## SUPPLEMENTARY INFORMATION

## Self-standing NASICON-type electrodes with high mass loading for fast cycling all-phosphate sodium-ion batteries

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Figure S1 XRD diffraction patterns and TG-DTA curves of carbon nanotube fabrics (CNFs) ((a) and (b)), NaTi<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>/CNFs ((c) and (d)) and Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>/CNFs ((e) and (f)). The CNFs were washed by concentrated hydrochloric acid and mixture of ethanol/water 1:1 (*vol./vol.*). The temperature range of TGA measurements is 30 to 700 °C with a heating rate of 2 °C min<sup>-1</sup> in O<sub>2</sub> atmosphere. The color of the TGA residue of CNFs is red, suggesting that it is Fe<sub>2</sub>O<sub>3</sub>.

The X-ray diffraction (XRD) pattern of pretreated carbon nanotube fabrics (CNFs) (**Figure S1**a) shows four characteristic peaks of carbon nanotubes (CNTs), as consistent with literatures.[S1,S2] The XRD patterns of  $NaTi_2(PO_4)_3/CNFs$  (NTP/CNFs) and  $Na_3V_2(PO_4)_3/CNFs$  (NVP/CNFs) are displayed in **Figure S1**c and e. Both electrodes adopted a rhombohedral structure with a space group of  $R^3c$ . The diffraction peaks at 26° and 44° that arises from CNFs. No impurity was detected by XRD. This result confirms that phase pure electrodes are obtained and the presence of carbon nanotubes did not affect the chemical composition of NTP and NVP during the preparation process.

The mass loading of the electrodes can be quantified by comparing the mass differences between CNFs and electrodes before and after syntheses, or by thermogravimetric analysis (TGA) to eliminate the presence of amorphous and graphitized carbon under oxygen flow at about 625 °C. Both methods were applied to calculate the mass loading of the electrodes. According to the weight differences, the calculated CNFs contents are 20.3 and 22.5 wt% in NTP/CNFs and NVP/CNFs, respectively. In such way, the amorphous carbon introduced by the carbonization of oxalic acid are counted as active materials. The mass percentages of active materials (79.7 wt% for NTP and 77.5 wt% for NVP) on CNFs are thus higher than their actual values.

According to the TGA results, 23.5 and 27.4 wt% carbon are removed respectively from NTP/CNFs and NVP/CNFs electrodes, as shown in **Figure S1**d and f. Since the NTP and NVP materials have negligible mass changes during TGA measurement in the temperature range of 30 to 700 °C,[S3,S4] the remaining specimens are mixture of NTP or NVP with tiny amount of Fe<sub>2</sub>O<sub>3</sub> that introduced by the Fe catalyst impurity in CNFs. The amount of Fe impurity in electrodes, according to the TGA results of CNFs in **Figure S1**b,

is roughly 0.8 wt%. Hence, the active material mass loading values of 75.7 wt% for NTP/CNFs and 71.8 wt% for NVP/CNFs are their actual values. On the basis of the TGA result and the total mass of both electrodes, high active loadings of 8.02 and 7.63 mg cm<sup>-2</sup> for NTP/CNFs and NVP/CNFs, respectively, have been achieved. Furthermore, the mass loading of electrodes can be easily controlled by adjusting the ratio of liquid precursor to CNFs surface ratio in the coating process.

## **Raman Characterization**



**Figure S2** Raman spectra of carbon nanotube fabrics (CNFs),  $NaTi_2(PO_4)_3/CNFs$  and  $Na_3V_2(PO_4)_3/CNFs$ . Raman spectra were recorded with an excitation wavelength of 532 nm and long working distance 50 × objective lens.

