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Nitrogen-containing graphene networks with high volumetric capacitance and exceptional rate capability

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ABSTRACT

Graphene has attracted more attention as advanced electrodes for supercapacitors due to its unique geometry structure and outstanding physicochemical property. But its low specific capacitance, especially low volumetric capacitance, has greatly restricted the practical application of graphene electrode materials. Herein, we synthesized nitrogen-containing graphene networks by using 2, 3-diaminopyridine (O-DAP) as functional agent in a facile hydrothermal route. During the hydrothermal process, not only the pyrrolic-N, but also the pyrazine-N is produced in the graphene lattice at the edge/defect site of graphene because of the double $-NH_2$ in DAP reactant. Owing to the high nitrogen content (17.5 at%), special nitrogen configuration, and high density (1.66 g cm⁻³), the N-containing graphene networks present high gravimetric capacitances up to 353 F g^{-1} and high volumetric capacitances over 586 F cm^{-3} in $1 \text{ M} \text{ H}_2\text{SO}_4$ electrolyte. More remarkably, the N-containing graphene electrodes exhibit exceptional rate capability with a capacitance retention of 80.6% at a high current density of 20 A g^{-1} and good cycling stability of 91.5% retention after 5000 cycles in a symmetrical two-electrode configuration.

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1. Introduction

Graphene is an attractive electrode material for supercapacitors due to its high theoretical specific capacitance (550 F g⁻¹), superior electrical conductivity (10^7 S m⁻¹), and good mechanical stability [1]. However, most pure graphene-based materials deliver small specific capacitances (below 200 F g⁻¹) because of irreversible agglomeration during the fabrication process [2]. Creating "porous graphene" has been recognized as a promising strategy to improve the mass specific capacity of graphene electrode materials [3]. The porosity of graphene could either come from the holes or pores in the graphene mesh surface [4–7], or from the three-dimensional network structure of graphene lamellae, such as aerosols [8–10], hydrogels and foams [11–13]. Unfortunately, the density of those porous graphene is generally less than 0.5 g cm⁻³ [14] (some even lower than 0.1 g cm⁻³ [9,12]), leading to a low volumetric capacity. Since supercapacitors are usually employed in a limited space, such

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as mobile electronics and electric vehicles, the volumetric capacity is a more important metric than gravimetric ones for practical application of supercapacitors.

Recently, numerous experimental studies [15-23] have shown that functionalizing and/or doping graphene with nitrogen can not only modulate local electronic structures and improve the electrical conductivity, but also facilitate the access of electrode surface area to the electrolyte ions. Taking advantage of abundant functionalities on graphene oxide (GO) surface. N-containing graphene can be easily synthesized in large scale by hydrothermal or solvothermal treatment of GO with nitrogen containing precursors. Various nitrogen containing molecules, such as non-aromatic diamine/triamine [15], phenylenediamine [16,17], hydroxylamine [18], formamide [2], ammonium bicarbonate [19], urea [20,21], hexamethylenetetramine [22], amitrole [23] et al., have been utilized as the nitrogen source for N-containing graphene. Despite its improved gravimetric performance, N-containing graphenes, in most cases, remains have low volumetric performance because of their porous structure as a result of well-spaced graphene framework or activation. Depressing the porosity of N-containing graphenes is expected to assure high density and high volumetric capacitance, but the rate performance would be limited due to the







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long ion diffusion path. Hence, it is still a big challenge to obtain graphene-based electrode materials with both high volumetric capacity and good rate capability.

It has been found that nitrogen characteristic configuration, such as pyrrolic-N, pyridinic-N, and quaternary-N, has significant influence on the electrochemical performance of N-containing graphene [20]. For examples, pyridinic-N and pyrrolic-N have been proven to improve the charge mobility and increase the capacitance through its reversible redox reaction especially in aqueous electrolytes, whereas quaternary-N could increase the electrical conductivity of graphene. Moreover, the nitrogen content and functional sites also play an important role in their performance, especially in terms of improving the rate capability [24]. In this work, N-containing graphene network (up to 17.5 at%) was successfully fabricated by employing 2, 3-diaminopyridine (O-DAP) as functional agent. The chemical interaction between monomers and GO and nitrogen configurations in graphene on the charge transport properties were experimentally studied. The specific surface of N-containing graphene was significantly reduced due to an accelerated restacking phenomenon with functionalizing process [25]. Even with a reduced specific surface area $(43 \text{ m}^2 \text{ g}^{-1})$, the N-containing graphene presents a considerably improved electrochemical performances with a high specific capacitance (up to 353 Fg^{-1} and 586 Fcm^{-3} at 0.1 Ag^{-1} in $1 \text{ MH}_2\text{SO}_4$ electrolyte measured in three-electrode system, $263 F g^{-1}$ at $0.5 A g^{-1}$ measured in two-electrode system), exceptional rate capability $(212 \text{ Fg}^{-1} \text{ at } 20 \text{ Ag}^{-1} \text{ in two-electrode system})$, and good cycling stability (91.5% retention after 5000 cycles).

