Low-Temperature Plasma Exfoliated N-Doped Graphene for Symmetrical Electrode Supercapacitors

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Abstract

Radio frequency (RF) dielectric barrier discharge plasma was used to exfoliate graphite oxide (GO) into graphene. The GO was synthesized from a modified Hummers method. The exfoliation occurred swiftly once the RF power and gas pressure reached a level that enabled sufficient energy transfer from the plasma to the GO. X-ray diffraction (XRD) and transmission electron microscopy (TEM) confirmed that graphene or carbon nanosheets were successfully prepared. The plasma exfoliation mechanism was revealed based on the microstructure characterization and optical emission spectroscopy, which indicated that oxygen was released at the moment of exfoliation. Inspired by the success of GO exfoliation, N-doping was realized by treating polypyrrole-modified GO with plasmas. The N concentration in the resulted graphene depended strongly on the plasma gas. Of the gases studied, CH₄ treated polypyrrole-modified

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GO (GO-PPY-CH₄) contained considerable concentration of N that was beneficial to electrical double layer capacitors (EDLCs). Supercapacitors made of the N-doped graphene exhibited promising capacitive characteristics. Electrochemical measurements showed that the GO-PPY-CH₄ presented an initial specific capacitance of ~312 F g⁻¹ under 0.1 A g⁻¹ charge/discharge current and ~100% retention after 1000 consecutive cycles under currents ranging from 0.1 to 10.0 A g⁻¹ in 6 mol L⁻¹ KOH electrolyte. This study demonstrated that the plasma exfoliation was an efficient approach to fabricating graphene and N-doped graphene that had promising potential to be high-performance electrode materials for EDLCs.

Keywords: plasma, graphene, exfoliation, N-doped, supercapacitor

1. Introduction

Supercapacitors are electrical-energy-storage devices that have recently attracted considerable interest due to their long life cycle, fast charge/discharge capability, and high power [1-4]. Based on the working principles, supercapacitors can be classified into two major types: pseudocapacitors and electrical double layer capacitors (EDLCs). In pseudocapacitors, fast redox reactions, also known as faradic reactions, occur between the electrode and electrolyte during charge/discharge. Subsequently electrical energy is stored[5]. Thus, metal oxides (e.g. MnO₂, NiO, Ni(OH)₂, Co₃O₄[6-9]) are commonly used as the electrode materials to enable the redox reactions with the electrolyte. In contrast to pseudocapacitors, no chemical reaction is involved in EDLCs and carbon materials are commonly used for the electrodes. Energy storage in EDLCs is achieved *via* adsorption and desorption of electrolyte ions. In this process, charge accumulation occurs due to electrostatic attraction between the positive and negative charges that separately reside at the electrode/electrolyte interface[10]. Pseduocapacitors have been demonstrated with very high capacitive performance. However, their capacity usually decreased

sharply with increasing cycles, especially at high current densities. On the other hand, EDLCs possess superior stability under a wide range of current densities and excellent tolerance to a broad variety of electrolytes, due to the inherent stability of carbon materials. In the past few years, a variety of carbon materials (e.g. carbon nanotubes, carbon fibers, activated carbon and graphene [11-14]) have been investigated as the electrodes for EDLCs. The desired characteristics for the carbon electrode materials include[15]: i) high specific surface area (SSA) to provide large accessible area to the electrolyte; ii) low resistance to minimize energy loss; iii) suitable pore size to allow fast transfer of electrolyte ions; and iv) sustainable and abundant to keep the cost low. These requirements have driven the research for various porous carbon and carbon nanomaterials for high-performance supercapacitors. Current challenges that limit the capacitive performance of porous-carbon-based electrodes include relatively low conductivity and structural degradation due to swelling and shrinkage during the charge/discharge process. Among the reported carbon materials, graphene has showed extraordinary potential for EDLCs [16-18].

Graphene is a two dimensional sp^2 hybridized carbon layer that has proven excellent properties including mechanical flexibility (high Young`s modulus 1.0 TPa) [19], exceptional thermal conductivity ($5,000 \text{ W m}^{-1} \text{ K}^{-1}$) [20], high electrical conductivity ($\sim 10^6 \text{ S cm}^{-2}$) [21], high theoretical surface area ($2,630 \text{ m}^2 \text{ g}^{-1}$ for single layer graphene) [22], and high transmittance (97.7%) [23] to visible light. These unique physical and chemical properties make graphene promising for many applications, such as energy storage and conversion (supercapacitors, fuel cells, solar cells and Li-ion batteries) [24-27], biomedical technologies (biosensors and drug carriers) [28, 29], and electronic components [30].

