## **Electronic Supplementary Information for**

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

Liying Liang,<sup>a</sup> Yang Xu,<sup>a</sup> Yueliang Li,<sup>b</sup> Huishuang Dong,<sup>c</sup> Min Zhou,<sup>a</sup> Huaping Zhao,<sup>a</sup> Ute Kasier<sup>b</sup> and Yong Lei<sup>a,c,\*</sup>

<sup>a</sup> Institute of Physics & IMN MacroNano (ZIK), Ilmenau University of Technology, Professor Schmidt Strasse 26, 98693 Ilmenau, Germany. \*E-mail: yong.lei@tuilmenau.de

 <sup>b</sup> Central Facility for Electron Microscopy, Electron Microscopy Group of Materials Science, Ulm University, Albert-Einstein-Allee 11, 89081 Ulm, Germany
 <sup>c</sup> Institute of Nanochemistry and Nanobiology, School of Environmental and Chemical Engineering, Shanghai University, Shanghai 200444, China.



Fig. S1 Scheme illustration of the formation of fern leaf-like Sb on Ti foil.



**Fig. S2** Fern leaf-like Sb prepared in different electrodeposition time: (a) 3 min, (b) 5 min, (c) 10 min, (d) 15 min.

Materials	Current density	Reversible Capacity (mAh g <sup>-1</sup> )		
	(A g <sup>-1</sup> )	2 <sup>nd</sup> cycle	150 <sup>th</sup> cycle	Capacity retention
Bi <sub>0.36</sub> Sb <sub>0.64</sub> -C <sup>1</sup>	0.2	~494	~320	~64.8%
Sb/C fibers <sup>2</sup>	0.1	~422	~380	~90%
rGO/nano Sb composite <sup>3</sup>	0.328	~590	~528	~89.5%
Sb/MWCNT nanocomposite4	0.2	~502	~382 (120th)	~76.1%
Porous Sb/Cu <sub>2</sub> Sb <sup>5</sup>	0.066	~616	~485 (120th)	~78.7%
Bulk Sb <sup>6</sup>	0.33	~540	~570	~105.6%
Sb@C coaxial nanotubes7	0.1	~500	~410	~82%
Nanoporous Sb <sup>8</sup>	0.1	~630	~600	~95.2%
Sb-NiSb-Ni heterostructures9	0.066	~500	~450	~90%
Rod-like Sb-C composite <sup>10</sup>	0.05	~560	~450 (110th)	~80.4%
Sb porous hollow microspheres <sup>11</sup>	0.66	~575	~502	~87.4%
Sb/graphene <sup>12</sup>	0.328	~600	~530	~88.3%
Sb nanocrystals <sup>13</sup>	0.66	~600	~580 (100th)	~96.7%
Fern leaf-like Sb	0.5	~612	~589	~96.2%

**Table S1** Cycling performance comparison of the as-prepared fern leaf-like Sb with some previously reported Sb-based anodes.

## References

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Fig. S3 SEM image of fern leaf-like Sb after 100 cycles at 0.5 A  $g^{-1}$ .







Fig. S5 SEM images of layered P2-Na<sub>2/3</sub>Ni<sub>1/3</sub>Mn<sub>2/3</sub>O<sub>2</sub>.



**Fig. S6** Electrochemical performance of layered P2-Na<sub>2/3</sub>Ni<sub>1/3</sub>Mn<sub>2/3</sub>O<sub>2</sub> in a Na cell. (a) Cyclic voltammetry at a scan rate of 0.1 mV s<sup>-1</sup> between 1.5 to 4.0 V (*vs.* Na<sup>+</sup>/Na). (b) Cycling performance at a current density of 30 mA g<sup>-1</sup>, and (c) Galvanostatic voltage profiles in different cycles between 2.7 to 4.0 V (*vs.* Na<sup>+</sup>/Na).



Fig. S7 (a) XRD pattern and (b) SEM image of  $Na_3V_2(PO_4)_3/C$ .



Fig. S8 Electrochemical performance of  $Na_3V_2(PO_4)_3/C$  cathode. (a) Cyclic voltammetry at a scan rate of 0.1 mV s<sup>-1</sup> between 1.7 to 4.0 V (*vs.* Na<sup>+</sup>/Na). (b) Galvanostatic charge/discharge voltage profile, and (c) cycling performance at a current density of 80 mA g<sup>-1</sup> between 2.7 to 4.0 V (*vs.* Na<sup>+</sup>/Na).



**Fig. S9** Electrochemical performance of fern leaf-like Sb//Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>/C full cell. (a) CV curves at a scan rate of 0.3 mV s<sup>-1</sup>. (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>.