Large Scale One-Pot Synthesis of Monodispersed Na$_3$(VOPO$_4$)$_2$F Cathode for Na-Ion Batteries

Qiangqiang Zhang$^{1,3,*}$, Xing Shen$^2$,* Quan Zhou$^{1,3,*}$, Kaixuan Li$^1$, Feixiang Ding$^{1,3}$, Yaxiang Lu$^1$, Junmei Zhao$^{2,4,*}$, Liquan Chen$^{1,3}$, Yong-Sheng Hu$^{1,3,*}$

$^1$ Key Laboratory for Renewable Energy, Beijing Key Laboratory for New Energy Materials and Devices, Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing, 100190, China

$^2$ CAS Key Laboratory of Green Process and Engineering, State Key Laboratory of Biochemical Engineering, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, China

$^3$ Center of Materials Science and Optoelectronics Engineering, University of Chinese Academy of Sciences, Beijing, 100049, China

$^4$ China Innovation Academy for Green Manufacture, Chinese Academy of Sciences, Beijing 100190, China

* Corresponding authors. E-mails: jmzhao@ipe.ac.cn (J.Z.), yshu@iphy.ac.cn (Y.-S.H.)

# These authors contributed equally to this work.

Abstract

Na-ion batteries (NIBs) have received significant interest as potential candidates for large-scale energy storage owing to the widespread distribution of sodium and superior low-temperature
performance. However, their commercial application is usually hindered by the high production
cost and inadequate performance for electrode materials, particularly for cathodes. Na$_3$(VOPO$_4$)$_2$F
(NVOPF) has been recognized as one of the most promising cathodes for high-energy NIBs owing
to the high working voltage and energy density. Here we report a facile highly efficient
room-temperature solution protocol for large scale synthesis of NVOPF cathode for NIBs. By
simply regulating pH, NVOPF can be obtained, which delivered a discharge capacity of 120.2
mAh g$^{-1}$ at 0.1 C and 72% capacity retention over 8000 cycles at 25°C. Besides, the kilogram-level
NVOPF products have been synthesized and 26650 cylindrical cells were fabricated, which
exhibit excellent cycling stabilities, remarkable low-temperature performance with comparable
safety features. We hope our findings could provide insights on the industrial application of
NVOPF in NIBs.

Keywords

Na$_3$(VOPO$_4$)$_2$F, monodisperse submicron-cuboids, cathode, Na-ion batteries, high safety, low
temperature performance, long cycle life, energy storage

1. Introduction

Rechargeable Na-ion batteries (NIBs) have attracted extensive attention owing to the outstanding
virtues, including abundant sodium resources, low cost, and similar working principle to
lithium-ion batteries (LIBs), making NIBs the promising candidate for highly efficient and
large-scale energy storage systems (ESSs).[1-4] The cathode, as the critical component
determining the energy density of NIBs, has accordingly captured comprehensive attention.[5-7]
Up to now, substantial efforts have been devoted to the development of high-performance cathode materials including layered oxides, Prussian blue analogues and polyanionic materials, which show distinguishable electrochemical behavior owing to the varied intrinsic structure characteristics.[8-11] Among them, V-based polyanionic compounds usually exhibit superior long-term cycling stability due to their open 3D host skeleton and strong inductive effects, such as Na$_3$V$_2$(PO$_4$)$_3$,[12, 13] NaVOPO$_4$,[14] Na$_3$(VPO$_4$)$_2$F$_3$,[15] Na$_3$(VOPO$_4$)$_2$F,[16] Na$_7$V$_3$(P$_2$O$_7$)$_4$.[17] et al.[18-20] In particular, the series compounds Na$_3$(VO$_{1-x}$PO$_4$)$_2$F$_{1+2x}$ (0 ≤ x ≤ 1, NVPFs) have been extensively investigated because they could offer high capacity (128-130 mAh g$^{-1}$) with a two-electron transfer and high operating voltage (3.6-4.1 V).[21-30] Besides, they often present high ionic-conductivity property and stable crystal structure, which is suitable well for the high-energy NIBs.[26, 31-34] However, the high preparation cost rooted in the synthetic strategy limits the scale-up production for sodium vanadium fluorophosphates.

