Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

(Supporting Information)

For

Solvent-free, deep eutectic systems assisted synthesis of nanoarchitectonics of hierarchical porous carbons for high rate supercapacitor

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2. Experimental Section

2.1 Materials:

All reagents are used directly without purification. Polyacrylonitrile(PAN) was purchased from Shanghai Petrochemical, urea (AR), potassium carbonate (AR), and N-methylpyrrolidone (AR) were purchased from China National Pharmaceutical Group, methionine (AR) was purchased from Shanghai Aladdin, and polyvinylidene fluoride (AR) was purchased from Aldrich.

2.2 Characterization:

The morphology of carbon materials was analyzed using scanning electron microscopy (Regulus 8100) and transmission electron microscopy (JEM-2100Plus). Thermal Gravimetric Analyzer (DTG-60). X-ray diffraction (XRD-6100, Cu radiation), Raman spectroscopy (Witec Alpha300R, excitation wavelength 488 nm), X-ray photoelectron spectroscopy (XPS, Thermo Fisher ESCALAB Xi^+), N_2 isothermal adsorption desorption curve (JW-BK200C).

2.3 Electrochemical Experiment:

The electrochemical performance of Cyclic voltammetry (CV), Galvanostatic Charge-discharge (GCD), and Electrochemical impedance spectroscopy (EIS) were tested using an electrochemical workstation (Chenhua, Shanghai, CHI660E).

The electroactive material, acetylene black and Polyvinylidene fluoride (PVDF) were mixed with the mass ratio of 8:1:1 in NMP. Then the slurry was coated on the square foam nickel of 1 cm^2. The average load of the electrode was 1.5 mg cm^{-2}. Dry at 100 ^oC for 12 h, then press under a pressure of 10 MPa for 30 s in a tablet press to obtain the working electrode. In the three-electrode testing system, 6 M KOH was used as the electrolyte, with Pt as the counter electrode and Hg/HgO as the reference electrode. The specific capacity of a single electrode was calculated from the GCD curves based on the following formula:

$$C_g = \frac{I \times \Delta t}{m \times \Delta V}$$

where C_g, I, $\triangle$t, m, and $\triangle$V are the gravimetric specific capacitance (F g^{-1}), discharge current (A), discharge time (s), the mass loading of electroactive material (g), and discharge voltage range (V), respectively.

As for the two-electrode symmetric cell:

$$C_s = \frac{2I \times \Delta t}{m \times \Delta V}$$

where Cs, I, $\triangle$t, m, and $\triangle$V are the gravimetric specific capacitance of a single electrode (F g^{-1}), discharge current (A), discharge time (s), the mass loading of electroactive material (g), and discharge voltage range (V), respectively.

$$C_{cell} = \frac{C_s}{4}$$

Where C_{cell} are the specific capacitance of the symmetric cell.

The energy density (E, Wh kg^{-1}) and power density (P, W kg^{-1}) of the symmetric cell were respectively calculated according to the following equations:

$$E = \frac{C_{cell} \times (\Delta V)^2}{3.6 \times 2}$$

$$P = \frac{3600 \times E}{\Delta t}$$

2.4 Synthetic Process

DES synthesis: Dissolve 0.89 g of methionine and 1.44 g of urea in 20 mL of deionized water, then mix the two solutions together, let them solidify at 0 °C, after that freeze dry the solid to obtain amino acid-urea DES.

Porous carbon nanospheres preparation: Mix 0.4 g PAN, 0.32 g DES, and 0.5 g K_2CO_3 directly through solid-phase stirring to obtain the precursor. The precursor was calcined at 240 °C for 2 h in a tubular furnace under an air atmosphere at a heating rate of 5 °C min^{-1}, and then in an Ar atmosphere at a heating rate of 5 °C min^{-1} to the pyrolysis temperature and calcined for 1 h. After completion, the obtained carbon material is first washed with 1 M HCl, then washed with deionized water to neutral, and finally dried at 120 °C for 10 h to obtain porous carbon nanospheres. The prepared porous carbon is named PDKP-X (X=700, 800, 900), where X is the pyrolysis temperature. For comparison, PDP-800 without adding K_2CO_3 and PKP-800 without adding DES were prepared at a pyrolysis temperature of 800 °C.

