Supplementary information

Mask-painting symmetrical micro-supercapacitors based on scalable, pore size adjustable, N-doped hierarchical porous carbon

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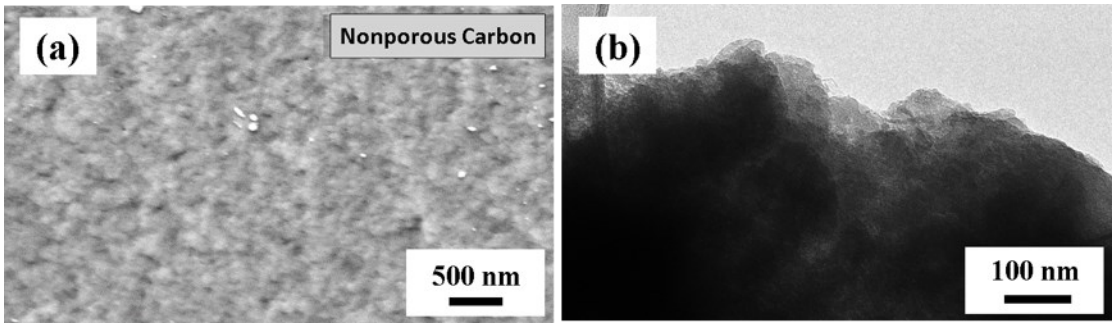

Fig. S1 (a)SEM image and (b) TEM image of nonporous carbon prepared from poly(acrylonitrile) (PAN) by air drying and carbonization.

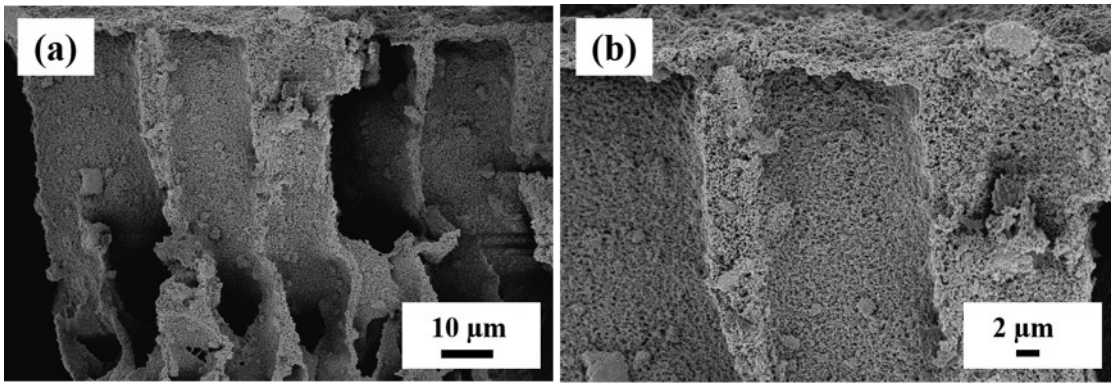

Fig. S2 SEM images porous carbon prepared from poly(acrylonitrile) (PAN) by a phase inversion method (a), and carbonization (PI carbon) (b).

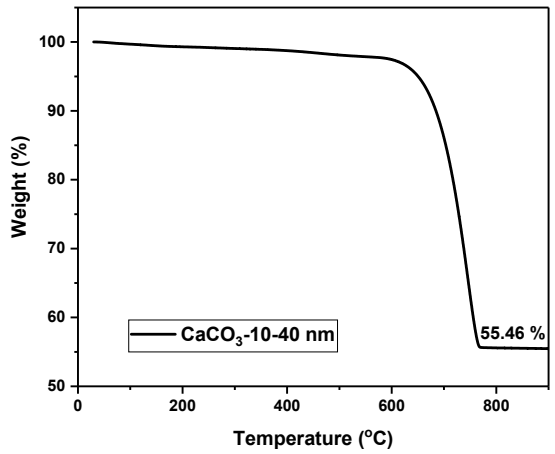

Fig. S3 Thermogravimetric analysis of nano-$CaCO_3$.