Up to now, various methods for the preparation of NVPFs have been reported. Among them, the solid-state approach based on high temperature was typically adopted in the synthesis of NVPFs. There is no doubt that high energy consumption from the solid-state method will increase the cost of ESSs. Meanwhile, the products usually show irregular morphologies or even heterogeneous compositions accompanied by impurity derived from the severe volatilization of VF$_3$, leading to poor electrochemical performance.[30, 32, 35-37] Furthermore, HF would corrode the equipment at high temperature. Beyond that, liquid-phase syntheses were developed rapidly in recent years, to reduce energy consumption and rationally regulate the morphologies for better electrochemical performance. As an example, Goodenough et al. synthesized NVOPF via solvothermal method, which marks the evolution from high temperature to mild condition.[38] In 2015, Qi et al.
developed a solvothermal low-temperature strategy for NVOPFs and firstly reported the room temperature preparation within dozens of days.[39] Very recently, our group developed a facile large-scale room-temperature controllable synthesis of NVOPF via a solution-phase method, which can remarkably reduce the manufacturing cost of the cathode materials within 6 days to get nearly 100% yield.[30] However, the long reaction cycle restricts the conversion rate of space and equipment, leading to a low production efficiency. Besides, like many other phosphate electrode materials, NVOPFs showed a low intrinsic electronic conductivity due to the separation of V atoms by [PO$_4$] tetrahedral,[40] which affects the Na$^+$ ion diffusion and then hinders its rate capabilities. To solve this problem, different strategies, such as coating with carbon,[26, 36, 41-43] doping with heteroatoms,[44, 45] have been energetically developed and proven to have positive effects on improving the apparent and intrinsic electronic conductivity. While these modification methods always rely on the complicated high-temperature synthesis, which is not suitable for the common solution-based syntheses. Accordingly, to achieve high-performance polyanionic cathode via a simple low-cost approach requires precise regulation in the size and morphology of products, which offers shortened ion/electron transport pathways and sufficient prerequisites for high tap density NIBs.

In this work, a facile and highly efficient room-temperature solution-phase strategy for the fabrication of NVOPF was investigated. And the high-purity monodispersed NVOPF submicron-cuboids have been prepared by precisely regulating the solution’s pH and substrate concentration. More importantly, the one-pot synthesis provided in this study can be easily scaled up to kilogram-level preparation of NVOPF to construct commercial cylindrical batteries. The potential mechanism for morphology formation and superior electrochemical performance has
also been investigated by multidimensional experimental characterizations. Thus, the proposed
room-temperature large-scale synthesis provides essential reference significance for the industrial
application of NVPFs in NIBs.

2. Experimental

2.1 Materials

Vanadylsulfate hydrate (VOSO₄·xH₂O, 99.9%, Alfa), sodium phosphate monobasic dihydrate
(NaH₂PO₄·2H₂O, 99%, Sigma), sodium fluoride (NaF, 99.99%, Aladdin), ammonium hydroxide
(NH₃·H₂O, 28-30 wt% solution of NH₃ in water, Acros), sodium perchlorate (NaClO₄, 98-102%,
Alfa), propylene carbonate (PC, 99.7%, Sigma-aldrich), 4-fluoro-1,3-dioxolan-2-one (FEC, 98%,
Alfa), and sodium metal (Na, 99%, Alfa). All above reagents were used as received without
further treatment.

2.2 Synthesis of the Na₃(VOPO₄)₂F (NVOPF)

Firstly, a certain amount of VOSO₄·xH₂O was dissolved in deionized water to form a
homogeneous solution labeled as S1, and a certain NaH₂PO₄·2H₂O, NaF, and NH₃·H₂O were
dissolved in deionized water to form a homogeneous solution labeled as S2. Then, S1 and S2 were
rapidly mixed to get solution S3 at 30°C, and the molar ratio of V: P: F in S3 was maintained at
1:3:1.7. Finally, the products were collected by filtration and washed several times with deionized
water and ethanol and dried at 100 °C for 6 h to obtain the final product.

