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Journal Name

ARTICLE

Electronic Supporting Information

Utilization of Biomass Pectin Polymer to Build High Efficient Electrode Architecture with Sturdy Construction and Fast Charge Transfer Structure to Boost Sodium Storage Performance for NASICON-type Cathode

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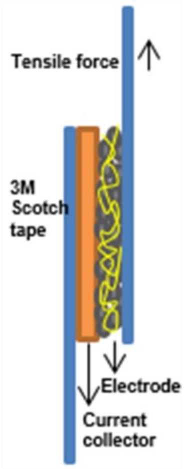
Supplementary Figures



Scheme 1 Illustration of tensile adhesion strength test.

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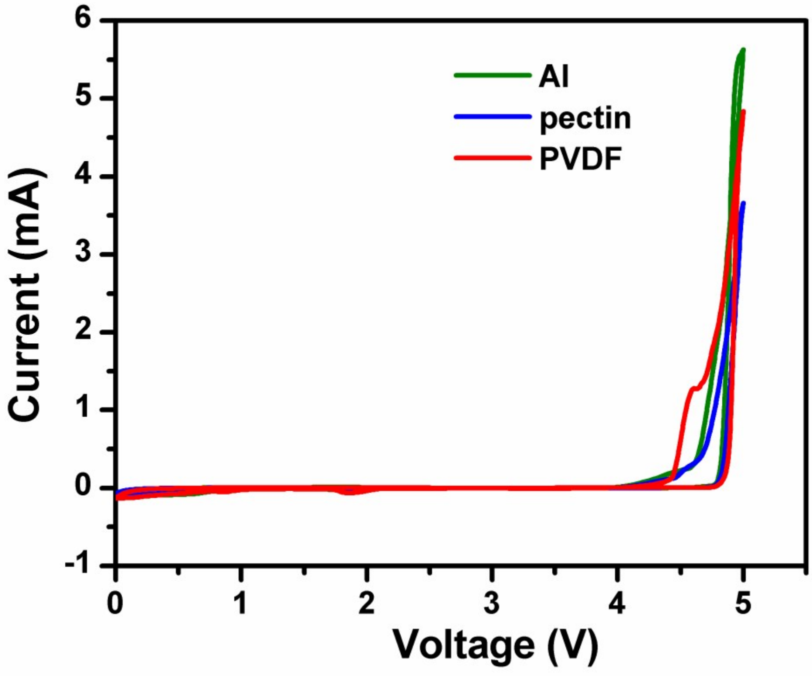

Fig. S1 CV curves of pure pectin/PVDF films on Al foil and Al foil in half-cell configurations at a scan rate of 0.2 mV s^{-1}.

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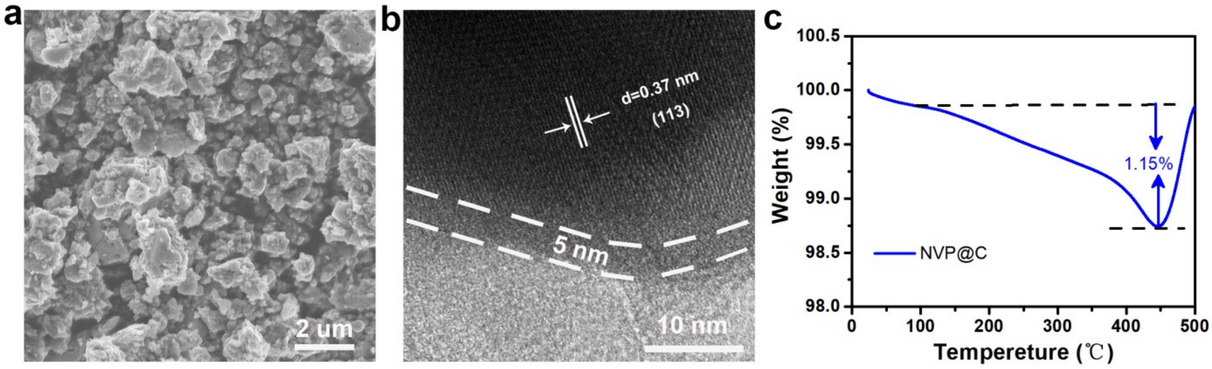

Fig. S2 Morphological analysis of the NVP nanocomposite: (a) SEM image. (b) HRTEM image and (c) TG curve.

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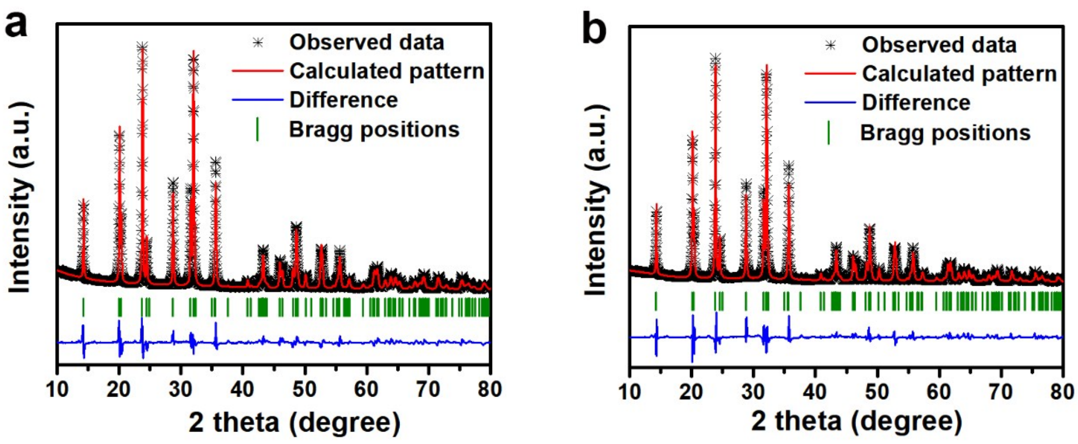

Fig. S3 Rietveld refinement based on the powder X-ray diffraction pattern of (a) NVP nanocomposite and (b) after being soaked with pectin and water for 1 day.

