Electronic Supplementary Information (ESI)

From Biomolecule to Na₃V₂(PO₄)₃/Nitrogen-Decorated Carbon Hybrids: Highly Reversible Cathodes for Sodium-ion Batteries

Ping Nie, Yaoyao Zhu, Laifa Shen, Gang Pang, Guiyin Xu, Shengyang Dong, Hui Dou and Xiaogang Zhang*

College of Material Science and Engineering and Key Laboratory for Intelligent Nano Materials and Devices of Ministry of Education, Nanjing University of Aeronautics and Astronautics, Nanjing, 210016, P. R. China.
*Corresponding author, azhangxg@163.com; Tel: +86-25-52112918; Fax: +86-25-52112626

Experimental Details

Materials Synthesis

The bundle-like Na₃V₂(PO₄)₃/nitrogen-doped carbon (Marked as NVP-1) nanocomposites were synthesized by a solvothermal method. Typically, stoichiometric amounts of 1.2 mmol V₂O₅, 0.9 mmol ascorbic acid, and 20 ml distilled water were mixed together and stirred in a Teflon-lined stainless steel autoclave with a volume capacity of 30 ml, and then 0.6 mmol Na₂CO₃ and 1.2 mmol adenosine 5’-triphosphate disodium salt (98%, Aladdin Industrial Inc.) were added to this mixed solution and kept vigorously stirred for 1 h. Afterwards, 0.9 ml of polyethylene glycol (PEG-400) was added as solvent to the solution with continued stirring. The vessel was then sealed and heated at 180 °C for 24 h. Upon cooling to room temperature naturally, the brown suspension and precipitate were heated on a
hotplate at 80 °C under stirring to get a precursor. The resulting power was ground and annealed at 350 °C for 4 h, following by further treatment at 700 °C for 6 h under a flow of nitrogen with a heating rate of 2 °C min⁻¹ in a tube furnace. For the synthesis of pristine Na₃V₂(PO₄)₃/C (Marked as NVP-2), the procedure was similar but NH₄H₂PO₄ was added as the phosphorous source.

Materials Characterization

The morphologies of the samples were characterized by field-emission scanning electron microscopy (FESEM, LEO 1430VP, Germany) and transmission electron microscopy-energy dispersive X-ray spectroscopy (HRTEM, JEOL JEM-2100). FTIR analysis of the sample was recorded on a Nicolet 750 Fourier transform infrared spectrometer using the KBr pellet method. The powder X-ray diffraction (XRD) pattern was collected on a Bruker D8 Advance diffractometer equipped with Cu Ka radiation over the 2θ range of 10-80°. The XRD profiles were refined by the Rietveld program RIETAN-FP.¹ The X-ray photoelectron spectroscopy (XPS) studies were performed on a Thermo escalab 250Xi spectrometer with a mono Al Kα radiation, and Raman spectra were collected with a Renishaw 2000 System. Thermogravimetric analysis was carried out under air flow from 30 to 600 °C with a temperature ramp of 10 °C min⁻¹. N₂ adsorption-desorption measurements were determined by using a Micromeritics ASAP 2020 instrument.

Electrochemical Measurements

Electrochemical performance characterization of the Na₃V₂(PO₄)₃ electrodes was performed in 2032 coin-type cells at the room temperature. The working electrode was prepared by casting a slurry of 80 wt% active materials, 10 wt% acetylene black, and 10 wt% poly(vinylidenedifluoride) in N-methyl-2-pyrrolidinone on an aluminum foil. Na metal was used as the reference and counter electrode, and a glass microfiber filter as the separator. The electrolyte was 1 M NaClO₄ dissolved in a mixture of ethylene carbonate (EC) and propylene carbonate (PC) with a volume ratio of 1:1. Coin cells were assembled in an argon-filled glove box in the laboratory.
Galvanostatic charge-discharge measurements were carried out on a Land Battery Test System (Wuhan, China) at various C rates (here 1C refers to 117.6 mAh g\(^{-1}\)). Electrochemical impedance spectra were measured on a CHI660C electrochemical workstation with amplitude of 5 mV in the frequency range 100 kHz to 0.01 Hz.

**Fig. S1** Elemental mapping images of sodium, oxygen, vanadium, phosphorus, carbon and nitrogen in the bundle-like Na\(_3\)V\(_2\)(PO\(_4\))\(_3\)/C nanocomposites.

**Fig. S2** SEM images: the control Na\(_3\)V\(_2\)(PO\(_4\))\(_3\)/C sample prepared using NH\(_4\)H\(_2\)PO\(_4\).
**Fig. S3** Powder XRD patterns of the Na$_3$V$_2$(PO$_4$)$_3$/C samples prepared by using ATP and NH$_4$H$_2$PO$_4$ as the phosphorus sources.

**Fig. S4** Nitrogen adsorption/desorption isotherm of the as-prepared bundle-like Na$_3$V$_2$(PO$_4$)$_3$/C nanostructures.
**Fig. S5** TG curves of Na$_3$V$_2$(PO$_4$)$_3$/C samples obtained by using different phosphorus sources.

**References**