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# **Supporting Information**

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Novel  $K_3V_2(PO_4)_3/C$  Bundled Nanowires as Superior Sodium-Ion Battery Electrode with Ultrahigh Cycling Stability

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## Supporting Information

### Novel K<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>/C bundled nanowires as superior sodium-ion battery electrode

#### with ultra-high cycling stability

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**Figure S1.** Schematic illustration for the fabrication process and proposed formation mechanism of the  $K_3V_2(PO_4)_3/C$  bundled nanowires and blocks.



Figure S2. The photos for solution precursor of  $K_3V_2(PO_4)_3$  bundled nanowires (A) and blocks (B). The photos for dried precursor of  $K_3V_2(PO_4)_3$  bundled nanowires (C) and blocks (D).



Figure S3. (A, B) SEM images of the K<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> precursor baked at 180 °C for 2h.

Table S1.	The ICP	test results	of the	$K_3V_2$	$(PO_4)$	3/C	bundled	nanowires.
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Temperature	K: V: P
<b>700</b> °C	3.0 : 2.04 : 2.97
<b>800</b> °C	3.0 : 2.06 : 3.04
900 °C	3.0 : 1.99 : 3.08



Figure S4. SEM images of the  $K_3V_2(PO_4)_3/C$  bundled nanowires sintered at 800 °C.

<b>Table S2.</b> The ICP test results of the $K_3V_2(PO_4)_3/C$ blocks sintered at 8	00 °C.
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	Temperature	K: V: P
Blocks	800 °C	3.00 : 2.03 : 3.01



Figure S5. XRD patterns of the  $K_3V_2(PO_4)_3/C$  bundled nanowires and blocks sintered at 800 °C.



Figure S6. (A-C) SEM images of the K<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>/C blocks sintered at 800 °C.



Figure S7. Elemental mapping images of the  $K_3V_2(PO_4)_3/C$  blocks sintered at 800 °C.



Figure S8. Raman spectra (A) and FT-IR spectra (B) of the  $K_3V_2(PO_4)_3/C$  samples.



Figure S9. TGA curves of the  $K_3V_2(PO_4)_3/C$  bundled nanowires and blocks sintered at 800 °C.



Figure S10. XPS spectra of the V 2p3/2 core level region of the  $K_3V_2(PO_4)_3/C$  bundled nanowires.



**Figure S11.** The nitrogen adsorption-desorption isotherms of the  $K_3V_2(PO_4)_3/C$  bundled nanowires (A) and blocks (B). The pore size distribution of the  $K_3V_2(PO_4)_3/C$  bundled nanowires (inset of A) and blocks (inset of B).



**Figure S12.** In situ X-ray diffraction patterns during galvanostatic charge and discharge of the  $K_3V_2(PO_4)_3/C$  bundled nanowires at 100 mA g<sup>-1</sup>.



Figure S13. Ex situ XRD patterns of the  $K_3V_2(PO_4)_3/C$  bundled nanowires.



**Figure S14.** The galvanostatic intermittent titration technique (GITT) for  $K_3V_2(PO_4)_3$  bundled nanowires.



**Figure S15.** Cyclic voltammograms (CV) and corresponding dq/dv plots of the  $K_3V_2(PO_4)_3/C$  bundled nanowires (A and B) and blocks (C and D) at a scan rate of 2.0 mV s<sup>-1</sup> in the electrochemical window of 1.5 to 4.0 V *vs.* Na/Na<sup>+</sup>.



**Figure S16.** (A) Cycling performance of the three  $K_3V_2(PO_4)_3/C$  bundled nanowires at 100 mA g<sup>-1</sup> in the electrochemical window of 1.5 - 4.0 V. (B) Rate performance of the three samples. (C, D) AC impedance plots of the three samples before and after 100<sup>th</sup> cycles (from 0.1Hz to 100 kHz).

	K: Na: V
Before cycle	3.02 : 0.81 : 2.00
Charge to 4.0 V	1.01 : 0.01 : 2.00
Discharge to 1.5 V	1.16 : 2.10 : 2.00
After 2 cycles	1.07 : 2.26 : 2.00
After 30 cycles	1.02 : 2.25 : 2.00
After 100 cycles	1.01 :2.24 : 2.00
After 500 cycles	1.02 : 2.25 : 2.00

After 30 cycles 1.02 : 2.25 : 2.00After 100 cycles 1.01 : 2.24 : 2.00After 500 cycles 1.02 : 2.25 : 2.001.02 : 2.25 : 2.00



Figure S17. Columbic efficiency of the  $K_3V_2(PO_4)_3/C$  bundled nanowires and blocks at 100 mA g<sup>-1</sup>.



