Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

A binder-free carbon nano-network wrapped carbon felt with optimized heteroatom doping for vanadium redox flow batteries

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Figure S1 Polymerization processes during the preparations of a) the N-CN-CF electrode and b) NS-CN-CF electrode.

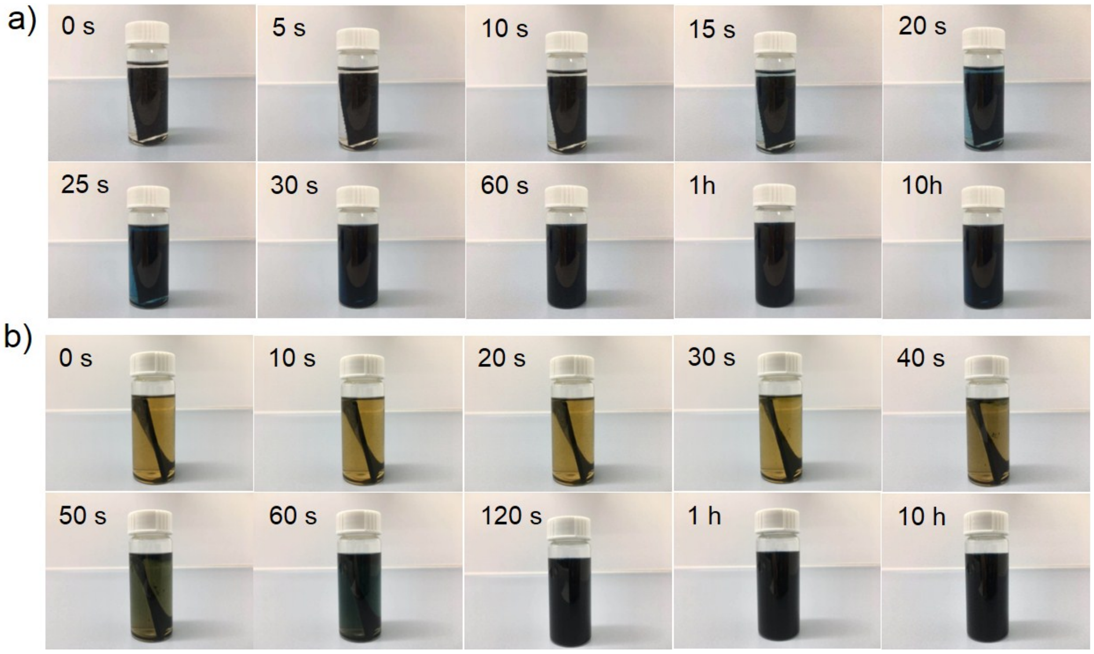

Figure S2 N_2 adsorption-desorption isotherm of the P-CF, T-CF, N-CN-CF and NS-CN-CF electrode.

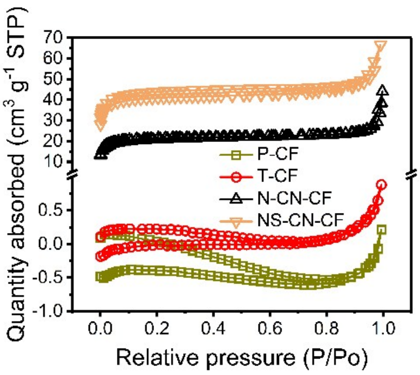

Figure S3 EDS elemental mapping of the NS-CN-CF electrode.

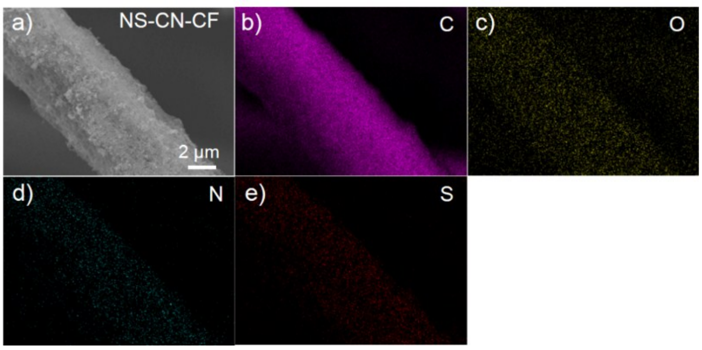

Figure S4 EDS elemental mapping of the N-CN-CF electrode.