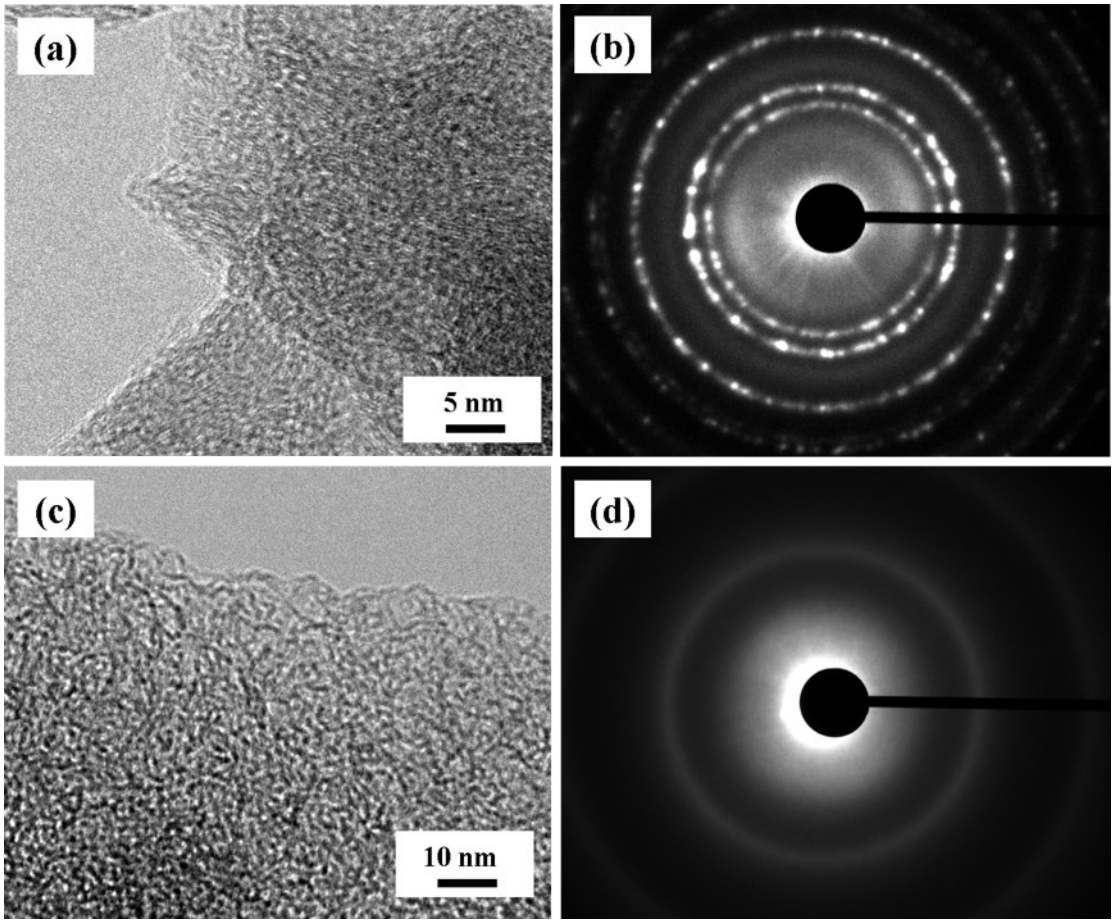

Fig. S4 TEM image and selected area electron diffraction (SAED) of (a, b) PIC carbon; (c, d) PICK carbon.

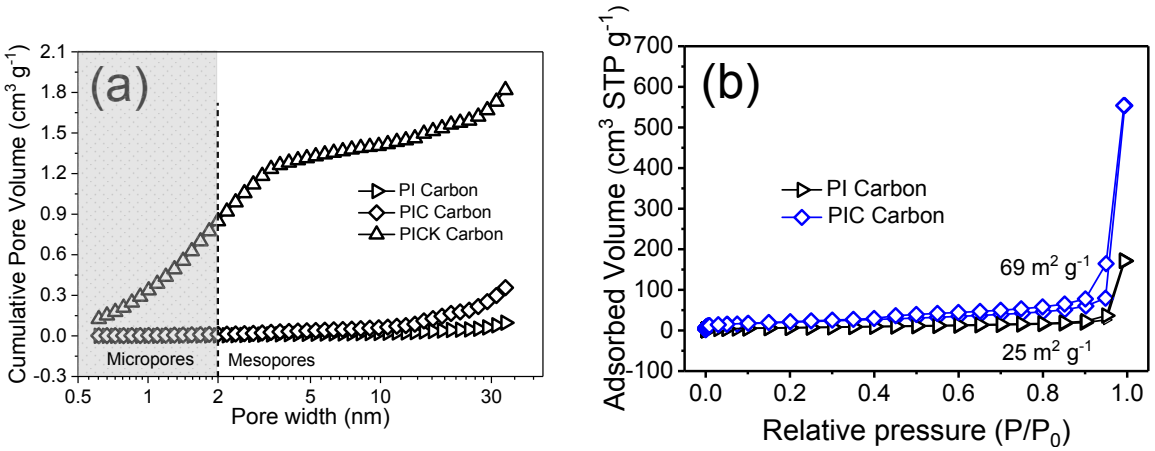

Fig. S5 (a) Cumulative pore volume of as prepared porous carbon; (b) Nitrogen adsorption-desorption isotherms of PI and PIC carbon

