Results and discussion

The crystal structure of the as-prepared Sb sample is revealed by X-ray diffraction (XRD) pattern. As shown in Fig. 1, except for the reflections of the substrate (Ti), the rest of diffraction peaks are in good agreement with rhombohedral Sb phase (JCPDS No. 35-0732), indicating the successful synthesis of pure crystalline Sb phase.

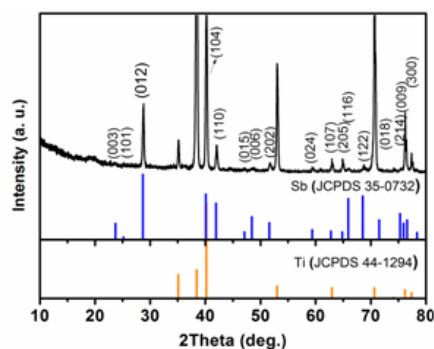


Fig. 1 XRD pattern of fern leaf-like Sb.

The morphologies and structures of the as-prepared Sb sample were characterized using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The low magnification SEM image in Fig. 2a proves the formation of large number of fern leaf-like Sb structures in a large-area, in which leaf-like Sb is uniformly dispersed on the Ti foil. Fig. 2b reveals leaf-like Sb with an average diameter of about 0.5–1  $\mu\text{m}$  and a length of 1.5–3  $\mu\text{m}$ . These fern leaf-like Sb structures still retain much space among the leaves, forming a porous morphology which can be expected to not only facilitate electrolyte penetration but also offer an extra space to relieve volume changes upon cycling. Fig. 2c and d show the magnified SEM images, in which many nanoparticles can be seen and they irregularly stack together forming a fern leaf-like structure.

TEM image (Fig. 3a) further presents the well-defined fern leaf-like structure, where the nanoparticles are exhibited in a much clearer way and some are highlighted in red circles. As seen in Fig. 3b, the average size of nanoparticles is 20–70 nm. The growth scheme of fern leaf-like Sb is illustrated in Fig. S1. In the initial stage, Sb nanoparticles are observed to uniformly disperse on Ti foil. With increasing deposition time, due to the strong crystalline anisotropy, Sb nanoparticles directionally aggregated, and the large aggregated particles grew along the preferred growth direction, leading to the formation of the fern leaf-like structure.<sup>24, 34–37</sup> The time-dependent morphology

is exhibited in Fig. S2. When the electrodeposition time is 3 min, a large number of nanoparticles are observed (Fig. S2a), indicating that the preferred morphology is nanoparticles in the initial stage. With the oriented aggregation process continuing, the increasing fern leaf-like structure is formed (Fig. S2b–c). Finally, well-defined fern leaf-like Sb is obtained (Fig. S2d). Fig. 3c presents a HRTEM image of this fern leaf-like Sb, where clear lattice fringes can be observed with distances of 3.73, 3.11, and 2.30 Å, corresponding to the (003), (012), and (104) planes of the rhombohedral Sb, further confirming the high crystallinity of the sample. The selected area electron diffraction (SEAD) pattern in Fig. 3d proves that the fern leaf-like Sb is polycrystalline.