The structural features of the CNFs, NTP/CNFs and NVP/CNFs were further studied by Raman spectroscopy as the results are shown in **Figure S2**. Three distinguishable Raman bands at 1580 (G band) with a shoulder around 1605 cm<sup>-1</sup>, 1349 (D band) and 2690 cm<sup>-1</sup> (2D band) are observed for pristine CNFs, which originate from the Raman-active, in-plane atomic displacement E2g mode, disorder-induced features of the CNTs and the overtone of D band.[S5] When comparing the Raman spectra of all three samples, the similar high intensity G band suggesting the presence of highly graphitized carbon which kept stable after active material decorations. The appearance of the D band at the same wavenumber for all samples indicates the existence of defects sp<sup>3</sup> carbon. Both of the carbon phases could help overcome the intrinsic poor electronic conductivity of phosphate electrode materials and improve the binding properties between the particles of active material and CNFs.[S3,S4,S6,S7] Recognizable differences between pristine CNFs and the self-standing electrodes are the presence of P-O Raman vibrations about 1010 and 1070 cm<sup>-1</sup> in both electrodes. It is also worth noting that the position of the G band is shifted to lower wavenumbers in both electrodes owing to the increased bond length of the graphite carbon, which arising from the embedded active materials since the G-band is quite sensitive to doping and minor strains.[S8,S9] Moreover, the D band's relative intensity (referred to the intensity of G band) of CNFs, NTP/CNFs and NVP/CNFs is 31.2%, 44.5% and 49.8%, respectively. The differences are a consequence of the carbonization of oxalic acid during annealing step in the synthesis process, which are consistent with the TGA data shown in **Figure S1**.



Figure S3 SEM image of field view and EDX element maps of  $Na_3V_2(PO_4)_3/CNFs$ . The element characteristics for the  $Na_3V_2(PO_4)_3$  (Na, V, P, O) are distributed over the complete focused area, indicating the presence of small  $Na_3V_2(PO_4)_3$  particles in the bulk CNFs.



Figure S4 Cyclic voltammetry profiles of pretreated carbon nanotube fabrics (CNFs) (a),  $NaTi_2(PO_4)_3/CNFs$  and  $Na_3V_2(PO_4)_3/CNFs$  versus metallic sodium respectively at 25 °C (b).



Figure S5 (a) Cyclic voltammetry curves of the NaTi<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>/CNFs||Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>/CNFs full cell measured with different scan rates from 0.5 to 10 mV s<sup>-1</sup> at 25 °C. (b) Peak current as a function of scan rate, *v*, and (c) peak current as a function of root square of scan rate, *v*<sup>1/2</sup>, of NaTi<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>/CNFs||Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>/CNFs full cell.