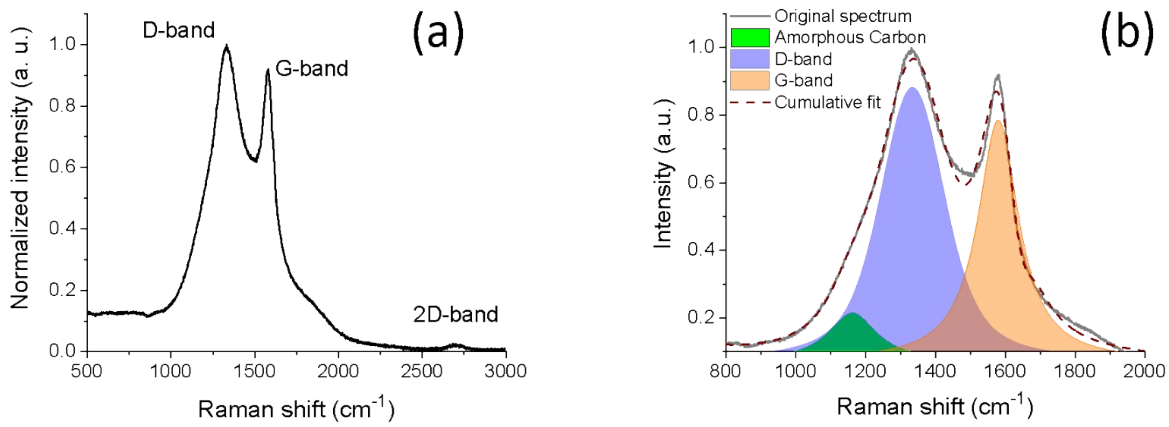

Fig. S6 (a, b) Raman spectra of PICK carbon.

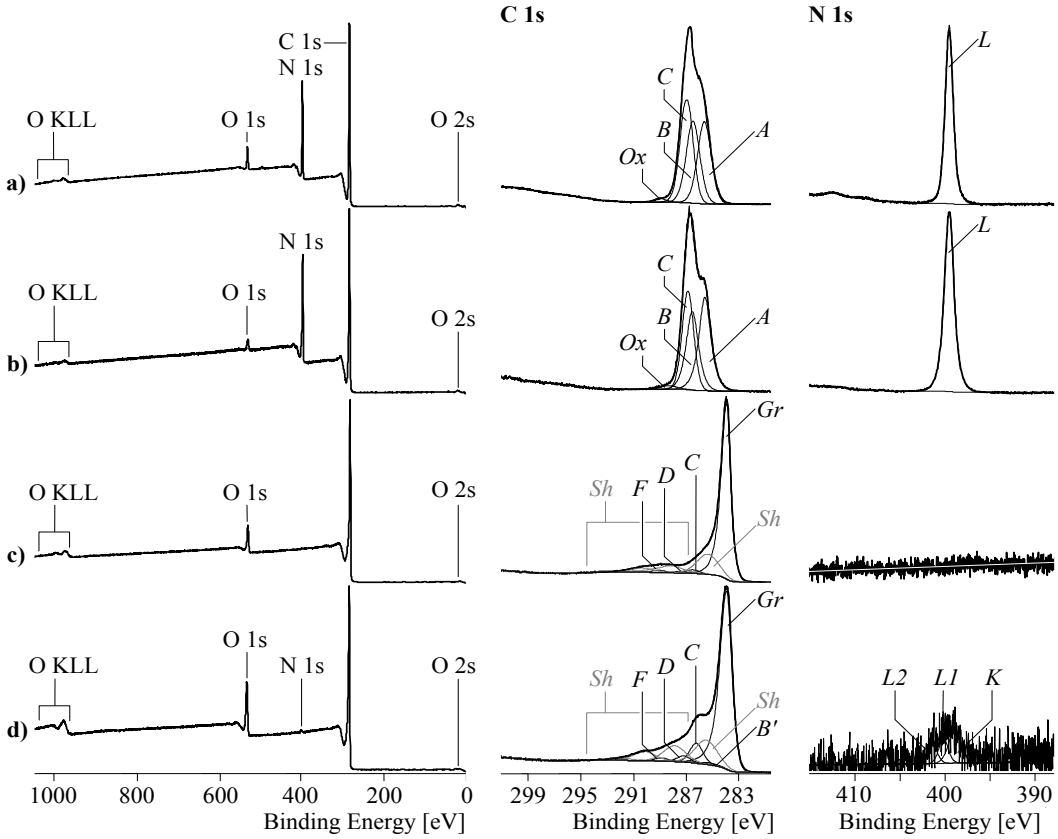

Fig. S7 XPS wide-scan (left column), C 1s middle column), and N 1s (right column) high-resolution element spectra recorded from (a) pristine PAN (b) PAN films, (c) YP-80F and (d) PICK carbon.

