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From Biomolecule to $Na_3V_2(PO_4)_3$/Nitrogen-Decorated Carbon Hybrids: Highly Reversible Cathodes for Sodium-ion Batteries

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Experimental Details

Materials Synthesis

The bundle-like $Na_3V_2(PO_4)_3$/nitrogen-doped carbon (Marked as NVP-1) nanocomposites were synthesized by a solvothermal method. Typically, stoichiometric amounts of 1.2 mmol V_2O_5, 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 Na_2CO_3 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 ℃ for 24 h. Upon cooling to room temperature naturally, the brown suspension and precipitate were heated on a

hotplate at 80 ℃ under stirring to get a precursor. The resulting power was ground and annealed at 350 ℃ for 4 h, following by further treatment at 700 ℃ for 6 h under a flow of nitrogen with a heating rate of 2 ℃ min^{-1} in a tube furnace. For the synthesis of pristine $Na_3V_2(PO_4)_3$/C (Marked as NVP-2), the procedure was similar but $NH_4H_2PO_4$ 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 10-80º. 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 ℃ with a temperature ramp of 10 ℃ min^{-1}. N_2 adsorption-desorption measurements were determined by using a Micromeritics ASAP 2020 instrument.

Electrochemical Measurements

Electrochemical performance characterization of the $Na_3V_2(PO_4)_3$ 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(vinlylidenedifluoride) 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 $NaClO_4$ 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 impendence spectra were measured on a CHI660C electrochemical workstation with amplitude of 5 mV in the frequency range 100 kHz to 0.01 Hz.

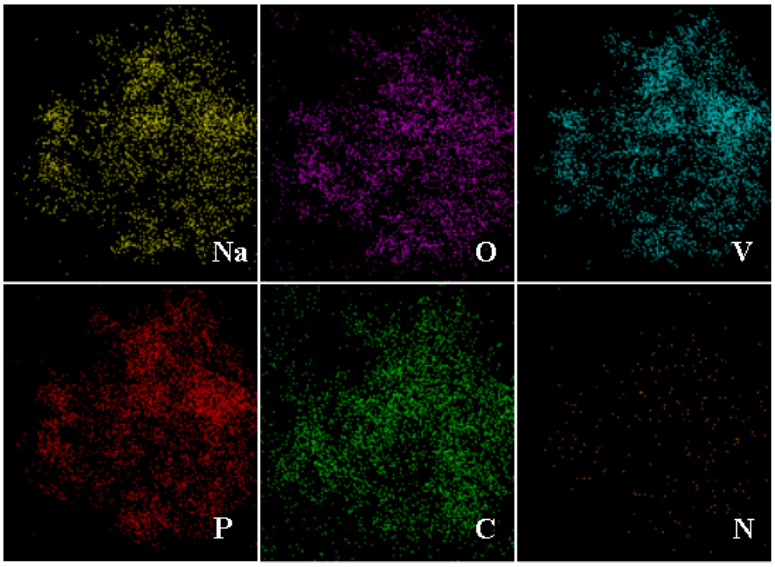

Fig. S1 Elemental mapping images of sodium, oxygen, vanadium, phosphorus, carbon and nitrogen in the bundle-like $Na_3V_2(PO_4)_3$/C nanocomposites.

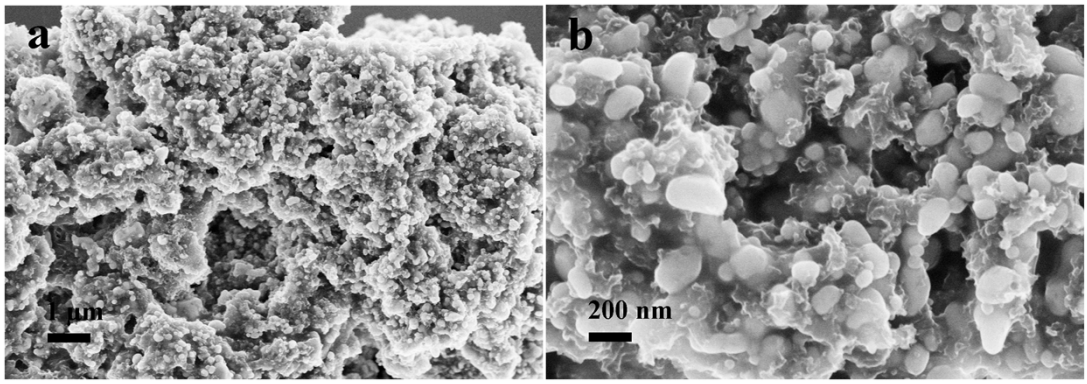

Fig. S2 SEM images: the control $Na_3V_2(PO_4)_3$/C sample prepared using $NH_4H_2PO_4$.

