# Supporting information

## Section I: Supporting preparation & calculation processes

### *S1*: Preparation processes of the reference samples

i) Low-carbon aggregated reference sample

To prepare the low-carbon aggregated reference sample, the precursor of $NaV_3(PO_4)_3$ was prepared by a sol-gel process. The starting materials of ammonium metavanadate, sodium carbonate, ammonium dihydrogen phosphate and oxalic acid were dissolved in 30 mL distilled water to form a uniform solution. Then the mixture was stirring at 80 $^oC$ for six hours, followed by drying in an oven over a night to achieve the precursor. Finally, the precursor was calcinated at 900 $^oC$ for 10 hours under $Ar/H_2$ (95/5 in volume) atmosphere to achieve the aggregated low-carbon reference sample.

ii) Random arranged hybrid nanofiber

To prepare the random arranged $NaV_3(PO_4)_3$@C hybrid nanofiber, the precursor of $NaV_3(PO_4)_3$ was prepared firstly. The starting materials of ammonium metavanadate, sodium acetate and phosphate acid were dissolved in 30 mL distilled water to form a uniform solution. Then the mixture was stirring at 80 $^oC$ for six hours, followed by drying in an oven over a night to achieve the precursor. Next, the sol for electrospinning is prepared through mixing the prepared precursor, PVA polymer and acetic acid (30 wt.%) at room temperature. After continuously stirring for 12 hours, the transport and viscid solution was obtained. The resulting precursor was transferred into a syringe connected a stainless steel needle. A high potential of 16 kV was applied on the needle relative to a flat plate positioned at about 12 cm from the tip of the needle. The flow rate of the precursor sol was controlled using a syringe pump at 0.8 mL $h^{-1}$. After electrospinning, the collected fibers film was peeled off from the collector and calcinated at 900 $^oC$ for 10 hours under $Ar/H_2$ (95/5 in volume) atmosphere.

## *S2*: Calculation process for sodium intercalation coefficients

The diffusion coefficient of sodium-ion ($D_{Na}$) can be calculated on the basis of the Randles-Sevcik equation,

$$i_p = 0.4463(\frac{F}{RT})^{1/2} n^{3/2} A D_{Na}^{1/2} C^* v^{1/2} \quad (1)$$

Where $i_p$, $n$, $A$, $C^*$ and $v$ are the peak current, number of exchanged electrons, surface area, sodium concentration and sweep rate, respectively.