Many methods have been reported to fabricate graphene. In 2004, Geim and coworkers reported a scotch-tape method, in which graphene was prepared *via* mechanical exfoliation of graphite [31]. In 2006, planar carbon with a few layers of graphene was grown by chemical vapor deposition [32]. In 2007, epitaxial growth of graphene on SiC was reported [33]. In 2009, graphene was prepared *via* chemical exfoliation [34]. Of these methods, Hummers-method [35]-based chemical exfoliation was easier to implement than the others. In Hummers approach, concentrated sulfuric acid (H_2SO_4), sodium nitrite (NaNO_3) and potassium permanganate (KMnO_4) were used to exfoliate graphite flake to graphite oxides (GOs) and subsequently graphene was obtained *via* further chemical reduction and physical treatment.

The electrochemical properties of graphene could be modified by doping. Several groups have demonstrated N-doping that greatly promoted the specific capacitance of graphene. In 2011, *Choi* and *Yang* [36, 37] reported N-doped graphene prepared *via* plasma enhanced chemical vapor deposition and thermal nitridation, respectively. They prepared EDLCs using the N-doped graphene electrodes and obtained specific capacitance of 280 and 144.9 F g^{-1} . In 2012, specific capacitance of 245.9 F g^{-1} was reported by *Chen* [36] who used pyrolysis to prepare N-doped graphene. In 2013, *Chen* and *Yang* [38, 39] developed a solvothermal method to prepare N-doped graphene and achieved specific capacitance of 301 F g^{-1} . In 2015, *Gomes* [40] reported a simple thermal treatment method to prepare N-doped graphene and attained a specific capacitance of 210 F g^{-1} . However, all the above processes required high temperatures and were time consuming.

The demands for graphene and N-doped graphene have driven the research on efficient fabrication of these carbon nanomaterials. In this work, the authors demonstrated an effective plasma exfoliation to prepare graphene, which was particularly suitable for high-performance

supercapacitors. GOs prepared *via* modified-Hummers method were rapidly exfoliated into graphene or N-doped graphene at low temperatures using a radio frequency dielectric barrier discharge plasma. This study revealed the plasma exfoliation mechanisms by combining optical emission spectroscopy of the plasma discharge with materials microstructure analysis. The promising potential of the plasma exfoliated graphene for EDLCs was confirmed by a variety of electrochemical characterizations.

2. Material and methods

2.1 Preparation of graphite oxides

Graphite oxides were synthesized via modified Hummer's method[35]. Typically, 2.5 g graphite (Fisher Scientific) was added into 100 ml concentrated sulfuric acid (98 wt%, Fisher Scientific) and kept stirring at 0 °C for 4 h. Afterwards 7.5 g potassium permanganate (Fisher Scientific) was slowly added into above solution before 2.5 g sodium nitrate (Fisher Scientific) being dissolved. The mixture was continuously stirred for 12 h and 50 ml distilled water was added into the solution drop by drop under a temperature of 98 °C. Subsequently, 150 ml distilled water was added to further dilute the solution under stirring for 4 h. To reduce the residual permanganate and manganese dioxide to colorless soluble manganese sulfate, 15 ml hydrogen peroxide (30 wt%, Fisher Scientific) was added. The prepared colloid was transferred into dialysis tubing (14,000 MWCO Daltons, Fisher Scientific) to dialyze in DI water for 2 days. Finally, the dialyzed sample was further separated by centrifugation at 8,000 rpm and washed with DI water till the pH was close to 7, and then dried at 60 °C in a vacuum oven for 24 h. The prepared graphite oxide was denoted in short for GO.

2.2 Preparation of N-modified graphite oxides

N-modified graphite oxide was prepared by immersing the synthesized GO (2 g) into 2 ml pyrrole for 48 h. During that period, the pyrrole spontaneously polymerized and became polypyrrole. The GO sample was subsequently covered with polypyrrole. The polypyrrole-modified graphite oxide was denoted as GO-PPY.