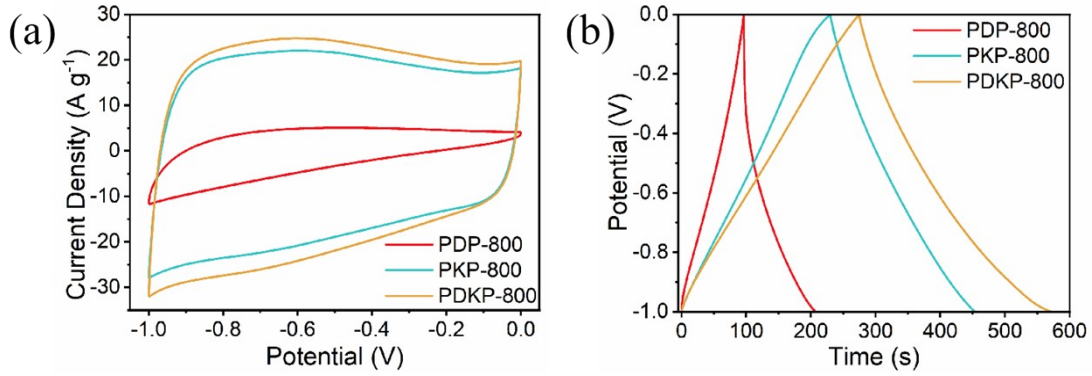

Fig. S1 (a) CV curves (100 mV s^{-1}), (b) GCD curves (1 A g^{-1}) of PDP-800, PKP-800 and PDKP-800.

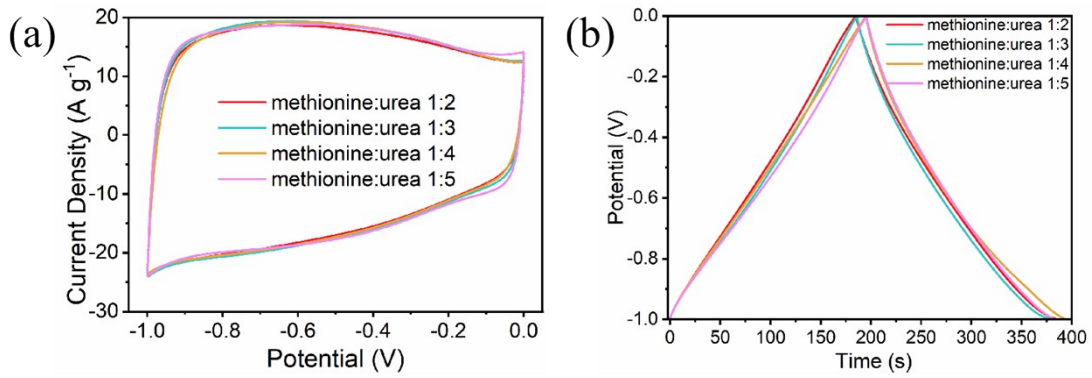

Fig. S2 (a) Cyclic voltammetry (CV) curves (100 mV s^{-1}), (b) galvanostatic charge-discharge (GCD) curves (1 A g^{-1}) of different molar ratios of methionine and urea.

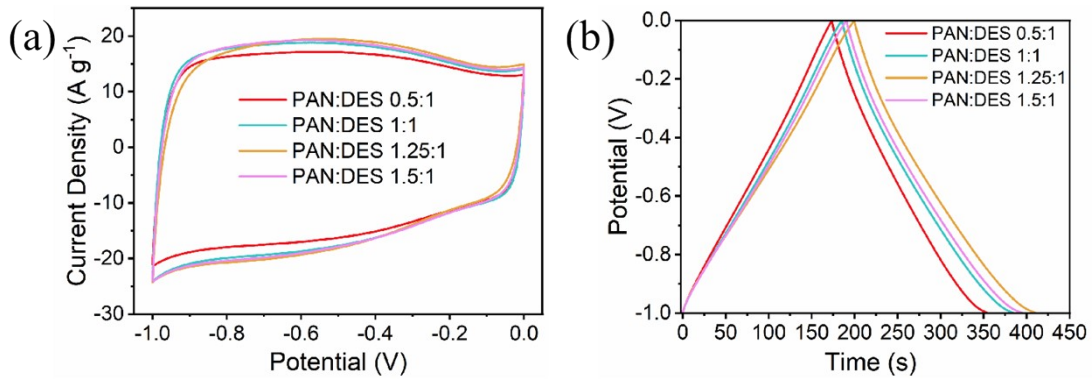

Fig. S3 (a) CV curves (100 mV s^{-1}), (b) GCD curves (1 A g^{-1}) of different mass ratios of PAN and DES.

