Supplementary Information

Porous $Na_3V_2(PO_4)_3$@C Nanoparticles Enwrapped in Three-dimensional Graphene for High Performance Sodium-Ion Batteries

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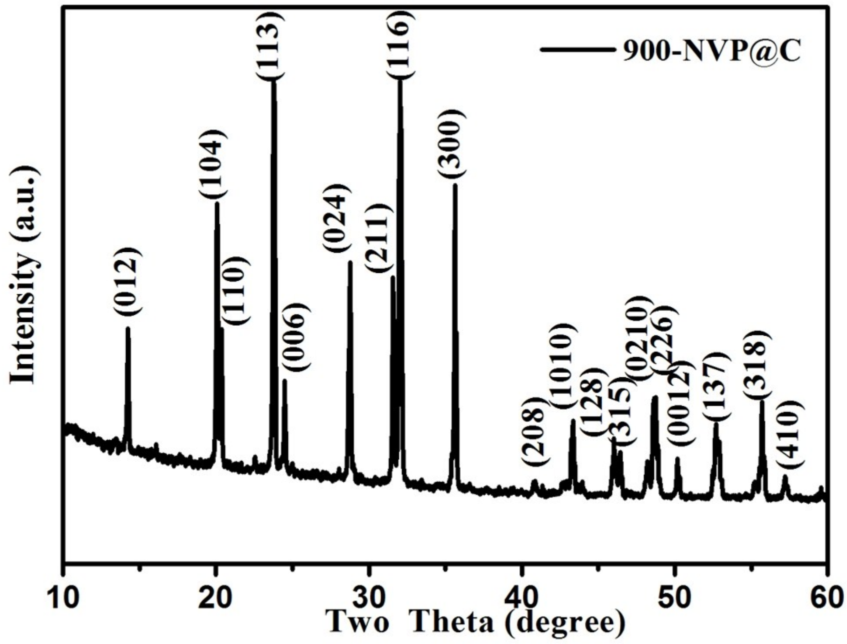

Figure S1. X-ray diffraction (XRD) pattern of 900-NVP@C.

