Supplementary Information

Rapid and Efficient Microwave-Assisted Solid-Phase Synthesis of Na₃V₂(PO₄)₂F₃ and Exploration of the Synthesis Process

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1. Experiment section

1.1. Synthesis of pristine Na₃V₂(PO₄)₂F₃/C

NH₄VO₃, NH₄H₂PO₄, NH₄F, Na₂CO₃, and glycerol (C₃H₈O₃) were weighed according to a molar ratio of 4:4:6:3 and placed in a high-speed ball mill for 2 hours. The resulting precursors were then transferred to an alumina crucible and pre-sintered at 310 °C for 4 hours in a flowing argon (Ar) atmosphere inside a tube furnace. Subsequently, they were sintered at 700 °C for 8 hours. As the furnace cooled down, the pristine samples, labeled as NVPF-Solid, were obtained.

1.2. Synthesis of Sol-gel Na₃V₂(PO₄)₂F₃/C

Citric acid (C₆H₈O₇), V₂O₅, NH₄H₂PO₄, and NaF were weighed and dissolved in 30 ml of deionized water in a molar ratio of 1:1:2:3. The solution was heated and evaporated at 70 °C, then dried at 100 °C for 12 hours. The resulting ground precursors were placed in an alumina crucible and sintered following the same steps as the original procedure to obtain the samples labeled as NVPF-Solgel.

1.3. Synthesis of microwave-assisted Na₃V₂(PO₄)₂F₃/C

NH₄VO₃, NH₄H₂PO₄, NH₄F, Na₂CO₃, and glycerol (C₃H₈O₃) were weighed according to a molar ratio of 4:4:6:3 and placed in a high-speed ball mill for 2 hours. The precursors prepared using the same method as NVPF-Solid were placed in a silicon carbide crucible and pre-sintered at 310°C for 10 minutes in a flowing argon (Ar) atmosphere using a microwave-assisted tube furnace. They were then sintered at 700 °C for 30 minutes, resulting in the microwave-assisted samples labeled as NVPF-Microwave.

1.4. Materials characterization

The crystal structures of precursors and as-prepared samples were characterized by X-ray diffraction (XRD, Bruker D8 Advance) using Cu Ka radiation operating at 40kV from 10 to 80° (20). Moreover, Rietveld refinement of XRD was used by assuming space group P42 to calculate detailed structure information. The surface morphology of precursors and as-prepared samples was observed by a scanning electron microscope (SEM, Thermo Scientific, Apreo 2C) and High-resolution Transmission Electron Microscopy (HR-TEM, FEI TF20). The energy dispersive spectrometer (EDS) was employed to analyze the elemental composition of the pre-NVPF and MW-NVPF. The surface area of the pre-NVPF and MV-NVPF was measured via Brunauer-Emmett-Teller (BET, Micromeritics ASAP2460) method, using a high-purity N2 adsorption/desorption isotherm. Preliminary calibration was performed using a monocrystalline Si sample to obtain a reference peak around 520.6 cm⁻¹. The number of acquisitions was 20, while the nominal laser power and the measuring time were 1 mW and 20 s for each measurement, respectively. The element types and corresponding ion valence distribution of the electrode materials were explored by X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha). All the data were calibrated by the standard spectrum of C 1S at 284.8 EV, and the fine spectrum of the elements was fitted by XPS peak.