2. Experimental section

2.1. Synthesis of N-containing graphene networks

GO was prepared through a modified Hummers process with natural graphite powder (average particle size of $20 \,\mu m$) [26]. The N-containing graphene was synthesized as follows. First, a homogeneous GO solution was prepared by dispersing 160 mg GO and 0.2 mL ammonia solution in 40 mL deionized water after ultrasonication in a water bath at 100 W for 3 h. Then, 3.67 mmol O-DAP were dissolved completely in 40 mL deionized water by stirring. Next, the precursor O-DAP solution was mixed with the GO dispersion under ultrasonication in a water bath at 100 W for 2 h and transferred to autoclaves to perform a one-step hydrothermal process at 165 °C for 12 h. Then, the hydrothermal products were washed with diluted ethanol and water sufficiently to remove residual precursor and freeze-dried. The obtained products were denoted as O-DAP-NG. In order to figure out the influence of nitrogen configuration on the electrochemical performance, 1,2diamino cyclohexane (O-DACH) was also used as functional agent at the same procedure and denoted as O-DACH-NG. For comparison, the reduced GO was prepared under the same hydrothermal procedure without adding nitrogen precursor and denoted as RG.

2.2. Characterizations

The morphology characteristics of samples were observed by scanning electron microscope (SEM, JSM-6700F, Japan) and transmission electron microscopy (TEM, JEM3010, Japan), respectively. The surface area and pore structure of samples were analyzed on aN₂ adsorption/desorption apparatus (Micromeritics ASAP Tristar 3020, USA) after degassing at 300 °C for 3 h. Raman spectra were obtained on a spectrophotometer (LABRAM-010, France) using a wave length of 633 nm. Fourier transform infrared spectroscopy (FT-IR) spectra were recorded by a TENSOR27 spectrometer. X-ray photoelectron spectroscopy measurements (XPS) were characterized using an ESCALAB 250Xi spectrometer (USA). The electrical conductivity was measured by a four-probe method (RTS-8 Four-Point probe meter, China).

2.3. Electrochemical measurements

The working electrode was fabricated by loading a mixture of active material (80 wt%), acetylene black (10 wt%) and polytetrafluoroethylene (10 wt%) on a stainless-steel mesh (as current collector, $1 \text{ cm} \times 1 \text{ cm}$). Then, the electrodes were dried at 80 °C under vacuum overnight. The mass loading of the active material on the current collector was measured to be 2 mg cm^{-2} . The electrochemical performance was evaluated on a CHI660E electrochemical workstation (China) at 25 °C, including galvanostatic charging/ discharging (GCD), cyclic voltammetry (CV), and electrochemical impedance spectroscopy (EIS). In a three-electrode configuration, platinum sheet and Ag/AgCl electrode were used as the counter and the reference electrode, respectively. GCD and CV tests were recorded between -0.2 and 0.8 V (vs. Ag/AgCl) in 1 mol L⁻¹ H₂SO₄ aqueous electrolyte. EIS was carried out at an open circuit potential of a 5.0 mV amplitude in a frequency range of 0.01 Hz-100 kHz. In the symmetrical two-electrode configuration, two N-containing graphene electrodes with the same mass were used as electrodes and separated by a glassy fibrous separator. CV and GCD tests of the two-electrode system were recorded between 0 and 1 V.

The specific gravimetric capacitance (C_g , F g⁻¹) in the threeelectrode system was calculated by equation (1) [27]:

$$C_g = \frac{2I \int V dt}{mV^2 \Big|_{V_i}^{V_f}} \tag{1}$$

where C (F g⁻¹) is the specific capacitance, I (A) is the discharge current, t (s) is the discharge time, $\int Vdt$ is the integral current area, V (V) is the potential with initial and final values of V_i and V_f , respectively, and m (g) is the mass of active materials loaded in working electrode.

