Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Supporting Information:

Engineering crystal orientation of $Na_3V_2(PO_4)_2F_3$@rGO microcuboids for advanced sodium-ion batteries

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Table S1 Comparison of reported $Na_3V_2(PO_4)_2F_3$ cathode materials for Na-ion batteries.

Materials	a(=b) [Å]	c [Å]	V [Å^3]
NVPF@rGO-0	9.0235	10.6398	866.3
NVPF@rGO-1	8.8149	10.6338	826.3
NVPF@rGO-2	9.0307	10.6547	868.9
NVPF@rGO-3	9.0086	10.6150	861.5

Scherrer equation S1

$$D = \frac{0.9\lambda}{\beta cos\theta}$$

where D is the crystallite size, β is the FWHM in radian, θ is the diffraction angle, and λ is the wavelength.

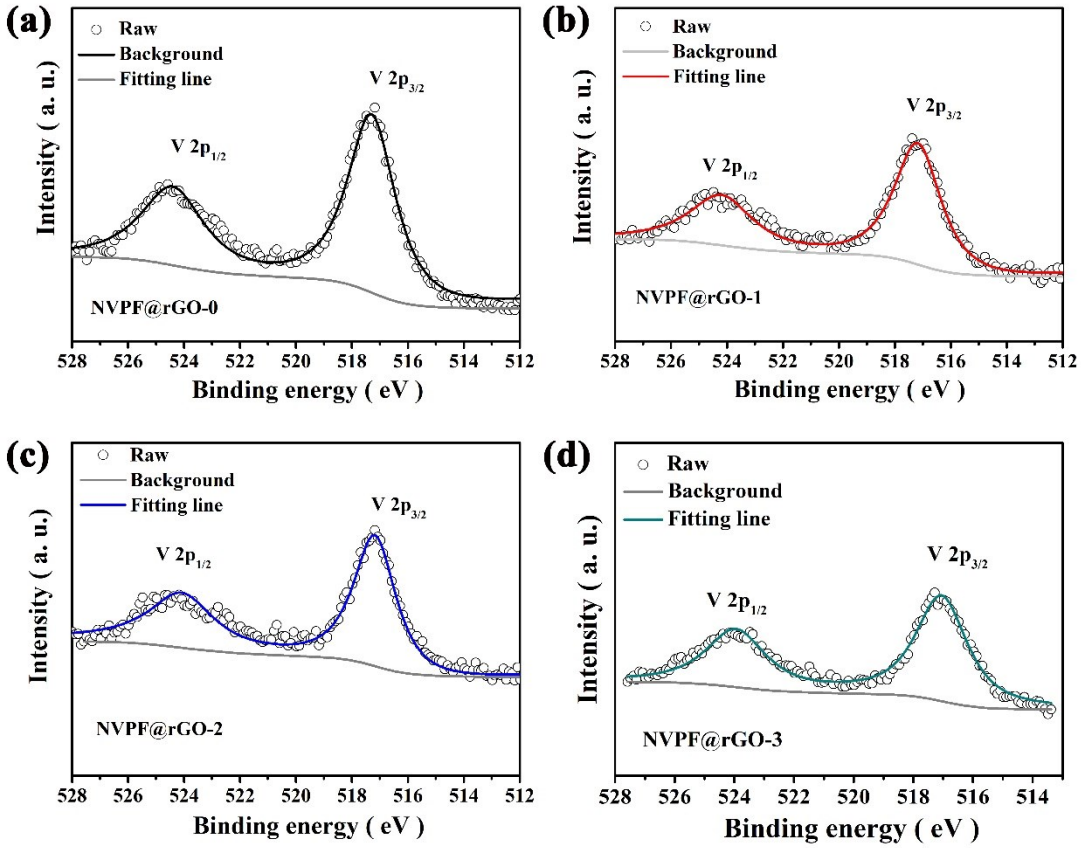

Fig. S1 V 2p XPS spectra of NVPF@rGO-0, NVPF@rGO-1, NVPF@rGO-2 and NVPF@rGO-3.