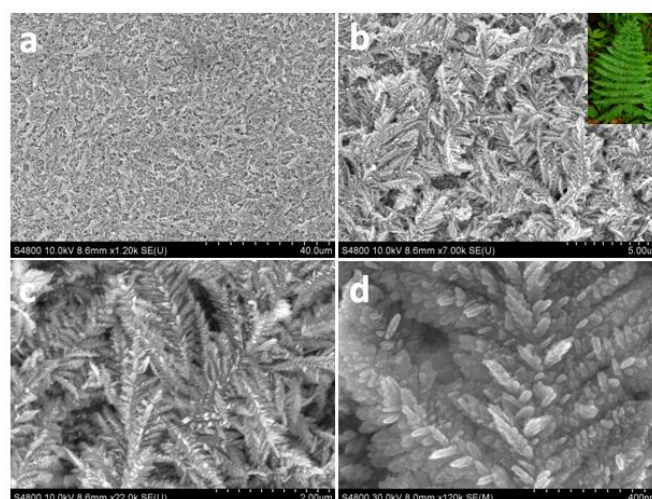
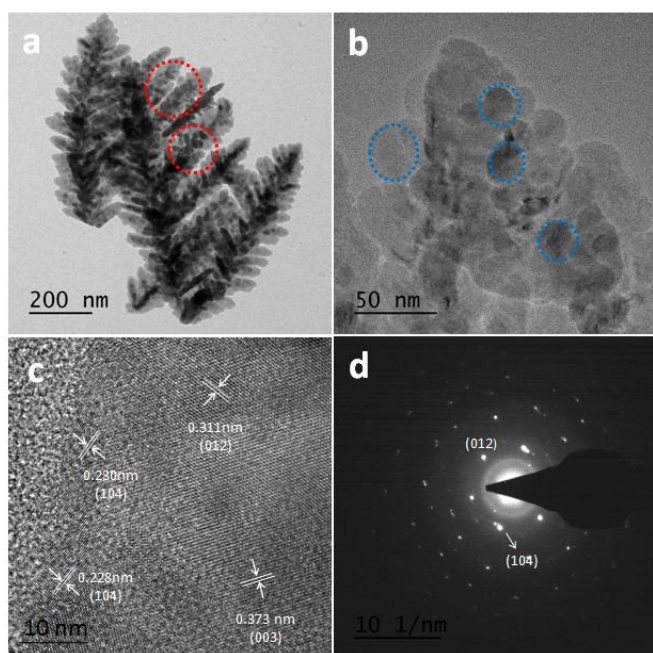


Fig. 2 SEM images of fern leaf-like Sb, (b inset) a photo of a fern leaf.

Motivated by its unique structural features, fern leaf-like Sb was used as an additive-free anode for SIB. Fig. 4a shows the CV curves of the fern leaf-like Sb in the initial three cycles at a sweep rate of 0.5  $\text{mV s}^{-1}$ . In the first cathodic scan, only a strong broad peak located at 0.33 V is observed, which could be attributed to the combination of the formation of a solid electrolyte interface (SEI) layer and  $\text{Na}_x\text{Sb}$  alloy which is subsequently transformed into  $\text{Na}_3\text{Sb}$ .<sup>38</sup> During subsequent cathodic scan, there are three peaks at 0.6, 0.4 and 0.35 V, corresponding to the multistep transformation of Sb into hexagonal  $\text{Na}_3\text{Sb}$  alloy phase by Na-ion insertion. The difference between the first and following cathodic scans is mainly ascribed to the formation of SEI layer and the rearrangement of the structure.<sup>39</sup> In all of the anodic scans, a strong peak at 0.94 V is clearly observed, resulting from the phase transformation from  $\text{Na}_3\text{Sb}$  to Sb.<sup>38</sup> Fig. 4b shows the charge-discharge curves of fern leaf-like Sb cycled at a current density of 0.5  $\text{A g}^{-1}$ , which shows typical characteristics of Sb anodes.<sup>13, 38</sup> The voltage profiles with different flat plateaus suggest the redox reactions associated with Na alloying and dealloying in the discharge and charge curves, respectively, which is in good agreement with CVs results in Fig. 4a. The voltage profiles of both charge and discharge have excellent

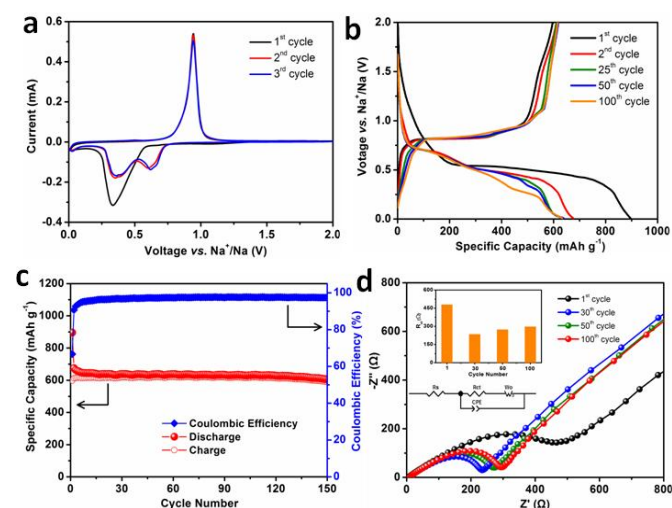
reproducibility from the 1st to 100th cycles, implying the stable structure of fern leaf-like Sb and high reversibility during cycling.