2.3 Preparation of graphene

A dielectric barrier discharge plasma system was used to prepare graphene from the GO and GO-PPY samples. The plasma system (Fig. S1) included a quartz tube that served as the vacuum chamber, a mechanical vacuum pump, a 13.56 MHz RF power supply, a matching network, a vacuum gauge, and a gas flow controller. Firstly, 300 mg GO or GO-PPY was placed into the quartz tube. Then, the tube was evacuated with the vacuum pump and purged with the process gas (i.e. nitrogen, oxygen, or methane). This step was repeated three times to make sure the residual air in the tube was negligible. After that, the gas flow was adjusted to maintain a stable pressure of ~28 mTorr. Then the RF power was turned on and the matching network was tuned manually to achieve almost zero watt reflection power. The gas pressure was subsequently increased to 3 Torr and the RF power was gradually increased to 70 W, during which the graphite oxides exfoliated. After the exfoliation (please watch the supplemental video for the exfoliation process), the RF power, gas flow, and vacuum valves were turned off in sequence and the quartz tube was vented to collect the exfoliated sample. Corresponding to the plasma gas, the prepared samples were named as GO-O₂, GO-N₂, and GO-CH₄.

2.4 Preparation of N-doped graphene

N-doped graphene was prepared following the same procedure of the GO samples, but the raw material was GO-PPY. Corresponding to the applied plasma gas, the prepared samples were denoted as GO-PPY-N₂, GO-PPY-O₂, and GO-PPY-CH₄.

2.6 Preparation of supercapacitor electrodes

The electrodes were prepared by mixing the graphene samples of GO-O₂, GO-N₂, GO-CH₄, GO-PPY-N₂, GO-PPY-O₂, or GO-PPY-CH₄ (80 wt%) with acetylene black (10 wt%) and PTFE (10 wt%), and then pressing onto a nickel foam (EQ-bcnf-16m, MTI Corp.) of 1 cm² surface area. The electrodes were dried at 60 °C for 12 hours in an oven. Afterwards, a sandwich structure was formed by placing two pieces of microporous PP separator celgard-3501 between two electrodes in a 2032 type coin cell. Finally, the cell was pressed under a pressure of 1,000 kg cm⁻² to finish the assembly.

2.7 Physical characterization

X-ray photoelectron spectroscopy (XPS) was performed on an SSX-100 system (Surface Science Laboratories, Inc.) equipped with a monochromated Al K_α X-ray source. For high resolution data, the lowest binding energy C 1s peak was set at 285.0 eV and used as the reference for all of the other elements. Raman spectra were obtained on a Horiba LabRAM confocal Raman microscope system with excitation wavelength of 532 nm from a diode pumped solidstate laser. A transmission electron microscope (TEM) (JEM-2100 LaB6, JEOL) equipped with energy-dispersive X-ray spectroscopy (EDX) (Gatan Inc.) was used to study the morphology, microstructure, and elemental mapping of the materials at an acceleration voltage of 200 kV. The plasma emission was monitored using an optical spectrometer (USB2000+, Ocean Optics, Inc. USA)

2.8 Electrochemical characterization:

Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) tests of the supercapacitors were performed on an electrochemical work station (SP-150, BioLogical, France) using 6 mol L⁻¹ KOH electrolyte. The galvanostatic charge/discharge curves were obtained from a battery test system (BTS series, NEWARE, China).

3. Results and discussion

The XRD patterns of GO, GO-N₂, GO-O₂ and GO-CH₄ were recorded in Fig. 1. A featured peak located at ~10° was observed for the GO, which corresponded to the (001) planes of crystalline graphite. On the contrast, the peak at ~10° vanished after the plasma treatment and a broad peak at ~24° corresponding to graphitic (002) plane emerged for GO-N₂, GO-O₂ and GO-CH₄. These results indicated that the pristine GO was successfully exfoliated into disordered and loosely packed graphene [41, 42]. The exfoliation process was also recorded by video. As can be seen, the GO was exfoliated at RF power about 70 W and gas pressure ~3 Torr in a short time of a few seconds. In comparison with the tightly stacked GO hard flakes, the plasma treated samples (GO-N₂, GO-O₂ and GO-CH₄) became flocculent and soft particles with much larger volume (Fig. S2).