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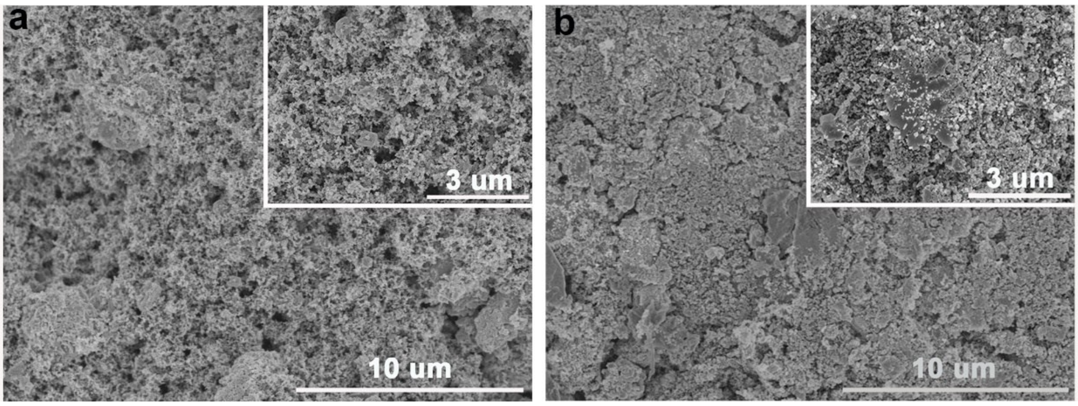

Fig. S4 SEM images of (a) NVP-pectin and (b) NVP-PVDF electrode.

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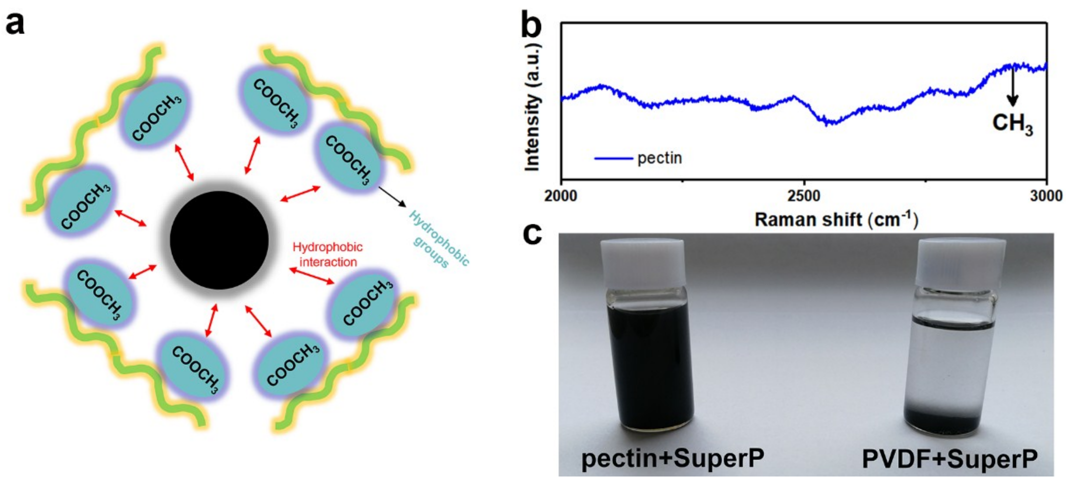

Fig. S5 (a) Illustration of the interaction between pectin and Super P. (b) Raman spectrum of pectin powder. (c) Photos of pectin and PVDF binders mixed with Super P, showing the dispersal property of the pectin binder with Super P.

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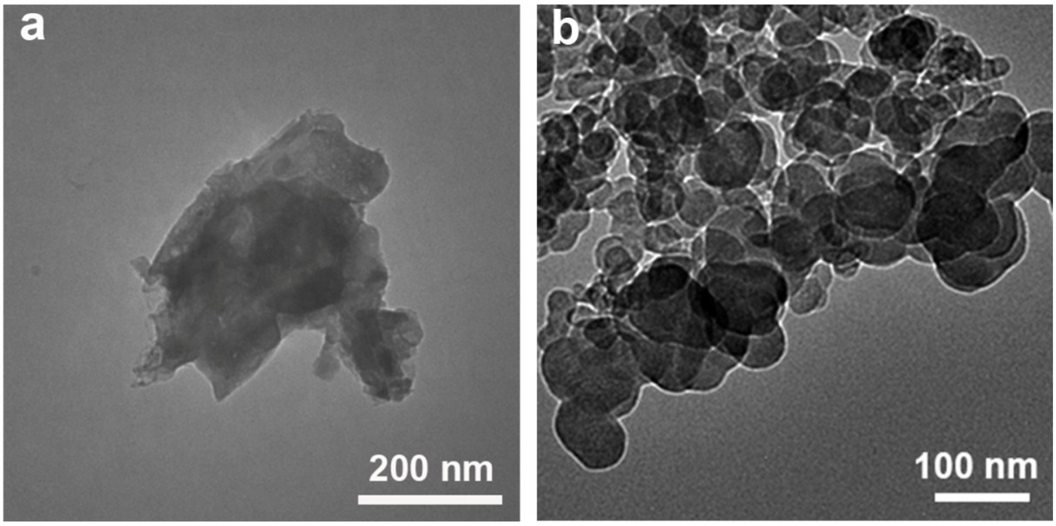

Fig. S6 TEM images of (a) NVP and (b) Super P powders.

