

# Green Functionalization and Supercapacitive Properties of Carbon Nanotubes by Atmospheric Pressure Non-Thermal Plasma Treatment

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**Abstract:** Functionalization of carbon nanotubes proceeds by using atmospheric pressure non-thermal plasma treatment, where  $\text{NH}_3$  is used as nitrogen sources which is excited either by alternating currents (AC) or direct currents (DC). The content and species of the functional groups are analyzed by XPS which displays that heteroatom content increases 1.6 at.%, the main nitrogen groups are pyridinic nitrogen (N-6) and amino ( $-\text{NH}_2$ ), and  $\text{HO-C=O}$ ,  $\text{C=O}$  and  $\text{C-OH}$  surface groups are also incorporated. The supercapacitive performance of the pristine CNTs, CNT-DC and CNT-AC electrodes are measured and the specific capacitance of CNTs is increased after plasma treatment, which indicate that the surface functionalization facilitate the improvement on supercapacitive properties.

**Keywords:** Atmospheric non-thermal plasma; Carbon nanotubes; Functionalization; Nitrogen doping; Supercapacitive performance

## 1. INTRODUCTION

Since carbon nanotubes (CNTs) were found by Iijima and co-workers in 1991[1], which have been widely applied in many fields, such as polymer reinforcement, energy storage, gas storage, sensing and actuating, nanoscale electronics, catalysts and et al. Due to the wide range of use, the surface functionalization such as surfactant and/or heteroatoms modification is important for enhancing their performance in many fields[2-7]. In the field of energy storage device, for example, as electrode materials of supercapacitors, the functionalization of CNTs is used to strengthen the connection between the CNTs and other materials including conductive polymer and metal compounds[6-7], which also promote the electron transfer, enhance the pseudocapacitance, and improve the stability of the supercapacitors. The heteroatoms modification is widely applied for the adjustment of surface property from inert to active. Due to the incorporation of heteroatoms groups[8-9], faradic reactions can occur to increase pseudocapacitance for CNTs while whose specific capacitance is mainly electrochemical double layer capacitors (EDLC) due to their conductive inert carbon surface. Moreover, functionalization of CNTs can improve the surface wettability to solution which is important to an energy storage material because the electrochemical reaction take place at

the interface of the electrode material and electrolyte.

Heteroatoms groups including oxygen and nitrogen species are the most common groups for carbon materials. As for oxygen groups, such as ketone, phenol, lactone, carboxyl groups, acid anhydride, etc., can be generated by controlled oxidation of CNTs<sup>[10]</sup>, however the usage of concentrated acid is not suitable for large scale preparation for the sake of environment. Nitrogen species including pyrrolic nitrogen (N-5), pyridinic nitrogen (N-6), quaternary nitrogen (N-Q), pyridine-N-oxide (N-X),  $-\text{NO}_2$ , or  $-\text{NH}_2$  can be introduced into CNTs by chemical vapor deposition (CVD)[11-12], post thermal treatment[13-14] or plasma treatment[15-16] in the presence of nitrogen sources. In the CVD process, nitrogen groups can be incorporated in the formation process of CNTs, resulting in the bamboo-like twisted structure[17], and the device is complicated and expensive. In contrast, nitrogen groups introduced by post thermal or plasma treatment are normally located in the outer and/or sub surface of CNTs, the original structure of CNTs are preserved. Plasma treatment is facile and environment-friendly, which provides with ionized particles available for effective functionalization of CNTs. However, the widely used plasma treatment, such as retarding field (RF) plasma[15] and microwave plasma[16] and etc. works under the vacuum. Heteroatom doping of carbon nanotubes by plasma treatment under atmospheric pressure and room temperature is seldom reported.

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In this paper, CNTs are functionalized by non-thermal plasma treatment with  $\text{NH}_3/\text{air}$  as heteroatom sources in atmosphere. The device is simple and the treatment condition is mild leading to the functionalization process easy to be realized. Moreover, nitrogen and oxygen groups are simultaneously introduced onto the surface of carbon nanotubes (CNTs) for both direct and alternating current (DC and AC). The treated CNTs are used as supercapacitor electrode materials, the capacity is enhanced compared to the untreated CNTs, and the role of the oxygen and nitrogen groups in the as-treated CNTs is discussed.

## 2. EXPERIMENTAL

### 2.1. Chemicals and Materials

Ammonia ( $\text{NH}_3$ , 28%), anhydrous calcium chloride ( $\text{CaCl}_2$ ) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Raw multi-walled carbon nanotubes (CNTs, 5-15  $\mu\text{m}$  in length and 20-50 nm in diameter) were obtained from Shenzhen Nanotech Port Co., Ltd., China. Ar gas with the purity of 99.9% was used.