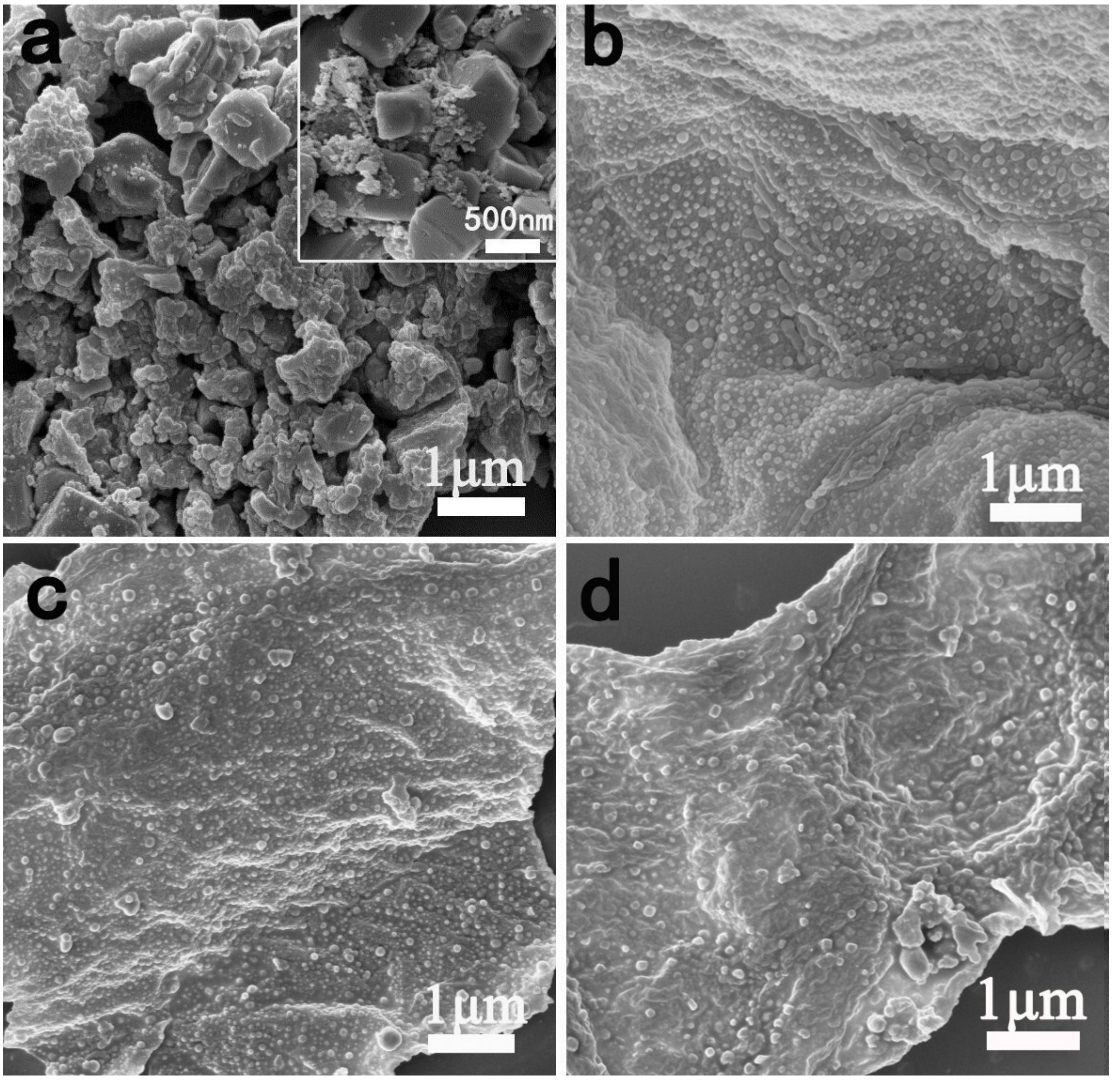

Figure S2. SEM images of (a) 900-NVP@C, (b) 700-NVP@C/G, (c) 800-NVP@C/G and (d) 900-NVP@C/G.

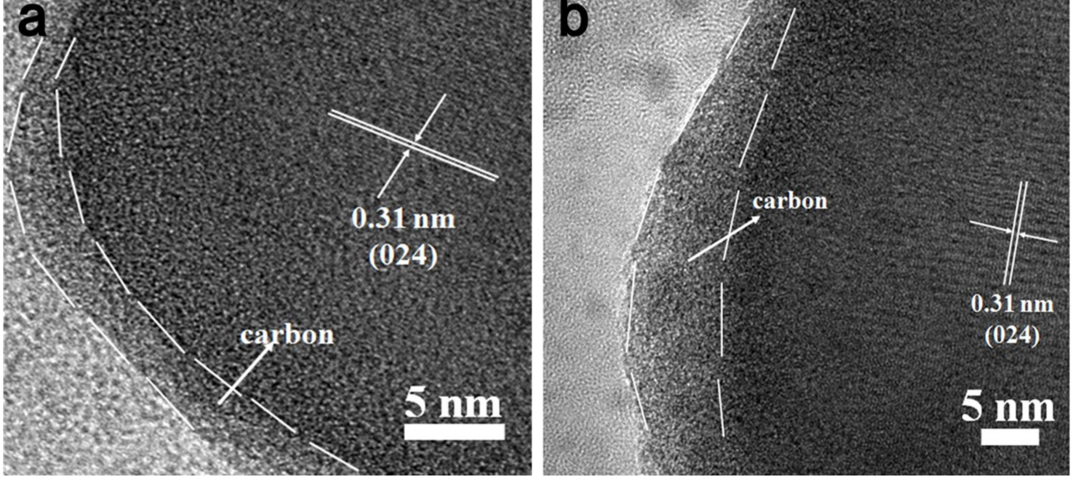

Figure S3. HRTEM images of (a) 700-NVP@C/G and (b) 800-NVP@C/G.