1.5. Electrochemical measurements

The cathode slurry consisted of active material, carbon black, and polyvinylidene fluoride(PVDF) with a mass ratio of 80:10:10 in N-N-methyl pyrrolidinone(NMP) as solvent. Then, the blended slurry was cast onto aluminum current collector foil and dried under vacuum at 120°C for 12h. The loading mass was around 2.3 mg/cm². Afterward, the prepared cathodes were sliced into circular with a diameter of 14mm. The coin-type cells (CR2025) were assembled into half-cells with cathodes, electrolyte (1 M NaClO₄ in a mixture of ethylene carbonate and diethyl carbonate with a volume ratio of 1:1), separator and lithium tablet in an argon-filled glovebox (the contents of both O_2 and H_2O are ≤ 0.1 ppm). the The electrochemical measurements were carried out using a cell test instrument (Neware) with a voltage range from 2.50 to 4.40 V. The current density corresponding to 1C is 128 mAh g^{-1} . According to the capacity balance between the cathode and anode electrodes, the N/P ratio was approximately 1:1.15. The size of the cathode electrode is 14mm, the anode electrode is 16mm, the load of the rate performance test is 6.02 mg/cm², and the load of the cycle performance test is 10.4 mg/cm². The Hard Carbon anode was assembled into a half battery and activated by Na+ insertion. Finally, the activated Hard Carbon and NVPF-Microwave were used to assemble a full battery with 1 M sodium NaPF6 in diglyme as an electrolyte. The electrochemical performance tests were performed in a voltage range of 2.0 - 4.5 V. The capacity of the full battery was calculated based on the mass of the active material in the NVPF-Microwave.



Figure S1 NVPF-Microwave charge and discharge curves at different cycles at 1C cycle test.



Figure S2 Cycling performance at 2 C.

Samples			NVPF-Solid	NVPF-Solgel	NVPF-Microwave	
Formula			$Na_3V_2(PO_4)_2F_3$			
		а	9.04549	9.03563	9.04233	
Lattice parameters (Å)		b	9.04549	9.03563	9.04233	
		с	10.74936	10.77419	10.96410	
Cell volume (Å ³)			879.47	879.63	896.26	
the c/a ratio			1.1884	1.1924	1.2125	
Reliability factors(%)	R		9.49	5.39	3.45	
	Е		5.83	2.59	1.30	

Table S1 Crystallographic data of NVPFs obtained from Rietveld refinements



Figure S3 (a) SEM of NVPF-Solid: (a) at the scale of 2μ m; (b) at the scale of 500 nm; (c) at the scale of 200 nm;(d-e) TEM of NVPF- Solid.



Figure S4 Full XPS spectra of NVPF-Solgel and NVPF-Microwave;



Figure S5 TG curves of NVPFs from 75 °C to 500 °C at a heating rate of 10 °C/min in air flow.



Figure S6 The nitrogen adsorption–desorption curve with inset pore-size distribution of (a) NVPF-Solgel and (b) NVPF-Microwave;

Sample	BET Surface Area	t-Plot Micopore	Adsorption Average
	(m^{2}/g)	Volume (cm ³ /g)	Pore Diameter (nm)
NVPF-Microwave	45.50	0.004993	2.8555
NVPF-Solgel	17.20	0.000544	4.5288

Table S2 Samples specific surface area and pore information from BET test



Figure S7 Nyquist plots after the first cycle activation of NVPFs and Equivalent circuit model.

Sample	R ₀ (ohm)	R ₁ (ohm)	R ₁ (ohm)	R ₂ (ohm)
NVPF-Solid	16.60524	680.5609	435.7628	137.6512
NVPF-Microwave	7.453769	0.002242	123.2499	156.9796
NVPF-Solgel	3.122561	4.515054	206.9996	176.9655

Table S3 Impedance fitting results of NVPFS.



Figure S8 Linear fitting relationship between true resistance and $\omega^{-0.5}$, and sodium ion diffusion coefficients of NVPFs.

Table S4 Sodium ion diffusion coefficients of NVPFs

Sample	NVPF-Solid	NVPF-Microwave	NVPF-Solgel
$D_{Na}^{+}(\mathrm{cm}^{2}\mathrm{s}^{-1})$	2.3861×10 ⁻¹¹	3.4455×10 ⁻¹¹	6.1094×10 ⁻¹¹

For the synthesis of one ton of NVPF, the solid-phase method and the microwaveassisted solid-phase synthesis (MASS) utilize raw material combination **I**, whereas the sol-gel method employs raw material combination **II**. The specific raw materials required, along with their respective unit prices and total costs, are detailed in Table S5.