Fig. 1 XRD patterns of GO, GO-N₂, GO-O₂ and GO-CH₄.

Fig. 2 shows the Raman spectra of GO-N₂, GO-O₂ and GO-CH₄ in comparison with GO. Two distinct peaks of *D*-band and *G*-band located at 1350 cm⁻¹ and 1580 cm⁻¹, respectively, were displayed. The *D*-band was associated with the *A_{1g}* mode breathing vibrations of six member *sp*² carbon rings, while the *G*-band was attributed to the first order scattering of the stretching vibration mode *E_{2g}* observed for the *sp*² carbon domain [43, 44]. Generally, the intensity ratio of *D*-band to *G* band (*I_D/I_G*) was used to estimate the disorder degree of graphene. The value of *I_D/I_G* was 1.24, 1.32, 0.92 and 0.91 for GO, GO-N₂, GO-O₂ and GO-CH₄, respectively. A *I_D/I_G* value larger than that of pristine GO implied that more defects were created after the nitrogen plasma treatment [43, 44]. The smaller *I_D/I_G* values for GO-O₂ and GO-CH₄ suggested the removal of oxygen-containing functional groups and partial restoration of the electronic conjugation in graphene sheets by repairing defects [43]. Such a difference most likely arose from the plasma gas during the exfoliation process.

Fig. 2 Raman spectra of GO, GO-N₂, GO-O₂ and GO-CH₄.

To confirm the morphology and microstructure of the prepared samples, TEM was employed (Fig. 3). As displayed, the treated GO-N₂, GO-O₂ and GO-CH₄ samples exhibited ultrathin and flat graphene nanosheets, which were essential to provide beneficial SSA. The TEM results clearly indicated that the RF plasma successfully exfoliated the pristine GO into graphene nanosheets which was in consistence with the XRD analysis. In addition, element mapping (Fig. S3) showed carbon and oxygen uniformly dispersed in these samples.

Fig. 3 Different magnifications TEM images of GO-N₂ (a, b), GO-O₂ (c, d) and GO-CH₄ (e, f).

To help understand the mechanism of the plasma exfoliation, the process was recorded by video (see Supplementary Information). Interestingly, no matter what kind of gas was used, the color of the plasma turned into bright blue at the very moment of explosion. The blue color was an indication of the presence of oxygen in the plasma. Inspired by this observation, the authors speculated that oxygen might be produced at the moment of explosion. To verify this speculation, optical emission spectra were recorded to study the reactions occurred during the exfoliation. The optical spectra are shown in Fig. 4, which includes the background spectra coming from the

202 process gases (N_2 , O_2 , or CH_4). After eliminating the background spectra, it was found that there
203 were three common peaks located at 491.8, 526.8 and 565.9 nm, respectively, for all the three
204 GO samples (GO-N_2 , GO-O_2 and GO-CH_4) and O_2 plasma background. This result supported the
205 speculation that oxygen was generated during the exfoliation. The suggested interactions
206 between the plasma and the GO sample are as following. In the dielectric barrier discharge, the
207 GO sample was electrically floating in the plasma. Electrons in the plasma moved faster than
208 ions and led to negative self-bias of the GO samples. Ions attracted by the negative potential
209 bombarded the GO and broke the bonds between the oxygen and carbon. Ion-GO interactions
210 also led to localized rapid increase in the temperature of the GO as a result of kinetic energy
211 transfer. Under the assistance of the ion bombardment, the dissociated oxygen species combined
212 to form oxygen molecules between the GO layers. When the RF power and gas pressure were
213 increased to certain levels (e.g. 70 W and 3 Torr), the thermal expansion of the oxygen gas
214 formed inside the GO led to the separation of the graphite layers and exfoliation occurred. The
215 plasma exfoliation was a swift process; it was completed in just a few seconds. Moreover, the
216 exfoliation did not require external heating. After the process, the surface temperature of the
217 quartz tube was low 80°C . Comparing with other methods used to prepare graphene (e.g. CVD,
218 PECVD, thermal solvent), RF dielectric barrier discharge plasma was highly efficient.

