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From Biomolecule to Na$_3$V$_2$(PO$_4$)$_3$/Nitrogen-Decorated Carbon Hybrids: Highly Reversible Cathodes for Sodium-ion Batteries

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Sodium ion batteries (SIBs) working at room temperature offer promising opportunities for renewable energy storage applications due to the abundant supply and low cost of sodium, yet low capacity, inferior rate capability and limited cycle life remain a significant challenge in their electrochemical operations. Herein, we report the preparation of hierarchically Na$_3$V$_2$(PO$_4$)$_3$/nitrogen-decorated carbon hybrids via solvothermal reaction by using biomolecule of adenosine 5’-triphosphate disodium salt (ATP), as a novel precursor and environmentally friendly multifunctional source, including sodium, phosphorus, carbon, nitrogen, simultaneously. The results demonstrate that Na$_3$V$_2$(PO$_4$)$_3$ nanocrystals are encapsulated in interconnected carbon nanosheets with moderate nitrogen doping (2.88 %) to form a bundle-like structure, where the carbon nanosheets not only serve as a highly conducting pathway facilitating electron and ion transport, but a shielding matrix to accommodate volume changes upon electrochemical cycling, thus improving stability and reversibility of the Na$_3$V$_2$(PO$_4$)$_3$ cathode. The obtained materials thus deliver a high reversible capacity of 110.9 mAh g$^{-1}$ at low current rate of 0.2C as well as outstanding rate performance, suggesting that the Na$_3$V$_2$(PO$_4$)$_3$/nitrogen-doped carbon hybrids are promising cathode materials for use in high-performance sodium ion batteries.

Introduction

Energy is most conveniently stored in fossil fuels in the form of chemical energy. The combustion of fossil fuels will pollute the environment and is responsible for changing climate situation. With the increasing environmental concerns and energy shortages, development of clean and renewable energy derived from wind and solar energy has been one of the most significant scientific and engineering duties recently. Thus, electric energy storage (EES) is of significance for modern society. Among various promising energy storage systems, electrochemical secondary battery technology has been considered to be the best choice for this application due to its flexibility, high energy efficiency, rapid response, and simple maintenance. In particular, Lithium ion batteries (LIBs) have attracted extensive attention for applications ranging from portable electronics to electric vehicles or other energy storage because they can provide much higher energy density compared to other rechargeable battery systems. However, the availability of LIBs has been questioned due to the ever increasing demand and limited lithium reserves in the Earth’s crust. Based on the data from the US Geological Survey and Meridian International Research, the existing lithium resources could be sustained for ca. 65 years from now considering an average growth of 5% per year (total world lithium consumption in 2008: ca. 21, 280 tons). Accordingly, the new generation of EES systems with low cost and long life is extremely required.

In the word of “Post Lithium-ion”, sodium ion batteries have been taken into consideration as ideal alternatives to LIBs because of the abundance and ubiquitous distribution of sodium, safety, no toxicity as well as the ability to use electrolytes at lower decomposition potentials and aluminum current collector for anodes. Recently, there are an increasing volume of reports on possible materials in both cathodes and anodes for Na-ion batteries, also studies on the stability of various electrolytes. Unfortunately, a drawback for the sodium-ion battery is the relatively large ionic radius of sodium (about 55% larger than that of lithium), resulting in insufficient electrochemical properties, including low reversible capacity, poor cycle stability and inferior rate performance. Therefore, a great deal of efforts should been made to develop suitable host structures with sufficiently large interstitial space to accommodate Na ions and enable reversible and rapid ion insertion and extraction. Na$_3$V$_2$(PO$_4$)$_3$ with NASICON structure is a good cathode material that has received considerable attention for Na-ion batteries due to its high theoretical energy density (~400 Wh kg$^{-1}$, 117.6 mAh g$^{-1}$×3.4 V), good thermal stability (450 °C), open 3D framework with large interstitial channels. Moreover, this material has two different voltage plateaus at around 3.4 V and 1.6 V, corresponding to the V$^{3+}$/V$^{4+}$ and V$^{3+}$/V$^{2+}$ redox couples, respectively. The unique double potentials property makes it a
perfect candidate for used as an anode and a cathode in symmetric batteries, simultaneously. However, one obstacle delaying the commercialization of Na$_3$V$_2$(PO$_4$)$_3$ is the poor electronic conductivity, which leads to low Coulombic efficiency and poor cycle performance. More recently, research and development efforts to address the issues are focused on the improvement of the conductivity, reduction in grain size, and prevention of the particle aggregation. As a result, high specific capacities in terms of ultrafast rate performance have been achieved by many research groups. Despite continuous progress made in recent years, only a few reports of Na$_3$V$_2$(PO$_4$)$_3$ as electrodes for sodium ion batteries exist in the literature. Developing a facile and reliable synthesis procedure for producing high-rate and long-life Na$_3$V$_2$(PO$_4$)$_3$ with well-defined architectures is highly desirable and still remains a challenge.

