Supplementary Information (SI) for Green Chemistry.

Supporting information for

Utilize rather than create: transforming phthalonitrile resin into N-rich hierarchical porous carbon for supercapacitor materials

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Content of Supporting Information

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The preparation of working electrode:

When preparing the working electrode, the DMF solution of polytetrafluoroethylene (concentration 10 mg/ml) was prepared, and carbon black was used as the conductive additive and polytetrafluoroethylene(PTFE) was used as the adhesive. The weight ratio of synthetic carbon material (active material), carbon black and PTFE is 8:1:1. After ultrasonic mixing, a proper amount of solution was dripped on carbon paper and dried at 80 ℃ for 12 h. This working electrode is assembled into a three-electrode system including an additional platinum counter electrode (2×2 cm^2) and a Hg/HgO reference electrode. The electrolyte is 1 M KOH.

Electrochemical performance measurements:

For the three-electrode system, the specific capacitance (C_g, F g^{-1}) was calculated from GCD curves according to the following equation (1):

$$C_g = \frac{\mathrm{I}/m}{\Delta \mathrm{V}/\Delta \mathrm{t}} \tag{1}$$

where I (A) is the current, m (g) is the mass of porous carbon, Δt is the discharge time, and ΔV is the voltage change during discharge. The frequency range of EIS measurement is 100 kHz to 0.01 Hz.

Table S1. C, N and O contents of RKCs based on XPS survey spectra.

Samples	C (%)	N (%)	O (%)
RKC@500	79.82	2.25	17.94
RKC@600	78.49	1.82	19.69
RKC@700	78.32	1.42	20.26
RKC@800	80.24	0.88	18.88
RKC@900	77.33	0.96	21.71

Table S1 lists the elemental ratios of C, O and N in all the porous carbon samples, showing that the nitrogen content decreased from 2.25% of RKC@500 to 0.96% of RKC@900, which may be closely related to temperature and KOH corrosion. With the increase of temperature, the decrease of nitrogen doping may have a negative impact on electrochemical performance.

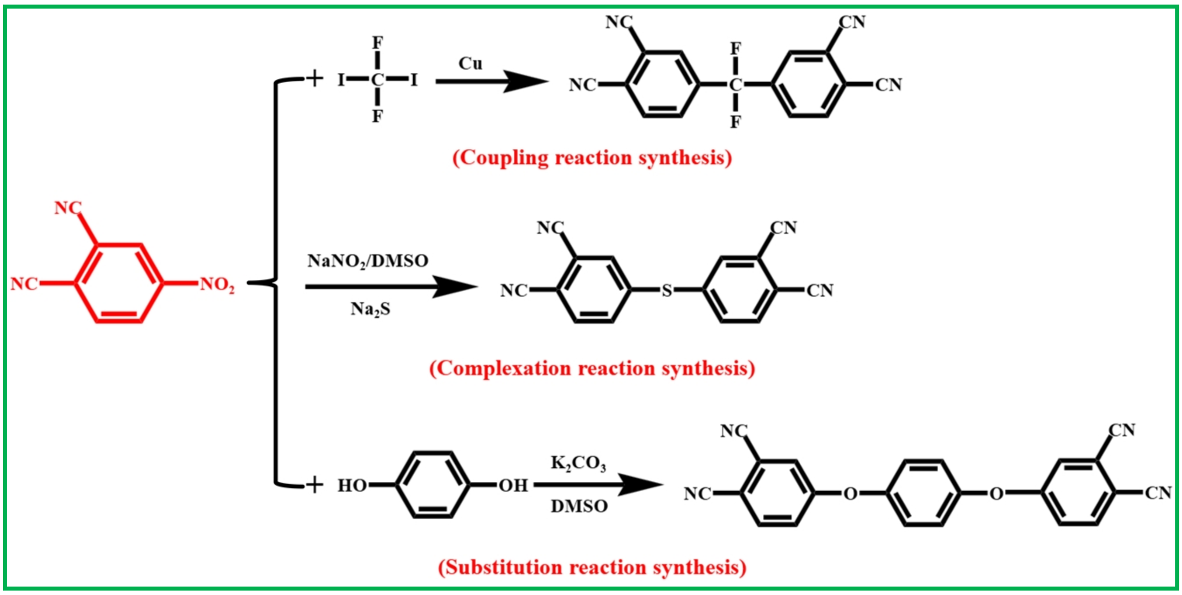


Fig. S1 Typical examples of synthesis methods of PN resin monomers reported in literature.[1, 2, 3]

