Supporting Information

Renewable Graphene-Like Nitrogen-Doped Carbon Nanosheets as Supercapacitor Electrodes with Integrated High Energy–Power Property

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Figure S1. The FESEM images of shrimp shell (a) and RGNC (b).



Figure S2. TGA and DTG curves of dried shrimp shells. The first weight loss around 200°C is ascribed to the exclusion of adsorbed water. The second (300-400°C) and third (around 700°C) weight losses are mainly the decomposition of biopolymers to chars. With the temperature higher than about 750°C, the gradual weight loss is attributed to the elimination of heteroatom groups from chars. The carbonization temperature is the key factor for pore structures and nitrogen-doped content of result carbons. The carbons with a good balance of surface area and nitrogen content may be obtained at 800°C.



Figure S3. FETEM images at the edge of chars from carbonized shrimp shell. The chars were obviously embedded by hard phases of laminated or granular calcium carbonates as the template and auto-activation agents, which can be successfully removed by washing with dilute acid.



Figure S4. XPS analyses of the chars carbonized from shrimp shell, RGNC and RGNC-NS. The chars carbonized from shrimp shell contain mainly carbons (285 eV), nitrogen (400 eV) and oxygen (532 eV), as well as calcium (348 eV) and phosphorus (133 eV) from the calcium carbonate and slight hydroxyapatite. Those inorganic salts were removed by washing with dilute acid, confirmed by the XPS curves of RGNC and RGNC-NS without the calcium and phosphorus peaks.



Figure S5. The C 1s and N 1s spectra of RGNC. As shown in the deconvoluted C1s spectrum, the high percentage of sp² C indicates that the conjugated graphitic domains are built successfully during the carbonization process. The C-N peak demonstrates the successful incorporation of nitrogen groups to carbon framework. The percentage of different nitrogen groups is shown in Table 2.



Figure S6. CV curves and charge-discharge voltage profiles of the RGNC-NS-SC (a and c) and RGNC-SC (b and d) in 6 M KOH. To avoid the overestimation of the specific capacitance for the samples, only the upper half of the discharge curves was used to determine the capacitance value. As a result, in aqueous electrolyte the RGNC-SC exhibits a specific capacitance of 219 F g⁻¹ at a low current density of 0.5 A g⁻¹ lower than a value of > 330 F g⁻¹ that was calculated from the whole discharge curve. The outcome is attributed that the lower half of the discharge voltage profile is obviously distorted (Figure S6d) because of the existence of pseudocapacitance in consistent with the CV analysis (Figure S6b). Whereas, a high specific capacitance of 322 F g⁻¹ at 0.5 A g⁻¹ was obtained for RGNC-NS-SC due to the more linear discharge voltage profile (Figure S6c).

The nearly rectangular CV curves and symmetrically linear charge/discharge voltage profiles of RGNC-NS-SC even at high rates (Figure S6a and c) indicate a mainly significant capacitance contribution from the double-layer capacitance superimposed with a partial pseudocapacitance.^[S1-53] The observation is further confirmed by the EIS analysis of RGNC-NS-SC with a most vertical curve in low-frequency region indicating a significant double-layer capacitance behavior (Figure 3e).^[S1] The less than 5% capacitance loss and close 100% Coulombic efficiency after 20 000 cycles at 10 A g⁻¹ was obtained for RGNC-NS-SC, also demonstrating that the outstanding performance is not mainly ascribed to parasitic reactions.^[S4] This is attributed that the high-aspects-ratio graphene-like structures with a good integration of specific surface area (1946 m² g⁻¹) and nitrogen-doped content (8.75 wt.%) in the RGNC-NS can enhance ionic/electronic transports and surface charge storage capacity, a feature which is still desired in synthesis of advanced nitrogen-doped supercapacitor electrodes.^[S2] The results are consistent with the observation of reported nitrogen-doped carbon nanocages (7.9% N and 1794 m² g⁻¹ specific

surface area)^[S1] and nitrogen-doped mesoporous few-layer carbons (8.2~11.9% N and ~1580 m² g⁻¹ specific surface area),^[S3] which also show rectangular CV curves and symmetrically linear charge-discharge voltage profiles in symmetric twoelectrode basic electrolyte systems.

In contrast, RGNC-SC exhibits the quasi-rectangular CV curves with one pair of prominently wide redox peaks (Figure S6b) and curved charge/discharge voltage profiles under 0.5 V (Figure S6d) at low rates but severe distortion at high rates, indicating a major capacitance contribution from pseudocapacitive which is inefficient in the symmetric electrochemical system.^[53, 55] The outcome is further confirmed by EIS analysis with a distorted curve in low-frequency region and large EDR (Figure 3e). It is attributed to the RGNC with high nitrogen-doped content (9.04 wt.%) but low specific surface area (446 m² g⁻¹). Furthermore, a high content of pyridinic nitrogen of 36.04% was achieved for RGNC compared with 25.55% for RGNC-NS based on the deconvolution of XPS N1s spectrum (Table 2). The pyridinic nitrogen could generate more pseudocapacitance effects than the other nitrogen functionalities due to only two electrons involved in the electrochemical process.^[S5, 56] The higher heteroatom-doped content of 16.2 wt.% was also obtained for RGNC than 15.3 wt.% for RGNC-NS (Table 2). These observations are in agreement with reported carbonized eggshell membrane (8% N and 221 m² g⁻¹ specific surface area)^[S7] and nitrogen-doped porous carbon monolith (11.9% N and 679 m² g⁻¹ specific surface area).^[S6]



Figure S7. (a) The area-normalized capacitances, and (b) electrode specific capacitance C_{electr} versus square root of charge/dischage time of the RGNC-NS-SC and RGNC-SC in 6 M KOH at current densities from 1 to 100 A g⁻¹.