Currently, naturally biological materials which are abundant, renewable, and eco-friendly, have been widely utilized as new raw materials for functional materials with novel morphologies and properties. For example, Su et al. fabricated LiFePO$_4$ nano/microspheres by using phytic acid as a biomass precursor, which showed excellent performance for lithium ion batteries. Mitlin et al. reported the hydrothermal-based synthesis of two-dimensional and interconnected carbon nanosheets from hemp bast fiber with superior electrochemical capacitance properties. The resultant nanosheets electrodes can work even down to 0 °C and display some of the best power-energy combinations reported in the literature for any carbon material, also the peat moss-derived carbon nanosheets anode for sodium ion battery. Activated carbons derived from coconut shells also exhibits favorable energy density and extraordinary cyclability when used as cathode materials for Li-ion capacitors. Wang and co-workers investigated a hierarchical porous carbon obtained from fish scales for lithium sulfur batteries. The resultant electrode displayed superb electrochemical performance in numerous respects, including high reversible capacity, rate capability, and cycling stability. These amazing achievements light the way to using renewable biomolecules as precursors for the preparation of electrode materials for sodium ion battery application.

![Fig. 1 Chemical structure of adenosine 5'-triphosphate disodium salt.](image)

In this paper, a facile template-free solvothermal method has been developed for the first time to fabricate bundle-like Na$_3$V$_2$(PO$_4$)$_3$/nitrogen-doped carbon nanoarchitectures by using adenosine 5'-triphosphate disodium salt, the most common energy carrier of the cell in biological systems, as novel and green phosphorus, carbon, nitrogen and sodium sources, simultaneously. Na$_3$V$_2$(PO$_4$)$_3$ nanocrystals were encapsulated in thin carbon nanosheets with nitrogen doping to form a bundle-like composite, in which the carbon nanosheets not only serve as a highly conducting pathway facilitating electron and ion transport, but a shielding matrix to accommodate volume changes upon electrochemical cycling, thus improving stability and reversibility of the Na$_3$V$_2$(PO$_4$)$_3$ cathode. Consequently, the hybrid exhibits a high specific capacity of 110.9 mAh g$^{-1}$ at a 0.2C rate, and a remarkable cyclability, suggesting a potential application as a new cathode for sodium ion batteries.

**Results and discussion**

![Scheme 1 Schematic illustration of the synthetic process of Na$_3$V$_2$(PO$_4$)$_3$/nitrogen-doped carbon nanosheet composites and decomposition reaction of adenosine 5'-triphosphate disodium salt under solvothermal environment.](image)
a complicated dissolution-recrystallization process, bundle-like Na$_3$V$_2$(PO$_4$)$_3$/C hybrids are obtained followed by annealing under nitrogen atmosphere.