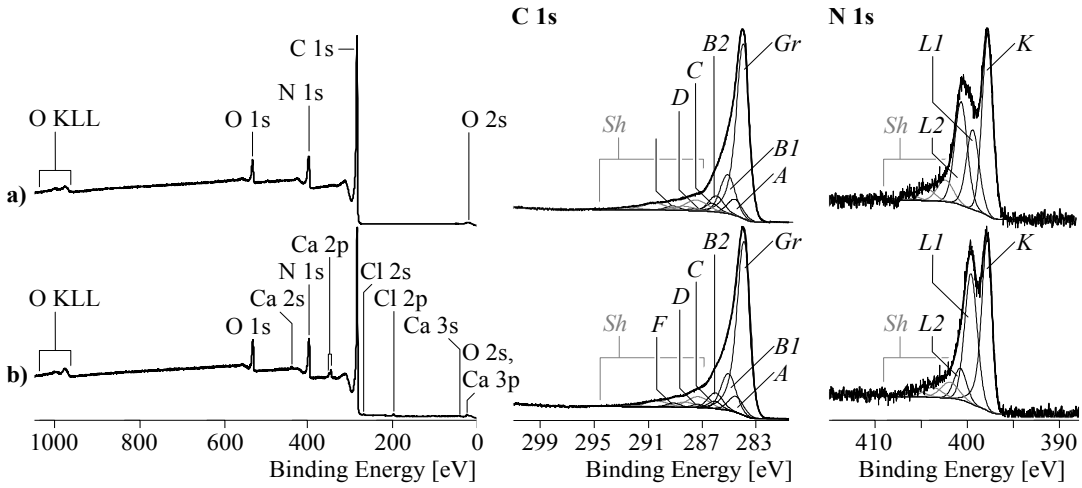

Fig. S8 XPS wide-scan (left column), C 1s middle column), and N 1s (right column) high-resolution element spectra recorded from (a) PI carbon and (b) PIC carbon.

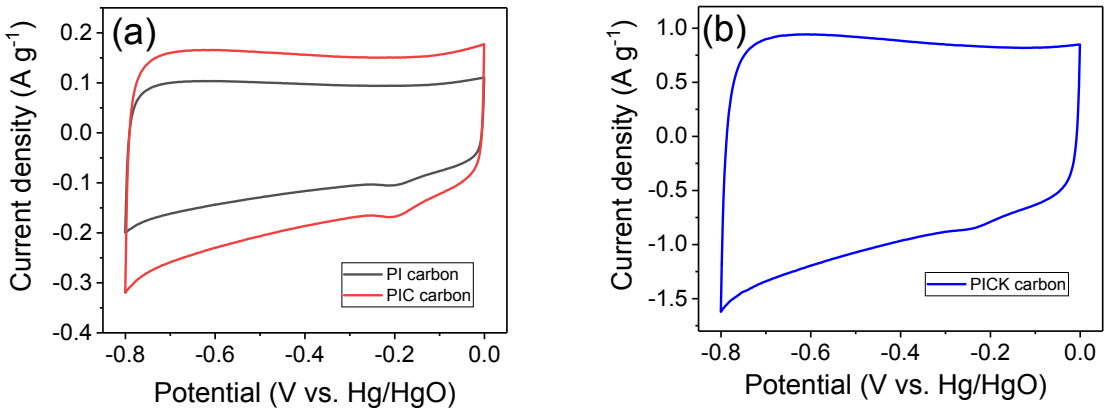

Fig. S9 (a) CV curves of PI and PIC carbon at a scan rate of 5 mV s^{-1} in 6.0 M KOH. (b) CV curves of PICK carbon at a scan rate of 5 mV s^{-1} in 6.0 M KOH.

Table S1 Synthesis parameters, Surface area, Pore volume and Capacitance of as prepared carbons.

Sample	Mass ratio (PAN: $CaCO_3$)	Mass ratio (PIC: KOH)	S_{BET} ($m^2\ g^{-1}$)	Pore Volume (CC g^{-1})	Capacitance (F g^{-1})
PI	-	-	25	0.05	12.8
PIC	1：1	-	69	0.17	28.1
PICK	1：1	1：3	2315	1.72	231.3
PICK-1	1：1	1：1	1120	0.74	113.2
PICK-2	1：1	1：2	1414	1.03	138.6
PICK-3	2：1	1：2	1216	0.89	124.6
PICK-4	2：1	1：3	1506	1.09	156.4
PICK-5	3：1	1：3	1469	1.04	142.5