The density of electrode materials was determined by pressed 200 mg sample into a thick molds with a 10 mm diameter under 10 MPa for 2 min [28]. The press density was calculated by equation (2):

$$\rho = M/(\pi^* r^{2*} T) \tag{2}$$

where M(g) is weight of sample, r(cm) is the diameter of the mold and T(cm) is the thickness.

The volumetric capacitance (C_v , F cm⁻³) was calculated from the following equation [28]:

$$C_{\rm v} = \rho \ C_{\rm g} \tag{3}$$

where ρ is the density of electrode materials (g cm⁻³).

Specific capacitances of a single electrode derived from galvanostatic tests in the two-electrode system can be calculated from equation (4) [29,30]:

$$C_m = \frac{4I}{(dU/dt)m} \tag{4}$$

where C_m (F g⁻¹) is the specific capacitance, *I* (A) is the constant current, *m* (g) is the total mass of active materials loaded in the two working electrodes, *U* (V) is the voltage.

Specific gravimetric and volumetric energy density (E_m , Wh kg⁻¹ and E_v , Wh L⁻¹), as well as power density (P_m , W kg⁻¹ and P_v ,

W L^{-1}) of the symmetric supercapacitors were obtained from equations (5)–(8) [28–30]:

$$E_m = \frac{I \int U(t)dt}{3.6 \times m} \tag{5}$$

$$P_m = \frac{E_m}{\Delta t} \tag{6}$$

$$E_V = \rho E_m \tag{7}$$

$$P_V = \frac{E_v}{\Delta t} \tag{8}$$

where *I* (A) is the applied current, *m* (g) is the total mass of electrodes, $\int Udt$ is the area under the GCD curve, $\Delta t(s)$ is the discharge time.

3. Results and discussions

3.1. Structural and morphological characterization of samples

The possible formation mechanism of the hydrothermal reaction of GO and O-DAP is shown in Fig. 1. GO sheets have their basal planes decorated mostly with hydroxyl and epoxide groups, in addition to carboxyl, hydroxyl and carbonyl groups located presumably at the edges. Therefore, GO reacted with DAP in the hydrothermal process can lead to the incorporation of pyridinic nitrogen moieties into graphene sheets. Imine (-C=N-) group was assembled by the reaction of 2,3-diaminopyridine with monoketone (C=O), while the reaction of 2,3-diaminopyridine with *o*diketone (O=C-C=O) can produce more stable pyrazine ring [31]. In the meanwhile, DAP reacted with carboxyl (COOH) to form amide and imidazole ring [16]. DACH reacted with GO in the hydrothermal process is similar to DAP with GO.

The morphologies and microstructures of N-containing graphene networks and reduced graphene oxide (RG) were observed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). It can be discerned that the RG displays a typical three-dimensional crumpled sheet-linked morphology (Fig. 2a and b) [8]. O-DAP-NG and O-DACH-NG possess a similar morphology but has much larger sheet size (Fig. 2c and e) than that of RG. This might be due to the accelerated coalescing behavior ascribe to the deoxygenation during hydrothermal reduction of GO with O-DAP and O-DACH molecules [32,33]. The O-DAP-NG displays a flexible graphene-like nanosheets with abundant wrinkles from the high magnification SEM observation in Fig. 2d. Severe basal plane-to-

basal plane aggregation of the nanosheets was observed in the O-DACH-NG (Fig. 2f). These results indicate that the overlapping and coalescing of the reduced graphene sheets may be accelerated due to nitrogen functionalization [33]. Meanwhile, by comparing the TEM images of O-DAP-NG and O-DACH-NG (Fig. 2g and h), it can be seen that the sheets of O-DAP-NG is thinner and more stretchable than that of O-DACH-NG.