**Fig. 3** (a, b) TEM images, (c) HRTEM image, and (d) SAED pattern of fern leaf-like Sb.

The cycling performance of fern leaf-like Sb anode was investigated at a current density of  $0.5 \text{ A g}^{-1}$ , as revealed in Fig. 4c. The Sb anode presents an excellent cycling stability, and the reversible capacity is  $589 \text{ mAh g}^{-1}$  after 150 cycles, which is 98.5% of the initial reversible capacity. Except for the initial several cycles, the Coulombic Efficiency (CE) is about 97%, suggesting facile ion and electron transport in this fern leaf-like Sb anode.<sup>40</sup> Table S1 provides the cycling performance comparison of the as-prepared fern leaf-like Sb with some previously reported Sb-based anodes. It is clearly seen that both of the capacity and cycle life of fern leaf-like Sb are among the best values for reported Sb-based SIBs anodes. The electrochemical sodium storage behaviors of fern leaf-like Sb was further studied by electrochemical impedance spectroscopy (EIS) at different cycles (Fig. 4d). The Nyquist plots contain compressed semicircles in the high frequency region of each spectrum, which refer to the charge transfer resistance ( $R_{ct}$ ) for the electrode, and inclined lines in the low frequency region, which describe the Na ion diffusion in the electrode electrolyte interface.<sup>41-43</sup> An equivalent circuit model in the inset of Fig. 4d could be used to fit the impedance data. The resistor  $R_s$  and  $R_{ct}$  refers to the electrolyte resistance and charge transfer resistance, respectively. The constant phase element CPE and the Warburg element  $W_o$  represent double-layer capacitance and the ion diffusion in the host material, respectively.<sup>41-43</sup> The fitting values for charge transfer resistances ( $R_{ct}$ ) are shown in the inset of Fig. 4d. The large charge transfer resistance ( $480 \Omega$ ) in the high frequency region

of the first cycle may be attributed to the influence of SEI layer.<sup>44</sup> With the increasing cycling numbers, the charge transfer resistances ( $234 \Omega$  for 30<sup>th</sup>,  $273 \Omega$  for 50<sup>th</sup>, and  $297 \Omega$  for 100<sup>th</sup>) keep relatively stable only with minimal increase (inset of Fig. R3), implying well-maintained electrical contact and relatively stable SEI layer.<sup>45</sup> These results further prove that the ion diffusion pathways and electron conduction in the electrode were well maintained and the stable electrode structure well accommodated the large volume changes during charge/discharge cycles.<sup>46</sup>

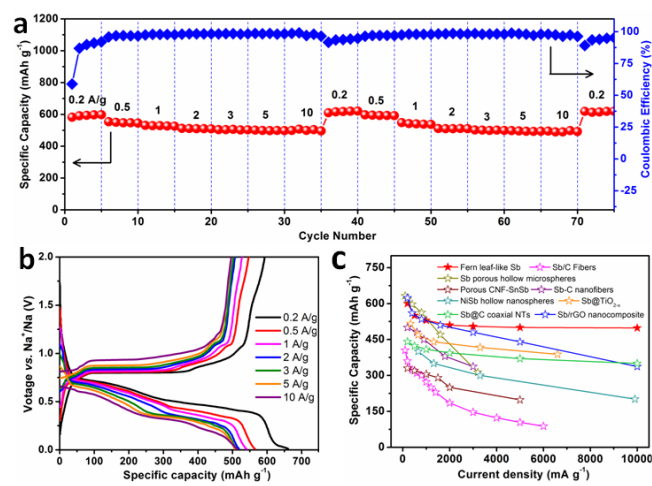


**Fig. 4** Electrochemical performance of the fern leaf-like Sb anode. (a) CV curves at a scan rate of  $0.5 \text{ mV s}^{-1}$  between 0.01 to 2.0 V (vs.  $\text{Na}^+/\text{Na}$ ). (b) Galvanostatic charge/discharge voltage profiles in different cycles at a current density of  $0.5 \text{ A g}^{-1}$ . (c) Cycling performance at  $0.5 \text{ A g}^{-1}$ . (d) Nyquist plots at charge state (2.0 V) from 1 MHz to 10 mHz.