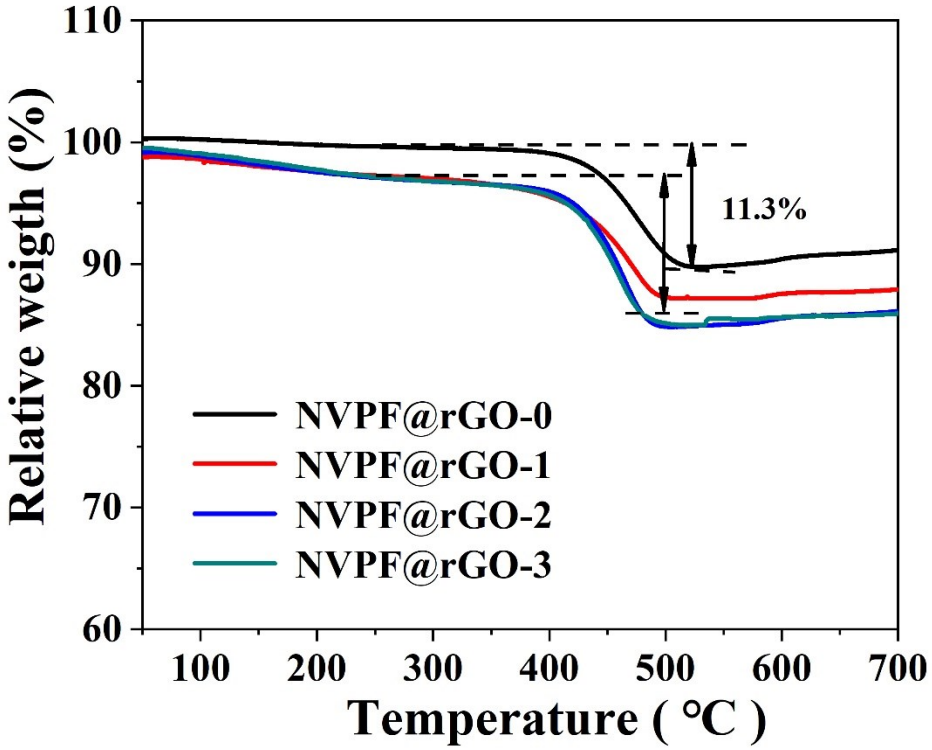

Fig. S2 TG curves of the NVPF@rGO-0, NVPF@rGO-1, NVPF@rGO-2, NVPF@rGO-3 materials.