Samples	Mass loading (mg cm <sup>-2</sup> )	Current density	Cycle number	Initial capacity (mAh g <sup>-1</sup> )	Capacity retention	Counter electrode	Ref.
Bi-CC	1.2	0.05A g <sup>-1</sup> 0.2A g <sup>-1</sup>	300 300	375.5 239.26	93.2% 74.0%	metallic sodium	[S10]
Sb <sub>2</sub> O <sub>3</sub> /CC	1.5	1A g <sup>-1</sup> 5A g <sup>-1</sup>	350 350	476.9 350.0	99.6% >95.0%	metallic sodium	[011]
Sb <sub>2</sub> S <sub>3</sub> /CC	1.0	2A g <sup>-1</sup> 10A g <sup>-1</sup>	400 400	697.8 530.0	93.0% 88.3%	metallic sodium	[511]
NiCo <sub>2</sub> O <sub>4</sub> /CC	1.3-1.5	0.05A g <sup>-1</sup>	50	669	81.0%	metallic sodium	[S12]
MoS <sub>2</sub> /N-Doped CC	0.5	1A g-1	1000	352.0	75.3%	metallic sodium	[S13]
MoS <sub>2</sub> -TiO <sub>2</sub> -CC	3.0	0.5A g <sup>-1</sup>	200	227.5	69.0%	metallic sodium	[S14]
FeFe(CN) <sub>6</sub> /CC	-	1C	1200	≈49.3	81.2%	metallic sodium	[S15]
Na <sub>2</sub> Ti <sub>3</sub> O <sub>7</sub> nanoarrays on Ti substrates	-	35C	10000	65	≈86.7%	metallic sodium	[816]
$Na_{2/3}Fe_{1/2}Mn_{1/2}\\O_2/G$	-	0.1C	140	95	63.2%	metallic sodium	[S17]
SnO <sub>2</sub> /CC	0.9	0.1C	100	468.8	80.0%	metallic sodium	[S18]
Na <sub>3</sub> V <sub>2</sub> (PO <sub>4</sub> ) <sub>3</sub> /C/r GO	≈0.64	5C 10C	400 400	97.6 89.7	96.1% 89.6%	metallic sodium	· [S19]
		3C	200	55.2	86.6%	Na <sub>3</sub> V <sub>2</sub> (PO <sub>4</sub> ) <sub>3</sub> / C/rGO	
Na <sub>3</sub> V <sub>2</sub> (PO <sub>4</sub> ) <sub>3</sub> /C/ CC	3.5	20C 50C	2000 2000	101.9 95.0	82.0% 78.4%	metallic sodium	· [S20]
		1C 5C	100 500	≈110 ≈100	89.2% 67.3%	NaTi <sub>2</sub> (PO <sub>4</sub> ) <sub>3</sub> @	
Na <sub>2/3</sub> [Ni <sub>1/3</sub> Mn <sub>2/3</sub> ] O <sub>2</sub> /rGO	5-6	1C	200	≈85	>95.0%	metallic sodium	[S21]
Na <sub>2</sub> FeP <sub>2</sub> O <sub>7</sub> /CC	1-1.5	10C	2000	67.5	83.0%	metallic sodium	[S22]
NaTi <sub>2</sub> (PO <sub>4</sub> ) <sub>3</sub> /CN Fs	8.02	1C	700	131.3	96.3%	metallic sodium	This work
Na <sub>3</sub> V <sub>2</sub> (PO <sub>4</sub> ) <sub>3</sub> /C NFs	7.63	1C	700	115.2	89.7%		
		1C 20C	1000 4000	125.1 119.5	91.0% 74.5%	NaTi <sub>2</sub> (PO <sub>4</sub> ) <sub>3</sub> /C NFs	

**Table S1.** Comparison of mass loading and electrochemical performance of different kinds of flexible electrode materials for sodium-ion batteries.

CC = carbon cloth; C = carbon; rGO = reduced graphene oxide; G = graphene film; CNFs = carbon nanotube fabrics



Figure S6 XRD patterns of the  $NaTi_2(PO_4)_3/CNFs$  (a) and  $Na_3V_2(PO_4)_3/CNFs$  (b) electrodes after 4000 cycles. The electrodes were cleaned with a mixture of EC/PC (1:1 *vol./vol.*) and their surface layers which were facing the electrolyte are peeled off before XRD measurement.



Figure S7 TEM images of the  $NaTi_2(PO_4)_3/CNFs$  ((a)~(c)) and  $Na_3V_2(PO_4)_3/CNFs$  ((d)~(f)) electrodes after 4000 cycles.



Figure S8 <sup>23</sup>Na static NMR spectra of 1M NaPF<sub>6</sub> in EC/PC, Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>/CNFs and NaTi<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>/CNFs electrodes.



**Figure S9** Ragone plots showing the performance of the batteries prepared in this work and conventional lithium-ion batteries and capacitors on device-level. The shaded curves in (a) and the performance targets for hybrid-electric (HEVs) and plug-in hybrid-electric vehicles (PHEVs) were estimated from Ref. [S23]. The shaded curves in (b) and the performance of high-power commercial A123 battery were estimated from Ref. [S24].

For the sodium-ion cells presented in this work, the weight (or volume) for the calculation of energy and power densities including the mass (or volume) of two electrodes, electrolyte and separator.