PN resin boasts a high degree of molecular design flexibility, which can be synthesized via coupling, complexing or substitution reaction [1-3], as depicted in **Fig. S1.** The coupling reaction method is seldom used for synthesizing PN monomers due to its demanding conditions, narrow product scope, and low yields. Moreover, it provides limited design flexibility for PN structures, which is insufficient for complex molecular engineering. While complexation reactions offer a simpler synthesis approach, they are marred by complicated product separation processes. Importantly, this method involves Na_2S, a hazardous material that can produce toxic hydrogen sulfide when exposed to air. This poses a significant safety concern. Additionally, complexation reactions are limited in their molecular design capabilities, making them less favored. On the other hand, the substitution reaction, conducted from 4-nitrophthalonitrile and phenol under the catalysis of potassium carbonate (K_2CO_3) in polar solvent, has become the predominant method. It is favored for its mild reaction conditions, straightforward purification and separation, and notably, its flexibility in molecular design due to the rich availability of phenol [4,5]. It is noteworthy that all three methods use 4-nitrophthalonitrile as a starting material and the current synthesis of PN is marred by the generation of the hazardous nitrite-containing by-product that poses significant environmental, safety, and health hazards.

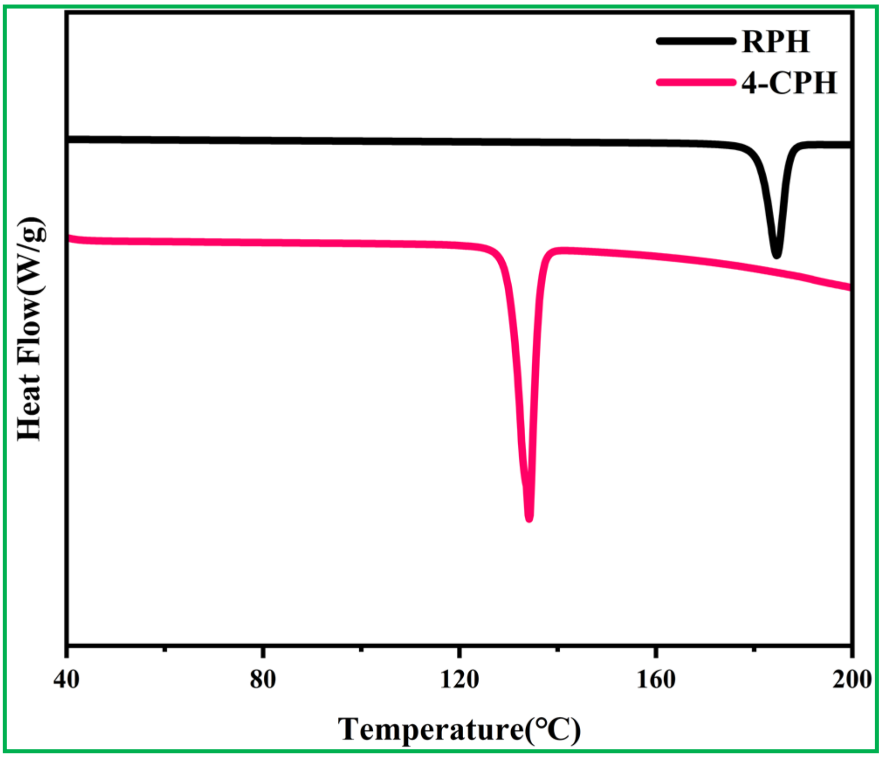
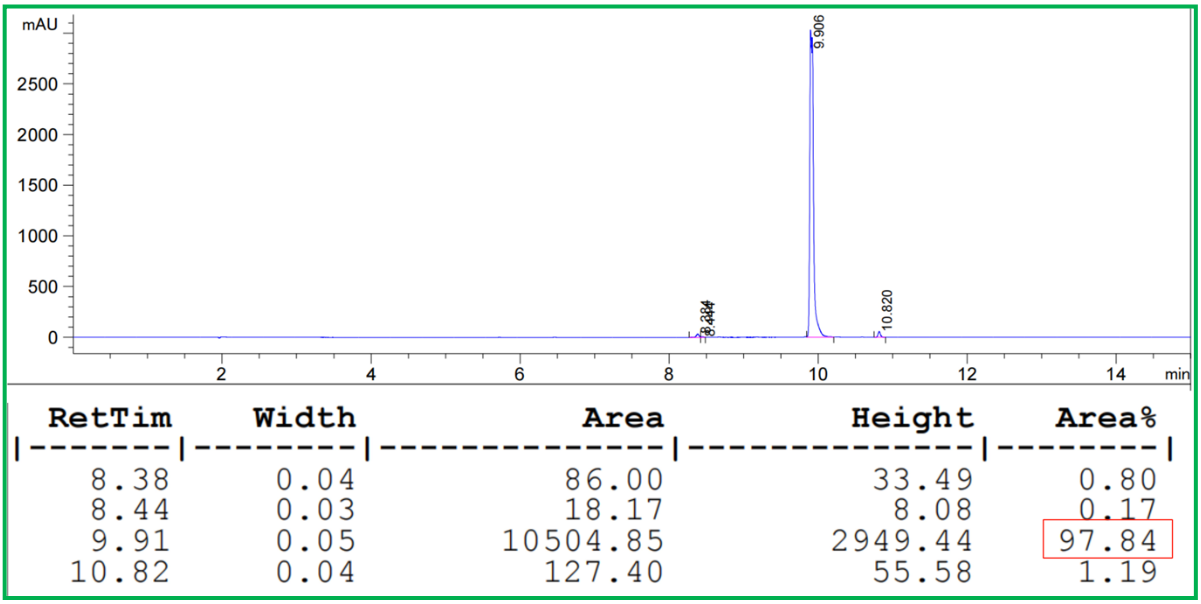