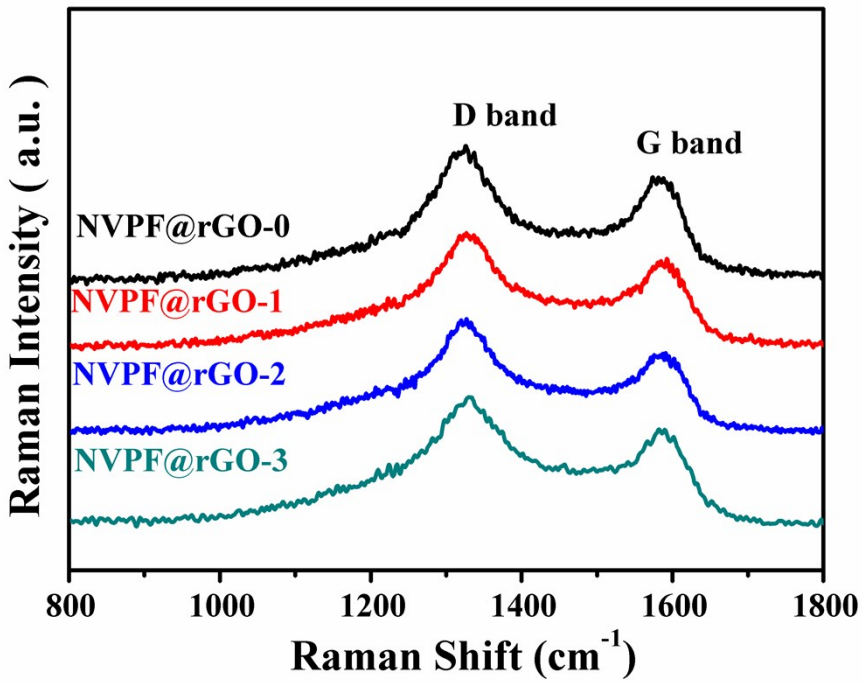

Fig. S3 Raman spectra of NVPF@rGO-0, NVPF@rGO-1, NVPF@rGO-2 and NVPF@rGO-3.

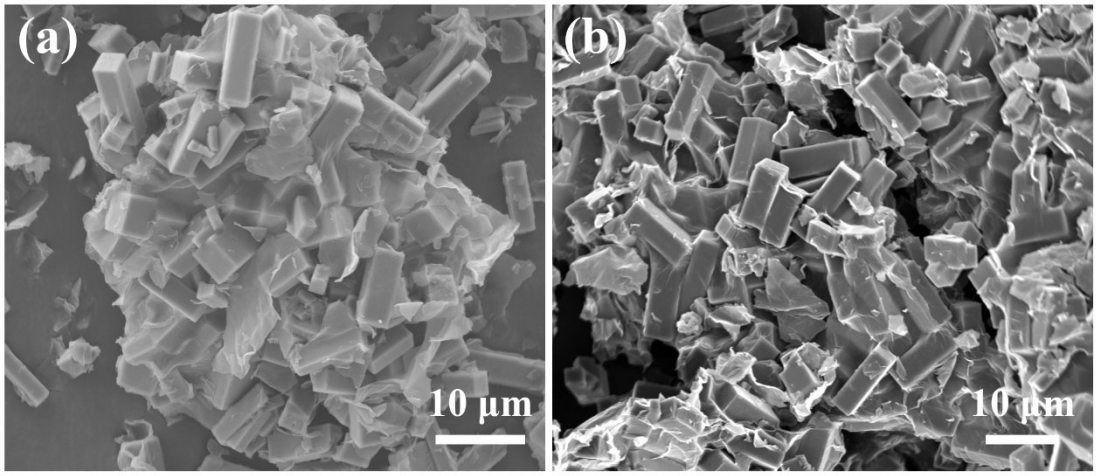

Fig. S4 SEM images of materials synthesized with (a) NaF and (b) NaBr.