Fig. 4 OES observed at the explosion moment for GO-N₂, GO-O₂ and GO-CH₄, and the background.

The exfoliated GO was expected to have a porous structure with large surface area. Hence, EDLCs with symmetrical electrodes were prepared to evaluate the specific capacitance of the plasma exfoliated GO. The following equation [45] was used to calculated the specific capacitance:

$$C = \frac{2I\Delta t}{m\Delta v} \quad (1)$$

where C is the specific capacitance, I is the charge/discharge current, Δt is the corresponding charge or discharge time, m is the mass of active materials on single electrode, and Δv is the total corresponding potential change.

Fig. 5a shows the CV curves of the electrodes prepared with GO-N₂, GO-O₂ and GO-CH₄ at a sweep potential window of 0 to 1 V at a scanning rate of 20 mV s⁻¹. All the three pairs of electrodes exhibited typical rectangular CV curves with only a little deformation for the GO-O₂ sample, indicating very good EDLCs behavior. At a scanning rate of 20 mV s⁻¹, the specific capacitance of GO-N₂, GO-O₂ and GO-CH₄ reached up to 93, 178 and 199 F g⁻¹, respectively, which indicated the potential of the materials for EDLC applications. In addition, the CV curves of GO-N₂, GO-O₂ and GO-CH₄ electrodes at different scanning rate ranging from 5 to 200 mV s⁻¹ were recorded in Fig. S4. With the increase in the scanning rate, the specific capacitance gradually decreased and the shape distortion appeared for all these three electrodes. However, GO-CH₄ showed the least distortion. EIS measurements of the supercapacitors were conducted in the frequency range of 10 Hz to 100 kHz in order to evaluate resistance of the device (Fig. 5b). The EIS consisted of an x -intercept at high frequency range, a semicircle in the middle frequency range, and a vertical line in the low frequency range, which corresponded to bulk electrolyte resistance, interfacial impedance between the electrode and bulk solution, and the impedance that was associated with intra-particle pores, respectively [46, 47]. The GO-O₂ sample presented the smallest resistance (6.6 Ω), while GO-N₂ (10.2 Ω) and GO-CH₄ (10.0 Ω) showed slightly higher resistance than the GO-O₂, but still small enough for high performance EDLCs electrode material.

Fig. 5 CV curves (a) at scanning rate 20 mV s⁻¹, nyquist plots (b) of GO-N₂, GO-O₂ and GO-CH₄ electrodes in 6 mol L⁻¹ KOH electrolyte.

The plasma exfoliated GO could be further modified to promote the specific capacitance. It was reported that introducing N could improve the capacitive performance *via* pseudocapacitance effect[48]. Therefore, N-modified GO (GO-PPY) was prepared and subsequently exfoliated by plasma.

Fig. 6 shows the XRD patterns of GO-PPY, GO-PPY-N₂, GO-PPY-O₂ and GO-PPY-CH₄. After the plasma treatment, the characteristic peak of GO located at ~10° (001) disappeared, but a broad peak around 24° (002) showed up, suggesting that the GOs were successfully exfoliated into graphene by the plasmas. Likewise, the same phenomenon as GO exfoliation was observed for GO-PPY with each of the plasma gases.

Fig. 6 XRD patterns of GO-PPY, GO-PPY-N₂, GO-PPY-O₂ and GO-PPY-CH₄.

Fig. S5 illustrated Raman spectra of GO, GO-PPY-N₂, GO-PPY-O₂ and GO-PPY-CH₄. Two distinct peaks of *D*-band and *G*-band located at 1350 cm⁻¹ and 1580 cm⁻¹, respectively, were observed, which were related to *A*_{1g} mode breathing vibrations of six member *sp*² carbon rings, and the first order scattering of the stretching vibration mode *E*_{2g} of the *sp*² carbon domain [43, 44], respectively. The intensity ratio of *D*-band to *G* band (*I*_D/*I*_G) was also used to estimate the disorder degree of graphene. The value of *I*_D/*I*_G was 1.24, 0.92, 0.98 and 0.86 for GO, GO-PPY-N₂, GO-PPY-O₂ and GO-PPY-CH₄, respectively, suggesting the removal of oxygen-containing functional groups and the partial restoration of the electronic conjugation in graphene sheets by repairing the defects [43].

