

**Supplementary Material for Journal of Materials Chemistry A**

**In-situ catalytic formation of graphene decoration on  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  particles for ultrafast and long-life sodium storage**

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**Experimental section**

*Synthesis of  $\text{Na}_3\text{V}_2(\text{PO}_4)_3@$ Graphene (NVP@G):* An appropriate amount  $\text{CH}_3\text{COONa}\cdot 2\text{H}_2\text{O}$  (A.R.),  $\text{NH}_4\text{VO}_3$  (A.R.),  $\text{NH}_4\text{H}_2\text{PO}_4$  (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 110°C oven, a homogeneous precursor was obtained. It was preheated at 400°C under a flowing  $\text{H}_2$  (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 750°C for 12 hours under the same  $\text{H}_2$  (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 K $\alpha$  radiation over a range of  $2\theta$  angles from  $10^\circ$  to  $60^\circ$ . 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  $80^\circ\text{C}$  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  $1.23\text{ mg cm}^{-2}$ . The electrolyte was composed of 1M NaClO $_4$  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  $0.1\text{ mV s}^{-1}$  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.

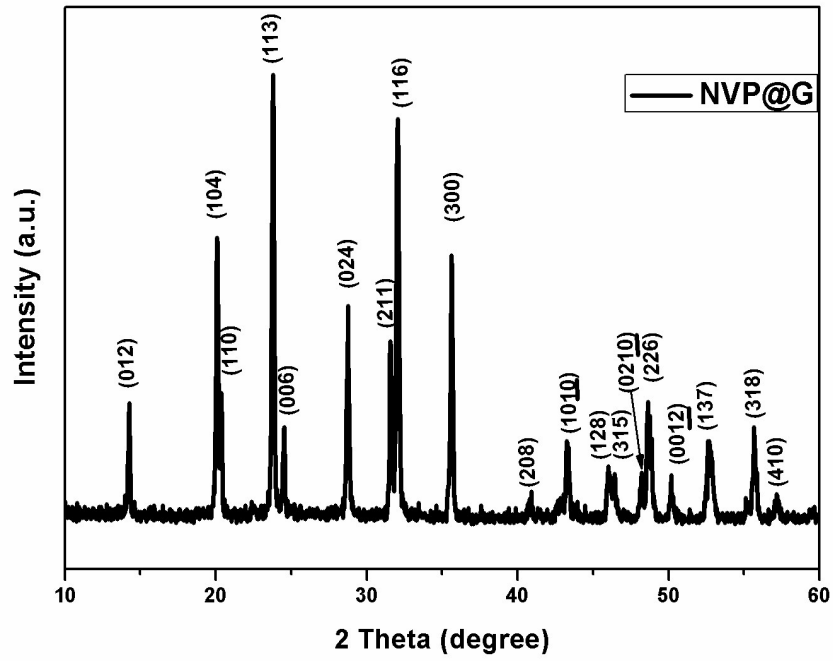


Fig. S1 XRD pattern of NVP@G.

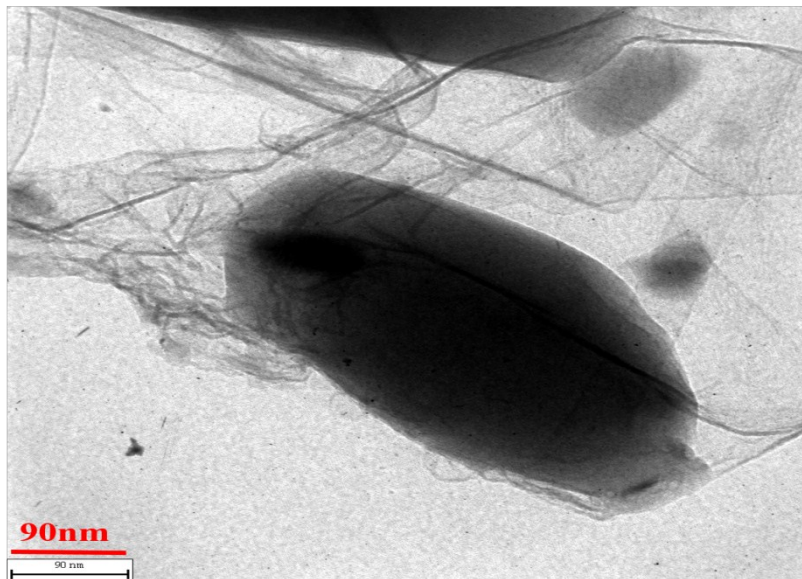


Fig. S2 TEM image of  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  (with PVA as the carbon source).