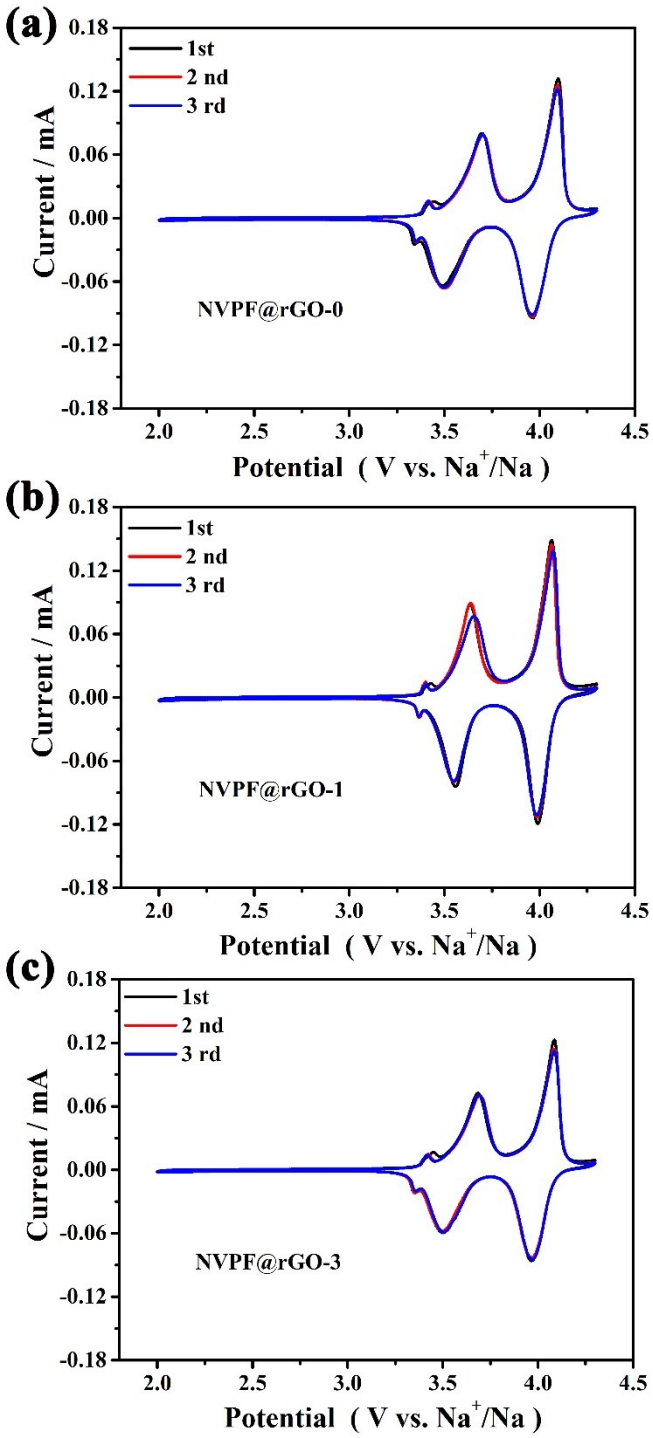

Fig. S5 CV curves of NVPF@rGO-0, 1, 3 at a scan rate of 0.1 mV s^{-1} in the electrochemical window of 2.0-4.3 V vs Na^+/Na.