Table S1. Elemental analysis and thermogravimetry results of carbon content

Samples	Elemental analysis of C/wt%	TG results of C/wt%
700-NVP@C/G	21.96	21.61
800-NVP@C/G	20.58	20.64
900-NVP@C/G	18.34	17.90
900-NVP@C	4.59	3.88

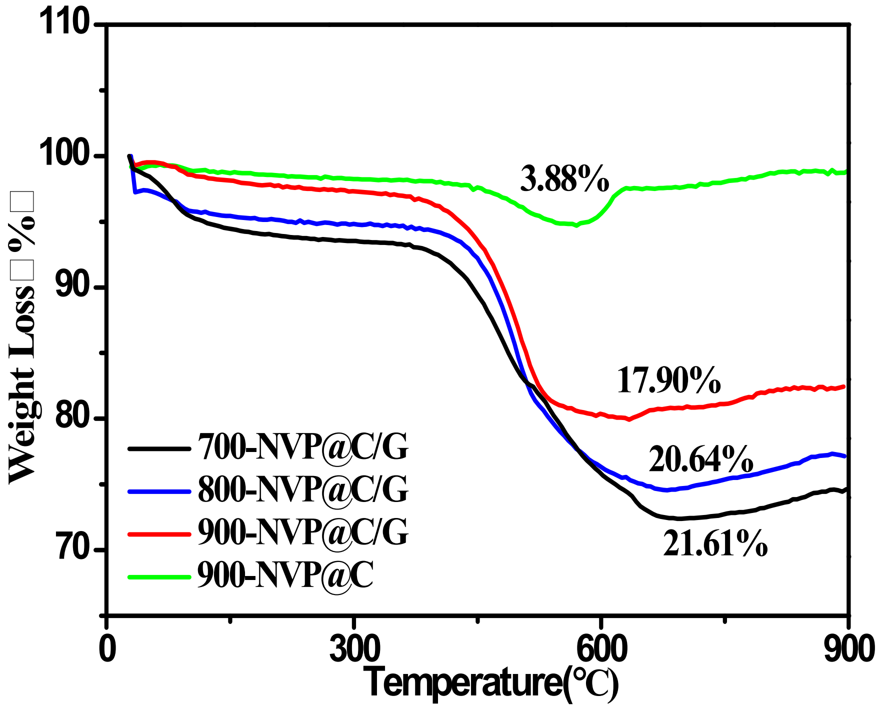

Figure S4. TG curves of 900-NVP@C, 700-NVP@C/G, 800-NVP@C/G and 900-NVP@C/G composites.