In order to investigate the effect of nitrogen functionalization on the specific surface area and pore structure of samples, N₂ adsorption/desorption measurements were performed and presented in Fig. 3. As shown in Fig. 3a, RG displays a typical Type-IV isotherm with a large hysteresis loop (H4) in the middle pressure range ($P/P_0 = 0.45 - 0.95$), suggesting the mesoporous characteristics. The porosity parameters of the samples are listed in Table 1. The BET specific surface area of RG was calculated to be $282 \text{ m}^2 \text{ g}^{-1}$, whereas the O-DAP-NG and O-DACH-NG show a much lower specific surface area, which is $43 \text{ m}^2 \text{ g}^{-1}$ and $9 \text{ m}^2 \text{ g}^{-1}$, respectively. Possible reasons for the diminished surface area are the high density of nitrogen functional moieties blocking the pores and the accelerated restacking and coalescing phenomenon of reduced graphene sheets induced by nitrogen functionalization [25,34]. The pore size distribution (determined by the density functional theory, DFT) is presented in Fig. 3b. The RG sample possesses a mesopore size within the range of 2-10 nm. However, the O-DAP-NG and O-DACH NG only have a weak and broad meso-to macroporous size distribution in the range from 20 to 100 nm.

FT-IR spectroscopy were performed to explore the chemical changes of the starting GO during the hydrothermal reaction, as shown in Fig. 4a. The characteristic peaks of GO at 1054, 1120, and 1730 cm⁻¹ can be assigned to the stretching vibration of alkoxyl (C-O), epoxy (C-O-C) and carbonyl (C=O) groups, respectively [35]. A broad adsorption band appeared at $3000-3500 \text{ cm}^{-1}$ is related to the hydroxyl (-OH) groups on the GO structure. In the FT-IR spectra of RG, residual oxygen functional groups were observed such as the symmetrical stretching vibration of C-O-C at 1120 cm⁻¹, C=O stretching at 1722 cm⁻¹, -OH group at 3423 cm⁻¹, suggesting partial reduction of GO under hydrothermal condition. For O-DAP-NG, the signal intensity of oxygen groups was remarkably decreased as most of them were removed during the hydrothermal process [36]. New peaks at 772 cm⁻¹, 1192 cm⁻¹ and 1566 cm^{-1} were observed. The peak at 772 cm^{-1} is attributed to N–H in plane bending vibrations. The strong peak at 1566 cm^{-1} can be attributed to the C=C/C=N stretching vibration mode of benzoid rings in pyridine and pyrazine [16,37]. And the peak at 1192 cm^{-1} also can be assigned to the characteristic peak of pyrazine [16,38]. The results indicate that pyrazine structures formed in hydrothermal process, as well as the pyridinic-N can be efficiently incorporated at the edge of graphene through them. It can be seen that the



Fig. 1. The possible formation mechanism of the hydrothermal process between GO and DAP



Fig. 2. SEM images of (a-b) RG, (c-d) O-DAP-NG, (e-f) O-DACH-NG and TEM images of (g) O-DAP-NG, (h) O-DACH-NG.



Fig. 3. N₂ absorption-desorption isotherms (a) and the corresponding DFT pore size distribution (b) of RG, O-DAP-NG and O-DACH NG. (A colour version of this figure can be viewed online.)

 Table 1

 Pore characteristics of RG and N-containing graphene networks.

Samples	RG	O-DAP-NG	O-DACH-NG
$S_{\rm BET} (m^2 { m g}^{-1})$	282	43	9
Pore volume ($cm^3 g^{-1}$)	0.29	0.12	0.036
Average pore width (nm)	4.1	11.0	15.7
ho (g cm ⁻³)	1.29	1.66	1.87

spectrum of O-DACH-NG also shows C–N bonds (1189 cm⁻¹) and C=N bonds (1572 cm⁻¹), implying the successful incorporation of nitrogen into the reduced graphene oxide. Fig. 4b compares the Raman spectrum of GO, RG, O-DAP-NG and O-DACH-NG. The Raman spectrum of GO shows a broad G band at 1594 cm⁻¹ and a D band at 1359 cm⁻¹, which correspond to the D (related to the disordered crystal structure) and G (associated with graphitic structure) bands, respectively. This D band is ascribed to the sp³ amorphous carbons originated by oxidation. The Raman spectrum of RG also displays the existence of D and G bands at 1345 and 1589 cm⁻¹, but with an increased D/G intensity ratio (1.30) compared to that in GO (0.86). This change suggests a greater number of sp² domains with smaller size created in RG upon reduction of the exfoliated GO [39]. Two major peaks at around

1325 cm⁻¹ (D) and 1584 cm⁻¹ (G) were observed for O-DACH-NG and O-DAP-NG. The intensity ratio of D band to G band (I_D/I_G) tends to increase in the order of RG, O-DACH-NG and O-DAP-NG, which is 1.30, 1.34 and 1.51, respectively. The highest I_D/I_G ratio of O-DAP-NG reveals more defects generating from nitrogen incorporation during hydrothermal process than in O-DACH-NG [6]. In addition, a small peak emerged at 1501 cm⁻¹ in O-DAP-NG further confirms the formation of pyrazine structure by reaction between the two amino groups on 2,3-DAP and two neighborhood oxygen functional groups at the edge of graphene [16].