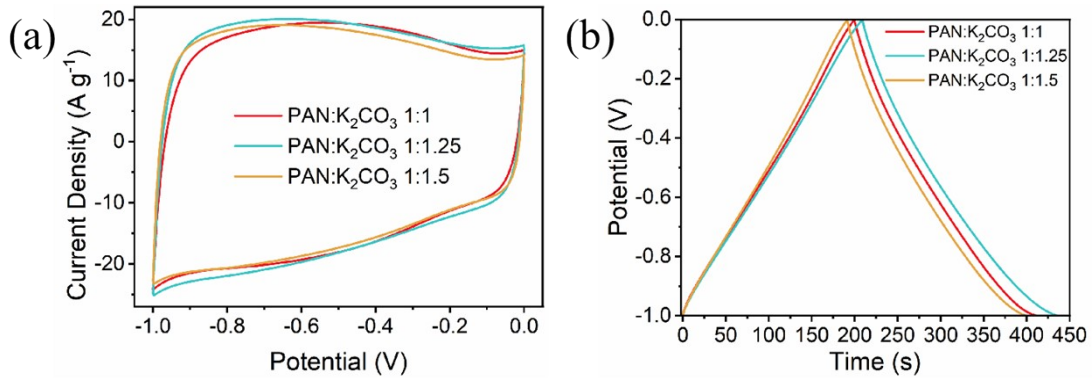

Fig. S4 (a) CV curves (100 mV s^{-1}), (b) GCD curves (1 A g^{-1}) of different mass ratios of PAN and K_2CO_3.

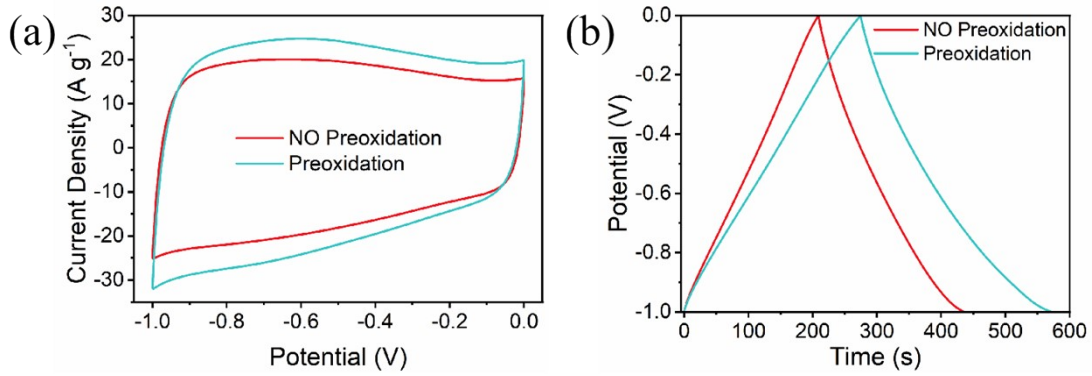

Fig. S5 (a) CV curves (100 mV s^{-1}), (b) GCD curves (1 A g^{-1}) of NO Preoxidation and Preoxidation.