	Raw material	Dosage/kg	unit price/(RMB/kg)	Total Price/RMB
I	NH ₄ VO ₃	559.5	25	13987.5
	NH4H2PO4	550.7	6	3304.2
	NH ₄ F	265.7	9	2391.3
	Na ₂ CO ₃	380.4	2	760.8
	Sum			20443.8
п	NH4H2PO4	550.7	6	3304.2
	V ₂ O ₅	435.60	102	44431.2
	NaF	300.8	7	2105.6
	Sum			49841.0

Table S5 Cost of different NVPF raw material combinations

In the industrial-scale synthesis of NVPF, the yield varies significantly depending on the method used: approximately 55% for the solid-phase method¹⁻³, 90% for the sol-gel method³⁻⁵, and 98% for the microwave-assisted solid-phase synthesis (MASS)⁶⁻⁹. As a result, raw material costs must be adjusted to reflect the actual consumption required for large-scale production. Additionally, it is important to note that certain additives and materials, such as the carbon source in the solid-phase method, the carbon source and absorber in the MASS, and the chelating agent in the sol-gel method, may differ between small-scale experiments and industrial applications. Therefore, these costs should be accounted for as part of the overall process cost rather than solely the raw material cost.

The process cost for the solid-phase and sol-gel methods is estimated to be 20% of the adjusted raw material cost, reflecting the higher energy and labor requirements. Conversely, due to its rapid synthesis and lower energy consumption, the process cost for MASS is estimated at 15% of the adjusted raw material cost. Table S6 provides a

comprehensive overview of the estimated costs for preparing NVPF using these three distinct methods.

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	Raw	Processing	Total
	Material/RMB	Cost/RMB	Cost/RMB
NVPF-Solid	37300	7500	44800
NVPF-Microwave	21000	2940	23940
NVPF-Solgel	55400	11120	66520

Table S6 Total cost of NVPF by different synthesis methods

Table S7 Comparison of full-cell electrical performance between this work and other works

Materials	Method	Average working voltage (V)	Reversible capacity (mAh/g)	Rate capability (mAh/g)	Cycling stability (capacity retention % (cycle numner))	Ref.
$Na_3V_2(PO_4)_2F_3$	MASS	3.17	127.41	60.83 at 20C	95.19% (500 cycles at 2C)	This work
$Na_3V_2(PO_4)_2F_3$	Microwave- assisted hydrothermal synthesis	2.2	116	101 at 5 A/g	94.3% (1300 cycles at 1 A/g)	6
$Na_3V_2(PO_4)_2F_3$	Carbon matrix loading	3.15	120.8	97.8 at 10C	91.4% (500 cycles at 5C)	10
$Na_3V_2(PO_4)_2F_3$	Hydrothermal method	3.44	123.8	98 at 5C	83.6% (300 cycles)	11
$Na_3V_2(PO_4)_2F_3$	Sol-gel synthesis	3.61	120.6	99.5 at 10C	95.0% (500 cycles at 5C)	12
$Na_3V_2(PO_4)_2F_3$	Sol-gel synthesis	3.8	95	/	65% (100 cycles at 1C)	1

$Na_{3}V_{1.95}Ti_{0.05}(PO_{4})_{2}F_{3}$	Sol-gel synthesis	3.1	121.29	52.26 at 20C	91.02% (200 cycles at 1C)	13
$Na_{3.6}V_{1.4}Mn_{0.6}(PO_4)_2F_3$	Hydrothermal microwave- assisted synthesis	3.25	90	/	/	7
$Na_{3}V_{1.96}Sc_{0.04}(PO_{4})_{2}F_{3}$	Sol-gel synthesis	3.5	112	71 at 10C	90.43% (60 cycles at 1C)	14

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