Fig. S2 DSC curves of RPH and 4-CPH.

As shown in **Fig. S2**, no melting peak for 4-CPH is detectable in DSC curve of RPH, suggest a thoroughly removal of unreacted 4-CPH.



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  RetTim     Width          Area          Height     Area%
|-------|---------|--------------|--------------|---------|
   8.38      0.04          86.00          33.49      0.80
   8.44      0.03          18.17           8.08      0.17
   9.91      0.05       10504.85        2949.44     97.84
  10.82      0.04         127.40          55.58      1.19
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Fig.S3 High performance liquid chromatography (HPLC) of RPH.

Fig. S3 shows that the purity of RPH is close to 98 %. This purity is relatively high to thermosetting monomer.

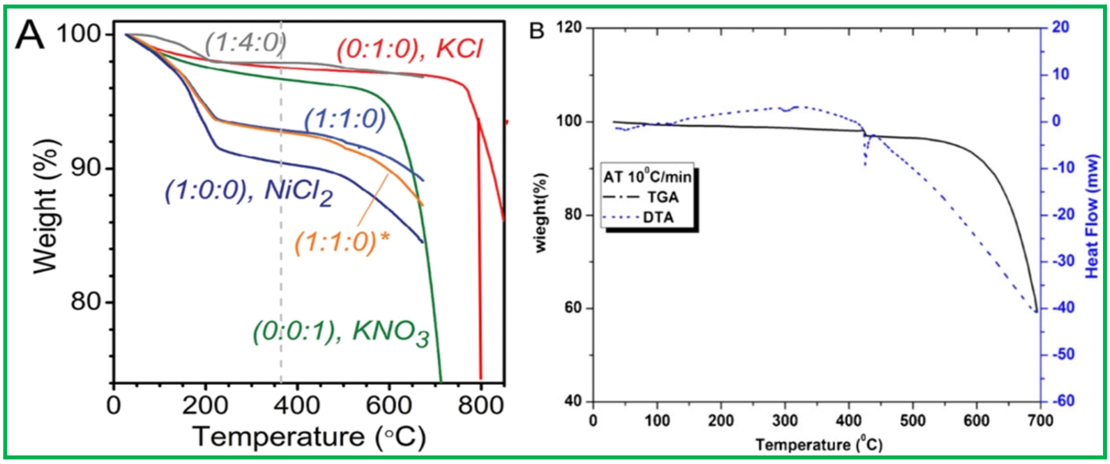

Fig. S4 Thermogravimetricanalyses (TGA) of (A) KCl and (B) KNO_2.[6, 7]

As shown in **Fig. S4**, it is reported that KCl maintains a residual weight of over 95% around 800 °C, demonstrating excellent thermal stability [6]. In contrast, KNO_2 begins to lose weight at approximately 350 °C, releasing a significant amount of NO_2 before this temperature, and has a residual weight of less than 60% at 700 °C [7]. Because the use environment of PN resin is usually above 300 °C [8, 9], this will lead to the decline of the performance of the final PN product. Furthermore, it has been reported that KNO_2 can explode around 537 °C [10], posing potential hazards.