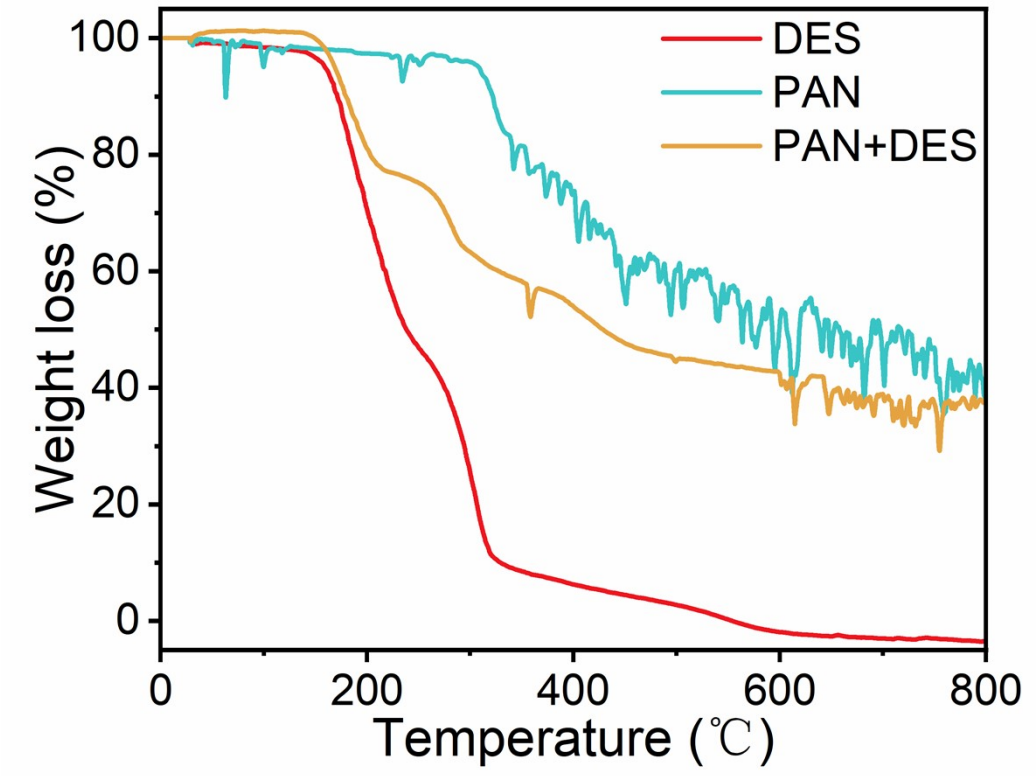

Fig. S6 TG of DES, PAN and PAN+DES.

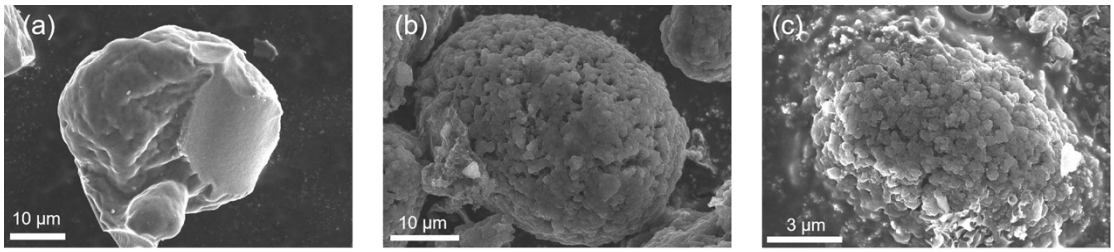

Fig. S7 (a)-(c) Scanning electron microscopy of PDP-800, PKP-800, and PDKP-800.

Table S1 Specific capacitances (1 A g^{-1}) of different molar ratios of methionine and urea, different mass ratios of PAN and DES, different mass ratios of PAN and K_2CO_3, NO Preoxidation and Preoxidation

Samples	Specific capacitance (F g^{-1})
Methionine:Urea 1:2	192.4
Methionine:Urea 1:3	193.8
Methionine:Urea 1:4	198.3
Methionine:Urea 1:5	187
PAN:DES 0.5:1	181.4
PAN:DES 1:1	198.3
PAN:DES 1.25:1	211.5
PAN:DES 1.5:1	205.3
PAN:K_2CO_3 1:1	200.9
PAN:K_2CO_3 1:1.25	227.5
PAN:K_2CO_3 1:1.5	208.4
NO Preoxidation	227.5
Preoxidation	297.3

Table S2 Char yield of DES, PAN and PAN+DES.