It could be seen from structural formula (Fig. 1a) that pectin is a chain polymer, which have the possibility of forming chain-like substance. Furthermore, it can be seen that morphology of NVP and Super P are far from chain-like. Considering that there are only three components in NVP-pectin and no chain-like material observed in NVP-PVDF electrode, the chain-like material in Fig. 2a could only be pectin.

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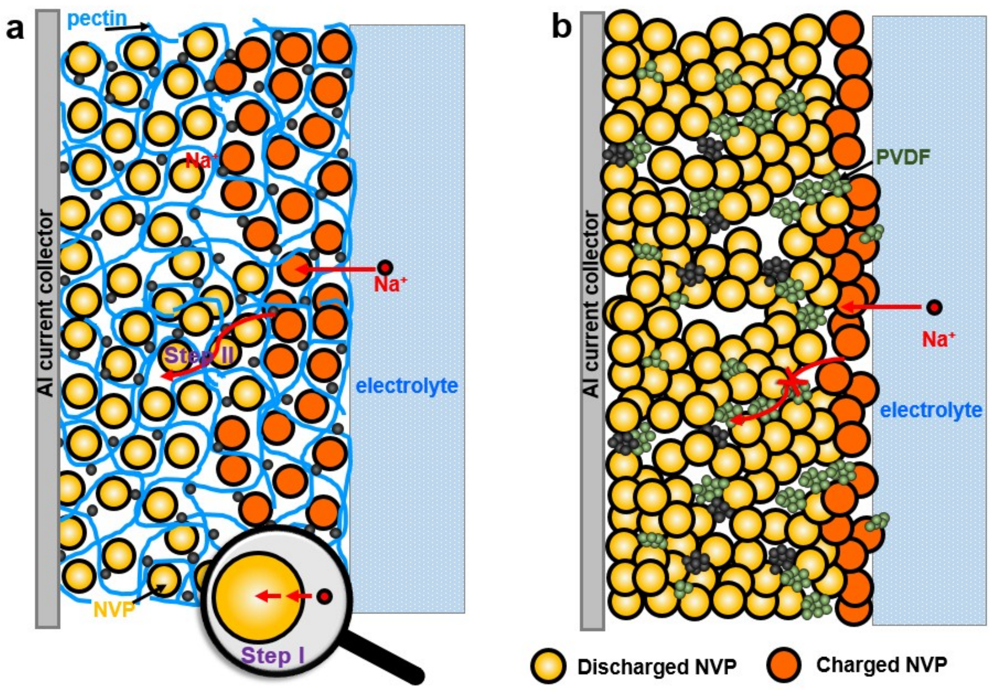

Fig.S7 Illustration of electrochemical process for NVP-pectin and NVP-PVDF.

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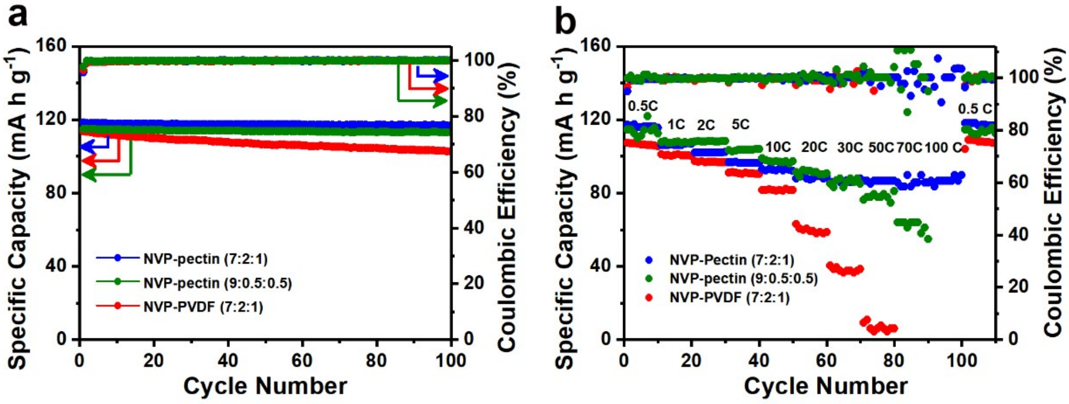

Fig. S8 Electrochemical performance of NVP-pectin (9: 0.5: 0.5), NVP-pectin (7: 2: 1) and NVP-PVDF (7: 2: 1) (a) cycle performance and (b) rate performance.