## References

- (S1) A. Cao, C. Xu, J. Liang, D. Wu and B. Wei, *Chem. Phys. Lett.*, 2001, **344**, 13–17.
- (S2) B. Che, B. Nguyen, L.-T. T. Nguyen, H. Nguyen, V. Nguyen, T. Van Le and N. Nguyen, *Chem. Cent. J.*, 2015, 9, 10.
- (S3) S. Yu, A. Mertens, R. Schierholz, X. Gao, Ö. Aslanbas, J. Mertens, H. Kungl, H. Tempel and R.-A. Eichel, J. Electrochem. Soc., 2017, 164, A370–A379.
- (S4) S. Yu, A. Mertens, H. Kungl, R. Schierholz, H. Tempel and R.-A. Eichel, *Electrochim. Acta*, 2017, 232, 310–322.
- (S5) K. McGuire and A. M. Rao, Characterization Techniques in Carbon Nanotube Research. In *Carbon Nanotubes: Science and Applications*; Meyyappan, M., Eds.; CRC Press LLC: Boca Raton, 2004; pp133-134.
- (S6) C. Wu, P. Kopold, Y. L. Ding, P. A. Van Aken, J. Maier and Y. Yu, ACS Nano, 2015, 9, 6610–6618.
- (S7) D. Wang, Q. Liu, C. Chen, M. Li, X. Meng, X. Bie, Y. Wei, Y. Huang, F. Du, C. Wang and G. Chen, ACS Appl. Mater. Interfaces, 2016, 8, 2238–2246.
- (S8) M. S. Dresselhaus, A. Jorio and R. Saito, Annu. Rev. Condens. Matter Phys., 2010, 1, 89–108.
- (S9) M. M. Hossain, H. Shima, M. A. Islam, M. Hasan and M. Lee, J. Phys. Chem. C, 2016, 120, 17670–17682.
- (S10) S. Liu, Z. Luo, J. Guo, A. Pan, Z. Cai and S. Liang, *Electrochem. commun.*, 2017, 81, 10–13.
- (S11) S. Liu, Z. Cai, J. Zhou, M. Zhu, A. Pan and S. Liang, J. Mater. Chem. A, 2017, 5, 9169–9176.
- (S12) Y. Mo, Q. Ru, J. Chen, X. Song, L. Guo, S. Hu and S. Peng, J. Mater. Chem. A, 2015, 3, 19765–19773.
- (S13) W. Ren, H. Zhang, C. Guan and C. Cheng, Adv. Funct. Mater., 2017, 27, 1-10.
- (S14) W. Ren, W. Zhou, H. Zhang and C. Cheng, ACS Appl. Mater. Interfaces, 2017, 9, 487–495.
- (S15) P. Nie, L. Shen, G. Pang, Y. Zhu, G. Xu, Y. Qing, H. Dou and X. Zhang, J. Mater. Chem. A, 2015, 3, 16590–16597.
- (S16) S. Fu, J. Ni, Y. Xu, Q. Zhang and L. Li, Nano Lett., 2016, 16, 4544–4551.
- (S17) H. Zhu, K. T. Lee, G. T. Hitz, X. Han, Y. Li, J. Wan, S. Lacey, A. V. W. Cresce, K. Xu, E. Wachsman and L. Hu, ACS Appl. Mater. Interfaces, 2014, 6, 4242–4247.
- (S18) Y. Liu, X. Fang, M. Ge, J. Rong, C. Shen, A. Zhang, H. A. Enaya and C. Zhou, *Nano Energy*, 2015, 16, 399–407.
- (S19) W. Wang, Q. Xu, H. Liu, Y. Wang and Y. Xia, J. Mater. Chem. A, 2017, 5, 8440– 8450.
- (S20) D. Guo, J. Qin, Z. Yin, J. Bai, Y. K. Sun and M. Cao, *Nano Energy*, 2018, 45, 136– 147.
- (S21) D. Yang, X. Z. Liao, J. Shen, Y. S. He and Z. F. Ma, J. Mater. Chem. A, 2014, 2, 6723–6726.

- (S22) H. J. Song, D. S. Kim, J. C. Kim, S. H. Hong and D. W. Kim, *J. Mater. Chem. A*, 2017, **5**, 5502–5510.
- (S23) S. W. Lee, B. M. Gallant, H. R. Byon, P. T. Hammond and Y. Shao-Horn, *Energy Environ. Sci.*, 2011, **4**, 1972–1985.
- (S24) J. H. Pikul, H. Gang Zhang, J. Cho, P. V. Braun and W. P. King, *Nat. Commun.*, 2013, 4, 1732–1735.