XPS were performed to further elucidate the chemical states and surface composition of the N-containing graphene (Fig. 5, Table 2). The survey spectrum (Fig. 5a) exhibits the presence of carbon (C), nitrogen (N) and oxygen (O) elements in O-DAP-NG and O-DACH-NG, whereas RG only has C and O elements. The oxygen content of RG is 13.7%, which is much lower than that of graphene oxide, suggesting a successful removal of oxygen functional groups. The content of nitrogen in O-DAP-NG is up to 17.5 at%, which is much higher than that of O-DACH-NG (6.9 at%), and also higher than most other N-containing carbon materials (see Table 3). Furthermore, the high-resolution N 1s spectrum of O-DAP-NG and O-DACH-NG (Fig. 5b and c) can be deconvoluted into four peaks locating at 398.8 eV, 399.4 eV, 400.4 eV and 401.5 eV, which can be assigned to



Fig. 4. FT-IR spectra (a), Raman spectra (b) of GO, RG, O-DAP-NG and O-DACH NG. (A colour version of this figure can be viewed online.)



Fig. 5. XPS of RG and N-containing graphene. (a) XPS survey scan, (b) N 1s XPS spectra of O-DAP-NG, (c) N 1s XPS spectra of O-DACH-NG. (A colour version of this figure can be viewed online.)

Table 2

The percentage mass content of elements, relative nitrogen content of samples determined by high-resolution XPS survey and the electronic conductivity.

Sample	C (at	0 (at %)	N (at %)	N distribution (%)				Electronic conductivity (S
	%)			Pyridinic-N (398.7 ± 0.1 eV)	Amine-N (399.4 ± 0.1 eV)	Pyrrolic-N $(400.4 \pm 0.1 \text{ eV})$	Quaternary-N (401.5 ± 0.1 eV)	cm ⁻¹)
RG	86.3	13.7	0.0	_	_	_	_	5.5
O-DAP-NG	77.2	5.4	17.5	44.6	21.4	26.8	7.1	7.3
O-DACH-	86.4	6.7	6.9	31.5	38.9	26.5	3.1	6.8
NG								

Table 3					
Comparison of volumetric	canacitance an	d rate canability	v of different	carbon	materials

Carbon sample	$S_{BET} (m^2 \; g^{-1})$	N content (at%)	Cv* (F cm ⁻³)	Cs (F g ⁻¹)	Rate (F g^{-1})	Electrolyte	Ref.
N-doped graphene	532	7.7		387 (1)*	234 (10)*	6 M KOH	[20]
N-doped porous carbon	1569	6.5		377 (0.2)	232 (20)	$1 \text{ MH}_2\text{SO}_4$	[45]
N-doping carbon	1004	8.7		180(1)	140 (20)	6 M KOH	[53]
N-doped graphene	29	5.3		214 (0.1) *	96 (5) *	$1 \text{ MH}_2\text{SO}_4$	[31]
3D N-doped graphene	627	9.2		408 (1)*	255 (10)*	$1 \text{ M} \text{H}_2\text{SO}_4$	[49]
N-doped mesoporous carbon sphere	439	5.3		231 (1)*	200 (20)*	6 M KOH	[43]
N-doped holey graphene	605	3.4	439 (0.1)	375 (0.1) *	196 (100)*	6 M KOH	[28]
N-doped graphene	197	7.7	438 (0.5)	334 (0.5)*	226.0 (20)*	6 M KOH	[54]
N-doped mesoporous carbons	489	5.3	200 (0.1)	190 (0.1)	152 (20)	$1 \text{ MH}_2\text{SO}_4$	[55]
N-doped graphene	485	4.4	390 (0.5)	255 (1)*	225 (20) *	6 M KOH	[2]
N-doped graphene film	-	13.9	711 (0.5)	458 (0.5)	443 (20)	1 MH ₂ SO ₄	[50]
N-enriched porous carbon/graphene	915	0.3	365 (0.05)	339 (0.05)	195 (20)	6 M KOH	[47]
Graphene hydrogel	39	1.2	294 (0.5)	151 (0.5)	120 (10)	6 M KOH	[48]
N-containing graphene	43	17.5	586 (0.1)	261 (1)	212 (20)	$1 \text{ M} \text{H}_2 \text{SO}_4$	This work

 C_v : the volumetric specific capacitance.