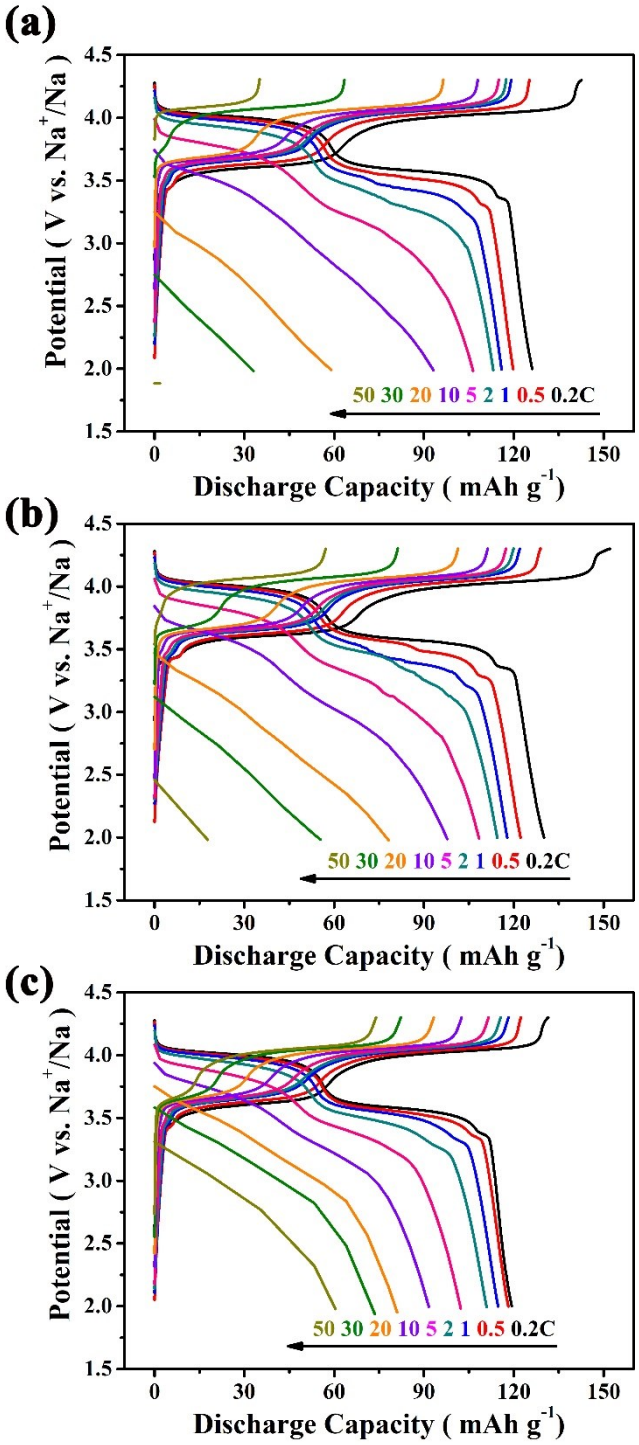

Fig. S6 Charge-discharge profiles of (a) NVPF@rGO-0, (b) NVPF@rGO-1 and (c) NVPF@rGO-3 at different rates.

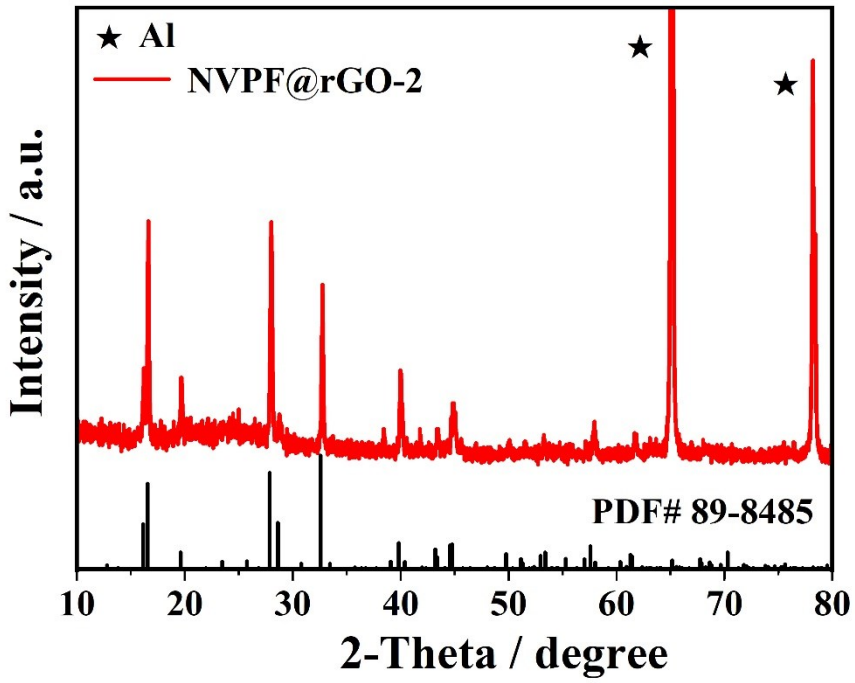

Fig. S7 XRD pattern of the NVPF@rGO-2 electrode after 1000 cycles at 5 C.