The area-normalized capacitances C_{area} were calculated using the formula $C_{area} = C_{electr}/S_{BET}$, where C_{electr} is the electrode specific capacitance and S_{BET} is the specific surface area of active electrode materials. The area-normalized capacitance of RGNC-NS-SC is to 12.4-16.5 μ F cm⁻² (Figure S7a), which is well comparable to the theoretical double-layer capacitance of 15-25 μ F cm⁻².^[S7, S8] But the area-normalized capacitance of RGNC-SC is obviously higher than 49.5-16.3 μ F cm⁻² (Figure S7a) due to a low S_{BET} value and a primary capcitance contribution from pseudocapacitance, which is in good agreement with same reported nitrogen-doped carbons, e.g., egg white-derived carbon of 48.5-29.1 μ F cm⁻².^[S8] and melaminederived carbon of 441-33 μ F cm⁻².^[S9]

The charging/discharging kinetic analysis was shown in Figure S7b. The electrode specific capacitance C_{electr} can take the form of $C_{\text{electr}} = k_1 + k_2 t^{1/2}$ where k_1 is a rate-independent component for reversible supercapacitance and $k_2 t^{1/2}$ is a diffusion-limited component controlled by the charge/dischage time t (s).^[S3] The k_1 can be obtained at the $t^{1/2} = 0$ intercept with the vertical axis. As showing in Figure S7b, the rate-independent component k_1 of RGNC-NS (~275 F g⁻¹) dominated the total C_{electr} , giving a high rate capability. However, the rate-independent component k_1 (< 140 F g⁻¹) of RGNC is obviously lower percentage in total C_{electr} , further suggesting the dominance of diffusion-limited component. Thus an obviously high rate capability of 75% was obtained for RGNC-NS-SC (holding 241 F g⁻¹) compared with 33% for RGNC-SC (holding 72 F g⁻¹) at a high current density of 100 A g⁻¹.



Figure S8. The charge/discharge voltage profiles of RGNC-NS-SC at a low current density of 0.5 A g^{-1} in the IL mixture electrolyte under different operating voltage windows from 2.5 to 4 V. The corresponding Coulombic efficiencies are of 99.8% for 2.5 V, 98.5% for 3 V, 81.3% for 3.5 V and 59.6% for 4 V, respectively.



Figure S9. (a) The charge/discharge voltage profiles at 0.5 A g^{-1} , (b) charge/discharge voltage profiles at current densities from 0.5 to 20 A g^{-1} , (c) CV curves at scan rates from 100 to 2000 mV s^{-1} , and (d) weight-normalized specific capacitances for RGNC-SC in the IL mixture electrolyte.

Using the operating voltage window of 3 V, a highly asymmetric charge/discharge voltage profile was presented for the RGNC-SC at low current density of 0.5 A g⁻¹, giving rise to a low Coulombic efficiency of 66.2 % (Figure S9a). But a stabilized RGNC-SC system could be obtained by using a small operating voltage window of 2.5 V, where the Coulombic efficiency is of >98%. The charge-discharge voltage profiles (Figure S9b) and CV curves (Figure S9c) of RGNC-SC indicate the low-rate supercapacitive performances with low capacitance values compared with RGNC-NS-SC. This is attributed the stacked multilayer structures with low specific surface area and inefficient ionic pathway especially in high viscosity IL electrolyte.



Figure S10. (a) The Nyquist plots and (b) the Bode plots of phase angle versus frequency for RGNC-NS-SC and RGNC-SC in the IL mixture electrolyte.

The ESR, R_{ct} and total cell resistance of RGNC-NS-SC is 0.82, 0.53 and 2.28 Ω in the IL mixture electrolyte system, respectively, while those of RGNC-SC is 0.90, 3.61 and 7.08 Ω . Furthermore, in the medium- to low-frequency region (insert of Figure S10a) the smaller EDR and more vertical curve were observed for RGNC-NS-SC than that of RGNC-SC, suggesting a better supercapacitive behaviour in the former. The characteristic frequency f_o was obtained of 1.69 Hz for RGNC-NS-SC and 0.31 Hz for RGNC-SC, corresponding to the relaxation time constant τ_o of 0.59 and 3.22 s, respectively.



Figure S11. CV curves of RGNC-NS-SC in two individual ILs and their IL mixture electrolytes at 5 mV s⁻¹ (a) and 50 mV s⁻¹ (b) under ambient condition.