Fig. 2 (a, b) FESEM and (c-f) TEM images of the as-synthesized bundle-like Na$_3$V$_2$(PO$_4$)$_3$/C nanostructures. The size and morphology of the as-synthesized Na$_3$V$_2$(PO$_4$)$_3$ were investigated by field-emission scanning electron microscopy (FESEM) and transmission electron microscope (TEM). As shown in Fig. 2a, b, the Na$_3$V$_2$(PO$_4$)$_3$/C composites consist of a bundle-like shape with the particle size of 500-800 nm. SEM image at higher magnification (Fig. 2b) reveals the highly interconnected sheet-like structure of the samples, and the nanosheets are interconnected and overlap to form a 3D porous structure. TEM images (Fig. 2c, d) further highlight the structure of Na$_3$V$_2$(PO$_4$)$_3$, one can interestingly find that the product consists of highly interconnected nanosheets and nanocrystals with sizes of a few tens of nanometers. The high resolution transmission electron microscopy (HRTEM) image of a selected nanoparticle in Fig. 2e clearly demonstrate the phase of Na$_3$V$_2$(PO$_4$)$_3$, where the clear lattice fringes with spacing of 6.1 Å, corresponding to the (012) plane of rhombohedral Na$_3$V$_2$(PO$_4$)$_3$.

For comparison, when NH$_4$H$_2$PO$_4$ was used as the phosphorus source under the same conditions, the control samples consist of agglomerated nanoparticles, as shown in Fig. S2. The results indicate that the biomolecules act as both a precursor for nitrogen, phosphorous, carbon, sodium source and a bio-template, which has a great effect on the morphology regulation and crystal growth during solvothermal process. In summary, nano-sized Na$_3$V$_2$(PO$_4$)$_3$ particles are modified by adenosine-derived nitrogen doped carbon nanosheets to form bundle-like hierarchical structures.

The crystal structure and phase purity of the resulting Na$_3$V$_2$(PO$_4$)$_3$/C samples were investigated by X-ray diffraction (XRD). Fig. S3 shows the XRD patterns of the two representative samples prepared by using ATP and NH$_4$H$_2$PO$_4$ as the phosphorus sources, respectively. All diffraction peaks are well in accordance with the NASICON structure with R-3c space group (rhombohedral unit cell, No.167). A Rietveld refinement analysis (Fig. 3b) was performed to estimate the bundle-like Na$_3$V$_2$(PO$_4$)$_3$ phase more precisely. As summarized in Table 1, the cell parameters obtained by Rietveld refinement were $a' = 8.734$ (1) Å, $c = 21.822$ (2) Å and $V' = 1441.8$ (2) Å$^3$, which correspond well with the existing values in literature and JCPDS card No.53-0018. Fig. 3a represents the schematic illustration of the NASICON type structure, which is built on a [V$_2$(PO$_4$)$_3$] unit of VO$_6$ octahedra sharing all the corners with PO$_4$ tetrahedra, where two octahedral VO$_6$ connected with three tetrahedral PO$_4$ constitute a basic unit. The two independent sodium atoms are located in the voids/channels of the framework with two different oxygen environments, one Na$^+$ occupies the 6b site (Na1) and the other one is located in 18e site (Na2). This open 3D framework offers large interstitial spaces for Na$^+$ accommodation, also channels allowing rapid transport of sodium ions and electron throughout the lattice.

Fig. 3 (a) Schematic representation of the crystal structure of Na$_3$V$_2$(PO$_4$)$_3$; (b) Rietveld refinement of the observed XRD pattern for Na$_3$V$_2$(PO$_4$)$_3$/C samples synthesis from ATP.
of N-doping, we analyzed the high-resolution N 1s peak of the hybrid (Fig. 4b). The N1s spectrum could be deconvoluted into four peaks centered at 398.5, 400.9, 402.5 and 406.4 eV, assigned to pyridinic N, pyrrolic N, graphitic N and oxygenated N, respectively. The total N content is calculated to be 2.88 atomic%. It has been widely established that the pyridinic-N species cause structural deformation and expose planar edges or defect sites in carbon materials, while pyrrolic N and graphitic-N will enable the surface adsorption and higher electronic conductivity of the carbon, respectively. Thus, nitrogen-doped carbon would be electrochemically more active. Compared with the post synthesized modification, our work opens new perspectives to develop functional materials with nitrogen doping for new energy storage systems.