The rate capability of the fern leaf-like Sb was tested at various current densities from 0.2 to  $10 \text{ A g}^{-1}$ , as shown in Fig. 5a. The anode affords reversible capacities of 600, 550, 530, 510, 505, 500 and  $498 \text{ mAh g}^{-1}$  at the current densities of 0.2, 0.5, 1.0, 2.0, 3.0, 5.0 and  $10 \text{ A g}^{-1}$ , respectively. At the rate of  $10 \text{ A g}^{-1}$ , the charging time is only 3 minutes. Fig. 5b exhibits the corresponding voltage profiles of the anode at various current densities. In spite of the increasing current densities from 0.2 to  $10 \text{ A g}^{-1}$ , both charge and discharge voltage profiles have quite similar shapes with minimal increase of the voltage offset. A second round of rate testing was performed to further demonstrate the excellent rate capability of the sample. The capacities are rather stable at each rate, regardless the rate cycling history. When the rate was returned to  $0.2 \text{ A g}^{-1}$ , the reversible capacity fully recovered to  $610 \text{ mAh g}^{-1}$ . The excellent rate performance indicates that the fern leaf-like Sb has good structure tolerance for repeated alloying/dealloying processes and can endure large rate changes while keeping high energy densities at the same time. To the best of our knowledge, the presented rate capability and specific capacities are among the best results of the reported Sb-based anodes (Fig. 5c).



The excellent electrochemical performance of the fern leaf-like Sb can be attributed to its special structure features. First, the hierarchical Sb structure inhibits the self-aggregation of Sb nanoparticles and ensures the surface remain uncovered to keep the effective and large contact areas. Therefore, the advantages of Sb nanoparticles can be fully achieved, resulting in short pathways both for Na ions and electrons. Second, the microsized structures contribute to the enough void space among the branches, which can relieve the volume change upon cycling and simultaneously offer more active sites for Na<sup>+</sup> ions. Third, metallic Sb with excellent electrical conductivity reacts with Na to form Na<sub>x</sub>Sb alloy which is also a good conductor. Therefore, the fern leaf-like Sb can be used as additive-free anodes without the addition of other conductive materials, where these leaves are closely associated with each other, easily transporting electrons from the substrate and forming a powerful conductive network, thereby promoting the efficient functioning of these leaves. Furthermore, the Sb anode shows the good structural stability, which still maintained the fern leaf-like morphology even after 100 cycles at a high rate of 0.5 A g<sup>-1</sup> (Fig. S3).

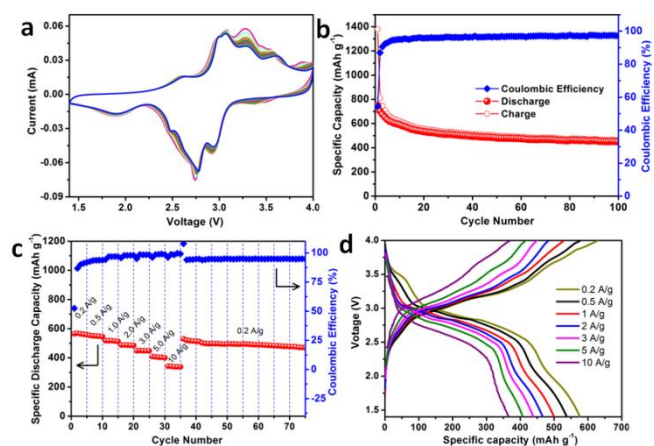


**Fig. 5** Electrochemical performance of the fern leaf-like Sb anode. (a) Rate performance at various current densities from 0.1 to 10 A g<sup>-1</sup>. (b) Charge/discharge voltage profiles at various current densities from 0.1 to 10 A g<sup>-1</sup>. (c) Ragone plots of fern leaf-like Sb anode and other Sb-based SIBs anodes from literature (Sb/C fibers<sup>47</sup>, Sb@TiO<sub>2-x</sub><sup>48</sup>, porous CNF-SnSb<sup>49</sup>, Sb-C nanofibers<sup>50</sup>, NiSb hollow nanospheres<sup>51</sup>, Sb/rGO nanocomposites<sup>52</sup>, Sb@C coaxial NTs<sup>53</sup>, Sb porous hollow microspheres<sup>14</sup>).