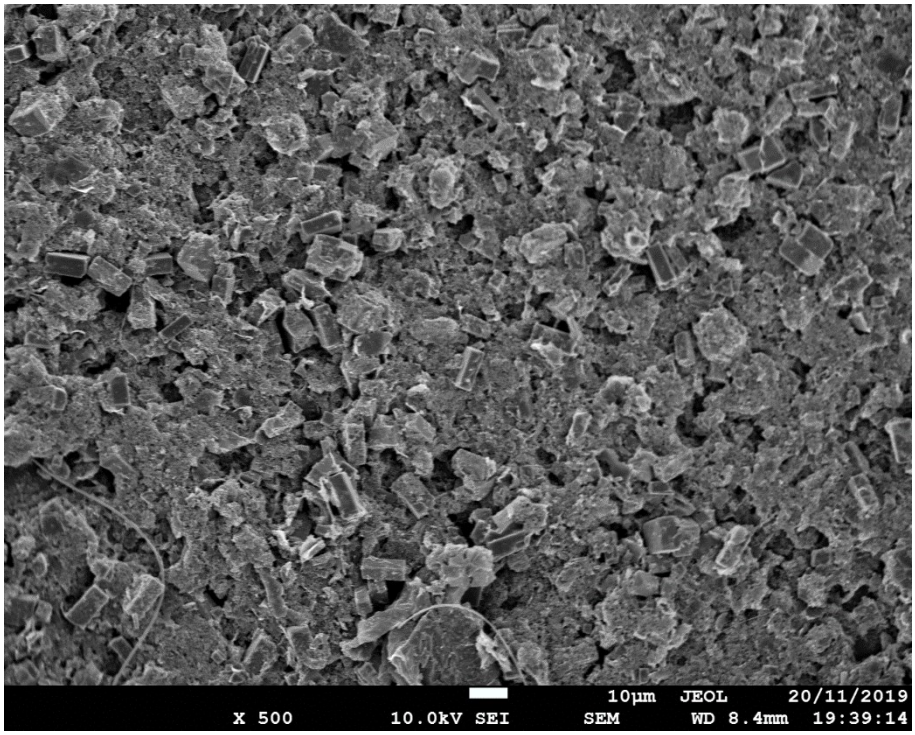

Fig. S8 SEM image of the NVPF@rGO-2 electrode after 1000 cycles at 5C.

Table S2 Comparison of reported $Na_3V_2(PO_4)_2F_3$ cathode materials for Na-ion batteries.

Materials	Low-rate capacity	High-rate capacity	Cycling stability	References
Carbon-coated $Na_3V_2(PO_4)_2F_3$ nanoparticles embedded in mesoporous carbon matrix	133 mAh g^{-1} at 0.5 C	74 mAh g^{-1} at 30 C	70% after 1000 cycles at 10 C	[1]
$Na_3V_2(PO_4)_2F_3$ is embedded in graphene network	105 mAh g^{-1} at 0.5 C	57 mAh g^{-1} at 10 C	80.8% after 1000 cycles at 10 C	[2]
Reduced graphene oxide (rGO) encapsulate $Na_3V_2(PO_4)_2F_3$ @Carbon nanoparticles	127 mAh g^{-1} at 0.5 C	64 mAh g^{-1} at 70 C	81% after 4000 cycles at 30 C	[3]
Uniform Hierarchical $Na_3V_{1.95}Mn_{0.05}(PO_4)_2F_3$@C Hollow Microspheres	126 mAh g^{-1} at 0.2 C	61 mAh g^{-1} At 10 C	86% after 500 cycles at 0.2 C	[4]
$Na_3V_2(PO_4)_2F_3$-SWCNT composite	118 mAh g^{-1} at 0.2 C	101 mAh g^{-1} at 10 C	96% after 500 cycles at 10 C	[5]
Y-doped $Na_3V_2(PO_4)_2F_3$ compounds	125 mAh g^{-1} at 0.5 C	80 mAh g^{-1} at 50 C	93.5% after 200 cycles at 1 C	[6]
$Na_3(VO)_2(PO_4)_2F$ nanoparticles encapsulated in conductive graphene network	116 mAh g^{-1} at 0.2 C	61 mAh g^{-1} at 20 C	82% after 1200 cycles at 10 C	[7]
Chromium doping on $Na_3V_2(PO_4)_2F_3$@C	111 mAh g^{-1} at 0.5 C	66 mAh g^{-1} at 10 C	93% after 125 cycles at 2 C	[8]
Carbon and aluminum oxide co-coated $Na_3V_2(PO_4)_2F_3$	128 mAh g^{-1} at 0.5 C	116 mAh g^{-1} at 5 C	96% after 100 cycles at 1 C	[9]
Carbon-coated $Na_3V_2(PO_4)_2F_3$ samples	117 mAh g^{-1} at 0.1 C	70 mAh g^{-1} at 8 C	90% after 100 cycles at 1 C	[10]
Three dimensional carbonous framework supported $Na_3V_2(PO_4)_2F_3$ nanoparticles	125 mAh g^{-1} at 0.1 C	44 mAh g^{-1} at 80 C	91% after 700 cycles at 1 C	[11]
Potassium doping $Na_3V_2(PO_4)_2F_3$@CNT particles	122 mAh g^{-1} at 0.2 C	50 mAh g^{-1} at 50 C	91% after 1600 cycles at 10 C	[12]
$Na_3V_2(PO_4)_2F_3$/C composites	103 mAh g^{-1} at 0.2 C	95 mAh g^{-1} at 10 C	92% after 500 cycles at 5 C	[13]
A doubled coated $Na_3V_2(PO_4)_2F_3$ material with polytetra-hydrofuran and carbon	120 mAh g^{-1} at 0.5 C	106 mAh g^{-1} at 10 C	92% after 100 cycles at 1 C	[14]
Porous nano-sized	109 mAh g^{-1}	74 mAh g^{-1}	95% after 200	[15]