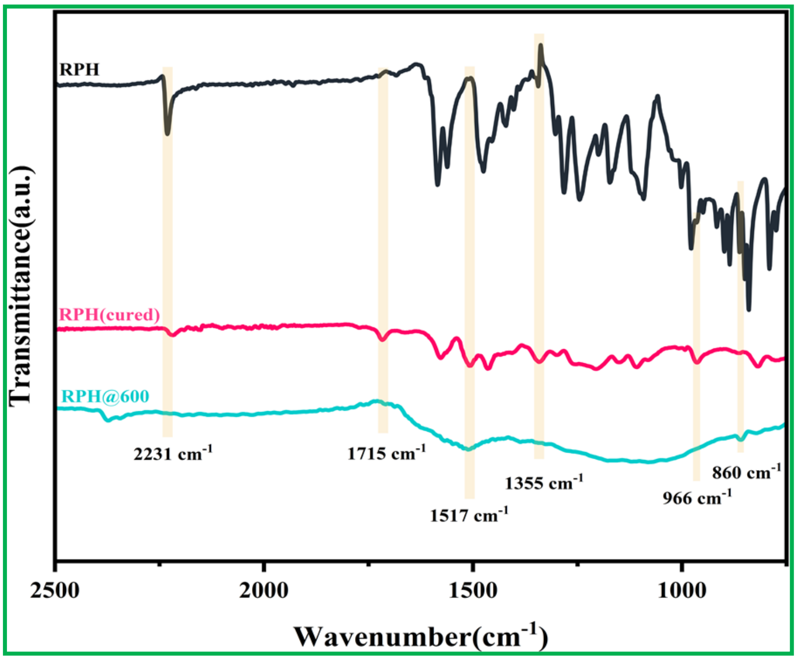

Fig. S5 FT-IR spectra of RPH, RPH(cured) and RKC@600.

Fig. S5 shows the infrared spectra of RPH, RPH(cured) and RPH@600 samples. For RPH(cured) samples, the vibration peak intensity of -CN at 2231 cm^{-1} is significantly lower than that of monomer RPH. Furthermore, the appearance of new peaks at 1517 cm^{-1} and 1355 cm^{-1} reflects the formation of triazine ring structure of RPH during polymerization [11]. In addition, it is worth noting that indoline (1715 cm^{-1}) and phthalocyanine (966 cm^{-1}) are also the main products in the polymerization process [12], which will lead to different N doping in porous materials. With the increase of treatment temperature, the one-pot process including polymerization, carbonization and activation was also monitored by FT-IR. The results showed that the polymerization could be effectively promoted with heating. Due to high temperature carbonization and KOH corrosion, the peak strength of nitrogen heterocyclic products gradually decreased.