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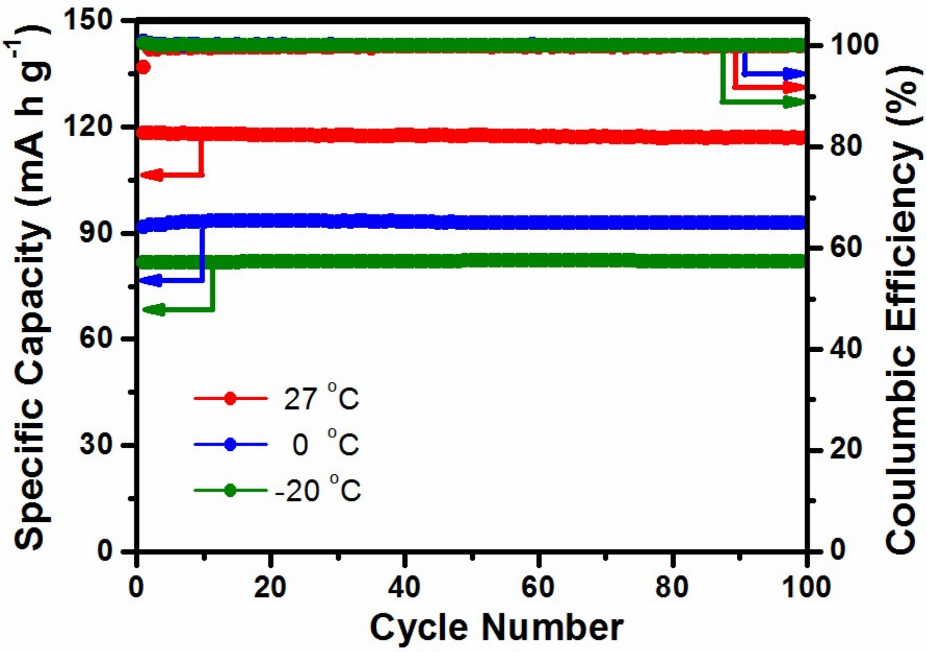

Fig. S9 Cycle performance of NVP-pectin electrode at different temperature.

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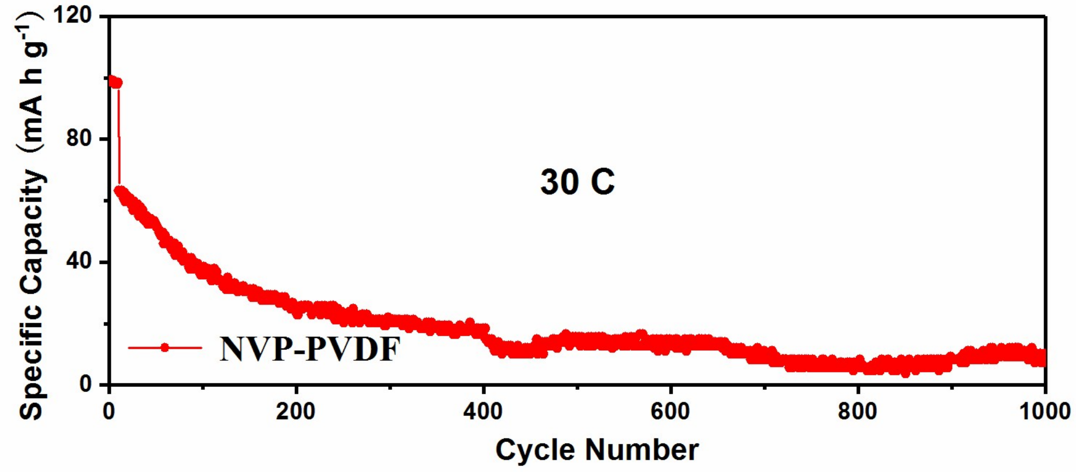

Fig. S10 Long cycle performance of NVP-PVDF electrode at 30 C rate.

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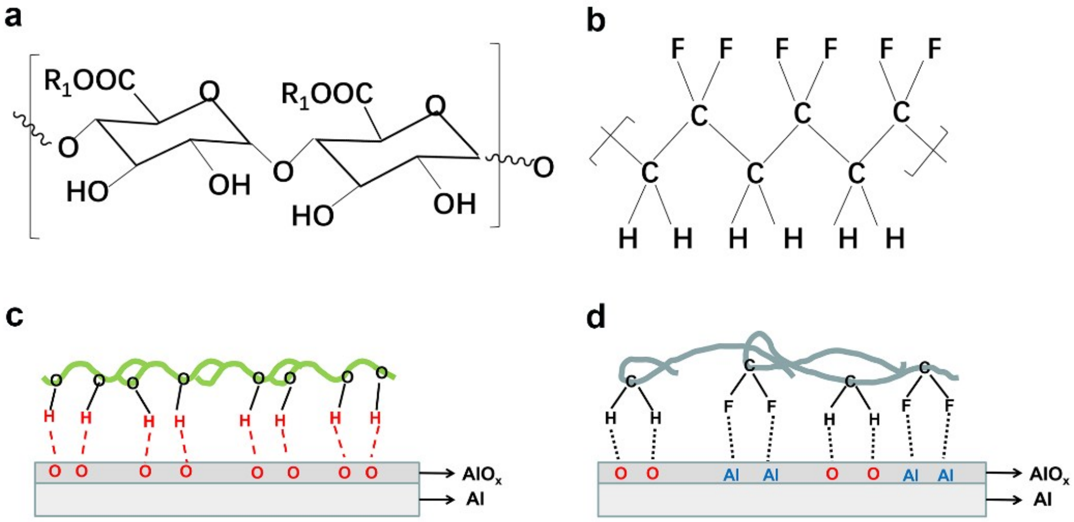

Fig. S11 Chemical structures of (a) pectin and (b) PVDF. Corresponding binding mechanisms with current collector (c) pectin and (d) PVDF.