2.3 Material Characterization
X-ray powder diffraction (XRD) was performed on a D8 advanced X-ray diffractometer (Bruker, Germany) using Cu Kα radiation (λ=1.5405 Å). Scanning electron microscopy (SEM) images were acquired on a Hitachi S-4800 equipped with EDS (energy dispersive X-ray spectrometry) (Hitachi, Japan). Transmission electron microscopy (TEM) was conducted on a JEM-2100Plus (JEOL, Japan). Fourier transform infrared (FTIR) spectra were carried out on a VERTEX 70v Bruker spectrometer (Bruker, Germany). UV-vis absorption spectra (UV) were measured on a U-4100 spectrometer (Hitachi, Japan). X-ray photoelectron spectroscopy (XPS) was recorded using Thermo Scientific ESCLAB 250Xi (Thermo Fisher Scientific, America) equipped with monochromic Al Kα radiation. All spectra were calibrated for the charging effect with the C1s peak at 284.8 eV. Cyclic voltammetry (CV) was conducted on the CHI800D electrochemical workstation (Chenhua, China). Inductively coupled plasma atomic emission spectrometry (ICP-OES) was used to analyze the concentration of vanadium in the aqueous phase, conducted on Optima 7000DV (PerkinElmer, America).

2.4 Electrochemical Measurements

All the galvanostatic measurements of NVOPF were conducted with a 2032-type coin cell on a Land BT2000 battery test system (LANHE, China). The cathode sheets were prepared by mixing NVOPF, KB, and polytetrafluoroethylene (PTFE) in a mass ratio of 7: 2: 1 followed by rolling the composite to square thin slices subsequently dried at 120 °C under high vacuum overnight, with the thickness of 0.1 mm. The active material loading is about 5-8 mg cm⁻² in the size of 6×6 mm. Coin cells were assembled in a glove box under Ar. The liquid electrolyte (200 μL) used here was 1M NaClO₄ in PC with 3 wt.% FEC as a functional additive. Na metal was adopted as an anode. The Whatman glass fiber was employed as the separator. During the charge and discharge process,
the same current rate was used (1 C=130 mA g⁻¹). The specific capacity is based on the mass of active material. The 26650 cylindrical cells using NVOPF as the cathode with hard carbon as the anode were manufactured at HiNa Battery Technology Co., Ltd.

3. Results and discussion

For the room-temperature solution-phase synthesis of NVOPF particles, it’s vital to balance different parameters, including raw materials, reaction time, additives, and pH etc. According to our previous experiments, VOSO₄ and NaH₂PO₄·2H₂O are ideal vanadium sources and phosphorus sources, respectively.[36, 46] NaF is widely used as a fluorine source for the synthesis of F-containing compounds. And the reaction of the three salts above has been written as below:[36]

\[
2\text{VOSO}_4 + 2\text{NaH}_2\text{PO}_4 + \text{NaF} \rightarrow \text{Na}_3(\text{VOPO}_4)_2\text{F}↓ + 2\text{H}_2\text{SO}_4
\]

We expect that the chemical reaction will go to the right following the chemical reaction balance if the by-product H₂SO₄ is removed from the reaction system. Furthermore, it has been reported that NVOPF would be dissolved in a strongly acidic solution. Therefore, we intentionally introduce NH₃·H₂O into the reaction system to eliminate H₂SO₄ and predict that NVOPF can precipitate rapidly at room-temperature under an appropriate pH value.

Beyond our expectation, NVOPF particles form immediately as the solution of VOSO₄ was poured into the mixed solution of Na, P, F sources with NH₃·H₂O, as recorded in Supplementary Video S1. The XRD pattern of as-prepared samples was shown in Figure S1, which is well
indexed to the standard card (PDF# 97-041-1950). In this case, the reaction time has been greatly
saved compared to the reported room-temperature synthetic process.[30] According to our
previous work, pH value acts as an important role in the preparation of the objective
products. Thus we prepared different-pH solutions where the concentrations of V, P and F
were 0.07 mol L$^{-1}$, 0.21 mol L$^{-1}$, and 0.119 mol L$^{-1}$, respectively, and the pH values ranged from 3
to 8 were adjusted through adding different amounts of NH$_3$·H$_2$O. As expected, the highest yield
of 99.2% can be reached at the pH of 6 with a fixed static time of 1 day. The vary of yields with
increasing pH was listed in Table S1, resulting from ICP-OES tests.