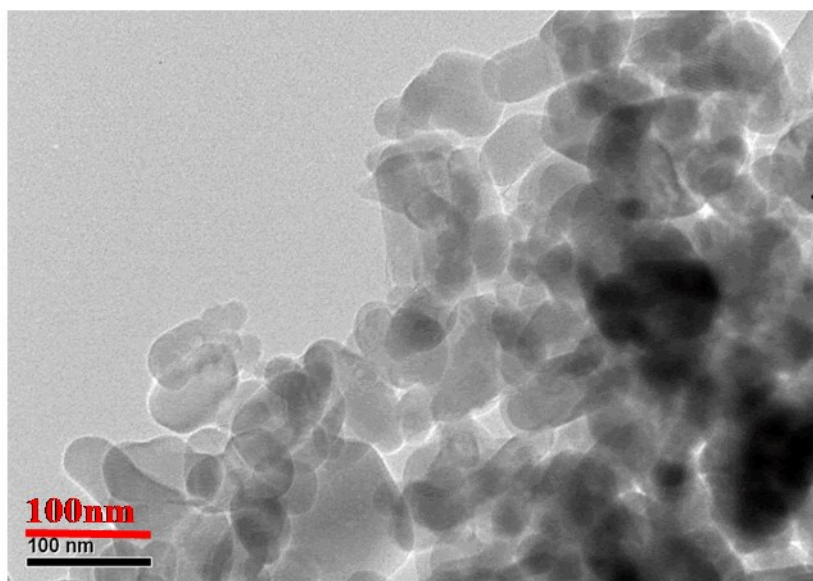


Fig. S3 TEM image of  $\text{LiMn}_{0.4}\text{Fe}_{0.6}\text{PO}_4$  (with PVA as the carbon source).

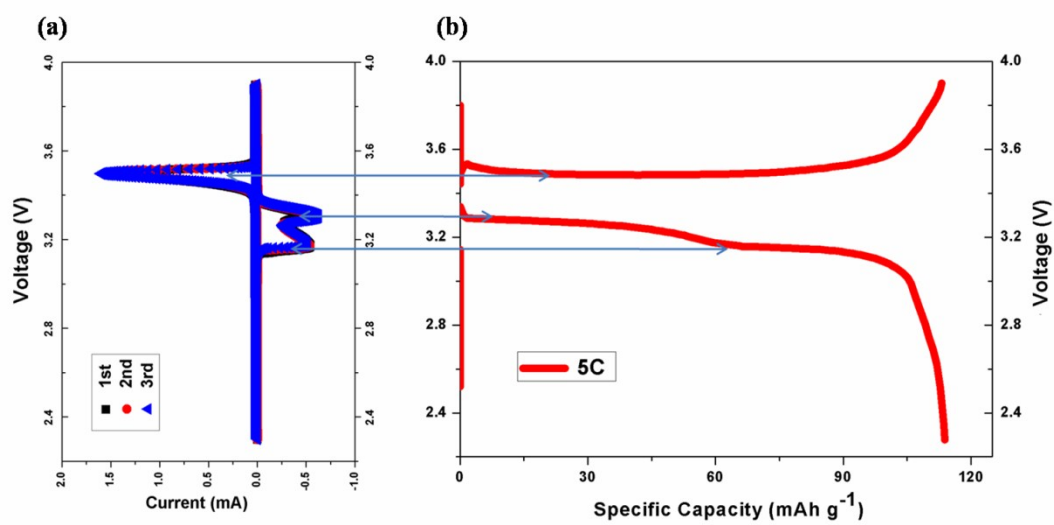


Fig. S4 CV curves of a Na/NVP@G cell (a) and its initial charge-discharge curves at 5C (b).

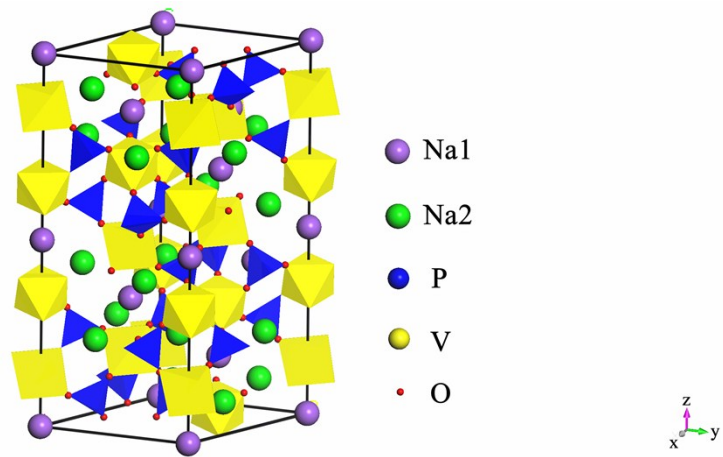


Fig. S5 Schematic illustration of the unit cell of  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ .