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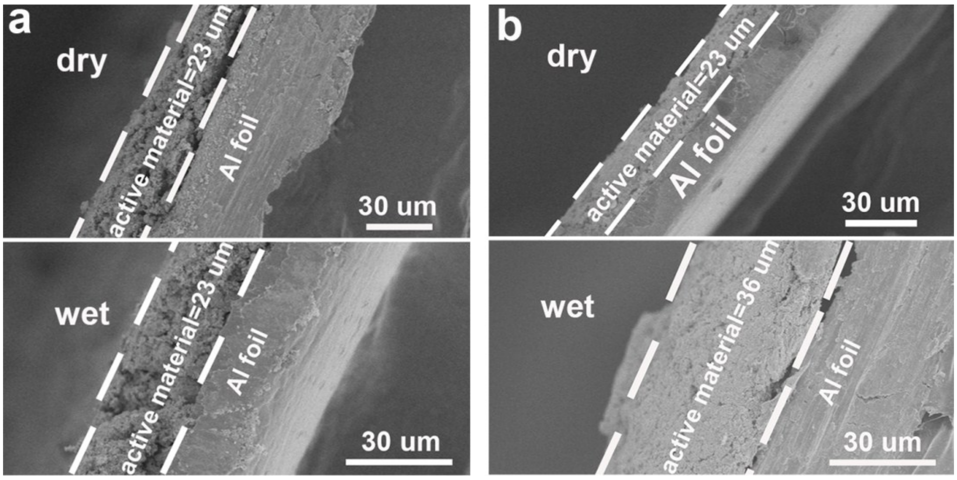

Fig. S12 SEM images of cross sections of (a) NVP-pectin and (b) NVP-PVDF electrode at before and after being soaked in electrolyte.

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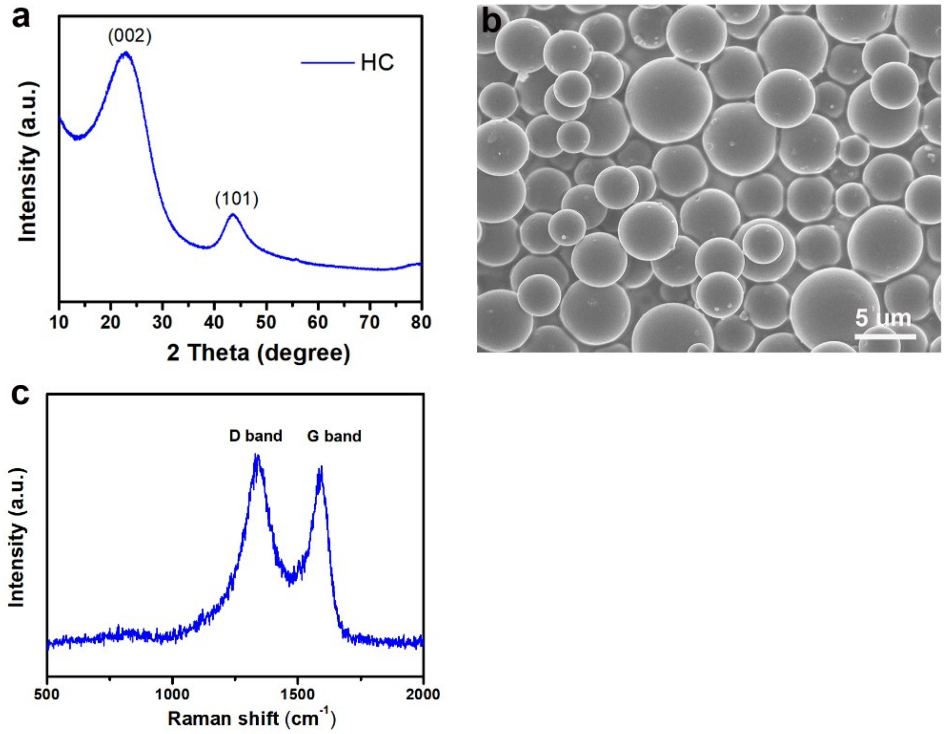

Fig. S13 (a) X-ray diffraction pattern. (b) SEM image and (c) Raman spectrum of hard carbon.

In **Fig. S13a**, the observed (002) and (101) peaks exhibit a typical character of hard carbon. The size of hard carbon is at the range of 3~7 μm (**Fig. S13b**). Subsequently, the intensity of *D*-band in Raman spectrum is observed at 1349 cm^{-1}, which corresponds to sp^2 carbon atoms with defects **(Fig. S13c**). And the *G*-band located at 1580 cm^{-1} arises from planar sp^2 configured carbon atoms. The rich defects is beneficial for storage of sodium ions.