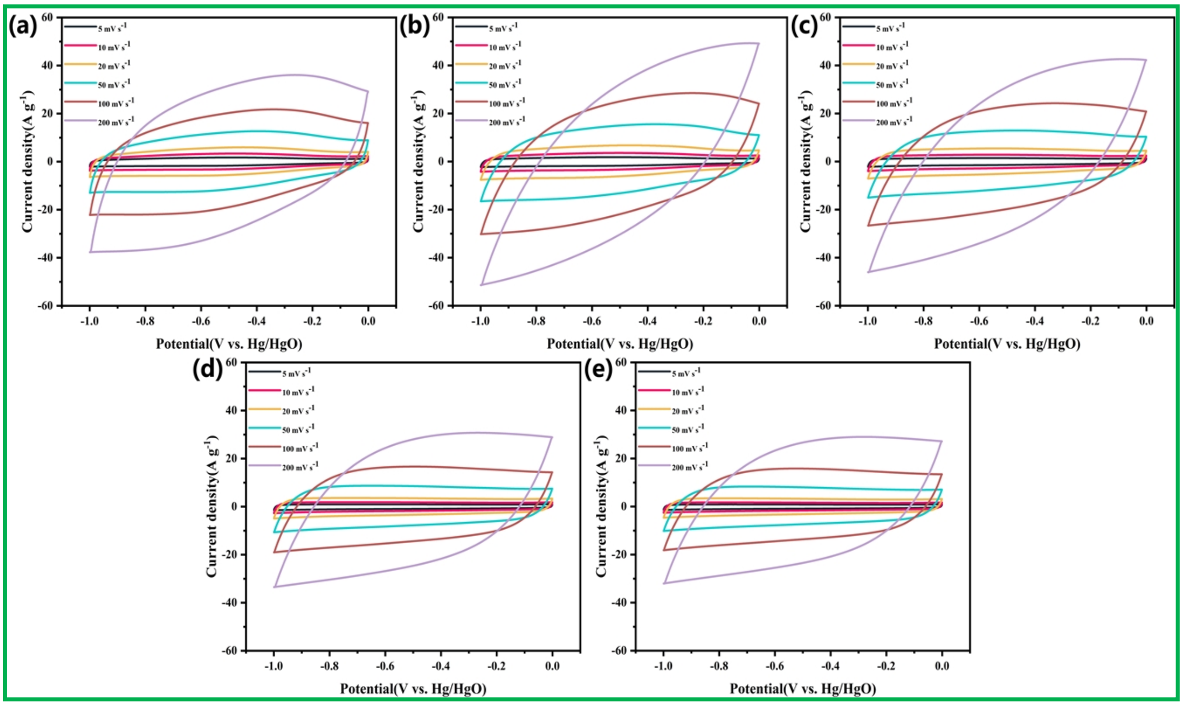

Fig. S6 CV curves of (a) RKC@500, (b) RKC@600, (c) RKC@700, (d) RKC@800 and (e) RKC@900 at different scan rates