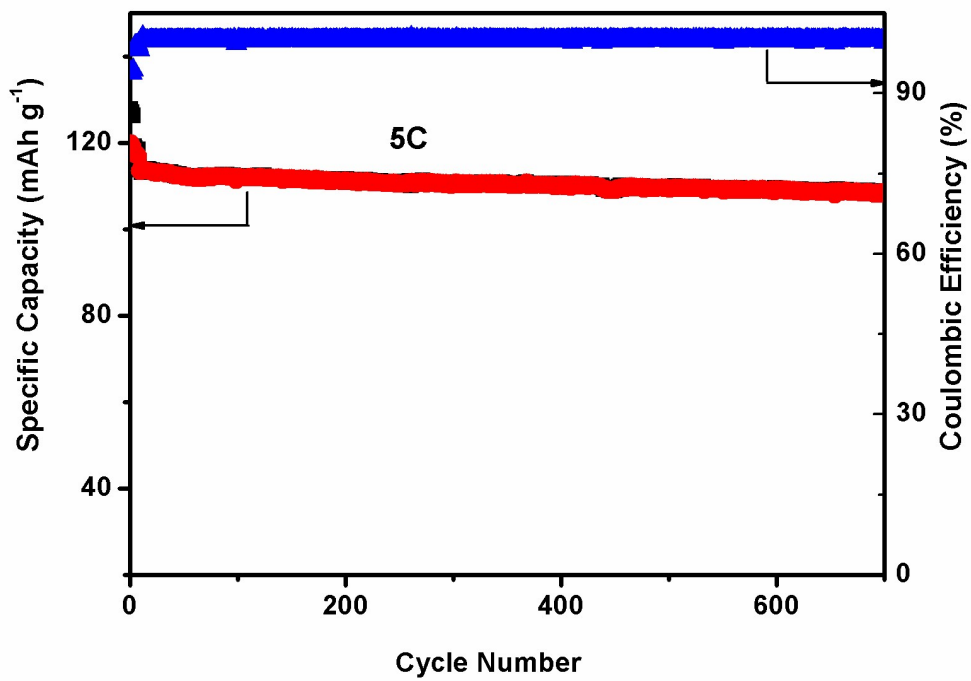


Fig. S6 Cycling performance of a Na/NVP@G cell at 5C in the voltage range from 2.3 to 3.9V.

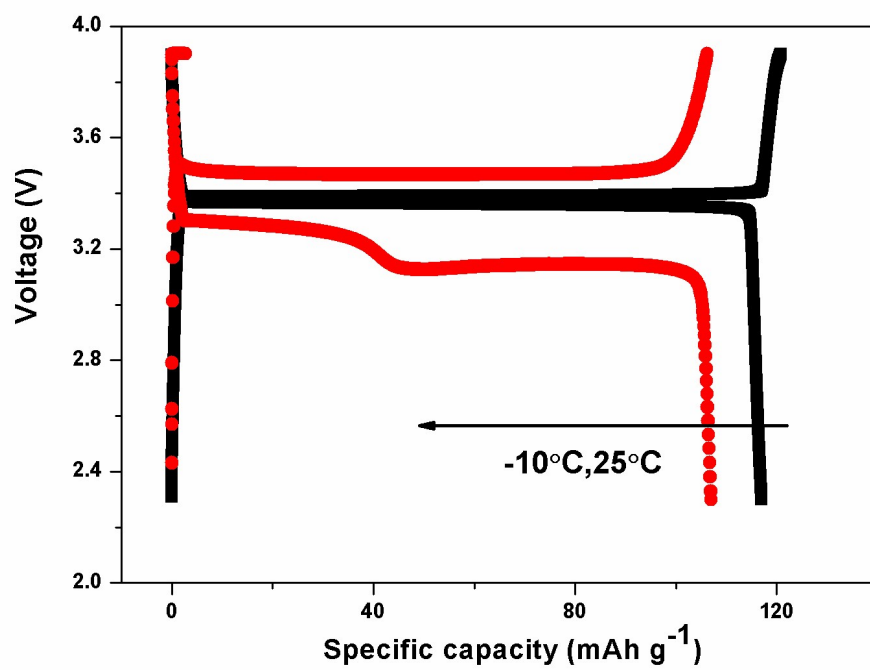


Fig. S7 Electrochemical performance of a Na/NVP@G cell at 0.1C at 25°C and -10°C.