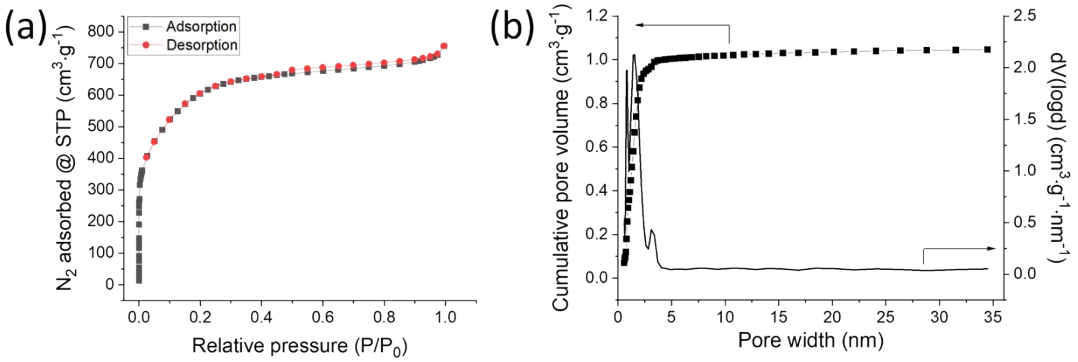

Fig. S10 (a) Nitrogen adsorption-desorption isotherms and (b) pore size distribution and cumulative pore volume of YP-80F.

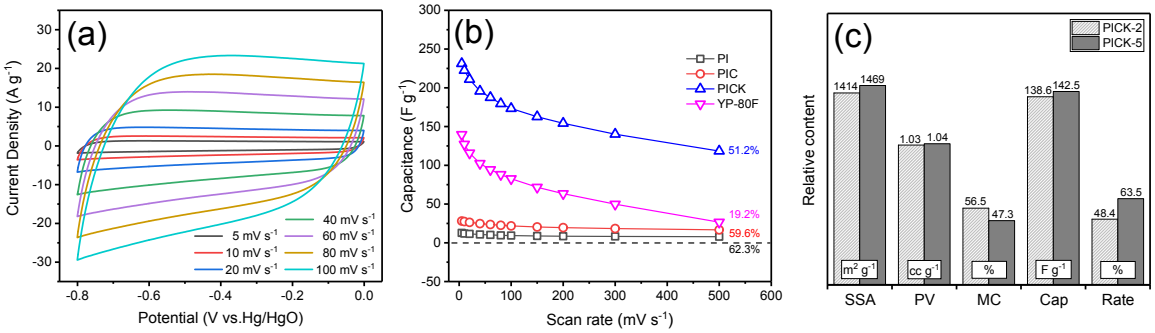

Fig. S11 (a) CV curves of PICK carbon; (b) Rate capability of as prepared porous carbon; (c) Comparison of two kinds of PICK on structure and electrochemical properties (SSA: Specific Surface Area; PV: Pore Volume; MC: Micropores content; Cap: capacitance; Rate: Rate capability)

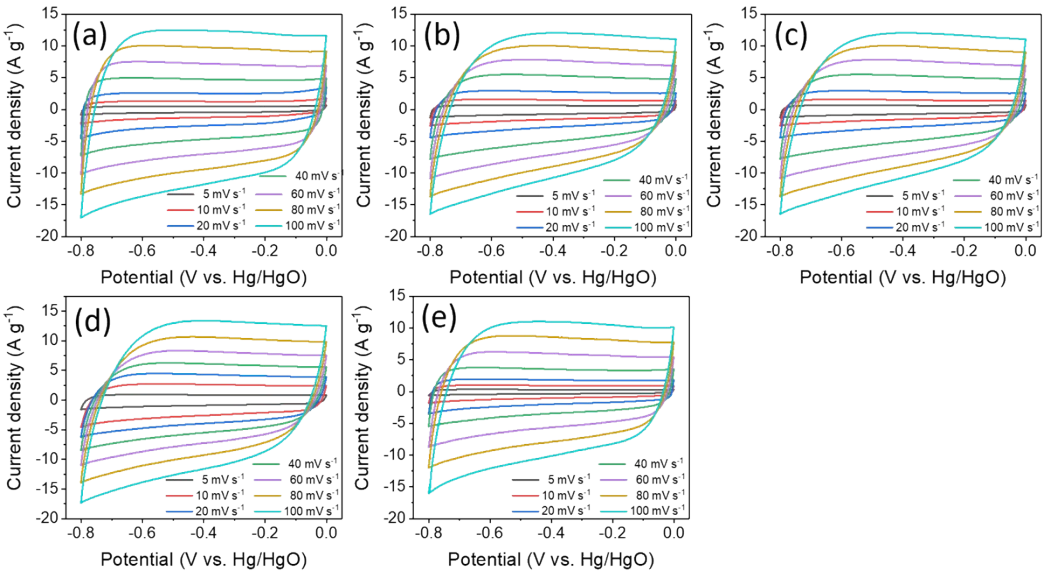

Fig. S12 CV curves of (a) PICK-1, (b) PICK-2, (c) PICK-3, (d) PICK-4, (e) PICK-5 in 1.0 M Na_2SO_4.