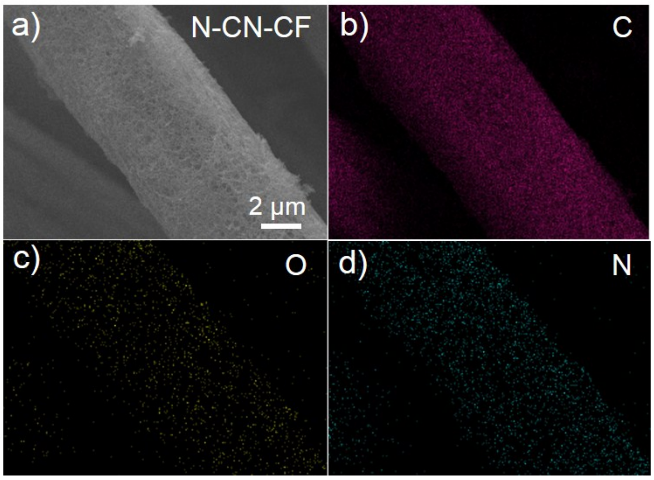

Figure S5 CVs of a) N-CN-CF electrodes synthesized with different concentrations of aniline and b) NS-CN-CF electrodes synthesized with different concentrations of aniline at the scan rate of 50 mV s^{-1}. N-CN-CF-2, N-CN-CF-5, N-CN-CF-10, and N-CN-CF-15 refers to N-CN-CF electrodes synthesized with 2, 5, 10, and 15 mmol L^{-1} aniline, respectively. Similarly, NS-CN-CF-5, NS-CN-CF-10 and NS-CN-CF-15 refers to NS-CN-CF electrodes synthesized with 5, 10 and 15 mmol L^{-1} aniline.

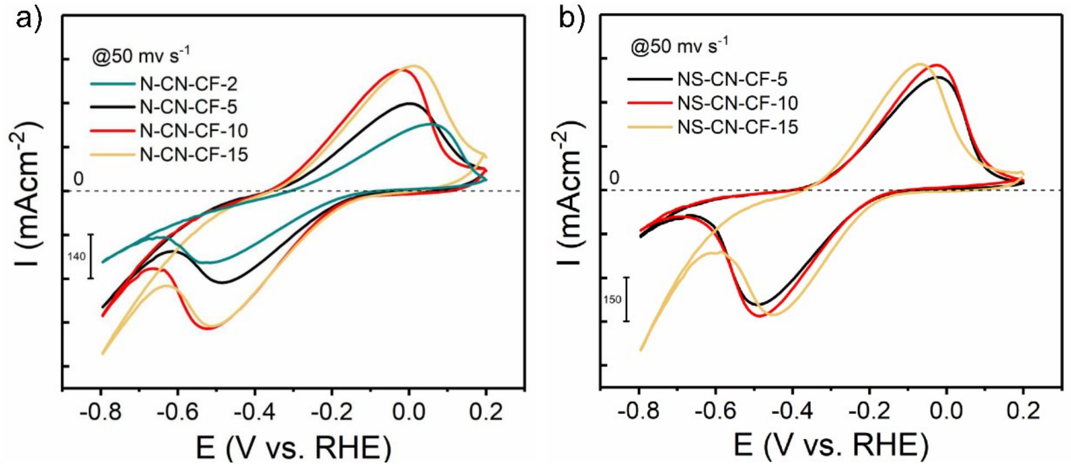

Figure S6 SEM image of the NS-CN-CF.

