Supplementary information

## Pore forming mechanisms and sodium ion storage performances in

## porous Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>/C composite cathode

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After calcination at 800 °C, vanadium in NVP was oxidized from trivalent to pentavalent. Each mole of NVP reacts with 1 mole of oxygen molecule, and the weight of NVP increases by about 7 wt% after oxidation reaction. The carbon content of NVP/C can be calculated by following equation: (

$$100 - x) \times (100 + y) = z$$

Where x is the carbon content of NVP/C sample. y is the weight increase caused by oxidation (wt%). z is the mass percentage of NVP/C sample at 750 °C in the TGA curve. As shown in Figure S2, the carbon contents of NVP/C-0, NVP/C-1, NVP/C-2, NVP/C-3, NVP/C-4 and NVP/C-5 sample are calculated to be 2.1 wt%, 4.3 wt%, 7.0 wt%, 6.3 wt%, 5.5 wt% and 4.8 wt%, respectively.



Figure S2. TGA curves of the NVP/C-0, NVP/C-1, NVP/C-2, NVP/C-3, NVP/C-4 and NVP/C-5 samples in air atmosphere.



Figure S3. The Nitrogen adsorption-desorption isotherms and embedded the Barrentt-Joyner-Halenda pore-size distribution curves. (a) NVP/C-0, (b) NVP/C-1, (c) NVP/C-2, (d) NVP/C-3 (e) NVP/C-4 and (f) NVP/C-5.

Sample	Surface area (m <sup>2</sup> g <sup>-1</sup> )	Pore volume (cm <sup>3</sup> g <sup>-1</sup> )	Average pore size (nm)
NVP/C-0	3.3862	7.6210×10 <sup>-3</sup>	9.0019
NVP/C-1	8.4653	1.5293×10 <sup>-2</sup>	7.2261
NVP/C-2	190.8046	1.4539×10 <sup>-1</sup>	3.0479
NVP/C-3	149.7236	1.2642×10 <sup>-1</sup>	3.1017
NVP/C-4	26.8464	3.7605×10 <sup>-2</sup>	3.4909
NVP/C-5	24.6400	2.1504×10 <sup>-2</sup>	5.6030

Table S1. Pore structural information of as-synthesized NVP/C composite cathodes.



Figure S4. XPS survey spectra of NVP/C-1, NVP/C-2, NVP/C-3, NVP/C-4 and NVP/C-5. (a) V 2p, (b) O 1s, (c) C 1s and (d) N 1s.



Figure S5. XPS survey spectrum of NVP/C-1, NVP/C-2, NVP/C-3, NVP/C-4 and NVP/C-5. (a) survey spectra, (b) Na 1s, (c) P 2p.