Generally speaking, for a solution-based strategy, the particle size and microstructure can be
rationally adjusted by regulating the concentration of the reactants. Herein, the concentrations of
the raw materials were monitored with the invariant pH value at 6 (the as-prepared samples were
marked as C1, C2, C3, C4, C5), whose details and yields have been listed in Table S2. It can be
seen that the yields have been slightly enhanced with the increasing concentration of precursors.
The XRD profiles of products were recorded in Figure S2a, from which pure NVOPF has been
obtained. And the microscopic morphologies of corresponding products were also recorded in
Figure S2b-f, from which the particle size becomes smaller and smaller with increasing
concentration. Although high reactant concentration favors the high yield, the small particle size
will induce severe side reactions that consumes electrolytes and reduces cycling stabilities.
Therefore, we choose the concentration of C5 (Table S2) for further optimization, from which
uniform cuboids in modest submicron-size successfully achieved. Besides, we investigated the
effect of aging time on the yield of NVOPF, as seen in Table S3. Results show that it could get a
98.7% yield at the moment of reactant mixing, and it slightly rises to 99.2% with a static time of 1
day. After 2 days’ aging, it could achieve the complete conversion of V with the yield of ~100%.

However, aging time benefits the crystallinity of as-prepared samples, as demonstrated in Figure S1. Based on the higher yield and better crystallinity, the 2 days’ aging sample was chosen as the referral target to be further explored.

The typical morphologies of as-synthesized NVOPF were precisely observed by combining SEM and TEM, as shown in Figure 1. Monodispersed cuboids in size about 800 nm have been obtained from Figure 1A-C from SEM. The lattice finger marked in Figure 1D from HR-TEM corresponds to the (101) plane of NVOPF. Figure 1E and 1F show the low-resolution images obtained from TEM, which further confirms the morphology observed from SEM. Considering the dynamic performance of NVOPF, the monodispersed submicron-cuboids could remarkably shorten transportation lengths for Na$^+$ and electrons, resulting in fast desodiation/sodiation transfer kinetics.[41] More importantly, differing from tens of submicron-sized particles that will consume lots of liquid electrolytes resulting in low Coulombic efficiencies and active materials utilization, the monodisperse 800 nm cuboids can efficiently reduce the consumption of liquid electrolyte and construct a uniform CEI on their surfaces. Furthermore, the uniform morphologies could efficiently homogenize current distribution and hence inhibit locally overcharge or over-discharge, contributing to utilizing the capacity of active materials sufficiently and holding the long-cycling stability. Besides, the EDS from SEM corroborates the uniform distribution of all containing elements in NVOPF, as shown in Figure S3.
**Figure 1. Material Synthesis** (A) (B) (C) SEM images of NVOPF in different magnifications. (D) HR-TEM image of NVOPF. (E) (F) TEM morphologies of NVOPF in different magnifications

Since NVOPF was first reported in 2002, there exists a debate about its crystal structure. In 2002, Massa showed a tetragonal NVOPF with $I4/mmm$ space group, while in 2011, Tsirlin et al. presented a tetragonal NVOPF with $P4_2/mnm$ space group.[47, 48] Up to now, some of groups have believed NVOPF to be $I4/mmm$ space group.[26, 30-33, 36, 39, 41, 42, 44, 46, 49-51] while others followed the $P4_2/mnm$ space group.[52-55] Herein, two Rietveld structural refinements for NVOPF have been carried out based on the $I4/mmm$ space group and $P4_2/mnm$ space group, respectively. The Rietveld refinement data of NVOPF have been listed in Table S4, from which it can be seen that better reliability factor values ($R_{wp} = 5.85\%, R_p = 4.5\%$) for $I4/mmm$ space group have been obtained than those ($R_{wp} = 11.96\%$ and $R_p = 8.12\%$) for $P4_2/mnm$. Hence, we believe that our synthesized NVOPF belongs to the $I4/mmm$ space group whose crystallographic data were listed in Table S5. It has been reported that Na atoms show the more disordered distribution in $I4/mmm$, which will lead to superior dynamic properties.[30] The XRD profile and the
Rietveld-refined results were shown in Figure 2A. No traces of impurities and intermediate phases are detected, indicating the high purity of the as-synthesized NVOPF. Figure S4 provides the tetragonal crystal structure diagram of NVOPF with a pseudo-layered framework formed by a repeating unit parallel to the ab plane. The repeating unit is composed of [V$_2$O$_{10}$F] biocahedra and [PO$_4$] tetrahedra connected by sharing O vertices. Along the c axis, in the [V$_2$O$_{10}$F] biocahedra, [VO$_5$F] octahedra are bridged by F vertices located in the same ab plane as the disordered Na atoms. It has been proved that Na$^+$ diffuses in 2D channels between these pseudolayers, which contributes to the rapid desodiation/sodiation during the charge/discharge processes.[33, 42, 56]
Figure 2. Crystal and Electronic Structure Characterizations (A) Rietveld-refined profiles of as-synthesized NVOPF from the proposed $I4/mmm$ space group according to Ref.2002. (B) FTIR spectrum of NVOPF. (C) UV-vis spectra of NVOPF, VCl$_3$, and VOSO$_4$.