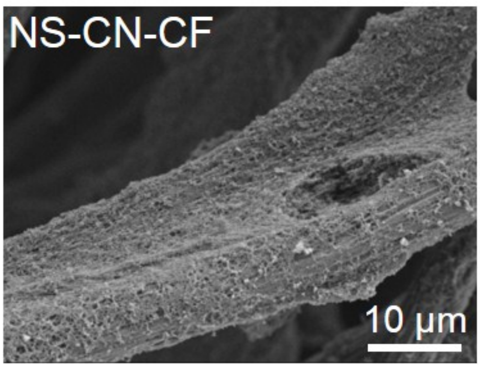

Figure S7 a) EIS of the battery with NS-CN-CF electrodes measured at static state (flow rate controlled to be 0), b) frequency dispersion of the resistance of the impedance vectors in a).

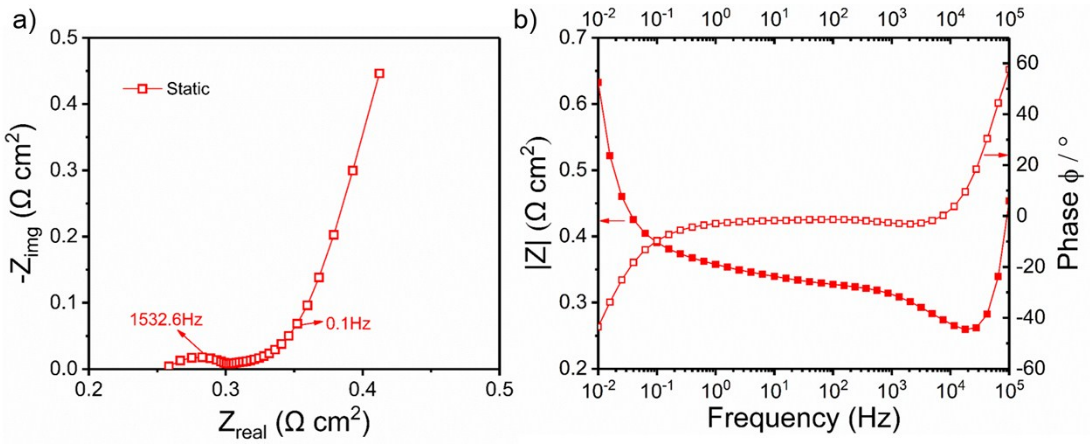

Table S1 Electrochemical data obtained from CV curves of the P-CF electrode for positive reactions.

Scan rate (mV s^{-1})	$-I_{pc}$ (mA cm^{-2})	I_{pa} (mA cm^{-2})	V_{pc} (V)	V_{pa} (V)	$-I_{pc}/I_{pa}$	ΔE (mV)
50	96.192	189.808	0.613	1.621	0.507	1008
20	56.022	111.549	0.840	1.469	0.502	629
10	39.844	68.506	0.909	1.400	0.582	491
5	26.482	38.938	0.960	1.349	0.680	389
1	5.718	8.266	1.036	1.256	0.692	220

Table S2 Electrochemical data obtained from CV curves of the T-CF electrode for positive reactions.

Scan rate (mV s^{-1})	$-I_{pc}$ (mA cm^{-2})	I_{pa} (mA cm^{-2})	V_{pc} (V)	V_{pa} (V)	$-I_{pc}/I_{pa}$	ΔE (mV)
50	192.356	281.104	0.795	1.558	0.684	763
20	100.084	143.949	0.900	1.454	0.695	554
10	59.348	81.939	0.954	1.385	0.724	431
5	32.512	43.651	1.005	1.334	0.745	329
1	9.497	12.186	1.081	1.226	0.780	145

Table S3 Electrochemical data obtained from CV curves of the N-CN-CF electrode for positive reactions.