![Image](image_url)

**Fig. 4** (a) Survey XPS spectrum, (b) N 1s XPS spectrum, (c) FTIR spectrum of bundle-like Na$_{1.9}$V$_2$(PO$_4$)$_3$/C nanostructures, and (d) Raman spectra of Na$_{1.9}$V$_2$(PO$_4$)$_3$/C samples prepared by using ATP (black curve) and NH$_3$H$_2$PO$_4$ (red curve) as the phosphorus sources.

The compositions of the as-prepared material were also identified by Fourier transform infrared (FT-IR) spectroscopy, as shown in Fig. 4c. The bands at 581 and 1058 cm$^{-1}$ suggest the presence of P-O bonds in PO$_4$ tetrahedra, and the vibration from V$^{3+}$-O$^2-$ bonds in isolated VO$_6$ octahedra is located at 633 cm$^{-1}$. In addition, the IR bands in the range of 1150-1250 cm$^{-1}$ can be ascribed to the stretching vibration of terminal PO$_4$ units, in agreement with the assignments previously reported in the literature. Raman spectroscopy studies were carried out to investigate the structure features of the resulting Na$_{1.9}$V$_2$(PO$_4$)$_3$/C composites. Fig. 4d displays the Raman spectra of the carbon coated Na$_{1.9}$V$_2$(PO$_4$)$_3$ and the nitrogen doped modified one. The peaks at 1350 cm$^{-1}$ (D band) and 1595 cm$^{-1}$ (G-band) can be seen clearly in both samples, suggesting the existence of carbon in the materials, which corresponds to the lattice defects, edges and disorder in the C-C system (sp$^3$ hybridization) and the C-C stretching mode of highly ordered graphitic carbon (sp$^2$ hybridization), respectively. Meanwhile, the Na$_{1.9}$V$_2$(PO$_4$)$_3$ exhibits characteristic peak located at 984 cm$^{-1}$. The Brunauer-Emmet-Teller (BET) specific surface area of Na$_{1.9}$V$_2$(PO$_4$)$_3$/nitrogen-doped carbon hybrid was further investigated by N$_2$ adsorption-desorption isotherm. As shown in Fig. S4, the composites possessed a relatively high specific surface area of 83.6 m$^2$ g$^{-1}$, and the pore volume was 0.279 cm$^3$ g$^{-1}$.

The carbon content is estimated to be 20.25 wt% and 5.40 wt% in bundle-like Na$_{1.9}$V$_2$(PO$_4$)$_3$ and the comparative one, respectively, as measured by thermogravimetric (TG) analysis in an air atmosphere (Fig. S5). The high carbon content in the former is closely related to the carbon compound backbone in the structure of ATP molecule.

![Image](image_url)

**Fig. 5** (a) Galvanostatic charge/discharge curves for the Na$_{1.9}$V$_2$(PO$_4$)$_3$ cells at a rate of 0.2 C in the voltage range of 2.5 and 3.8 V, (b) Cycling performance of the two samples at various current densities.