FTIR spectra were widely conducted in investigating the molecular structure of Na$_3$(VO$_{1-x}$PO$_x$)$_2$F$_{1+2x}$, $(0 \leq x \leq 1)$ compounds. As shown in Figure 2B, the FTIR spectrum of the synthesized product is highly consistent with the previously reported that of Na$_3$(VOPO$_4$)$_2$F.[27, 37] The strong broad band ranging from $1000 \text{ cm}^{-1}$ to $1200 \text{ cm}^{-1}$ represents the asymmetric stretching vibration of the PO$_4^{3-}$ group. The bands at $670 \text{ cm}^{-1}$ and $555 \text{ cm}^{-1}$ correspond to the P-O symmetric stretching vibration and bending vibration. More importantly, the V-O stretching vibration $(916 \text{ cm}^{-1})$ is remarkably stronger than the V-F vibration $(947 \text{ cm}^{-1})$, which is due to the more numbers of the V-O bonds than that of V-F bonds in the Na$_3$(VOPO$_4$)$_2$F lattice.[27, 30, 32, 37, 50] In addition, UV-vis spectrum is a valuable tool to characterize the valence of V.[30, 57]

Herein, the UV-vis spectra of the as-synthesized product, standard VCl$_3$ and VOSO$_4$ samples were obtained in Figure 2C. It can be identified that the absorption peaks of the synthesized product are similar to those of VOSO$_4$ but very different from those of VCl$_3$. A maximum adsorption peak at $764 \text{ nm}$ and a shoulder peak at $630 \text{ nm}$ indicate V$^{4+}$ in the synthesized product.[36]

The electrochemical Na$^+$-storage properties of as-synthesized NVOPF cuboids were gauged in coin half cells with sodium metal as the counter/reference electrode. The typical charge-discharge profiles of NVOPF at various current densities are displayed in Figure 3A. For the current density of 0.1 C, it presented two prominent charge-discharge plateaus located at around 3.6 V and 4.0 V with small polarizations, which can be described as a typical two-step reaction as follows:
Plateau at around 3.6 V:

\[
Na_3(VOPO_4)_2F - xNa^+ \Leftrightarrow Na_{3-x}(VOPO_4)_2F + xe^- (0 \leq x \leq 1) \tag{1}
\]

Plateau at around 4.0 V:

\[
Na_2(VOPO_4)_2F - xNa^+ \Leftrightarrow Na_{2-x}(VOPO_4)_2F + xe^- (0 \leq x \leq 1) \tag{2}
\]

As the current density increases, all the charge-discharge curves still exhibit two distinct plateaus accompanied by the increment of voltage hysteresis due to the increasing ohmic polarization, concentration polarization, and electrochemical polarization. The discharge capacities recorded at 0.1C, 1C, 2C, 5C, 10C, 15C, 20C and 25C are 120.2 mAh g\(^{-1}\), 119.5 mAh g\(^{-1}\), 117.5 mAh g\(^{-1}\), 116.3 mAh g\(^{-1}\), 109.7 mAh g\(^{-1}\), 103.4 mAh g\(^{-1}\), 93.5 mAh g\(^{-1}\) and 74.1 mAh g\(^{-1}\), respectively, suggesting superior rate capability. Furthermore, the discharge capacity at 0.1C could almost restore to its initial value of 118.2 mAh g\(^{-1}\) after the rate tests of 70 cycles as shown in Figure 3B, only 1.7% capacity loss, indicating that NVOPF could operate at arbitrarily varied current densities.
Figure 3. Na-storage Performance of Half Cell (A) Charge-discharge profiles of NVOPF electrodes at different rates from 0.1 C to 25 C, and corresponding rate capability (B). Cycling performance of NVOPF electrodes at (C) 25 C.