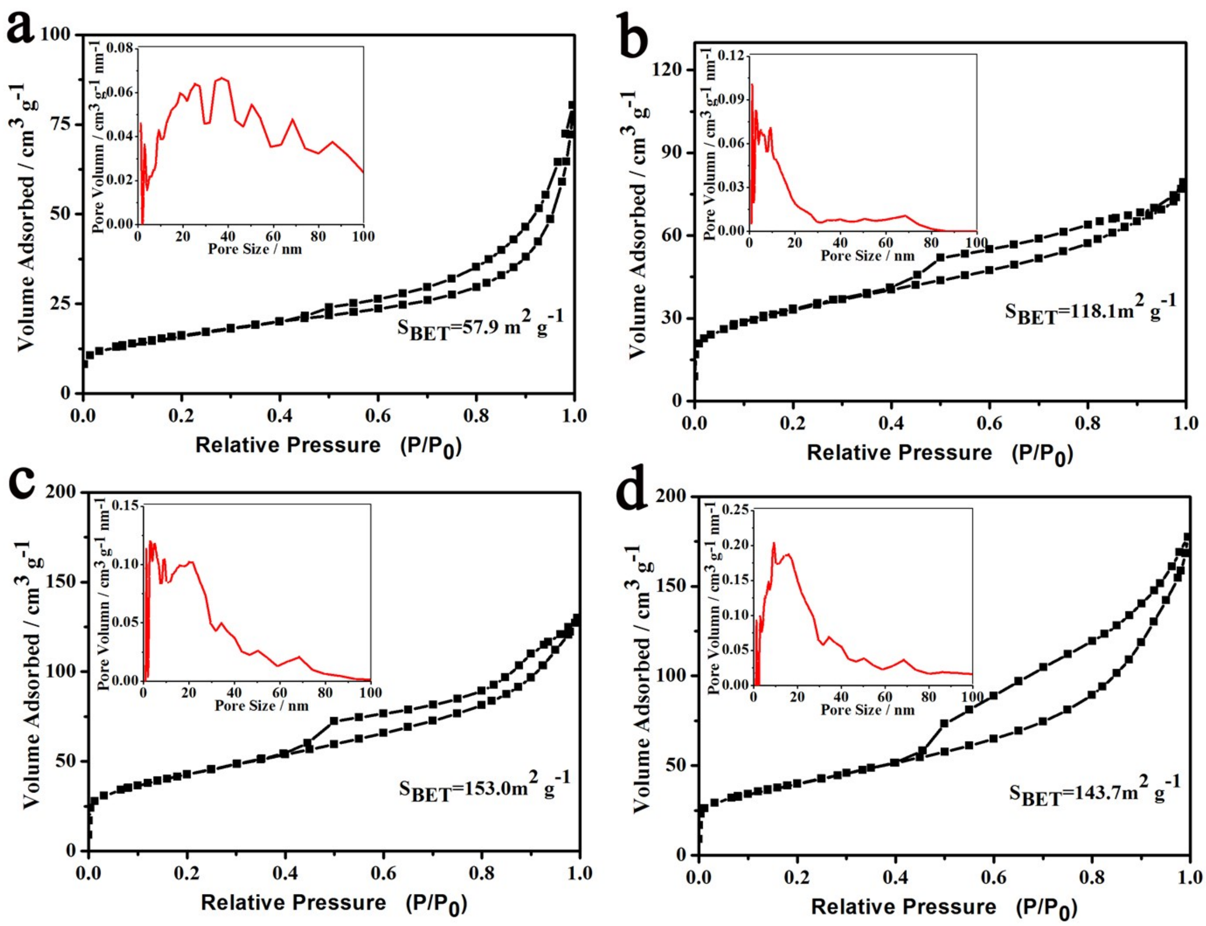

Figure S5. N_2 adsorption/desorption isotherms of (a)900-NVP@C,(b)700-NVP@C/G, (c) 800-NVP@C/G, (d) 900-NVP@C/G.