Intrigued by the structural features of the obtained composites, electrochemical measurements of the Na$_{1.9}$V$_2$(PO$_4$)$_3$ electrodes were performed in 2032 coin-type cells at the room temperature. Fig. 5a shows galvanostatic charge/discharge profiles of the Na$_{1.9}$V$_2$(PO$_4$)$_3$ electrodes in the potential window of 2.5-3.8 V vs. Na$^+$/Na at a rate of 0.2 C (1C = 117.6 mAh g$^{-1}$). The bundle-like Na$_{1.9}$V$_2$(PO$_4$)$_3$/C hybrids afford initial charge...
and discharge capacities of 121.7 and 110.9 mAh g\(^{-1}\), yielding an efficiency of 91.1%. The irreversible capacity loss may mainly stem from kinetic limitations by structural changes during sodium de/insertion.\(^\text{59}\) The distinct voltage plateaus demonstrate a two-phase reaction between Na\(_3\)V\(_2\)(PO\(_4\))\(_3\)/NaV\(_2\)(PO\(_4\))\(_3\), corresponding to the V\(^{4+}/V^{3+}\) redox couple, where the electrochemical Na\(^+\) insertion/extraction processes occurring at Na\(_3\)V\(_2\)(PO\(_4\))\(_3\) electrode can be expressed by Equation (1):

\[
\text{Na}_3\text{V}_2(\text{PO}_4)_3 \leftrightarrow \text{NaV}_2(\text{PO}_4)_3 + 2\text{Na}^+ + 2\text{e}^-
\]

(1) resembling the results in previous reports.\(^\text{59}\) In contrast, the nitrogen free Na\(_3\)V\(_2\)(PO\(_4\))\(_3\)/C nanocomposites delivered a discharge capacity of 85 mAh g\(^{-1}\). Interestingly, an obvious narrow gap between charge and discharge voltage profiles is observed for the bundle-like Na\(_3\)V\(_2\)(PO\(_4\))\(_3\) and the sample presents a higher Coulombic efficiency than the Na\(_3\)V\(_2\)(PO\(_4\))\(_3\) nanoparticles (86.7%). It is noted that the enhanced performances of bundle-like Na\(_3\)V\(_2\)(PO\(_4\))\(_3\)/C material may originate from highly conductive network represented by the interparticular nitrogen-doping carbon nanosheets located between Na\(_3\)V\(_2\)(PO\(_4\))\(_3\) nanocrystals.

![Nyquist impedance plots of the Na\(_3\)V\(_2\)(PO\(_4\))\(_3\) electrodes measured before cycling.](image)

**Fig. 6** Nyquist impedance plots of the Na\(_3\)V\(_2\)(PO\(_4\))\(_3\) electrodes measured before cycling.

The charge/discharge rate performance of the Na\(_3\)V\(_2\)(PO\(_4\))\(_3\)/C composite was investigated by cycling at various current densities. An extraordinary high-rate capability is demonstrated in Fig. 5b in which the cell delivers a high reversible capacity of 110.7, 104.7, 102.6, 76.6 mAh g\(^{-1}\) at current rates of 0.5C, 1C, 2C and 5C, respectively. Even when the C-rate was increased to 10C, a remarkably reversible and stable capacity of 46.8 mAh g\(^{-1}\) was still preserved. This corresponds to a charge or discharge time of 6 minutes, indicating the excellent rate capability of the cathode. It is worth noting that the as-prepared bundle-like Na\(_3\)V\(_2\)(PO\(_4\))\(_3\) material demonstrates much better performance compared to the bare Na\(_3\)V\(_2\)(PO\(_4\))\(_3\) without N-doping carbon nanosheets modification, indicating the positive effect of the unique structure. Overall, the sodium storage properties of bundle-like Na\(_3\)V\(_2\)(PO\(_4\))\(_3\)/carbon nanosheets hybrids in terms of specific capacity and rate performance are comparable or even superior to the reported Na\(_3\)V\(_2\)(PO\(_4\))\(_3\) cathode materials in the literature,\(^\text{26-30}\) which renders the nanocomposite highly desirable for applications in large-scale electric energy storage and electric vehicles.