*C*_s: the gravimetric specific capacitance.

*: the specific capacitance in three-electrode systems.

The value in the brackets means the current density (A g^{-1}).

pyridinic-N/pyrazine-N/imines [40], amines, pyrrolic-N, and quaternary nitrogen, respectively. Notably, the pyridinic-N content reaches 7.8 at% in O-DAP-NG and constitutes 44.6% of the total nitrogen content, while the pyridinic-N content in O-DACH-NG remains at relatively low levels (2.2 at%). Besides improving the wettability of electrode, the incorporation of pyridinic-N/pyrazine-N and pyrrolic-N could offer additional capacitance through the Faradaic redox reactions, especially in acidic aqueous electrolytes [41]. Furthermore, the presence of graphitic-N could improve the conductivity of the N-containing graphene [33], which can be confirmed by the measurements of intrinsic electronic conductivity, as shown in Table 2.

3.2. Electrochemical characterization of samples

Electrochemical performances of N-containing graphene and RG for supercapacitors were first estimated using a three-electrode system in 1 M H₂SO₄ aqueous solution. Fig. 6a compares the CV curves of the electrodes at a scan rate of 5 mV s⁻¹. The RG electrode shows a nearly rectangular CV shape, indicative of a typical electric double-layer capacitive (EDLC) behavior. Obviously, much larger capacitive response with distinct redox peaks can be seen for the O-DAP-NG and O-DACH-NG electrodes, indicating the presence of a strong pseudocapacitive behavior in addition to EDLC. These redox reactions probably based on the protonation of pyridinic-N and pyrrolic-N atoms in acidic medium [42]. Furthermore, the O-DAP-NG electrode exhibits a stronger capacitive response than O-DACH-NG, indicating that the high nitrogen content and suitable nitrogen configuration have greatly positive effect on enhancing the specific capacitance of graphene materials. The charge/discharge curves of electrode (Fig. 6b) were also recorded. The RG exhibits nearly linear in shape, again indicative of the ideal EDLC behavior. In contrast, the O-DAP-NG and O-DACH-NG electrodes show distorted triangular shape, further demonstrating the combination effect of pseudocapacitance and EDLC. The O-DAP-NG electrodes exhibit the longest charge-discharge time, in accordance with the CV results. The specific capacitance of O-DAP-NG, O-DACH-NG and RG calculated from the GCD curves is 353 F g⁻¹, 244 F g⁻¹ and 176 F g⁻¹ at a current density of 0.1 Ag^{-1} , respectively. Taking the very small specific surface area of the N-containing graphene into consideration, the capacitance should mainly come from pseudocapacitance. More importantly, the volumetric specific capacitance of O-DAP-NG is as high as 586 F cm^{-3} (353 F g^{-1} , 1.66 g cm^{-3}) at a current density of 0.1 A g^{-1} , which is superior to most N-containing carbon materials at the same current density (See Table 3). EIS was carried out to gain a deep understanding of the capacitive property of Ncontaining graphene electrodes, as shown in Fig. 6c. The resulting Nyquist plots can be well fitted by the equivalent circuit model (inset). The x-intercept of the semicircle in the high frequency region corresponds to the bulk solution resistance (R_s) [43]. The R_s of all three electrodes are similar (0.85Ω) . The diameter of the semicircle represents the charge-transfer resistance (R_{ct}) [43]. The R_{ct} values for the O-DAP-NG, O-DACH-NG and RG electrodes are 0.85, 1.63 and 1.96 Ω , respectively. The smallest diameter of O-DAP-NG electrode indicates fast charge transfer between the electrode material and electrolyte, which may be ascribed to the enriched N atoms and proper nitrogen configuration. Moreover, the more vertical line of the O-DAP-NG electrode in the low frequency region suggests better capacitive behavior and smaller diffusion resistance, which is desirable for high-rate capability. In addition, the stability of newly generated nitrogen-containing bonds in O-DAP-NG and O-DACH-NG were also investigated by a long-term cyclic voltammetry (CV) measurements at a fixed scan rate (10 mV s^{-1}) in a three-electrode configuration, as shown in Fig. 6d and e, respectively. CV curves of the first and 500 th cycles are almost identical in shape of the two electrodes, indicating a high reversibility of the pseudocapacitive interactions and excellent electrochemical stability of nitrogen containing graphene electrode.