To manifest the potential of NVOPF in high-power and long-life applications, we measured the ultrafast long-term charge-discharge performance at 25 C, as shown in Figure 3C, respectively. As a result, the batteries exhibit ultralong cycling stability with 72% retention after 8,000 cycles, and the first discharge capacity reaches 75.7 mAh g⁻¹. Besides, a series of batteries operating at lower rates of 1C, 2C, 5C, 10C, 15C, and 20C, respectively, were recorded in Figure S5. As a result, all batteries exhibit excellent cycling stabilities, suggesting the outstanding electrochemical
performance of the as-synthesized NVOPF. In terms of preparation cost and Na-storage performance, the current work shows the comparable comprehensive properties in contrast to the reported NVOPF cathodes for NIBs, as listed in Table S6. Besides, the half and full cell performances of the typical cathode materials prepared by room-temperature routes were summarized in Table S7. Compare to other materials, the current cathode exhibits the decent electrochemical performances.

Notably, the method proposed in this study can be easily scaled up. The synthesized kilogram-level NVOPF was shown in Figure 4A and made into large sheets on the coating production line, as shown in Figure S6a-b. Afterward, the prepared NVOPF cathode sheets were assembled into NVOPF-26650 cylindrical cells with the hard carbon as anodes, as shown in Figure 4B. The 0.2C charge and discharge results show that the prepared NVOPF-26650 cylindrical cell has a capacity of 1.78 Ah, as shown in Figure S6c, when cycled at 5C, the initial discharge capacity decreased to 0.99 Ah. And the capacity retention reaches up to 95.2% after 2000 cycles at 5C with high average Coulombic efficiency of near 100%, as shown in Figure 4D, demonstrating the remarkable electrochemical performance and the practicability of the current strategy. Furthermore, the low-temperature performance of the prepared NVOPF-26650 cylindrical cell is tested at 25°C, -20°C, and -30°C, respectively, as shown in Figure 4C. Before discharge, the charging process is conducted first at 0.2C at 25°C, and then discharging the cell at 0.2C at different temperatures. Taking the discharge capacity at 25°C as 100%, it can be seen that the discharge capacity retention rate is 78% at -20°C and 63.5% at -30°C, demonstrating the glorious low-temperature characteristic of the NVOPF-26650 cylindrical cell, superior to the LiFePO₄-based cell shown in Figure 4C.
Figure 4. Electrochemical Properties of 26650 Cylindrical Cell (A) Mass production of NVOPF, (B) NVOPF||carbon 26650 cylindrical cells, (C) low-temperature performance, (D) cycling performance of 26650 cylindrical cell at 5 C.