Table S2 Details of XPS results and capacitance of PICK-1, PICK-2, PICK-3, PICK-4 and PICK-5.

Sample	Peak	Position BE(eV)	Atomic Conc (%)	Mass Conc (%)	Capacitance (F g^{-1})
PICK-1	C 1s	284.2	80.22	72.54	113.2
	N 1s	399.25	1.71	1.81	
	O 1s	533.26	14.08	16.96	
PICK-2	C 1s	284.2	80.22	72.43	138.6
	N 1s	399.65	1.56	1.64	
	O 1s	532.78	14.02	16.87	
PICK-3	C 1s	284.2	80.3	70.2	124.6
	N 1s	399.89	1.5	1.5	
	O 1s	532.82	11.37	12.47	
PICK-4	C 1s	284.2	87.93	83.94	156.4
	N 1s	399.78	0.52	0.58	
	O 1s	532.37	10.76	13.68	
PICK-5	C 1s	284.59	86.93	80.47	142.5
	N 1s	399.84	0.54	0.58	
	O 1s	532.16	9.63	11.88	

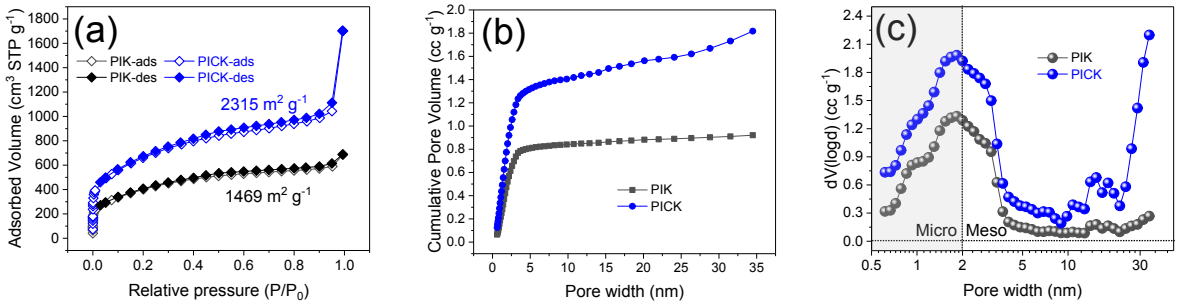

Fig. S13 (a) Nitrogen adsorption-desorption isotherms, (b) pore volume and (c) pore size distribution of PIK and PICK carbons.