To verify the microstructure of the prepared N-doped graphene, TEM was conducted (Fig. 7). As shown in Fig. 7 and Fig. S6, two-dimensional ultrathin graphene monolayer or multilayers were observed with some ripples. In addition, the existence of monolayer graphene for GO-PPY-CH₄ was further proved by SAED (the inset in Fig. 7d). A perfect hexagonal pattern was presented,

which confirmed the well-crystallized single layer graphene structure[48, 49]. Elemental mapping (Fig. S7) was made to verify the nitrogen inclusion. The signals of carbon, oxygen and nitrogen were all detected and distributed uniformly, indicating nitrogen was successfully introduced. In other word, the N-doped graphene was expected to be a suitable material for high performance EDLCs.

Fig. 7 TEM images of GO-PPY-CH₄ under different magnifications. The inset in (d) is SAED.

During the plasma exfoliation, OESs were recorded (Fig. S8). Interestingly, the same bright blue light appeared at the explosion moment for all the three gases. Besides, the featured peaks of oxygen located at 491.8, 526.8 and 565.9 nm were also observed. All these results revealed that the exfoliation mechanisms were similar to that of GO, the only difference was that N was incorporated in the treated sample.

288 XPS analysis was employed to analyze the functional groups in the surface of GO-PPY-N₂, GO-
289 PPY-O₂ and GO-PPY-CH₄. In Fig. 8a, signals of C 1s (532 eV), O 1s (284 eV) and N 1s (400 eV)
290 were detected, which indicated that N was successfully introduced into the prepared graphene.
291 The XPS analysis also verified the results of TEM elemental mapping. High resolution O 1s
292 spectrum (Fig. 8b and Fig. S9a, c) was deconvoluted into three peaks at binding energy
293 of ca. 531 eV, 532 eV, and 533.5 eV, which were assigned to O-I, O-II and O-III, respectively.
294 The three O species represented C=O groups for O-I, C-OH groups and/or C-O-C groups for O-
295 II, and O-C=O groups for O-III, respectively[50, 51]. Among them, O-I and O-II were the
296 dominant functionalities that would contribute to the pseudocapacitance through the
297 quinone/hydroquinone redox [50]. Besides, two peaks were detected at binding energy ca.398.9
298 and 401.0 eV for N species, which were attributed to pyridinic-N, and quaternary-N, respectively
299 (Fig. 8c and Fig. S9b, d) [52, 53]. The significance of introducing N was that pyridinic-N could
300 lead to great pseudocapacitance effect and improve the conductivity, resulting in enhanced
301 capacitive performance. In addition, atomic element concentrations in the prepared GO-PPY,
302 GO-PPY-N₂, GO-PPY-O₂ and GO-PPY-CH₄ were summarized in Table 1. It was noted that GO-
303 PPY possessed the highest atomic content of nitrogen (10.9%), which was reasonable due to the
304 incorporation of polypyrrole before the plasma treatment. After exfoliation, 8.9%, 1.1% and 4.2%
305 N was detected in GO-PPY-N₂, GO-PPY-O₂ and GO-PPY-CH₄, respectively. This result
306 indicated that N was partially removed due to the interactions between the plasma species and
307 polypyrrole. Oxygen was most effective in removing polypyrrole. Further studied are underway
308 to reveal the chemical interactions between the plasma species and GO-PPY.

Fig. 8 XPS survey (a) of GO-PPY-N₂, GO-PPY-O₂ and GO-PPY-CH₄ and high resolution O 1s (b) and N 1s (c) XPS spectra of GO-PPY-CH₄.

Table. 1 Atomic elements content of prepared GO-PPY, GO-PPY-N₂, GO-PPY-O₂ and GO-PPY-CH₄.