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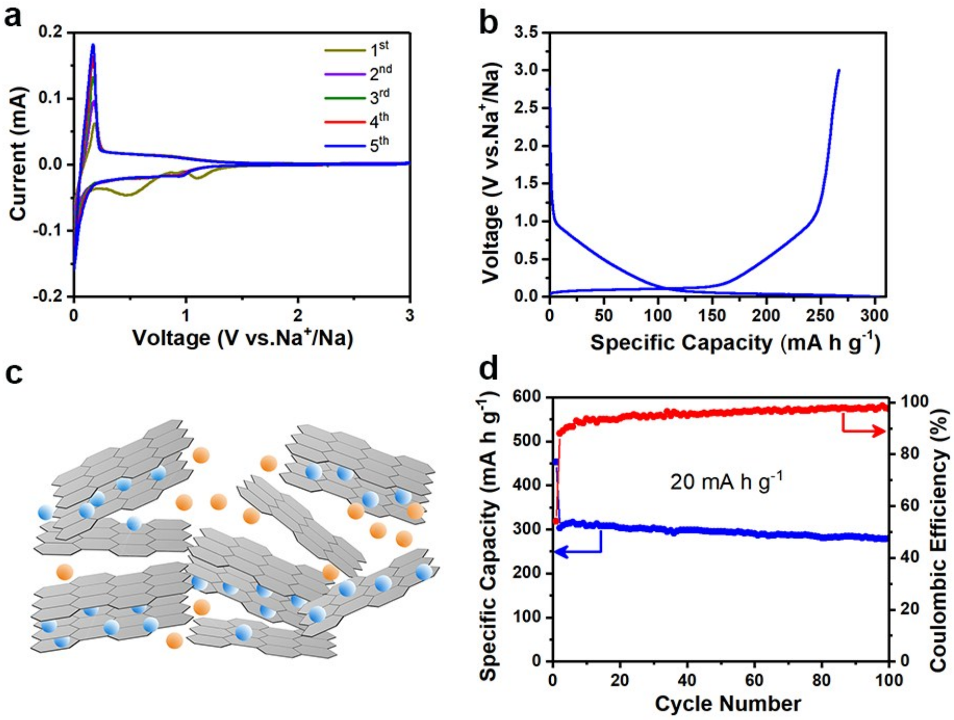

Fig. S14 (a) CV profile and (b) stable discharge/charge profile of hard carbon. (c) Schematic of Na-ion storage mechanism and (d) cycle performance of hard carbon.

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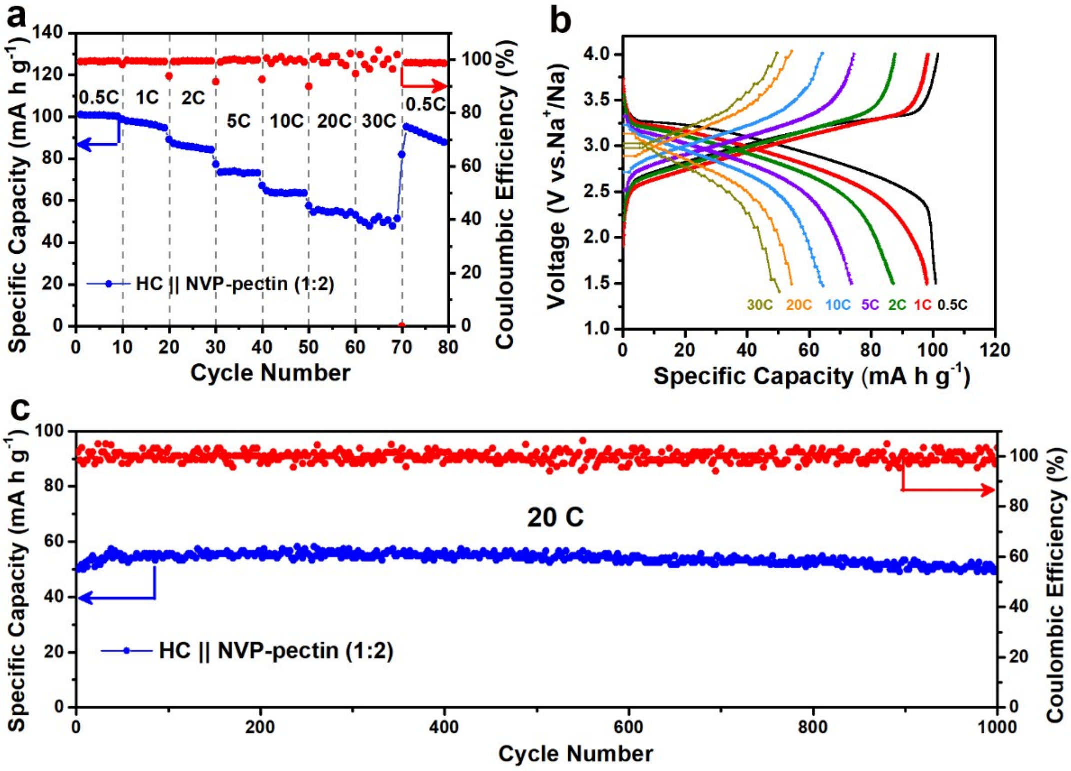

Fig. S15 (a) Rate performance of HC || NVP (1: 2) full cell. (b) Corresponding charging/discharging profiles at various rates from 0.5 to 30 C and (c) long-term cycle performance at 20 C rate.

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Table S1 Lattice parameters of NVP and NVP (soak) from XRD calculations.

Sample	a (Å)	b (Å)	c (Å)	Volume ($Å^3$)	R_{wp}
NVP	8.732(6)	8.732(6)	21.831(5)	1441.8(2)	10.91
NVP(soak)	8.713(0)	8.713(0)	21.766(5)	1431.0(6)	11.81

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Table S2 Calculated Na^+ diffusion coefficients of NVP-pectin and NVP-PVDF.

D_{Na}(cm^{2}S^{-1})	Anode	Cathode
NVP-pectin	6.43×10^{-9}	4.03×10^{-9}
NVP-PVDF	1.32×10^{-9}	1.09×10^{-9}

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Table S3 A survey of electrochemical properties of $Na_3V_2(PO_4)_3$ cathodes in sodium ion batteries.