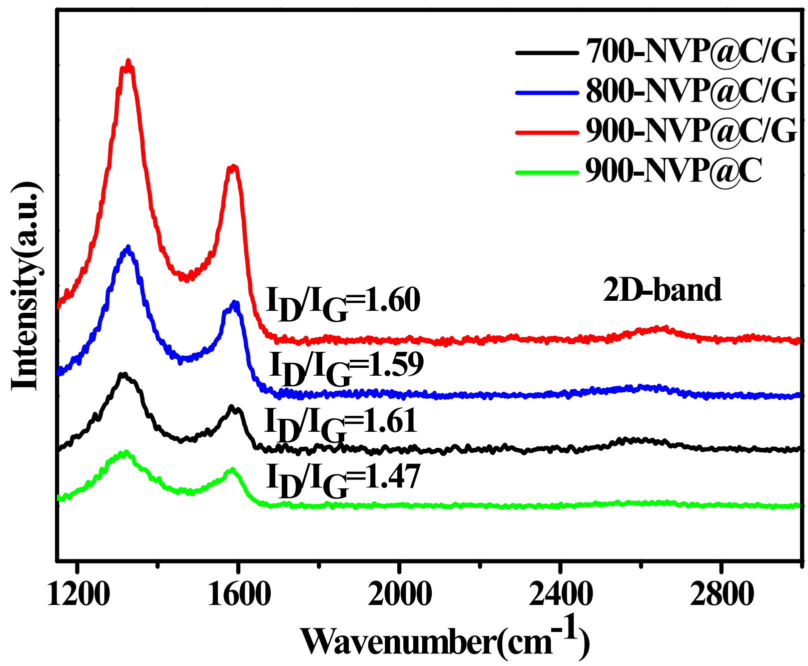

Figure S6. Raman spectrum of NVP@C and 3D porous NVP@C/G nanocomposites

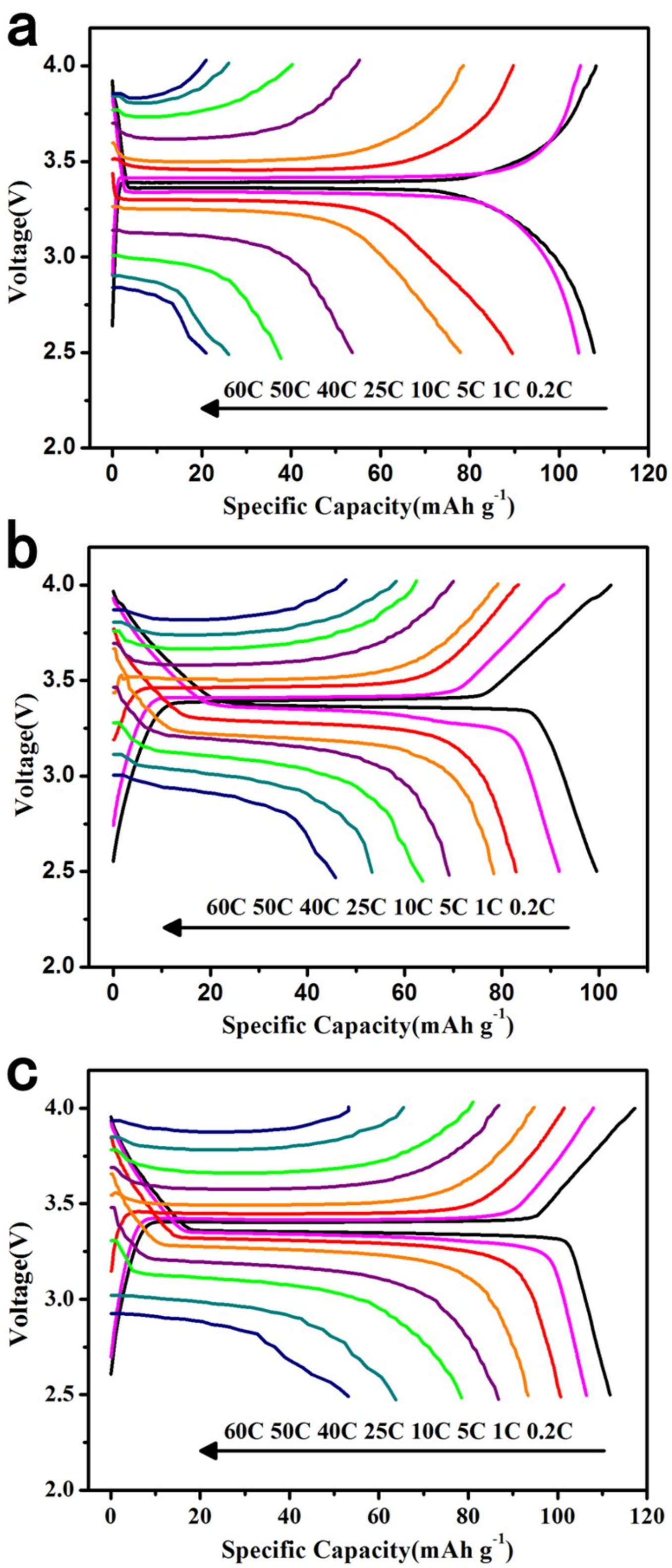

Figure S7. Representative discharge–charge curves of (a) 900-NVP@C, (b) 700-NVP@C/G and (c) 800-NVP@C/G.