	Carbon (Atomic %)	Oxygen (Atomic %)	Nitrogen (Atomic %)
GO-PPY	73.3	15.7	10.9
GO-PPY-N ₂	73.8	17.4	8.9
GO-PPY-O ₂	86.7	12.2	1.1
GO-PPY-CH ₄	81.4	14.5	4.2

EDLCs were prepared with the exfoliated N-doped graphene as the electrode materials. CV tests were conducted to evaluate the electrochemical performance. Fig.9a shows the CV curves of

GO-PPY-N₂, GO-PPY-O₂ and GO-PPY-CH₄ electrodes in 6 mol L⁻¹ KOH electrolyte at a scanning rate of 20 mV s⁻¹. All three cells exhibited characteristic rectangular shape CV curves, which were an indication of very good electrochemical EDLC behavior. The specific capacitance was calculated according to formula (1) to quantify the EDLCs' performance. The specific capacitance reached up to 130, 178 and 250 F g⁻¹ for GO-PPY-N₂, GO-PPY-O₂ and GO-PPY-CH₄, respectively. Although GO-PPY-N₂ contained the highest concentration of N from the XPS analysis, it produced the lowest specific capacitance. This result implied that only certain type of nitrogen doping, *i.e.* pyridinic-N, was effective in promoting the capacitive performance. CH₄ plasma promoted the incorporation of effective N in GO and/or created additional surface structures and functional groups that beneficial the capacitive performance. In addition, the better capacitance performance of GO-PPY-CH₄ may be arisen from two distinct effects of CH₄ plasma: i) hydrogen plasma etching of the graphite oxides, and ii) growth of nanostructured carbon on the produced graphene. These effects created defects and active surface that promoted the capacitance performance.

The impedance spectra were measured over a frequency range from 100 kHz to 10 Hz (Fig. 9). From the inset, a short *x*-intercept, small diameter of the semicircle, and high slope at low frequency revealed that the GO-PPY-CH₄ electrodes had small bulk electrolyte resistance, interfacial impedance and the inter-particle ionic impedance. A smaller resistance meant higher conductivity and less energy loss, as well as good performance of EDLCs.

Fig. 9 CV curves (a) at scanning rate 20 mV s^{-1} , nyquist plots (b) of GO-PPY- N_2 , GO-PPY- O_2 and GO-PPY- CH_4 electrodes in 6 mol L^{-1} KOH electrolyte; The inset in (b) shows the magnified view of the high-frequency region.

The specific capacitance was also recorded at different scanning rate ranging from 5 to 200 mV s^{-1} in CV test for all three samples (Fig. 9a and Fig. S10). GO-PPY- CH_4 showed much higher specific capacitance and rate capability with negligible distortion in comparison with that of GO-PPY- N_2 and GO-PPY- O_2 .

Meanwhile, as another important index for EDLCs, stability or cycle life of GO-PPY- CH_4 was assessed by charge/discharge at various current densities. In galvanostatic charge/discharge measurement, symmetric lines without IR_{drop} indicated a good capacitive behavior of EDLCs, which was consistent with the result of CV measurement. The cycling performance of GO-PPY- CH_4 electrode was also evaluated using the galvanostatic charge/discharge shown in Fig. 10b. The measurement yielded a specific capacitance as high as 312 F g^{-1} at beginning and ended at 250 F g^{-1} under 0.1 A g^{-1} charge/discharge current with little fluctuation. The specific capacitance remained at $220, 215, 196, 178 \text{ F g}^{-1}$ with a retention of almost 100% after 1000 consecutive cycles under larger currents of $0.5, 1.0, 5.0$ and 10.0 A g^{-1} , respectively. The results indicated that the electrodes were highly reversible during charge/discharge processes.

Fig. 10 CV curves (a) at various scanning rates ranging from 5 to 200 mV s⁻¹, galvanostatic charge/discharge curves (b) and cycle life plot (c) at different current density ranging from 0.1 to 10 A g⁻¹ for GO-PPY-CH₄ electrodes in 6 mol L⁻¹ KOH electrolyte, respectively.

3. Conclusion

Graphite oxides were successfully exfoliated into graphene and N-doped graphene using radio-frequency dielectric barrier discharge plasma. The plasma exfoliation required a certain power level and pressure to transfer sufficient energy. Optical emission spectroscopy revealed the mechanisms of plasma exfoliation, which was due to the breakage of the C-O bonds and combination of O atoms into molecules that expanded under plasma. Comparing with oxygen and nitrogen plasmas, CH₄ plasma exfoliated N-doped graphene exhibited better capacitive characteristics, including high specific capacitance ~312 F g⁻¹ and stable charge/discharge performance. The RF plasma exfoliation was a low-temperature and efficient approach to manufacturing graphene.

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