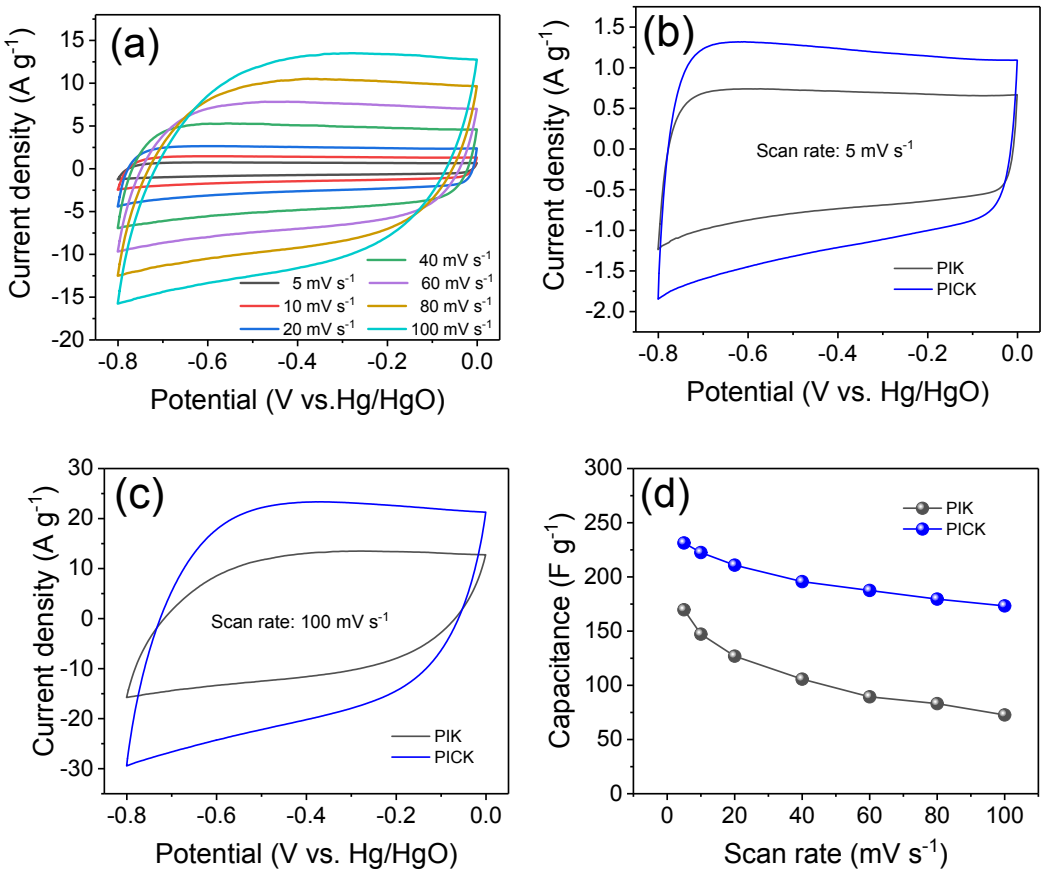

Fig. S14 (a) CV curves of PIK carbon at different scan rate; (b) CV curves of PIK carbon and PICK carbon at the scan rate of 5mV s^{-1}; (c) CV curves of PIK carbon and PICK carbon at the scan rate of 100 mV s^{-1}; (d) rate capability of PIK carbon and PICK carbon.

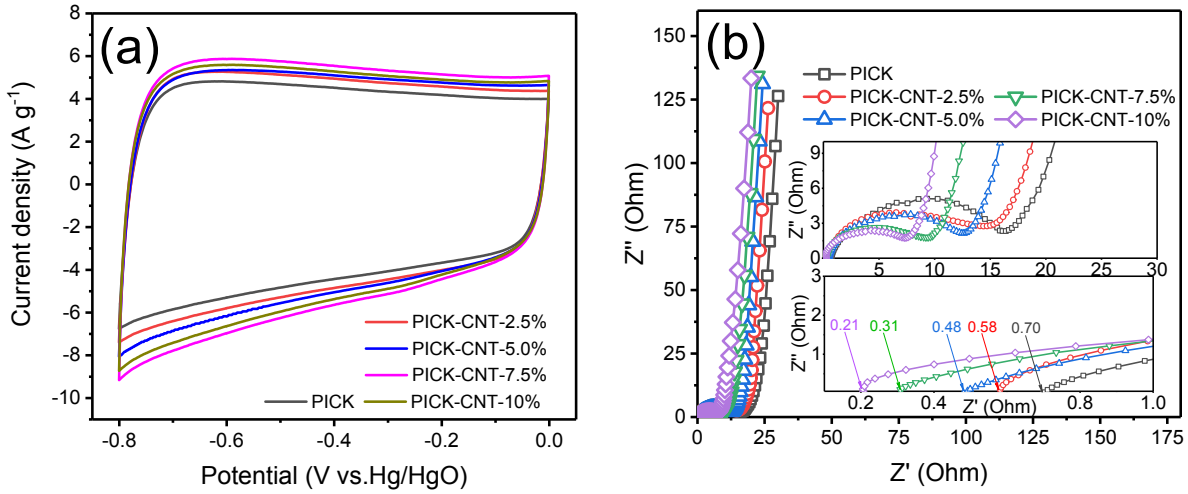

Fig. S15 (a) CV curves of a series of PICK-CNT electrode at a scan rate of 20 mV s^{-1}. (b) Electrochemical impedance spectrum at open circuit potential range from 0.01 Hz to 100 kHz with insert showing the high frequency region.

Table 3 Comparison on the electrochemical performance of some PAN based carbon.