Samples	char yield (%)
DES	Less than 3
PAN	41
PAN+DES	38

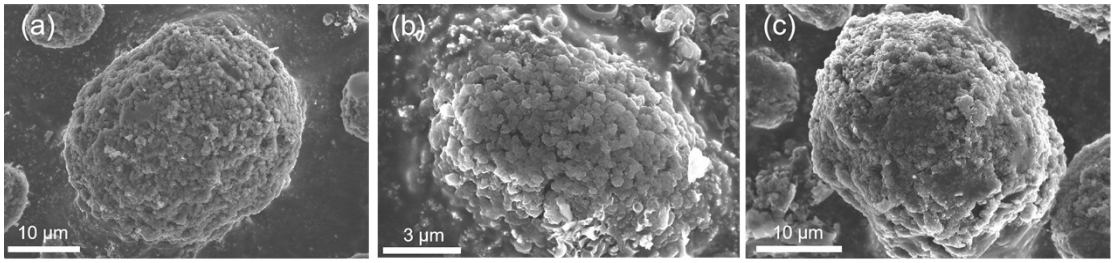

Fig. S8 (a)-(c) Scanning electron microscopy of PDKP-700, PDKP-800, and PDKP-900.

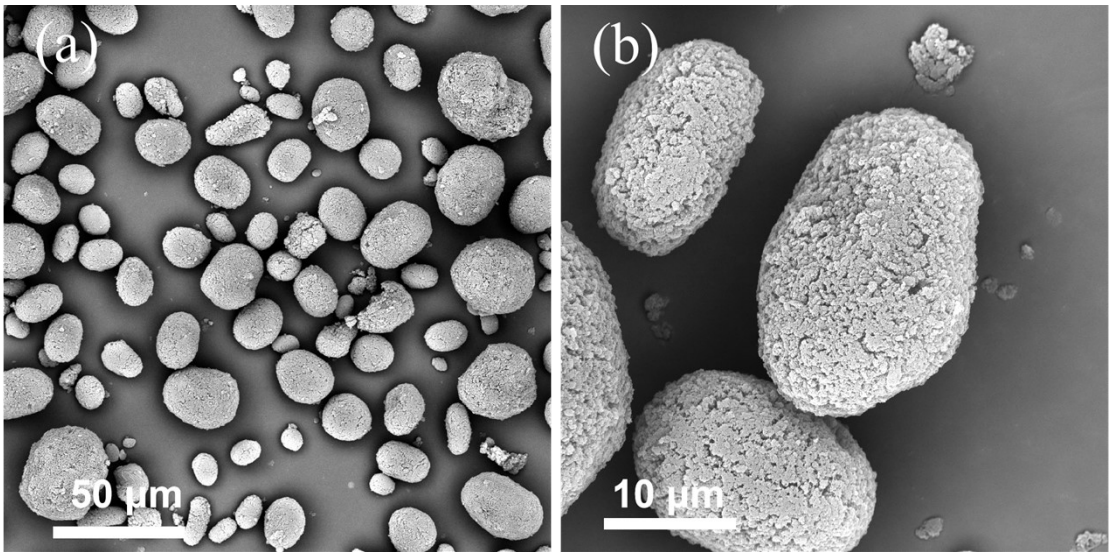

Fig. S9 Scanning electron microscopy of PAN.

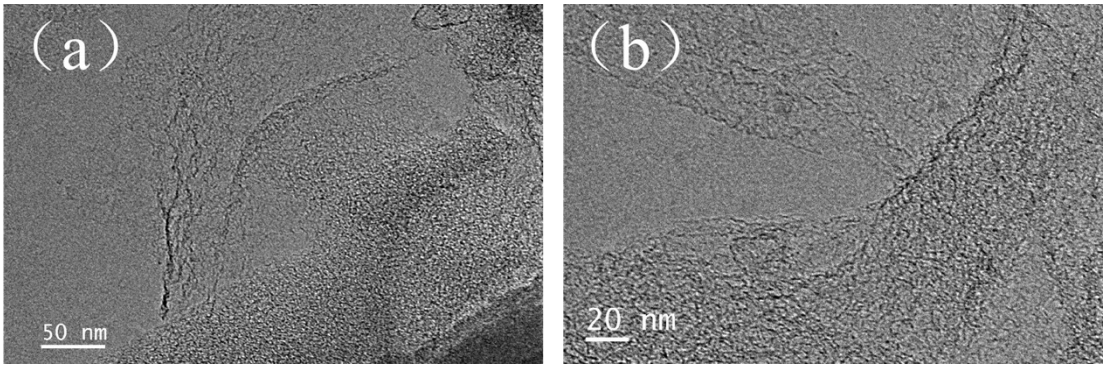

Fig. S10 high-resolution transmission electron microscopy images of PDKP-800.