$Na_3V_2(PO_4)_2F_3$@C nanospheres	at 0.1 C	at 5 C	cycles at 3 C	
Nitrogen-doped graphene encapsulated $Na_3V_2(PO_4)_2F_3$@C	121.6 mAh g^{-1} at 0.2 C	108 mAh g^{-1} at 5 C	96.5% after 300 cycles at 10 C	[16]
Nitrogen-doped carbon coated subglobose $Na_3V_2(PO_4)_2F_3$@C	121.5 mAh g^{-1} at 0.1 C	99.2 mAh g^{-1} at 10 C	90.1% after 1000 cycles at 10 C	[17]
$Na_xV_2(PO_4)_2F_3$@rGO cathode with exposed sodium- rich facet	127 mAh g^{-1} at 0.2 C	74 mAh g^{-1} at 50 C	83% after 1000 cycles at 5 C	This work

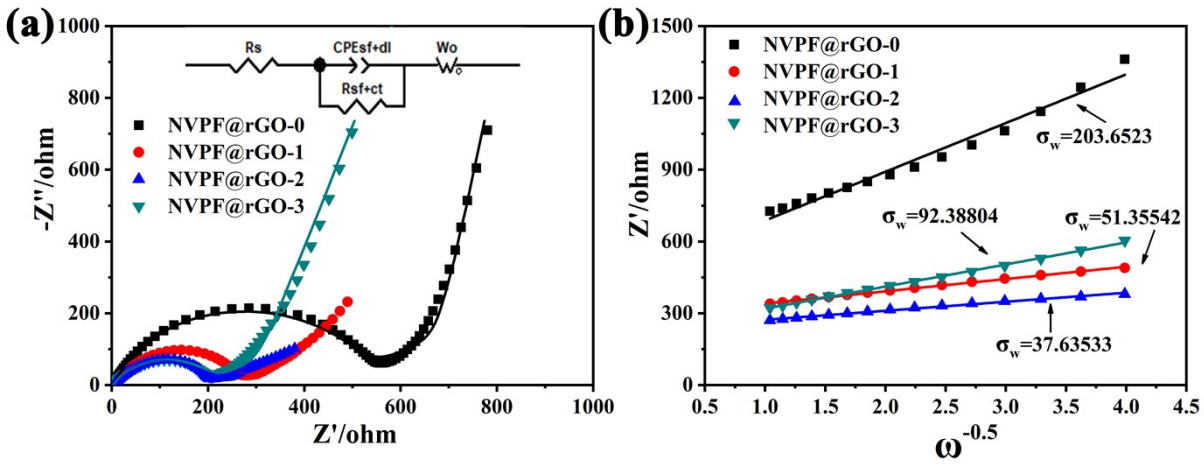

Fig. S9 (a) EIS plots of the electrodes (inset: corresponding fitted equivalent circuit model) and (b) corresponding Z'-$\omega^{-0.5}$ patterns.