Electrode/ precursor	S_{BET} ($m^2 g^{-1}$)	Scan rate/ Current density	electrolyte	Capacitance ($F g^{-1}$)	Cycling stability	Reference
PAN	1886	1.0 A g^{-1}	1.0 M Na_2SO_4	103.01	~92% (3,000)	Compos. Part B-Eng., **2019**, *161*, 10.
PAN-carbon	2370	10 mV s^{-1}	Pyr14TFSI:PC:EC (3;3;2)	128	75% (1,000)	Nanotechnology, **2019**, *30*, 355402.
PAN/PMMA	-	0.5 A g^{-1}	6.0 M KOH	140.8	95.4% (10,000)	J. Mater. Sci., **2018**, *53*, 9721.
LCNFs/PANI/N-9	483	1.0 A g^{-1}	1.0 M H_2SO_4	199.5	82% (1,000)	Ionics, **2020**, *26*, 465.
rGOPKS/PAN	203	2.0 A g^{-1}	4.0 M KOH	203	90% (5,000)	RSC Adv., **2021**, *11*, 11233.
PAN	1986	0.25 A g^{-1}	-	210	86.8% (3,000)	Electrochem. Commu., **2018**, *96*, 98.
NDP-ACMs	613.8	10 mV s^{-1}	1.0 M H_2SO_4	216	108% (3,000)	Sci. Rep., **2017**, *7*, 1.
NDP-CMs	840	2.5 Ag^{-1}	1.0 M H_2SO_4	246	110% (3,000)	Carbon, **2019**, *143*, 776.
PAN	1256.2	10 mV s^{-1}	$[BMIM]BF_4^-$	248.3	99.80%	Electrochim. Acta, **2018**, *282*, 97.
PAN/POSS	335.38	5 mV s^{-1}	-	257.7	-	Mater. Design, **2018**, *139*, 72.
PAN	852	0.2 A g^{-1}	1.0 M $ZnSO_4$	261.5	-	Batteries & Supercaps, **2021**, *680*.
ACNFs	2439	1.0 A g^{-1}	6.0 M KOH	267.32	96.7% (5,000)	J. Power Sources, **2019**, *437*, 226937.
PMC	1600	0.2 A g^{-1}	1.0 M H_2SO_4	270	100% (5,000)	RSC Adv., **2017**, *7*, 43172.
CNF-3	51.2	0.5 A g^{-1}	6.0 M KOH	272.05	92% (1,000)	Mater. Res. Express, **2019**, *6*, 125077.
PAN/CA	1355	0.1 A g^{-1}	6.0 M KOH	280	96.8% (2,000)	J. Mater. Sci. **2018**, *53*, 4527.
PICK-CNTs	**2315**	**5 mV s^{-1}**	**1.0 M Na_2SO_4**	**286.8**	**98.2% (20,000)**	**This work**
PAN	3066	0.5 A g^{-1}	2.0 M KOH	290	96% (3,000)	J. Mater. Chem. A, **2018**, *6*, 6891.
FSCs	763.8	1 mA cm^{-2}	6.0 M KOH	294.7	99.1 (10,000)	Chem. Eng. J., **2019**, *364*, 70.
PAN	2146	1.0 A g^{-1}	6.0 M KOH	302	86% (1,000)	RSC Adv., **2018**, *8*, 29767.
PAN	3292.3	0.5 A g^{-1}	6.0 M KOH	331	89.5% (10,000)	Chem. Eng. J., **2018**, *362*, 600.
PAN-800-1	2374	0.5 A g^{-1}	1.0 M Na_2SO_4 /1.0 M H_2SO_4	390	95.5% (10,000)	ACS Appl. Mater. Inter. **2020**, *12*, 50.
PS/PAN	955	0.5 A g^{-1}	6.0 M KOH	438.5	75.5% (10,000)	ACS Appl. Energy Mater. **2019**, *2*, 4402.
PPC	3751	0.5 A g^{-1}	1.0 M Na_2SO_4	448	96.5% (10, 000)	Carbon, **2019**, *152*, 120-127.

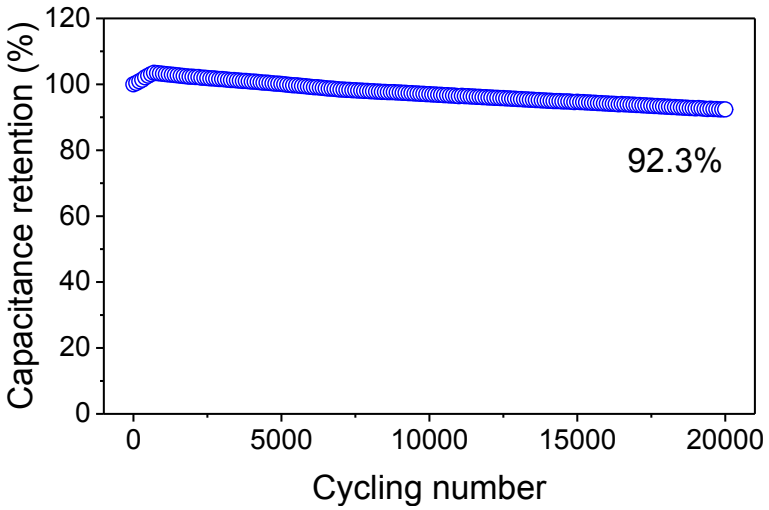

Fig. S16 Cycling stability of pure PICK carbon at a scan rate of 20 mV s^{-1}.

Fig. S17 Resistance testing of the device before active materials painting

Fig. S18 Image of MSC with logo “AK Sommer”.