To further establish the relationship between electrochemical performance and electrode kinetics for both Na\(_3\)V\(_2\)(PO\(_4\))\(_3\), cathodes, impedance Nyquist plots was collected on fresh cells (Fig. 6). The impedance spectra of both electrodes consist of a single depressed semicircle in the high frequency region and an inclined line at low frequency, corresponding to the charge-transfer resistance (R\(_ct\)) and the solid-state diffusion of ions in the active materials, respectively. The bundle-like Na\(_3\)V\(_2\)(PO\(_4\))\(_3\) electrodes show smaller diameter of semicircles in the Nyquist plots than those of the corresponding bare Na\(_3\)V\(_2\)(PO\(_4\))\(_3\) without N-doping carbon nanosheets, indicating lower R\(_ct\) and better kinetics for sodium ion insertion reactions. This result clearly implies that the electronic conductivity of Na\(_3\)V\(_2\)(PO\(_4\))\(_3\) has been remarkably improved by coupling N-doping carbon nanosheets.

In the light of the results, the superior performance of the Na\(_3\)V\(_2\)(PO\(_4\))\(_3\)/carbon nanosheets composite could be ascribed to its unique nanoarchitecture and favorable morphology. Firstly, the porous 3D structure and open channels between Na\(_3\)V\(_2\)(PO\(_4\))\(_3\) nanocrystals and carbon nanosheets offer favorable paths for electrolyte penetration, facilitating fast charge transfer across the electrolyte/electrode interface.\(^\text{60}\) Secondly, the nitrogen doping in the carbon matrix can introduce a lot of surface defects and enhance the electrochemical reactivity. Furthermore, the well-crystallized nature and nanoscale effect of the Na\(_3\)V\(_2\)(PO\(_4\))\(_3\) nanocrystals provide relatively shorter Na\(^+\) diffusion pathways, thus facilitating the fast kinetics of electrochemical reactions.\(^\text{61, 62}\)

Lastly, the Na\(_3\)V\(_2\)(PO\(_4\))\(_3\) nanocrystals are encapsulated in the large-area carbon nanosheets multiplexed networks, which further strengthen the structural integrity of the hybrids, prevent the aggregation and volume change during Na insertion and extraction, also enable reasonable electronic conductivity of the Na\(_3\)V\(_2\)(PO\(_4\))\(_3\) material. All in all, the above synergistic effect favors the high reversible capacity as well as superior rate performance of the bundle-like Na\(_3\)V\(_2\)(PO\(_4\))\(_3\)/nitrogen-doped carbon nanocomposite.

**Conclusions**

In summary, bundle-like Na\(_3\)V\(_2\)(PO\(_4\))\(_3\)/nitrogen-doped carbon composite has been synthesized via solvothermal reaction by using a high-energy biomolecule for the first time. In the system, ATP biomolecule acts as a multifunctional source, including sodium, phosphorus, carbon, nitrogen, also a biotemplate to control the formation of the hierarchical structure. The unique porous 3D structure offer favorable paths for electrolyte penetration and mass/charge transfer, and the newly found nitrogen-doped carbon nanosheets enable high electronic conductivity of the Na\(_3\)V\(_2\)(PO\(_4\))\(_3\), thus facilitating the fast kinetics of electrochemical reactions. These features combined with the nanoscale effect of the Na\(_3\)V\(_2\)(PO\(_4\))\(_3\) nanocrystals, the as-fabricated hybrids exhibit extremely high sodium storage capacities and impressive rate capability when used as cathode materials. Our design for the synthesis of Na\(_3\)V\(_2\)(PO\(_4\))\(_3\) by using ATP as precursors represents a promising direction and new prospect towards developing novel types of functional materials for energy storage devices.

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Notes and references

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Biomolecule for sodium ion battery: We present important findings related to a high energy biomolecule, adenosine 5’-triophosphate disodium salt (ATP), as a novel precursor and environmentally friendly multifunctional source for the synthesis of bundle-like Na₃V₂(PO₄)₃/nitrogen-decorated carbon nanocomposites.