In order to better illustrate the potential applications of the Ncontaining graphene, we assembled a symmetrical supercapacitor based on the N-containing graphene and tested in 1 MH₂SO₄ electrolyte. Fig. 7a compares the CV curves of the electrodes at a scan rate of 5 mV s⁻¹ in the symmetrical system. There are obvious redox humps in both anodic and cathodic curves of O-DAP-NG and O-DACH-NG electrodes, further demonstrating the pseudocapacitance is originated from the Faradaic redox reactions of pyridinic-N and pyrrolic-N atoms involving protons [44]. As shown in Fig. 7b, the CV curves of as-assembled O-DACH-NG supercapacitor exhibit evident distortion when the scan rate increased, indicative of large polarization for O-DACH-NG. In comparison, CV curves of O-DAP-NG (Fig. 7c) show a rectangle-like shape even at a high scan rate up to 200 mV s⁻¹, suggesting the low internal resistance and high rate delivery with rapid charging-discharging characteristic. Typical GCD curves of the O-DAP-NG at different current densities from 1 to 20 Ag^{-1} are illustrated in Fig. 7d. It can be seen that all the GCD curves in the two-electrode system are not strictly symmetrical, but slightly distorted due to the nitrogen incorporation. However, the IR drop is almost negligible even at the high current density of



Fig. 6. (a) CV curves of RG, O-DAP-NG and O-DACH-NG electrodes at 5 mV s⁻¹ in a three-electrode system, (b) Galvanostatic charge/discharge (GCD) curves at 0.1 A g⁻¹, (c) Nyquist plots, inset shows the enlarged part and the corresponding equivalent circuit model, (d) the long-term CV measurements of O-DAP-NG electrode (500 cycles) at 10 mV s⁻¹, (e) the long-term CV measurements of O-DAP-NG electrode (500 cycles) at 10 mV s⁻¹, (e) the long-term CV measurements of O-DACH-NG electrode (500 cycles) at 10 mV s⁻¹. (A colour version of this figure can be viewed online.)

 20 Ag^{-1} (insert of Fig. 7d), further confirming the low internal resistance of the O-DAP-NG supercapacitor material. Fig. 7e displays the calculated specific capacitances from GCD curves of the three devices at different current densities from 0.1 to 20 Ag^{-1} . Both O-DAP-NG and O-DACH-NG have higher specific capacitance than RG even though they have much lower specific surface area and pore volume. Notably, the maximum gravimetric capacitances of O-DAP-NG is 263 Fg^{-1} , higher than that of O-DACH-NG

(217 F g⁻¹) and RG (117 F g⁻¹). This value is lower than the capacitance (353 F g⁻¹) of three-electrode system due to electrode polarization [45]. Significantly, the volumetric capacitance and gravimetric capacitances (Fig. 7f) still retain 352 F cm⁻³ and 212 F g⁻¹ at the current density of 20 A g⁻¹, respectively, much higher than those of nitrogen-doped graphene and porous carbons, meaning excellent rate capability (see Table 3). The exceptional rate capability of O-DAP-NG could be explained by the increased





Fig. 8. The schematic illustration of the effect of DAP functionalization on the electrochemical performances of graphene based materials. (A colour version of this figure can be viewed online.)