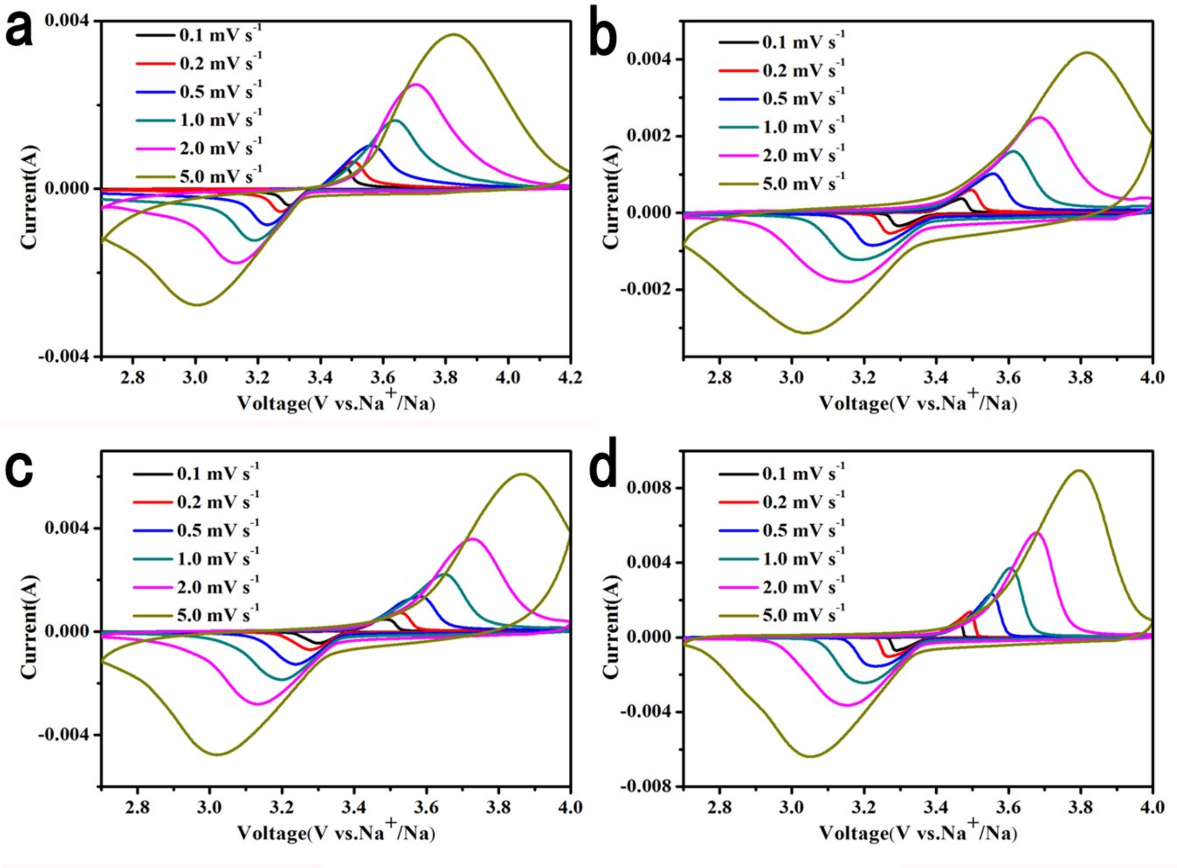

Figure S8. CV curves of the the (a) 900-NVP@C, (b) 700-NVP@C/G, (c) 800-NVP@C/G and (d) 900-NVP@C/G electrode at different scan rates. (e) The corresponding relationship between the square root of the scan rate $v^{1/2}$ and peak current.

The Na-ion diffusion coefficient D (cm^2 s^{-1}) can be calculated from the straight slope according to the following Randles Sevcik equation:

$$I_p=2.69 \times 10^5 n^{3/2} A D_{Na}^{1/2} C_{Na} \nu^{1/2} (25°C)$$

where n is the number of electrons in reaction (n=1 for V^{3+}/V^{4+}redox pair), A is the effective contact area between electrode and electrolyte (0.9 cm^2) and C is the concentration of Na ions in the electrode (6.92×10^{-3} mol cm^{-3}). The D values of the anodic and cathodic reactions are shown in Table S2.

Table S2. D values of the anodic and cathodic reactions

Samples	Anodic peaks	Cathodic peaks
900-NVP@C	6.61×10^{-10} cm^2 s^{-1}	3.51×10^{-10} cm^2 s^{-1}
700-NVP@C/G	8.97×10^{-10} cm^2 s^{-1}	4.59×10^{-10} cm^2 s^{-1}
800-NVP@C/G	2.0×10^{-9} cm^2 s^{-1}	1.14×10^{-9} cm^2 s^{-1}
900-NVP@C/G	4.11×10^{-9} cm^2 s^{-1}	1.99×10^{-9} cm^2 s^{-1}

Table S3. Kinetic parameters obtained from equivalent circuit fitting

Samples	$R_s(\Omega)$	$R_{ct}(\Omega)$
700-NVP@C/G	31.59	515.7
800-NVP@C/G	29.84	425.5
900-NVP@C/G	16.92	323.6
900-NVP@C	35.07	372.5

Table S4. Comparison of this work versus state -of-the-art $Na_3V_2(PO_4)_3$ for Na-ion