Scan rate (mV s^{-1})	$-I_{pc}$ (mA cm^{-2})	I_{pa} (mA cm^{-2})	V_{pc} (V)	V_{pa} (V)	$-I_{pc}/I_{pa}$	ΔE (mV)
50	256.192	340.693	0.838	1.546	0.752	708

20	136.348	175.654	0.929	1.441	0.776	512
10	79.801	98.627	0.981	1.374	0.809	393
5	42.760	51.323	1.109	1.335	0.833	316
1	11.564	13.078	1.088	1.231	0.884	143

Table S4 Electrochemical data obtained from CV curves of the NS-CN-CF electrode for positive reactions.

Scan rate (mV s^{-1})	**$-I_{pc}$ (mA cm^{-2})**	**I_{pa} (mA cm^{-2})**	**V_{pc} (V)**	**V_{pa} (V)**	**$-I_{pc}/I_{pa}$**	**ΔE (mV)**
50	303.128	339.532	0.855	1.454	0.893	599
20	156.801	174.097	0.945	1.334	0.901	389
10	82.165	90.870	0.969	1.295	0.904	326
5	36.489	39.929	0.990	1.289	0.914	299
1	12.356	12.951	1.086	1.225	0.959	139

Table S5 Atomic fractions of C, O, N from XPS spectra of the N-CN-CF electrodes synthesized with different concentrations of aniline.

Components (%)	**N-CN-CF-2**	**N-CN-CF-5**	**N-CN-CF-10**	**N-CN-CF-15**
C 1s	93.11	90.68	92.64	89.69
O 1s	5.37	7.02	3.41	2.36
N 1s	1.52	2.30	3.95	5.46
Pyridinic N	0.22	0.62	1.02	1.33
Pyrrolic N	0.17	0.20	0.41	1.02
Graphitic N	0.77	1.24	1.94	2.43
Oxidized N	0.36	0.24	0.58	0.68

Table S6 Atomic fractions of C, O, N, S from XPS spectra of the NS-CN-CF electrodes synthesized with different concentrations of aniline.

Components (%)	**NS-CN-CF-5**	**NS-CN-CF -10**	**NS-CN-CF -15**
C 1s	90.38	91.24	89.69
O 1s	6.99	4.60	3.44
N 1s	1.94	2.82	5.01
Pyridinic N	0.10	0.58	1.57
Pyrrolic N	0.29	0.31	0.39
Graphitic N	0.95	1.55	2.42
Oxidized N	0.60	0.38	0.63
S 2p	0.69	1.34	1.86
C-S	0.18	0.60	0.67
C=S	0.10	0.32	0.64
$C-SO_X$	0.41	0.42	0.55

Table S7 Area specific resistances of various electrodes with a compression ratio of 70%.

Electrodes	P-CF	T-CF	N-CN-CF	NS-CN-CF
Area specific resistance (mΩ cm^2)	51.52	71.84	26.08	25.36

Table S8 Summary of performance of VRFBs assembled with advanced electrodes in the open literature.

Year	Modification method	Current density (mA cm^{-2})	Energy efficiency (%)	Specific surface area (m^2 g^{-1})	Membrane	Reference
2013	CNF/CNT	100	65.6	1.4	Nafion 117	1
2014	Nb_2O_5	150	77.6	-	Nafion 115	2
2014	Corn protein-derived N-doped carbon	150	68.6	-	Nafion 117	3
2016	B/N-co-doped porous carbon	150	70	-	Nafion 212	4
2016	Graphene nanowall	125	73	11.8	Nafion 212	5
2016	Edge-halogenated graphene	50	86.8	-	Nafion 117	6
2017	Reduced graphene oxide	200	72	-	Nafion 115	7
2018	Boron doping	320	77.97	-	Nafion 212	8
2018	PB/PBA	100	78.5	-	Nafion 212	9
2019	$Ti_3C_2T_x$ MXene	300	75	-	Nafion 212	10
2019	Gradient pore	300	74.06	21.16	Nafion 212	11
2019	**NS-CN-CF**	**320 (160)**	**82.4 (89.7)**	**160.82**	**Nafion 212**	**This work**

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