The safety of the battery is the most crucial parameter of the battery. As shown in Figure S7a-d, we performed a nail penetration experiment on a fully charged NVOPF-26650 cylindrical cell. It can be seen that there is no fire or explosion in the cylindrical cell during the nail penetration process. Figure S7e shows the cylindrical cell after the nail penetration test, indicating that the NVOPF-26650 cylindrical cell has an excellent safety characteristic.
To elucidate the evolution process of NVOPF crystal structure during desodiation/sodiation and understand the underlying reasons for the outstanding electrochemical performance of the as-synthesized NVOPF, we carried out the in-situ XRD measurement of the NVOPF electrode for the first two cycles at 0.1C, as presented in Figure 5A. For the new electrode, the XRD pattern is similar to that of the original NVOPF powder, except for several diffraction peaks of the Al current collector (38.6° (111), 44.8° (200)). The detailed structural evolutions during cycling are monitored by the changes of selected peaks of 27.9° (200), 28.8° (103), 32.7° (202), 39.9° (220), 40.5° (213), 43.3° (301), 49.9° (303), 51.5° (006), 53.2° (224), 57.7° (400), 60.5° (402) and 61.6° (330). During the desodiation process, the (200) peak at 27.9° weakens gradually while shifts to
higher degrees and finally merges with the (103) peak at 28.8°. Inversely, the (103) peak shifts to lower degrees with diminished intensity. The variations in the same trend are also detected for several other couples of adjacent peaks during the desodiation process, such as 39.9° (220)-40.5° (213), 49.9° (303)-51.5° (006), and 60.5° (402)-61.6° (330). Besides, several other peaks at 32.7° (202), 43.3° (301), 53.2° (224), and 57.7° (400) also exhibit lower and lower intensity when moved to higher degrees. As a result, two-Na extractions are achieved through the transformation from Na$_3$(VOPO$_4$)$_2$F to Na$_2$(VOPO$_4$)$_2$F and final Na(VOPO$_4$)$_2$F, as presented in equation (1) and (2). As expected, the XRD patterns change in the opposite direction and return to the pristine state during the subsequent sodiation process, demonstrating the excellent reversibility of NVOPF during electrochemical cycling. Furthermore, the second desodiation/sodiation cycling of NVOPF shows an entirely consistent trend of XRD patterns with that of the first cycling. Similar to earlier reports, no new phase appears during desodiation/sodiation, indicating the characteristics of a single-phase solid solution.[27, 30, 31, 33, 55] According to Bragg’s law, we can evaluate the changes in lattice parameters $a$ and $c$ values with the Na content in the NVOPF electrodes during desodiation, as shown in Figure S8. The $a$ value decreases continuously with extracting Na$^+$ from the crystal lattice, originating from the increasing positive electricity and decreasing cationic radius of V. In contrast, the $c$ value constantly increases due to the rising repulsive force between the pseudolayers. The volume change is only 2.7% at the end of desodiation by calculating the volume of unit cells, suggesting a minimal lattice strain during the desodiation/sodiation processes. Accordingly, this explains that the high cycling stability of NVOPF is due to the high structural reversibility and minor lattice strain during the desodiation/sodiation.

To illuminate the root cause of the high-rate electrochemical capabilities of NVOPF, we
conducted CV measurement at various scan rates to explore the Na\(^{+}\)-migration kinetics in NVOPF crystal lattice, as shown in Figure 5B-D. The CV profile recorded at 0.03 mV s\(^{-1}\) equaling to 0.1 C reveals two couples of redox peaks (O1/R1 and O2/R2) as presented in Figure 5B. The first couple centered at 3.65/3.56 V corresponds to the activity of V\(^{4+}/V^{5+}\) attributed to the reversible Na\(^{+}\) extraction and insertion. The second couple centered at 4.07/3.97 V corresponds to the activity of V\(^{4+}/V^{5+}\) attributed to the reversible Na\(^{+}\) extraction and insertion.[26] The good linear relationships for plots of \(I_p\ vs \ \nu^{1/2}\) have been obtained as shown in Figure 5D, resulting from CV curves at different scan rates as presented in Figure 5C. The excellent fitting results imply that the electrochemical desodiation/sodiation processes are diffusion-controlled.[26, 35, 43, 50, 58] Therefore, the Na\(^{+}\)-diffusion coefficient (\(D_{Na^{+}}\)) is calculated on the basis of Randles-Sevcik equation:[29, 35]

\[
I_p = 2.69 \times 10^5 n^{3/2} A C_0^{\ast} D_{Na^{+}}^{1/2} \nu^{1/2}
\]

Where \(I_p\) is the peak current (A), \(n\) stands for the number of transferred electrons, \(A\) is the area between electrode and electrolyte, \(C_0^{\ast}\) is Na\(^{+}\) concentration in the electrode, \(D_{Na^{+}}\) is Na\(^{+}\) diffusion coefficient (cm\(^2\) s\(^{-1}\)), and \(\nu\) is the scan rate (V s\(^{-1}\)). For simplification, here \(A\) is approximated to be the electrode area (0.64 cm\(^2\)), and \(C_0^{\ast}\) is estimated from the crystallographic cell parameter of NVOPF.