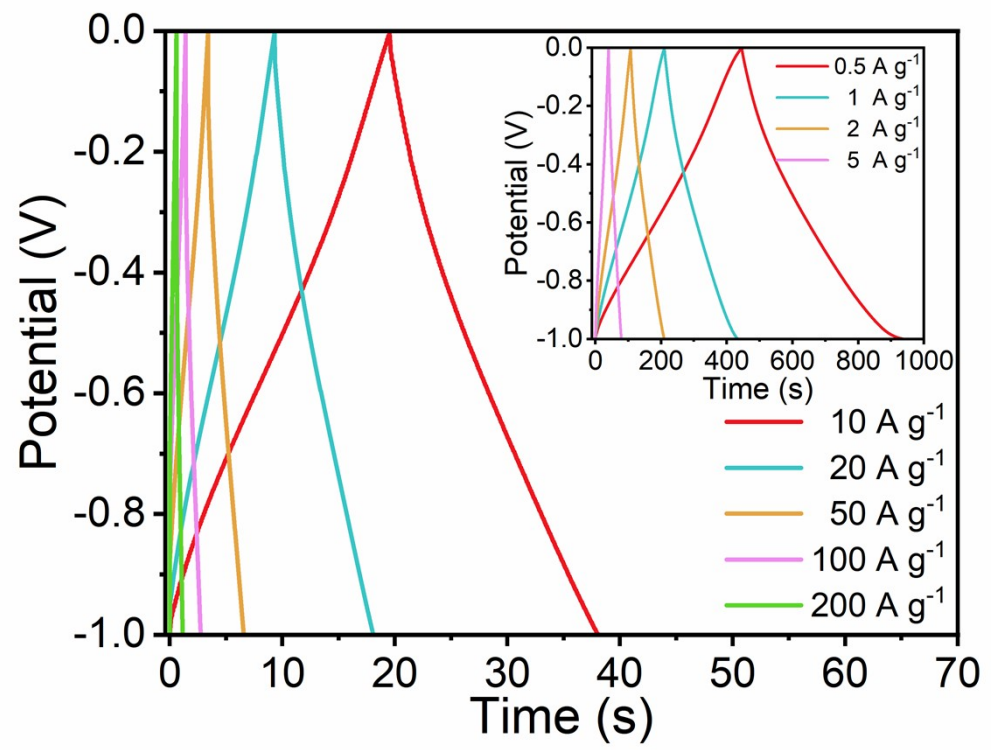

Fig. S11 GCD curves of PDKP-700 at different current densities.