As shown in Figure S11, the obvious increase of the capacitance response near the low- and high-voltage limits, or the appearance of small reaction peaks in the voltage windows were observed in both individual IL systems especially at low scan rate of 5 mV⁻¹. This indicates the existence of electrolyte decomposition, which could be ascribed to the different charge storage capacity of the two symmetric electrodes toward the cation and anion of the individual ILs that creates the asymmetry operating potential windows in the positive and negative electrodes.^[S10] Compared to the individual IL systems, the CV curves in the mixture IL is flat without obvious reaction peak, signifying almost no electrolyte decomposition in favor of cyclic stability.



Figure S12. The Ragone plots of RGNC-NS-SC and RGNC-SC in 6 M KOH (a) and in IL mixture electrolyte (b). The RGNC-NS-SC always exhibits higher energy–power properties than that of RGNC-SC, due to its unique high-aspect-ratio graphene-like nitrogen-doped nanosheet microstructures.

 Table S1. Comparison of the symmetric supercapacitive performance of RGNC-NS with that of the reported state-of-the-art

Electrode material	S _{BET} ^{a)} [m ² g ⁻¹]	N content	Electrolyte	C ^{b)} [F g ⁻¹] / / ^{c)} [A g ⁻¹]	Rate capability	Cyclic stability	Ref
Carbonized chicken eggshell membranes	221	8 wt%	1 M KOH	297 / 0.2 ^{d)} 196 / 20	66% (10 A g ⁻¹)	97% (10 000, 4 A g ⁻¹)	[11]
Hierarchical nitrogen- doped carbon nanocages	1794	7.9 at%	6 М КОН	313 / 1 234 / 100	75% (100 A g ⁻¹)	98 % (20 000, 10 A g ⁻¹)	[56]
Functional carbon derived from dead	1230		$1 \text{ M H}_2\text{SO}_4$	400 / 0.5 258 / 10	64.5% (10 A g ⁻¹)		[44]
Mesoporous nitrogen-rich carbons from egg white protein	805.7	10.1 wt%	$1 \text{ M H}_2\text{SO}_4$	390 / 0.25 ^{d)} 265 / 30	67.9 % (30 A g ⁻¹)	93 % (10 000, 2 A g ⁻¹)	[54]
Human hair-derived carbon flake	1306	4.38 at%	6 М КОН	445 / 0.5 ^{d)} 128 / 80	27.8% (80 A g ⁻¹)	98 % (20 000, 2 A g ⁻¹)	[12]
Functionalized activated carbons from egg white	1217	6.5 wt%	1 M KOH	525 / 0.25 ^{d)} 297 / 30	56. 6% (30 A g ⁻¹)	90.6% (10 000, 2 A g ⁻¹)	[53]
Nitrogen-doped graphene		1.86 at%	6 М КОН	282 165 / 33	58.5% (33 A g ⁻¹)	>70% (230 000, 2 A g ⁻¹)	[31]
Graphene/polyaniline nanofiber	~ 20		2 M H ₂ SO ₄	260 / 0.5		70 % (1 000, 1.5 A g⁻¹)	[S11]
Biochar nanosheets from corn cob	543.7	1.2 at%	0.5 M H₂SO₄	221 / 0.5 ^{d)}	78% (40A g ⁻¹)	97% (5 000,)	[S12]
Porous carbon nanosheets from gelatin	2774	0.5 at%	6 М КОН	228/1	83% (40A g ⁻¹)		[S13]
Porous carbon nanosheets from gelatin	2774	0.5 at%	1 M TEABF ₄ /AN	106 / 1	81% (40A g ⁻¹)		[S13]
Interconnected carbon nanosheets from hemp	1505		BMPY TFSI	139/1	72% (100A g ⁻¹)	96% (10 000, 10 A g ⁻¹)	[21]
Human hair-derived carbon flake	1306	4.38 at%	1 M LiPF ₆ /(EC/DEC)	126 / 1 107/2			[12]
Porous carbon nanosheets from coffee grounds	1945	4.1 at%	BMIM BF ₄ /AN	121 / 0.5 55.3 / 20	45.7% (20 A g ⁻¹)	90.5% (5 000, 1 A g⁻¹)	[49]
Nitrogen-doped carbon nanosheets from silk	2494	4.7 wt%	EMIMBF ₄	242 / 0.1 155 / 10	64% (10 A g ⁻¹)	92 % (10 000, 2 A g ⁻¹)	[10]
RGNC-NS	1946	8.75 wt%	6 М КОН	322 / 0.5 241 / 100	75% (100 A g ⁻¹)	98.3% (20 000, 10 A g ⁻¹)	Our
			IL mixture	162 / 0.5 95 / 80	59% (80 A g ⁻¹)	93.2% (8 000, 5 A g ⁻¹)	work

IL mixture 95 / 80 (80 Å g⁻¹) (8 000, 5 Å g⁻¹) ^{a)} S_{BET} is the specific suface area. ^{b)} C is weight-normalized specific capacitance. ^{c)} / is the current density. And ^{d)} the specific capacitance was obtained from the three-electrode system, which is 15-20% higher than that obtained from two-electrode setup, and the others were obtained from the two-electrode system.

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