Electrode description	Mass loading (mg cm^{-2})	Carbon content（wt %）	Binder	Rate performance	Ref.
NVP -pectin	1.3 - 1.8	1.15	pectin	86.6 mA h g^{-1} at 100 C	This work
NVP-NFs	1.2-1.4	6.70	PVDF	75.9 mA h g^{-1} at 200 C	1
NVP@C@rGO	0.8 - 1.0	10.10	PVDF	86.0 mA h g^{-1} at 100 C	2
NVP:rGO-CNT	0.5 - 1.0	21.00	free	82.0 mA h g^{-1} at 100 C	3
NVP/AC	～2.7	8.46	PTFE	42.2 mA h g^{-1} at 10 C	4
HCF-NVP	～1.0	6.41	PVDF	78.0 mA h g^{-1} at 100 C 38.0 mA h g^{-1} at 500 C	5
(C@NVP)@pC	～1.0	~17.00	PVDF	44.0 mA h g^{-1} at 200 C	6
NVP@C@CMK-3	-	17.88	PVDF	81.0 mA h g^{-1} at 30 C	7
NVP@rGO	1.5 - 2.0	3.50	PVDF	73.0 mA h g^{-1} at 100 C 41.0 mA h g^{-1} at 200 C	8
NVP-nanofiber	1.5 - 2.0	6.50	PVDF	94.0 mA h g^{-1} at 100 C	9
900-NVP@C/G	～1.5	18.34	PVDF	76.0 mA h g^{-1} at 60 C	10
NVP/C porous hollow spheres	-	7.50	PVDF	9.6 mA h g^{-1} at 8.5 C	11
NVP-CNF-6 h	～1.9	8.34	PVDF	88.9 mA h g^{-1} at 50 C	12
NVP@C	-	12.50	PVDF	94.9 mA h g^{-1} at 5 C	13
NVP@C-GF	～0.9	12.10	PVDF	83.0 mA h g^{-1} at 100 C 56.0 mA h g^{-1} at 200 C	14
NVP@C+N@CNTs	2.0 - 2.6	12.68	PVDF	70.0 mA h g^{-1} at 70 C	15
NVP/C/rGO	1.5 - 2.0	4.34	PVDF	80.0 mA h g^{-1} at 30 C	16
NVP/MCNTs	～1.8	13.36	PVDF	70.0 mA h g^{-1} at 10 C	17
NVP/C	1.9 - 2.5	3.14	PVDF	92.0 mA h g^{-1} at 5 C	18
NVPC-800	-	7.60	PVDF	73.0 mA h g^{-1} at 100 C 55.0 mA h g^{-1} at 200 C	19
NVP/C-10	～1.0	3.38	PVDF	97.5 mA h g^{-1} at 5 C	20
PL-NVP@C	～1.0	5.93	PVDF	92.0 mA h g^{-1} at 50 C	21
NVP/C	1.5 - 2.0	17.60	PVDF	81.0 mA h g^{-1} at 40 C	22
NVP-graphene	-	6.14	PVDF	70.1 mA h g^{-1} at 30 C	23
NVP/N-CNT	2.5	6.57	PVDF	100.0 mA h g^{-1} at 20 C	24

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Electrode description	Mass loading (mg cm^{-2})	Carbon content（wt %）	Binder	Rate performance	Ref.
NVP@rGO	～1.5	3.28	PVDF	79.2 mA h g^{-1} at 100 C	25
NVP@C@HC	2.0	14.69	PVDF	61.0 mA h g^{-1} at 50 C	26
NVP/graphene	～1.0	5.00	PVDF	60.4 mA h g^{-1} at 30 C	27
NVP nanoflakes	-	10.53	PVDF	87.7 mA h g^{-1} at 100 C	28
NVP/N-doped C	-	20.25	PVDF	46.8 mA h g^{-1} at 10 C	29
NVP/C	-	2.80	PVDF	54.3 mA h g^{-1} at 50 C	30

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Table S4 A survey of electrochemical properties of advanced sodium-ion full cells.

Sodium-ion full cell description	**Voltage range (V)**	**Potential (V)**	**Current density (mA g^{-1})**	**Capacity retention**	**Ref.**
NVP||1M $NaClO_4$/EC+PC+FEC||HC	1.5 - 4.0	3.2	2352	83.5% (1000 cycles)	This work
NVP||1M $NaClO_4$/PC+FEC||HC	0.8 - 3.0	1.7	100	-	2
NVP||1M NaFSI/PC||HC	2.0 - 3.4	2.7	11.76	-	31
NVP||1M $NaClO_4$/EC +DMC||HC	2.0 - 4.0	3.3	59	58% (100 cycles)	32
NVP||1M $NaClO_4$/EC +DMC||HC	0.7 - 4.1	1.5	300	80% (1000 cycles)	33
NVP||1M $NaClO_4$/PC||HC	0.5 - 3.5	1.6	500	77.9% (50 cycles)	34
NVP||1M $NaClO_4$/EC+DMC||HC	2.0 - 3.5	-	50	83% (50 cycles)	35
NVP||1M $NaClO_4$/EC+DMC||WC	2.0 - 3.4	2.8	60	95% (350 cycles)	36
$NaNi_{0.5}Ti_{0.5}O_2$||1 M $NaClO_4$/PC||HC	1.5 - 4.0	2.9	30	72% (100 cycles)	37
NVP||1M $NaClO_4$/PC+FEC||3D graphene	0.7 - 3.7	2.7	100	77.1% (200 cycles)	1
NVP||1M $NaClO_4$/PC+FEC||NVP	1.0 - 2.2	1.7	1100	77% (100 cycles)	3
NVP||1M $NaClO_4$/EC+DMC||NVP	1.0 - 3.0	1.75	117.6	80% (200 cycles)	4
NVP||1M $NaClO_4$/EC+PC||NVP	0.8 - 2.0	1.7	117.6	-	38
NVP||1M $NaClO_4$/EC+DMC||NVP	1.0 - 2.5	1.8	235	81% (280 cycles)	39
NVP||1M $NaClO_4$/PC||NVP	1.0 - 2.2	1.7	235	81.4% (50 cycles)	13
$NaV_{2.91}Mn_{0.09}(PO_4)_3$||1M $NaClO_4$/EC+DEC||NVP	0.5 - 2.5	1.8	588	90.1% (300 cycles)	40
NVP||1M $NaClO_4$/PC||NVP	1.0 - 2.2	1.71	100	92% (100 cycles)	41
NVP||1M $NaClO_4$/EC+DMC||$NaV_3(PO_4)_3$	0.5 - 3.5	1.8	588	87.2% (1000 cycles)	42
NVPF-NTP||1M $NaClO_4$/EC+PC||Sb-CNT	1.5 - 3.9	3.0	650	80% (50 cycles)	43
NVP||1M $NaClO_4$/EC+DMC||NTP	0.7 - 2.4	1.3	590	96.9% (300 cycles)	9
NVPF||1M $NaClO_4$/PC||NTP	1.0 - 1.8	1.5	65	80% (100 cycles)	44
NVPF||1M $NaClO_4$/EC+PC||NTP	1.0 - 3.0	1.5	128	74% (100 cycles)	45
VOPO4||1M $NaClO_4$/PC||NTP	1.8 - 3.8	2.8	100	92.4% (100 cycles)	46
NiCoFe||1M $NaClO_4$/EC+DEC||NTP	0.5 - 2.2	1.4	150	100% (300 cycles)	47