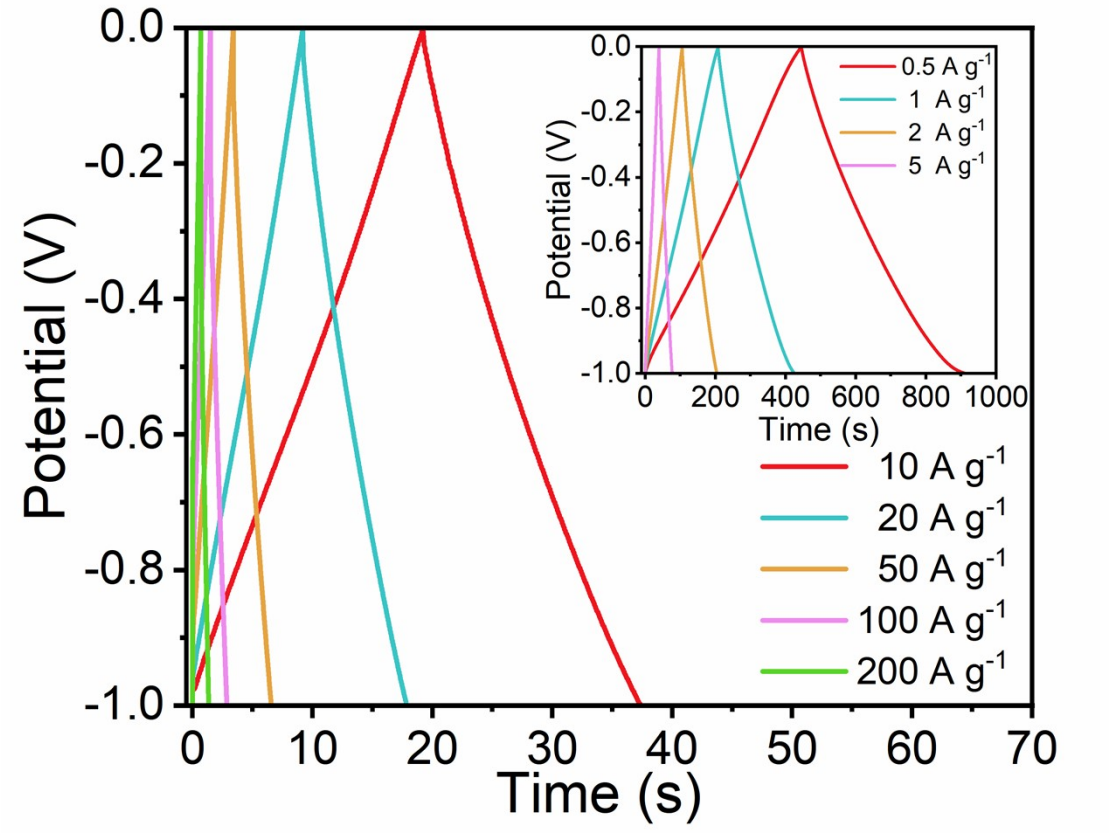

Fig. S12 GCD curves of PDKP-900 at different current densities.

Table S3 Specific capacitances and rate capacities of PDKP-700, PDKP-800 and PDKP-900.

Current density ($A\ g^{-1}$)	Specific capacitance ($F\ g^{-1}$) and rate capacity (%)		
	PDKP-700	PDKP-800	PDKP-900
0.5	245.8 100%	305.7 100%	234.55 100%
1	222.5 90.5%	297.3 97.3%	217.6 92.8%
2	204 83%	250.4 81.9%	197.6 84.2%
5	193 78.5%	233.5 76.4%	187.5 79.9%
10	186 75.7%	222.7 72.9%	181 77.2%
20	175.2 71.3%	210.6 68.9%	172.8 73.7%
50	158 64.3%	189.5 62%	158 67.4%
100	132.8 54%	170 55.6%	137.4 58.6%
200	111.2 45.2%	154 50.4%	130 55.4%

Table S4 The comparison of the capacitance of carbon materials.

Samples	SSA [$m^2 g^{-1}$]	electrolyte	C_g [$F g^{-1}$]	Ref.
PDKP-800	3352.8	6 M KOH	305.65 (0.5 A g^{-1})	This work
			210.6 (20 A g^{-1})	
			170 (100 A g^{-1})	
			154 (200 A g^{-1})	
PAN/Lignin-800-1	2041	6 M KOH	325. 7 (0.5 A g^{-1})	1
			182.2 (20 A g^{-1})	
HPCNFs-3-1	679	6 M KOH	251 (0.5 A g^{-1})	2
			160 (20 A g^{-1})	
NPCNFs/PANI-1.0	285	1 M H2SO4	275 (0.5 A g^{-1})	3
			165 (8 A g^{-1})	
HPCs-750	1579	6 M KOH	314 (0.5 A g^{-1})	4
			237 (20 A g^{-1})	
PAN-C1	2348.7	6 M KOH	282.7 (0.5 A g^{-1})	5
			219 (10 A g^{-1})	
PPLCNFs-0.5g	364	6 M KOH	233 (0.5 A g^{-1})	6
			127 (100 A g^{-1})	
HTPC	1508	6 M KOH	278 (1 A g^{-1})	7
			248 (20 A g^{-1})	
			208 (100 A g^{-1})	
HOMC	2033	6 M KOH	286 (0.2 A g^{-1})	8
			206 (20 A g^{-1})	

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