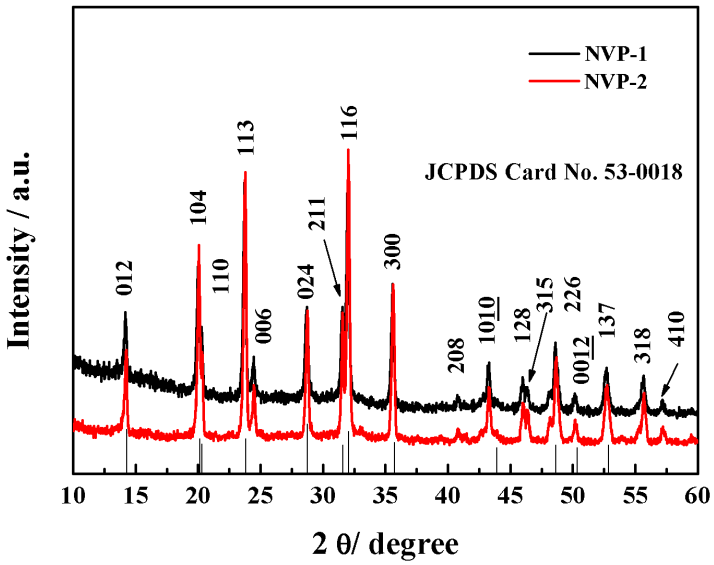

Fig. S3 Powder XRD patterns of the $Na_3V_2(PO_4)_3$/C samples prepared by using ATP and $NH_4H_2PO_4$ as the phosphorus sources.

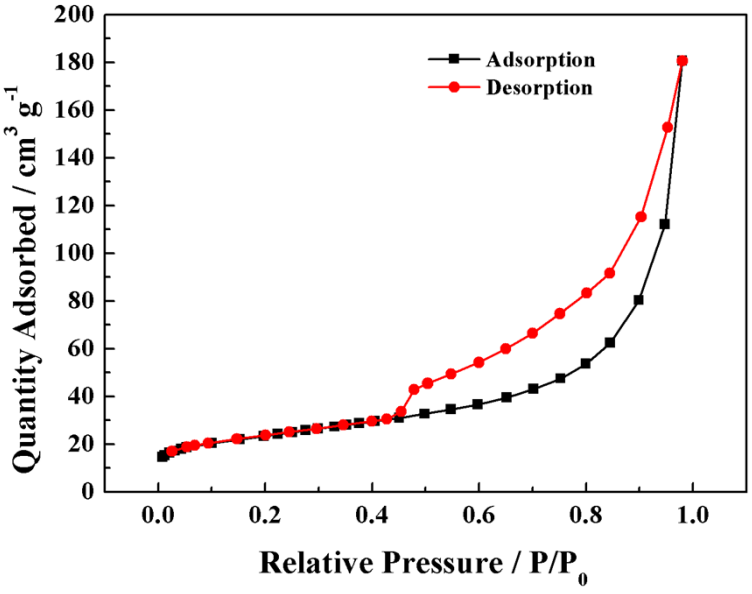

Fig. S4 Nitrogen adsorption/desorption isotherm of the as-prepared bundle-like $Na_3V_2(PO_4)_3$/C nanostructures.

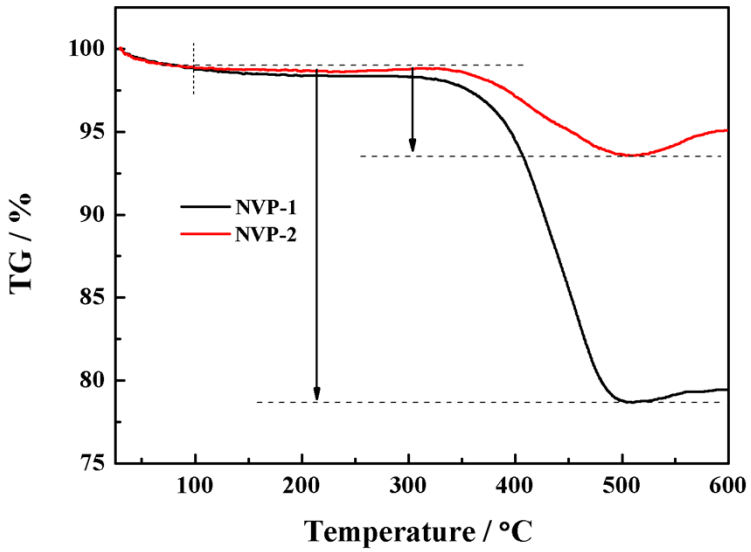

Fig. S5 TG curves of $Na_3V_2(PO_4)_3$/C samples obtained by using different phosphorus sources.

References

1. G. Pang, C. Yuan, P. Nie, B. Ding, J. Zhu and X. Zhang, *Nanoscale*, 2014, **6**, 6328-6334.