To evaluate the feasibility of the fern leaf-like Sb as additive-free anode in practice, two different full cells were assembled by using two different cathode materials (P2-Na<sub>2/3</sub>Ni<sub>1/3</sub>Mn<sub>2/3</sub>O<sub>2</sub> and Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>/C). The preparations and characterizations of the cathode materials can be found in Fig. S4-S8. Fig. 6 presents the electrochemical performances of the fern leaf-like Sb//Na<sub>2/3</sub>Ni<sub>1/3</sub>Mn<sub>2/3</sub>O<sub>2</sub> full cell. Fig. 6a is the CV curves of the full cell, which shows well-defined oxidation and reduction peaks and excellent reproducibility, indicating the good

stability of electrode materials again. The cycling performance can be seen in Fig. 6b. The full cell affords a high capacity retention of 70% (based on the anode mass) of the theoretical capacity of Sb (660 mAh g<sup>-1</sup>) after 100 cycles with a high CE of about 97.5 % at 0.5 A g<sup>-1</sup>.

The full cell also exhibits excellent rate capability, delivering the reversible capacities of 565, 540, 505, 470, 440, 405 and 370 mAh g<sup>-1</sup> at current densities of 0.2, 0.5, 1.0, 2.0, 3.0, 5.0 and 10 A g<sup>-1</sup>, respectively, with high CEs (Fig. 6c). When the current density was decreased to 0.2 A g<sup>-1</sup>, the reversible capacity recovered to 520 mAh g<sup>-1</sup>, which is 92 % of the initial reversible capacity, and kept stable up to 75 cycles. Fig. 6d presents the corresponding voltage profiles of the full cell at various current densities from 0.2 to 10 A g<sup>-1</sup>. The operation voltages are in the range of 2.5 and 2.8 V. The superior rate capability is attributed to the stable electrode structure. The fern leaf-like Sb//Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>/C full cell also presents a high capacity, good cyclability and rate capability (Fig. S9). The performances of the two full cells are much better than those of reported Sb-based full cells.<sup>48,51,54,55</sup> The above results fully prove that fern leaf-like Sb anode has strong feasibility for Na-ion storage in practice.



**Fig. 6** Electrochemical performance of fern leaf-like Sb//Na<sub>2/3</sub>Ni<sub>1/3</sub>Mn<sub>2/3</sub>O<sub>2</sub> full cell. (a) CV curves at a scan rate of 0.3 mV s<sup>-1</sup> with 10 cycles. (b) Cycling performance at a current density of 0.5 A g<sup>-1</sup> (with respect to the anode weight). (c) Rate capability (with respect to the anode weight) at various current densities from 0.2 to 10 A g<sup>-1</sup>. (d) Charge/discharge voltage profiles at various current densities from 0.2 to 10 A g<sup>-1</sup>.

## Conclusions

In summary, hierarchical Sb was firstly synthesized by using one-step electrodeposition method, which owns the morphology of fern leaf. Used as additive-free anode for Na-ion storage, the obtained fern leaf-like Sb shows excellent cycling stability and rate capability both in Na-ion half cells and

full cells. The excellent electrochemical performance can be attributed to morphological and structural features of the fern leaf-like Sb. It was demonstrated that the fern leaf-like Sb composed of self-assembled nanoparticles not only accommodates the volume expansion, but also facilitates the transport of Na ions and electrons. The synthesis method used in this work for hierarchical Sb structures is cost-effective, simple, high efficiency, and easily scaled up to large areas. We believe that our work may shed lights on the scalable fabrication of hierarchical additive-free electrode materials with special morphologies for improved electrochemical performance.

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