Material	**Cyclability**	**Rate Performance**
900-NVP@C/G (this work)	97.2 mAh g^{-1} at 1000th cycle at 10 C (95% capacity retention) 75.1 mAh g^{-1} at 1500th cycle at 40 C (82% capacity retention)	112 mAh g^{-1} at 0.2 C 106 mAh g^{-1} at 5 C 104 mAh g^{-1} at 10 C 92 mAh g^{-1} at 40 C 81 mAh g^{-1} at 50 C 76 mAh g^{-1} at 60 C
Carbon-Coated $Na_3V_2(PO_4)_3$ Particles in Mesoporous Carbon (ref S1)	90 mAh g^{-1} at 1000th cycle at 10 C (85% retention) 68.6 mAh g^{-1} at 1000th cycle at 20 C (67.3% retention)	115 mAh g^{-1} at 0.5 C 112 mAh g^{-1} at 1 C 109 mAh g^{-1} at 5 C 107 mAh g^{-1} at 10 C 94 mAh g^{-1} at 20 C 81 mAh g^{-1} at 30 C

Nitrogen-doped Carbon Coating $Na_3V_2(PO_4)_3$ (ref S2)	96.5 mAh g^{-1} at 50^{th} cycle at 0.2 C (95.5% capacity retention) 69 mAh g^{-1} at 50^{th} cycle at 0.2 C charge/5 C discharge (92.6% capacity retention)	100 mAh g^{-1} at 0.2 C 93.8 mAh g^{-1} at 3 C 84.3 mAh g^{-1} at 5 C
Porous $Na_3V_2(PO_4)_3$/C (ref S3)	90 mAh g^{-1} at 1000^{th} cycle at 10 C (84.9% retention)	114 mAh g^{-1} at 1 C 106 mAh g^{-1} at 10 C 91.2 mAh g^{-1} at 20 C 62 mAh g^{-1} at 40 C
Electrospun $Na_3V_2(PO_4)_3$/C (ref S4)	No reported	77 mAh g^{-1} at 2 C 58 mAh g^{-1} at 5 C 39 mAh g^{-1} at 10 C 20 mAh g^{-1} at 20 C
$Na_3V_2(PO_4)_3$/AC (ref S5)	97 mAh g^{-1} at 200th cycles at 5 C (96.4% retention)	105.1 mAh g^{-1} at 1 C 101.1 mAh g^{-1} at 2 C 97 mAh g^{-1} at 5 C
$Na_3V_2(PO_4)_3$/nit-rogen-decorated carbon hybrids (ref S6)	No reported	110.7 mAh g^{-1} at 0.5 C 104.7 mAh g^{-1} at 1 C 102.6 mAh g^{-1} at 2 C 76.6 mAh g^{-1} at 5 C 46.8 mAh g^{-1} at 10 C

Porous $Na_3V_2(PO_4)_3/C$ (ref S7)	86.5 mAh g^{-1} at 100^{th} cycle at 5 C (88.6% retention)	105 mAh g^{-1} at 0.2 C 99 mAh g^{-1} at 1 C 95 mAh g^{-1} at 3 C 92 mAh g^{-1} at 4 C 90 mAh g^{-1} at 5 C
Carbon-Coated $Na_3V_2(PO_4)_3$ Embedded in Porous Carbon Matrix (ref S8)	83 mAh g^{-1} at 1000^{th} cycle at 10 C (80.6% capacity retention) 73 mAh g^{-1} at 1000^{th} cycle at 50 C (80.2% capacity retention)	104 mAh g^{-1} at 1 C 103 mAh g^{-1} at 10 C 102 mAh g^{-1} at 20 C 96 mAh g^{-1} at 30 C 91 mAh g^{-1} at 50 C 74 mAh g^{-1} at 100 C 44 mAh g^{-1} at 200 C
Mg doping $Na_3V_2(PO_4)_3$ (ref S9)	104.6 mAh g^{-1} at 50^{th} cycle at 1 C charge/10 C discharge (96.5% capacity retention) 86.2 mAh g^{-1} at 50^{th} cycle at 1 C charge/20 C discharge (83.0% retention)	112.5 mAh g^{-1} at 1 C 111.3 mAh g^{-1} at 2 C 109.9 mAh g^{-1} at 5 C 108.5 mAh g^{-1} at 10 C 103.9 mAh g^{-1} at 20 C 94.2 mAh g^{-1} at 30 C
Graphene-supported $Na_3V_2(PO_4)_3$ (ref S10)	93% capacity retention over 100 cycles at 1 C 80 mAh g^{-1} at 300^{th} cycle at 1 C charge/10 C discharge	Fixed at 0.2 C charge: 90.6 mAh g^{-1} at 0.2 C discharge 89.5mAh g^{-1} at 1 C discharge 88.2mAh g^{-1} at 2 C discharge 83.5mAh g^{-1} at 10 C discharge 60.4mAh g^{-1} at 30 C discharge
Biochemistry Enabled 3D Na3V2(PO4)3 (ref S11)	approximate 100% retention over 1000 cycles at 1 C charge/100 C discharge	Fixed at 1 C charge: 109 mAh g^{-1} at 5 C discharge 99 mAh g^{-1} at 20 C discharge 87 mAh g^{-1} at 50 C discharge 51 mAh g^{-1} at 200 C discharge