Accordingly, a series of \(D_{Na^{+}}\) values can be calculated as 7.8 \(\times\) \(10^{-9}\) cm\(^2\) s\(^{-1}\) (O1), 2.6 \(\times\) \(10^{-9}\) cm\(^2\) s\(^{-1}\) (R1), 1.1 \(\times\) \(10^{-8}\) cm\(^2\) s\(^{-1}\) (O2) and 5.8 \(\times\) \(10^{-9}\) cm\(^2\) s\(^{-1}\) (R2). The high \(D_{Na^{+}}\) values at different reaction stages indicate that as-synthesized NVOPF would have superior rate performance. Besides, O2/R2 redox pair displays a higher \(D_{Na^{+}}\) values than those of the O1/R1
redox pair, suggesting that the desodiation/sodiation process kinetic at around 4.0 V is superior to
that at about 3.6 V, and the charge/discharge profiles at low temperatures further confirm this
point.

Furthermore, ex-situ XPS spectra were conducted to examine the changes of the V oxidation
state during the desodiation/sodiation process. Figure S9 shows that the binding energy in the
original powder is 517.12 eV/524.62 eV, corresponding to V$^{4+}$. During the desodiation process,
the characteristic peaks of V gradually moved towards high binding energies. Generally, in the
same crystal structure, the binding energies of elements will increase with increasing the oxidation
state of elements. Hence, the oxidation state of V in the NVOPF electrode gradually increased
with increasing the charging depth from the original V$^{4+}$ to fully charged-state V$^{5+}$. More
importantly, the binding energies changed in the opposite direction and almost returned to the
pristine state before desodiation during the subsequent sodiation process. The binding energy
values of V in the NVOPF electrode at different charge-discharge voltage were listed in Table S8.
During desodiation/sodiation, the slight difference of binding energies at the same voltage is due
to the electrochemical polarization. Therefore, the XPS spectra confirm the reversible
transformation of the V oxidation state between V$^{4+}$ and V$^{5+}$ in the NVOPF electrode during
desodiation/sodiation, indicating the electrochemical activity of the NVOPF is highly reversible.

Besides, the XPS results agree well with the results of in-situ XRD.

To further understand why capacity fading after cycles and provide valuable references for
further enhancement of electrochemical performance, a simple analysis of battery failure was
carried out. After cycled for 8,000 cycles, the coin cell has been disassembled, as shown in Figure
S10a, from which it can be seen that the electrolyte is almost dry. The XRD patterns of original
and cycled electrode sheets were compared, where there is little change, as shown in Figure S10b. Besides, SEM characterization was carried out to observe the change in morphology of NVOPF as presented in Figure S11; the submicron-cuboids morphology is maintained, indicating the excellent structure stability of NVOPF. Therefore, the fade of capacity could be ascribed to the degradation of the electrolyte. Consequently, we believed that the electrochemical performance of NIBs based on NVOPF would be further improved by optimizing the electrolyte.

4. Conclusions

In summary, a facile and room-temperature strategy for the large-scale fabrication of NVOPF submicron-cuboids has been developed for the first time. Besides, the controllable synthesis of monodispersed NVOPF particles can be realized through regulating pH value and reactants concentration. The as-prepared NVOPF cuboids present superior rate capability and excellent cycling performance of 72% capacity retention at 25°C over 8000 cycles, which can be attributed to the specific submicron-sized morphology with shortened diffusion path, and the reversible crystal structural evolution with small volume change. More importantly, kilogram-grade NVOPF product can be easily obtained via such a facile one-pot strategy. To demonstrate the practical application of NVOPF product, commercial 26650 cylindrical batteries were conducted to exhibit impressive cycling stabilities at 5C, remarkable low-temperature performance at -30 °C and great safety characteristics during nail penetration. The facile and high-efficient room-temperature strategy and commercial tests referred in the current work provides a critical reference to the future industrial manufacture of NVOPF.
Data Availability

The data and materials used to support the findings of this study are available from the corresponding author upon request.

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Author Contributions

Q.Q.Z., X.S., and Q.Z contributed equally to this work. J.M.Z and Y.S.H. proposed and designed the project. Q.Q.Z., X.S., and Q.Z performed the experiments. K.X.L prepared the 26650 cylindrical cells, and F.X.D carried out the in-situ XRD characterization. All the authors contributed to the write-up of the article.

Declaration of Interests

The authors declare no conflicts of interest.

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