Table S3 Fitting results of the Nyquist plots using the equivalent circuit.

Samples	R_s (Ω cm^{-2})	CPE_{sf+dl} (S $s^{1/2}$ cm^{-2})	R_{sf+ct} (Ω cm^{-2})	W_o (S $s^{1/2}$ cm^{-2})
NVPF@rGO-0	3.817	5.1516×10^{-5}	502.8	0.45179
NVPF@rGO-1	2.392	1.876×10^{-5}	244.5	0.314
NVPF@rGO-2	4.426	1.2903×10^{-5}	183.2	0.28801
NVPF@rGO-3	3.455	1.7868×10^{-5}	198.1	0.40941

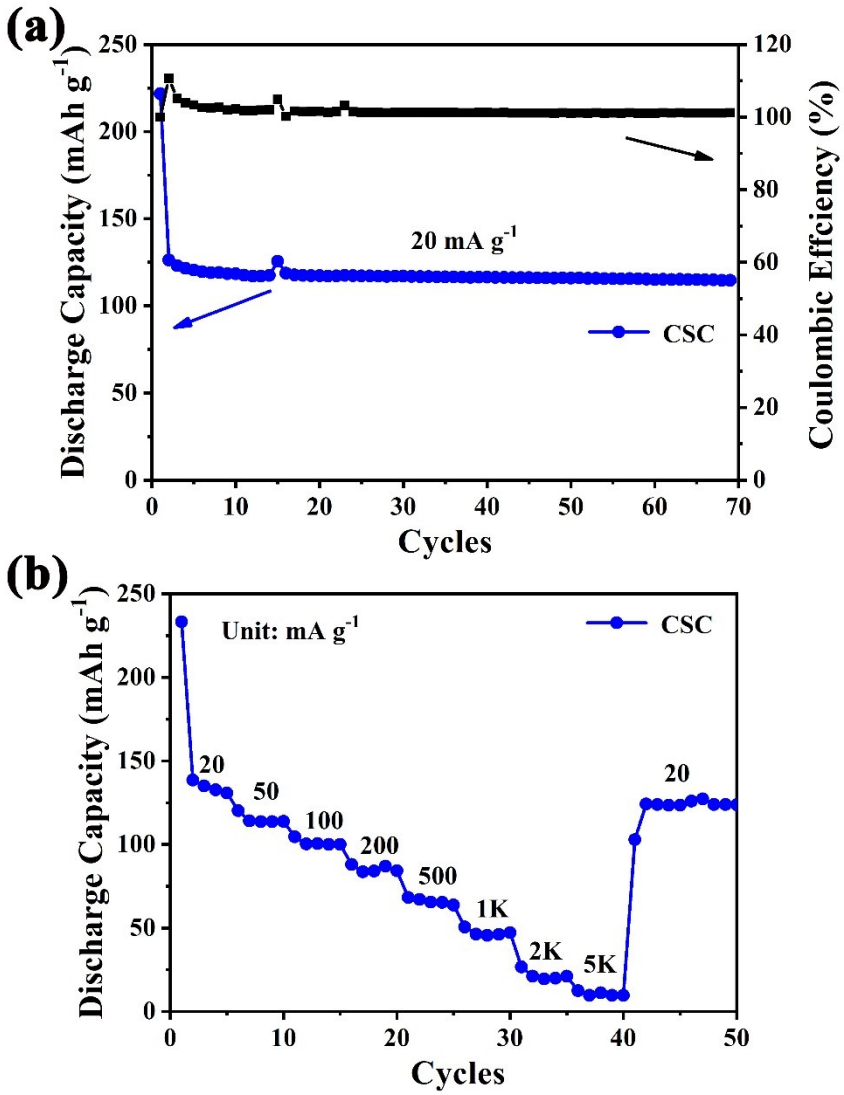

Fig. S10 (a) Cycling performance and (b) rate performance of commercial soft carbon.

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