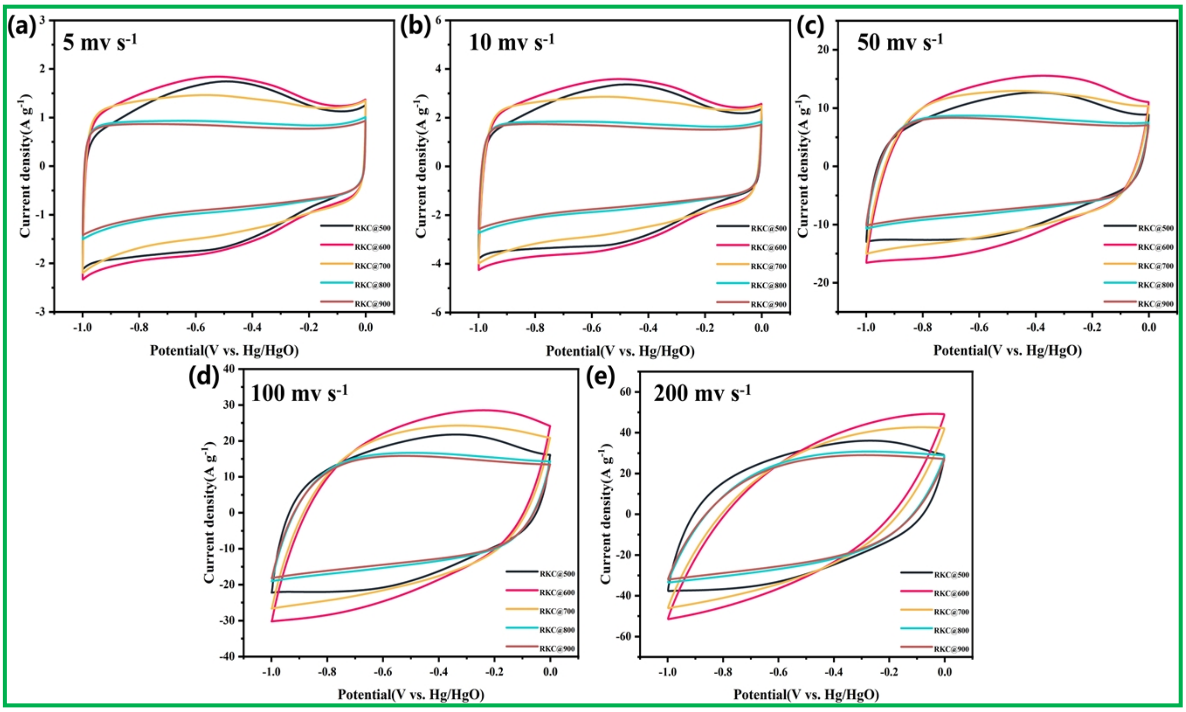

Fig. S7 CV curves of different electrodes at a scan rate of (a) 5 mV s^{-1} (b) 10 mV s^{-1}, (c) 50 mV s^{-1}, (d) 100 mV s^{-1}, and (e) 200 mV s^{-1}

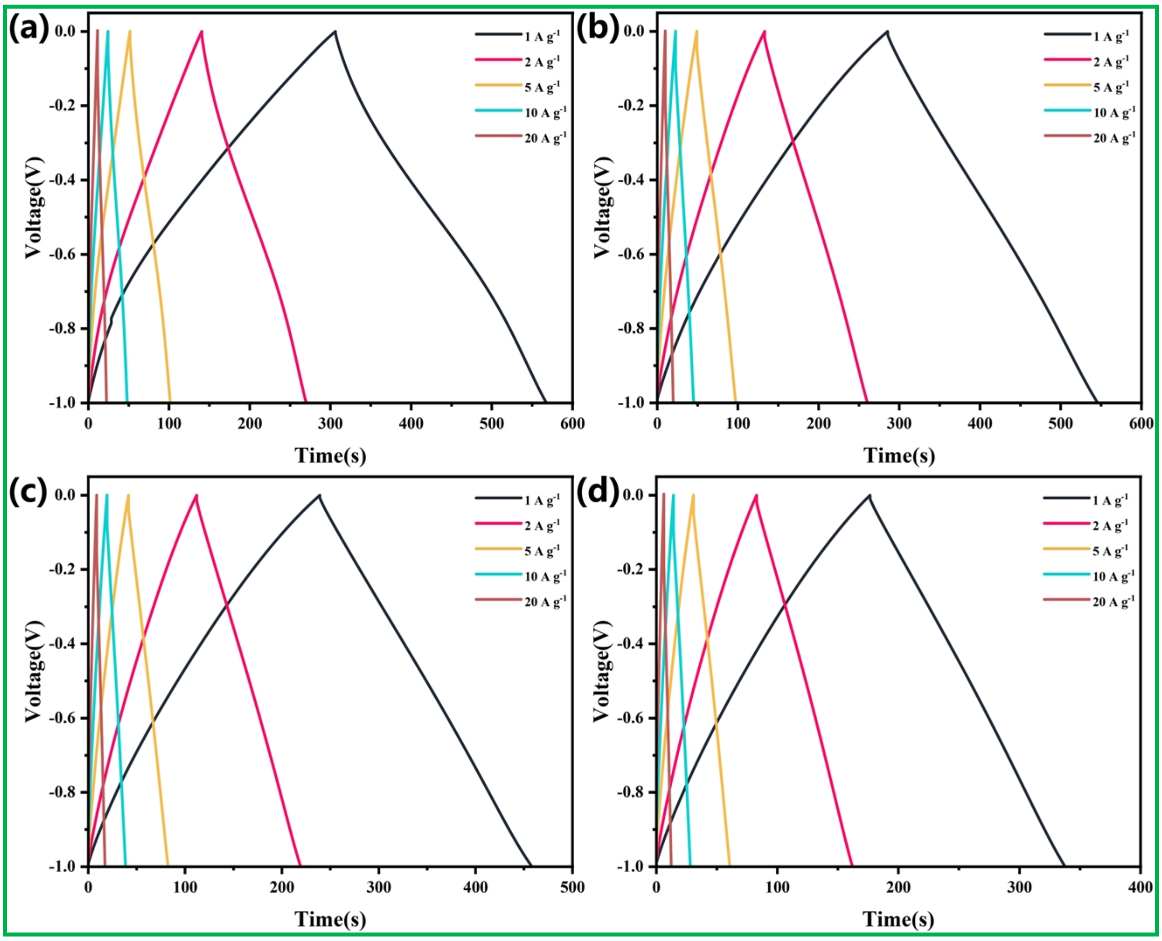

Fig. S8 GCD curves of (a) RKC@500, (b) RKC@700, (c) RKC@800 and (d) RKC@900 at different current densities

