Experimental section

Synthesis of Na$_3$V$_2$(PO$_4$)$_3$@Graphene (NVP@G): An appropriate amount of CH$_3$COONa·2H$_2$O (A.R.), NH$_4$VO$_3$ (A.R.), NH$_4$H$_2$PO$_4$ (A.R.) and citric acid were used as the starting materials. Citric acid (15%wt) was employed as both a reduction agent and a chelating agent. These mixtures were dispersed in acetone and mixed by ball-milling for 12 hours. After evaporating acetone in the 110ºC oven, a homogeneous precursor was obtained. It was preheated at 400ºC under a flowing H$_2$ (5%)/Ar for 6 hours and cooled to room temperature. Appropriate amount of polyvinyl alcohol (PVA) was mixed the grinded precursor for several minutes and then sintered at 750ºC for 12 hours under the same H$_2$ (5%)/Ar atmosphere to obtain NVP@G composite.

Structural Characterization: The phase and crystallinity of NVP@G was characterized...
by powder X-ray diffraction (XRD, Rigaku) with Cu Kα radiation over a range of 20 angles from 10° to 60°. Its particle morphology was studied by a scanning electron microscope (SEM, JSM-6390 LA, JEOL) and a transmission electron microscope (TEM, HRTEM, JEM-2010). The carbon content in NVP@G was measured by an Infrared Carbon-sulfur analyzer (CS-600). Its Raman spectroscopy analysis was conducted with a Renishaw inVia Raman Microscope.

Electrochemical Characterization: The electrochemical performances of NVP@G were investigated by CR2032 coin cells Na/NVP@G. The working electrode laminate was prepared by mixing NVP@G (80 wt%), acetylene black (10 wt%) and poly(vinylidene difluoride) (PVDF) (10 wt%) in NMP to form a homogeneous slurry, which was conformably coated on an aluminum foil. It was dried in oven at 80°C for 4 hours and then CR2032-type half-cells (Na/NVP@G) were assembled in an argon filled glove box (MBRAUN LABMASTER 130). The mass loading of NVP@G in electrodes was about 1.23 mg cm⁻². The electrolyte was composed of 1M NaClO₄ in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1, v/v,)/1% fluoroethylene carbonate (FEC). A Whatman glass-fiber was used as the separator. The cyclic voltammetry (CV) of the cell was measured on a CHI 660B electrochemical workstation at a scan rate of 0.1 mV s⁻¹ between 2.3 and 3.9 V. These cells were also tested on a NEWWARE BTS-610 multichannel battery test system in voltage range of 2.3-3.9 V.
Fig. S1 XRD pattern of NVP@G.

Fig. S2 TEM image of Li$_3$V$_2$(PO$_4$)$_3$ (with PVA as the carbon source).
**Fig. S3** TEM image of LiMn$_{0.4}$Fe$_{0.6}$PO$_4$ (with PVA as the carbon source).

**Fig. S4** CV curves of a Na/NVP@G cell (a) and its initial charge-discharge curves at 5C (b).
Fig. S5 Schematic illustration of the unit cell of Na$_3$V$_2$(PO$_4$)$_3$.

Fig. S6 Cycling performance of a Na/NVP@G cell at 5C in the voltage range from 2.3 to 3.9V.
Fig. S7 Electrochemical performance of a Na/NVP@G cell at 0.1C at 25°C and -10°C.