electrical conductivity [45] and strong affinity for H⁺ in the electrolyte [33] by abundant pyridinic-N/pyrazine-N at the edges and defect sites of graphitic domains. Ragone plots in Fig. 7g again display the highest energy density of O-DAP-NG, which delivers an energy density of 9.1 and 7.3 W h kg⁻¹ at a power density of 0.12 and 4.8 kW kg⁻¹ at 0.5 and 20 A g⁻¹, respectively, demonstrating an ultrafast ion/electron exchange/transport. More importantly, volumetric Ragone plot of O-DAP-NG symmetric supercapacitor shows a maximum volumetric energy density of $15.1 \text{ W} \text{ h} \text{ L}^{-1}$ with the corresponding power density of 0.2 kW L^{-1} and retains 12.2 \mathbf{W} h L⁻¹ at 7.9 kW L⁻¹. It is noteworthy that such high volumetric capacitive performance of N-containing graphene outperforms to the behaviors of other previously reported Ncontaining carbon-based electrodes for supercapacitors in aqueous electrolytes, such as heteroatom-doped porous carbon-tube $(12.15 \text{ W h L}^{-1} \text{ at } 0.7 \text{ kW L}^{-1})$ [46], N-enriched porous carbon/graphene composites (6.7 W h L^{-1} at 5.0 kW L^{-1}) [47], functionalized graphene hydrogel [48] (11.2 W h L^{-1} at 0.125 kW L^{-1}) etc. The cycle stability was performed at a current density of 2 Ag^{-1} (Fig. 7h). In addition to the high volumetric capacitance and excellent rate capability, O-DAP-NG based symmetric supercapacitor demonstrates good cycling stability. Approximately 91.5% of its initial capacitance is retained after 5000 cycles, which is comparable to many pseudocapacitive electrodes [20,49,50] and some commercial activated carbons [51,52].

Fig. 8 is provided to illustrate the effect of nitrogen incorporation on the electrochemical performances of O-DAP-NG electrode. Under hydrothermal conditions, DAP molecules tend to functionalize at the edge of graphene through the formation of the pyrazine structure or imidazole structure, as confirmed by Raman and XPS results, rather than intercalate into the interlayer of the graphene sheets as molecular spacers. On the other hand, the epoxy and hydroxyl groups on the basal planes can be significantly removed during hydrothermal reduction at DAP-induced basic pH. The overlapping and coalescing of graphene sheets are accelerated due to the promoted $\pi-\pi$ attractive interactions and result in a very low specific area and pore volume. Benefiting from the N-enriched (pyridinic, pyrazine or imidazole-N) edge/defects sites, the agglomerated graphene sheets have a strong affinity for H⁺ and high electrochemical activity in the acidic electrolyte, which is beneficial for the penetration of electrolyte and fast ion transport. Due to the massive electroactive sites, strong affinity for electrolyte ions, together with high packing density, the as-prepared N-containing graphene electrodes exhibit an ultrahigh volumetric capacitance, superior rate capability, and outstanding cycle stability.

4. Conclusion

The nitrogen-containing graphene framework was successfully synthesized through a simple one-step hydrothermal reaction by employing DAP as functional agent. Specific pyridinic-N configuration can be effectively incorporated into graphitic network at edge/defect sites through newly formed pyrazine linkages. Because of its high nitrogen content, specific nitrogen configuration, appropriate functional sites and high density, the O-DAP-NG materials display a high specific capacitance up to 353 Fg^{-1} and an ultrahigh volumetric capacitance up to 586 Fcm^{-3} at a current density of 0.1 Ag^{-1} . More importantly, the two-electrode symmetric supercapacitor made of O-DAP-NG displays a high volumetric energy density of 12.2 Wh L^{-1} at 7.9 kW L⁻¹, exceptional rate capability (212 Fg^{-1} at a current density of 20 Ag^{-1}), and good cycling stability, indicative of their potential application for high-performance supercapacitors.

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Fig. 7. Capacitive behaviors of O-DAP-NG, O-DACH-NG and RG electrodes measured in the symmetric supercapacitor in 1 M H₂SO₄. (a) CV curves of samples at 5 mV s⁻¹, (b) CV curves of O-DAP-NG electrode at scan rates from 5 to 200 mV s⁻¹, (c) CV curves of O-DAP-NG electrode at the scan rates from 5 to 200 mV s⁻¹, (d) GCD curves of O-DAP-NG electrode at different current densities from 0.2 to 20 A g⁻¹, (e) Gravimetric capacitances of O-DAP-NG, O-DACH-NG and RG at different current densities, (f) Volumetric capacitance of O-DAP-NG electrode at different current densities, (g) Ragone plots of O-DAP-NG electrode and (h) Cycling stability of O-DAP-NG electrode at a current density of 2 A g⁻¹ over 5000 cycles. (A colour version of this figure can be viewed online.)

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