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Sodium-ion full cell description	Voltage range (V)	Potential (V)	Current density (mA g^{-1})	Capacity retention	Ref.
NVP‖1M $NaClO_4$/PC+FEC‖Sb	1.7 - 3.4	2.7	117.6	100% (100 cycles)	48
NVP‖1M $NaClO_4$/EC+PC‖Sb	1.2 - 3.8	2.5	12	-	49
NVP‖1M $NaClO_4$/PC+FEC‖SnS	0.8 - 3.0	2.2	1000	85.5% (300 cycles)	50
NVP‖1M $NaPF_6$/DME‖Sn_4P_3	1.6 - 3.6	2.9	20	-	51
NVP‖1M $NaClO_4$/PC+FEC‖MoS_2	0.6 - 3.0	2.4	50	-	52
NVP‖1M $NaClO_4$/EC+DEC‖MoS_3	0.1 - 3.0	1.8	500	84% (100 cycles)	53
$Na(Ni_{0.5}Mn_{0.5})O_2$‖1M $NaClO_4$/PC+FEC‖Sn	1.5 - 4.0	2.8	24	74% (50 cycles)	54
NVP‖1M $NaClO_4$/EC+DMC‖Cu_3P	2.0 - 4.0	2.6	600	38.2% (200 cycles)	55
NVP‖1M $NaPF_6$/EC+DMC‖HTO	1.8 - 3.8	2.7	200	-	56
NVP‖1M $NaClO_4$/EC+PC‖SPO	1.5 - 4.0	2.9	50	99.8% (100 cycles)	57
NVP‖1M $NaClO_4$/EC+PC‖MoO_3	0.2 - 3.0	1.4	111.7	-	58
NVP‖‖1M $NaClO_4$/EC+DEC‖TiO_2	1.0 - 4.0	2.2	24	-	59
NVOPF‖1M $NaClO_4$/EC+PC‖VO_2	1.0 - 4.0	2.0	520	80% (220 cycles)	60
NVP‖1M $NaCF_3SO_3$/DEGDME‖$CoSe_2$	0.5 - 3.0	1.2	500	97.9% (50 cycles)	61
NVP‖1M $NaClO_4$/PC‖$Co_{0.5}Fe_{0.5}S_2$	0.7 - 2.7	1.6	200	87% (100 cycles)	62
NVP‖1M $NaClO_4$/PC+FEC‖$NiFe_2O_4$	0.0 - 4.0	1.8	59	95% (30 cycles)	63
$Na_3V_{1.8}Al_{0.2}(PO_4)_3$‖1M $NaPF_6$/EC+DEC‖$Na_3Ti_{1.8}Fe_{0.2}(PO_4)_3$	0.4 - 2.0	1.2	59	-	64
$Na_{2/3}Ni_{1/3}Mn_{2/3}O_2$‖1M $NaClO_4$/EC+PC‖Sb	1.4 - 4.0	2.8	500	70% (100 cycles)	65
$[Ni_{0.6}Co_{0.2}Mn_{0.2}]O_2@Al_2O_3$‖0.5M $NaPF_6$/PC+FEC‖HC	1.0 - 4.1	2.5	75	75% (300 cycles)	66
$Na_{0.80}Li_{0.12}Ni_{0.22}Mn_{0.66}O_2$‖1M $NaPF_6$/EC+DEC‖SnS_2	1.0 - 4.2	2.5	37	74% (50 cycles)	67
$Na_{0.8}Ni_{0.4}Ti_{0.6}O_2$‖1M $NaPF_6$/EC+DEC‖$Na_{0.3}MoO_2$	0.6 - 3.6	2.1	20	94.8% (100 cycles)	68
$Na_xFe_2(CN)_6$‖1M $NaClO_4$/EC+DEC‖CNT/FeO_x	0.5 - 3.0	1.7	250	85% (400 cycles)	69
PB‖1M $NaClO_4$/EC+DMC‖NACF	0.01 - 3.5	-	100	-	70

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