$Na_3V_2(PO_4)_3$@C core-shell nanocomposites (ref S12)	91.2 mAh g^{-1} at 700th cycles at 5 C (96.1% retention)	104. mAh g^{-1} at 0.5 C 94.9 mAh g^{-1} at 5 C 88 mAh g^{-1} at 10 C
NVP particles embedded in CNFs (ref S13)	93% retention over 300 cycles at 1 C	112.5 mAh g^{-1} at 0.1 C 88.9 mAh g^{-1} at 50 C
Honeycomb-structured $Na_3V_2(PO_4)_3$ (ref S14)	93.6% retention over 200 cycles at 1 C	113 mAh g^{-1} at 0.2 C 97.2 mAh g^{-1} at 5 C 80.2 mAh g^{-1} at 20 C
NVP nanoparticles Confined in a 1D Carbon Sheath (ref S15)	74% retention over 50 cycles at 1 C	103 mAh g^{-1} at 0.2 C 88 mAh g^{-1} at 2 C

References:

[S1] Y. Jiang, Z. Yang, W. Li, L. Zeng, F. Pan, M. Wang, X. Wei, G. Hu, L. Gu, and Y. Yu, *Adv. Energy Mater.,* 2015, **5**,1402104.

[S2] W. shen, C. wang, Q. Xu, H. Liu, Y. Wang *Adv. Energy Mater.,* 2015,**5**, 1400982.

[S3] K. Saravanan , C.W.Mason, A rudola, K.H Wong, *Adv. Energy Mater.,* 2013,**3**, 445.

[S4] J. Liu, K. Tang, K. Song, P. A. V. Aken, Y. Yu and J. Maier, *Nanoscale,* 2014, **6**, 5081.

[S5] S. Li, Y. Dong, L. Xu, X. Xu, L. He and L. Mai, *Adv. Mater.,* 2014, **26**, 3545.

[S6] P. Nie, Y. Zhu, L. Shen, G. Pang, G. Xu, S. Dong, H. Dou and X. Zhang, *J. Mater. Chem. A,* 2014, **2**, 18606.

[S7] W. Shen, C. Wang, H. Liu and W. Yang, *Chem.Eur. J.,* 2013, **19**, 14712.

[S8] C. Zhu, K. Song, P. A. V. Aken, J. Maier, and Y. Yu, *Nano Lett.,* 2014, **3**, 2175-2180.

[S9] H. Li, X. Yu, Y. Bai, F. Wu , C. Wu, L. Liu and X. Yang, *J. Mater. Chem. A,* 2015, **3**,9578-9586.

[S10] Y. H. Jung, C. H. Lim and D. K. Kim, *J. Mater. Chem. A,* 2013, **1**, 11350.

[S11] Y. Zhou, X. Rui, W. Sun, Z. Xu, Y. Zhou, W. J. Ng, Q. Yan, and E. Fong, *ACS Nano,* 2015,**9**, 4628-4635

[S12] W. Duan, Z. Zhu, H. Li, Z. Hu, K. Zhang, F. Cheng and J. Chen, *J. Mater. Chem. A,* 2014, **2**, 8668-8675.

[S13] J. Yan g, D. Han, M. R. Jo, K. Son g, Y. Kim, S. Chou, H. Liu and Y. Kang, J. *Mater. Chem. A,* 2015, **3**, 1005-1009.

[S14] Q. Wang, B. Zhao, S. Zhang, X. Gao and C. Deng, *J. Mater. Chem. A,* 2015, **3**, 7732-7740.

[S15] S. Kajiyama, J. Kikkawa, J. Hoshino, M. Okubo, and E.Hosono, *Chem. Eur. J.,* 2014, **20**, 12636-12640.