**Figure S18.** Charge-discharge curves of the  $K_3V_2(PO_4)_3/C$  bundled nanowires (A) and blocks (B), at various current densities from 100 to 1,000 mA g<sup>-1</sup>.

Table S3. The *ex situ* ICP test results of the  $K_3V_2(PO_4)_3/C$  bundled nanowires.



Figure S19. The cycle performances of the  $K_3V_2(PO_4)_3/C$  blocks at 1,000 (A) and 2,000 mA g<sup>-1</sup> (B).

	Material	Current density (mA g <sup>-1</sup> )	Initial capacity (mAh g <sup>-1</sup> )	Cycle numbers	Per cycle decay (%)	Referance
		100	119	100	0.0213	
1 <b>K</b>	<b>K</b> .V.( <b>PO</b> .).	500	71.0	1,000	0.0026	Our work
	$\mathbf{K}_{3}$ <b>v</b> <sub>2</sub> ( <b>r U</b> <sub>4</sub> ) <sub>3</sub>	1,000	66.0	2,000	0.0023	Our work
		2,000	45.7	2,000	0.0016	
2		588	100.6	200	0.0015	<b>S1</b>
3	Na <sub>3</sub> V <sub>2</sub> (PO <sub>4</sub> ) <sub>3</sub>	1,176	103	1,000	0.0029	<b>S2</b>
4		4,700	60	30,000	0.013	<b>S</b> 3
5		1,176	86	300	0.023	<b>S4</b>
6		11.76	109	80	0.088	<b>S</b> 5
7		588	95	700	0.0056	<b>S6</b>
8		5.88	50	50	0.146	<b>S7</b>

**Table S4.** Comparison of the electrochemical performance of phosphate based electrodes for sodium-ion batteries.



**Figure S20.** SEM images of the  $K_3V_2(PO_4)_3/C$  bundled nanowires before cycling (A, B), after 100 cycles at 100 mA g<sup>-1</sup> (C, D), and after 2,000 cycles at 1,000 mA g<sup>-1</sup> (E, F).



Figure S21. (A, B) TEM images of the  $K_3V_2(PO_4)_3/C$  bundled nanowires after 100 cycles at 100 mA g<sup>-1</sup>.



Figure S22. SEM images of the  $K_3V_2(PO_4)_3/C$  blocks before cycling (A) and after 100 cycles at 100 mA g<sup>-1</sup> (B). TEM images of the  $K_3V_2(PO_4)_3/C$  blocks after 100 cycles at 100 mA g<sup>-1</sup> (C, D).



**Figure S23.** (A) CV curves of the  $K_3V_2(PO_4)_3/C$  blocks in the electrochemical window of 1.5 - 4.0 V at different scan rates. (B) Cycling response of the  $K_3V_2(PO_4)_3/C$  blocks analyzed by the Randles-Sevick equation.

#### Reference

S1. S. Li, Y. F. Dong, L. Xu, X. Xu, L. He, L. Q. Mai, Adv. Mat. 2014, 26, 3545.

- S2. C. B. Zhu, K. P. Song, Peter A. van Aken, J. Maier, Y. Yu, Nano Lett. 2014, 14, 2175.
- S3. K. Saravanan, C. W. Mason, A. Rudola, K. H. Wong, P. Balaya, Adv. Energy. Mater. 2013, 3, 444.
- S4. Y. H. Jung, C. H. Lim, D. K. Kim. J. Mater. Chem. A 2013, 1, 11350.
- **S5.** Z. L. Jian, W. Z. Han, X. Lu, H. X. Yang, Y. S. Hu, J. Zhou, Z. B. Zhou, J. Q. Li, W. Chen, D. F. Chen, L. Q. Chen. *Adv. Energy Mater.* **2013**, 3, 156.
- S6. W. C. Duan, Z. Q. Zhu, H. Li, Z. Hu, K. Zhang, F. Y. Cheng, J. Chen. J. Mater. Chem. A 2014, 2, 8668.

S7. W. Shen, C. Wang, H. M. Liu, W. S. Yang. Chem. -Eur. J. 2013, 19, 14712.