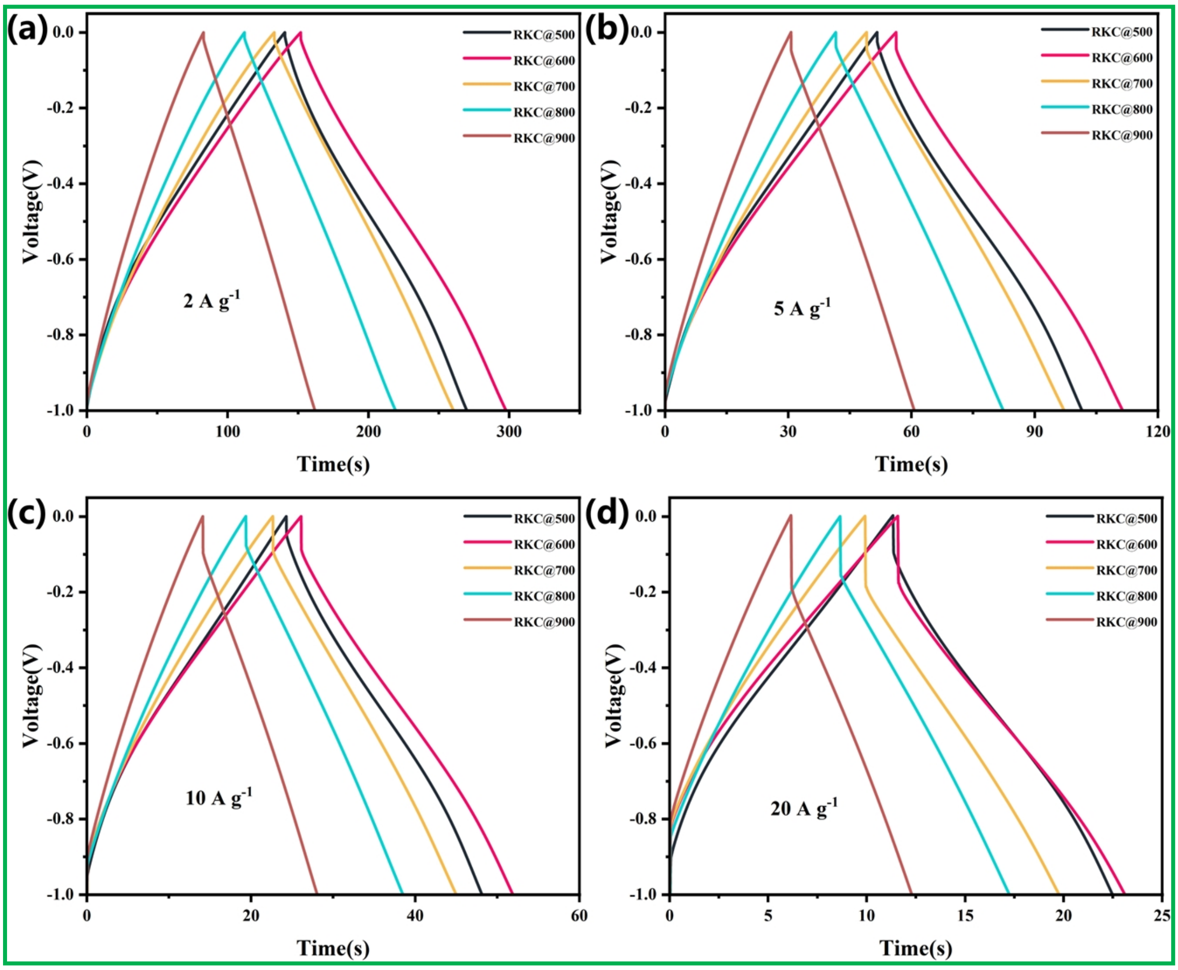

Fig. S9 GCD curves of different electrodes at the current density of (a) 2 A g^{-1}, (b) 5 A g^{-1}, (c) 10 A g^{-1} and (d) 20 A g^{-1}

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