## Section II: Supporting figures

**Figure S1** (a) Zigzag chain and (b) the rigid rod-shaped block in the $NaV_3(PO_4)_3$ crystal.

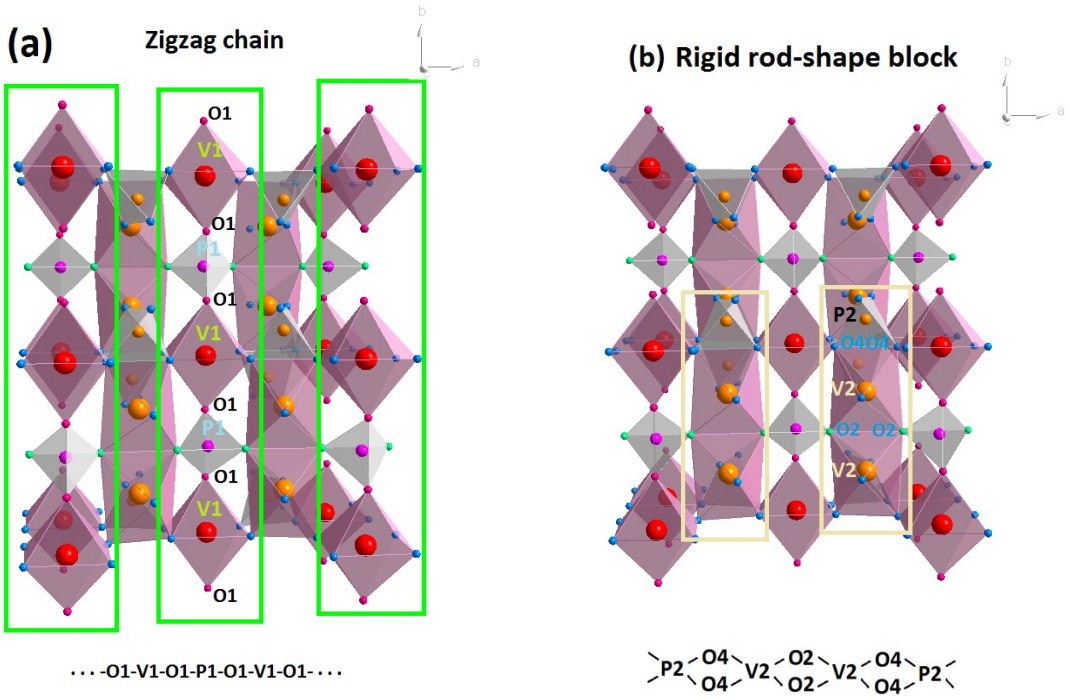

**Figure S2** Comparison of the XRD patterns of full discharged $NaV_3(PO_4)_3$ in aqueous (a) and organic (b) electrolytes.

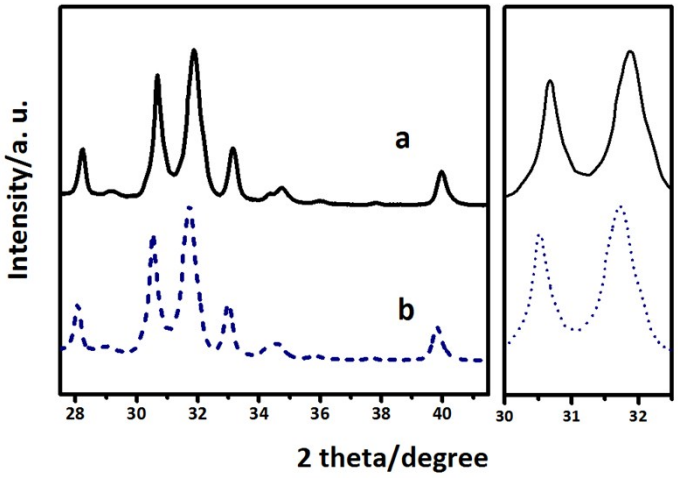

**Figure S3** Comparison of the physical characteristics, including carbon content (a), BET area (b) and pore volume (c) of the aligned nanofiber, random arranged nanofiber and large aggregated reference samples.

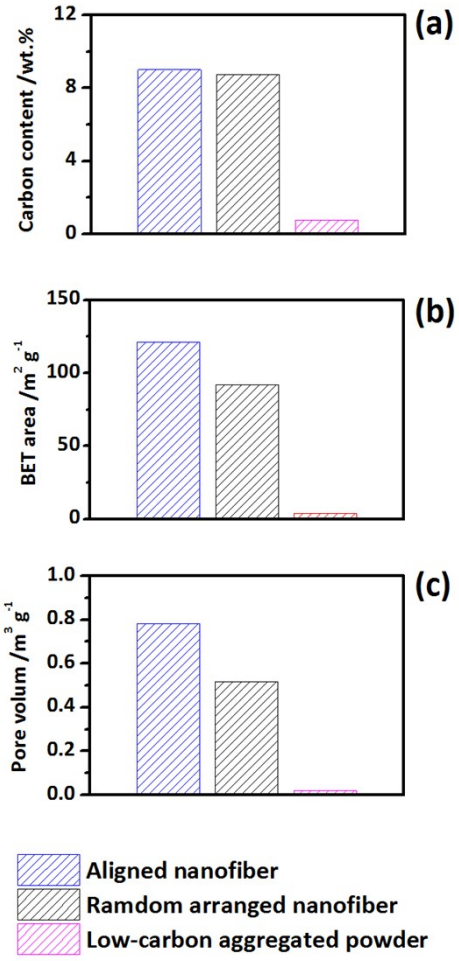

**Figure S4** Galvanostatic charge/discharge curves of the aligned $NaV_3(PO_4)_3$ nanofiber in different voltage ranges. The narrow voltage range (a) results in a higher coulombic efficiency and a lower capacity than those obtained in a wide voltage range (b) of present work.