### 2.2. Functionalization of CNTs by non-thermal plasma

A home-made device for generating non-thermal plasma was used to functionalize the as-received CNTs. Argon flow (1 L  $\text{min}^{-1}$ ) was bubbled into concentrated ammonia, which carried the mixture of  $\text{NH}_3$  and air into the chamber contained  $\text{CaCl}_2$ , where most of water vapor and  $\text{CO}_2$  in the argon flow was removed. The gas was then allowed to flow in the discharge chamber, where the pristine CNTs were placed. An Al electrode was wrapped on the outer wall of the tube to generate electric field, a wire connected the Al electrode and plasma generator which had another grounding electrode constitute a circuit. Steady and uniform flame could be seen when discharged in pure argon at a power of 36 W, which disappeared when Ar carried the mixture of  $\text{NH}_3/\text{air}$ , alternating current or direct current was applied to excite gas. The functionalization process proceeded for 30 min, during which the power was turned off in every other 5 min to allow the chamber to cool down. The samples excited by AC or DC non-thermal plasma were marked as CNT-AC or CNT-DC in the following text.

### 2.3. Characterizations

The element composition of the samples was determined by an X-ray photoelectron spectroscopic instrument (ESCALAB250Xi, Thermo). Raman spectra were recorded on a Thermo Fisher DXR Raman spectrometer equipped with a 532 nm incident laser light source. The morphology images were obtained on Field emission transmitting electron microscopy (JEOL, JEM-2100F) in low vacuum mode. A homogeneous slurry was prepared by mixing 20  $\mu\text{L}$  of ethanol, 5 mg of the CNTs samples and 10  $\mu\text{L}$  of 5% poly(tetrafluoroethylene) (PTFE), which was then spread and pressed on nickel foam substrates (1 cm  $\times$  1 cm) and dried at 60  $^\circ\text{C}$  for 5 h, leading to the working electrode. A Pt foil and a saturated calomel electrode (SCE) were used as counter and reference electrode. All electrochemical analyses were performed on an electrochemical workstation (CHI690, CH Instruments) with 6 mol  $\text{L}^{-1}$  KOH as electrolyte.

## 3. RESULTS AND DISCUSSION

### 3.1. Characterization of CNTs

The gas including  $\text{NH}_3$  and  $\text{O}_2$  is ionized at the electric field produced by Al electrode, and the resulted plasma acts on the pristine CNTs to generate functional groups, such as nitrogen and oxygen related groups. The species and content of these functional groups are measured by XPS analysis, the results are showed in the following.

The total content of the surface elements is organized in Table 1, where the content increments of oxygen and nitrogen are observed. The oxygen content of the pristine CNTs is measured as about 1.26 at.%, and no nitrogen is detected. After functionalization, the heteroatom content increase 1.6 at.% for CNT-AC and 1.58 at.% for CNT-DC, indicating the efficiency of AC and DC are almost identical. While for CNT-AC, the increased nitrogen content is 0.86 at.% higher to CNT-DC (0.65 at.%), and the increased oxygen content is 1.99 at.% lower to CNT-DC (2.19 at.%).

The deconvolution of the corresponding N1s and O1s XPS signals of the CNT-AC and CNT-DC are illustrated in Fig.1. For CNT-AC, the binding energies for the fitted peaks of nitrogen appear at 398.1 eV and 399.1 eV, corresponding to the N-6 and  $-\text{NH}_2$  groups; and those for the fitting of oxygen present at 530.8 eV, 531.8 eV and 532.6 eV, indicative of the HO-C=O, C=O and C-OH groups [18-20]. The same nitrogen and oxygen species are found in the CNT-DC but with different contents. Table 2 illustrates that the N-6 and  $-\text{NH}_2$  are the main nitrogen species in both CNT-AC and CNT-DC, CNT-AC contains more nitrogen groups and less oxygen groups, while C=O and C-OH is higher than CNT-DC which has larger amount of unstable group HO-C=O. The reason to the difference of functionalized groups introduced by AC and DC mode plasma is still under investigation.

The Raman analysis (Fig.2) indicates that the  $I_D/I_G$  ratios for the CNT-AC and CNT-DC are 1.19 and 1.2, which are a bit higher than the pristine CNTs ( $I_D/I_G = 1.11$ ), illuminating that the presence of the incorporated heteroatoms increase the defects of CNTs, in line with the XPS results. Fig.3 is the combined picture of the TEM images of the pristine CNTs, CNT-DC and CNT-AC. No notch or fracture is observed in the view field of plasma treated samples, the morphology of CNT-AC and CNT-DC are identical to the pristine CNTs, demonstrating that the non-thermal plasma treatment is a mild functionalization process because it worked under atmosphere and room temperature condition.

### 3.2. Electrochemical properties of the CNTs

Fig.4a shows the cyclic voltammograms of the pristine CNTs, CNT-DC and CNT-AC in a 6 mol  $\text{L}^{-1}$  KOH solution at a scan rate

Table 1. Content of C, O and N in the pristine CNTs, CNT-AC, CNT-DC samples

Samples	Atomic percentage [%]		
	C	O	N
CNTs	98.74	1.26	N/A
CNT-AC	97.14	1.99	0.87
CNT-DC	97.16	2.19	0.65

N/A means that the specie is not detected

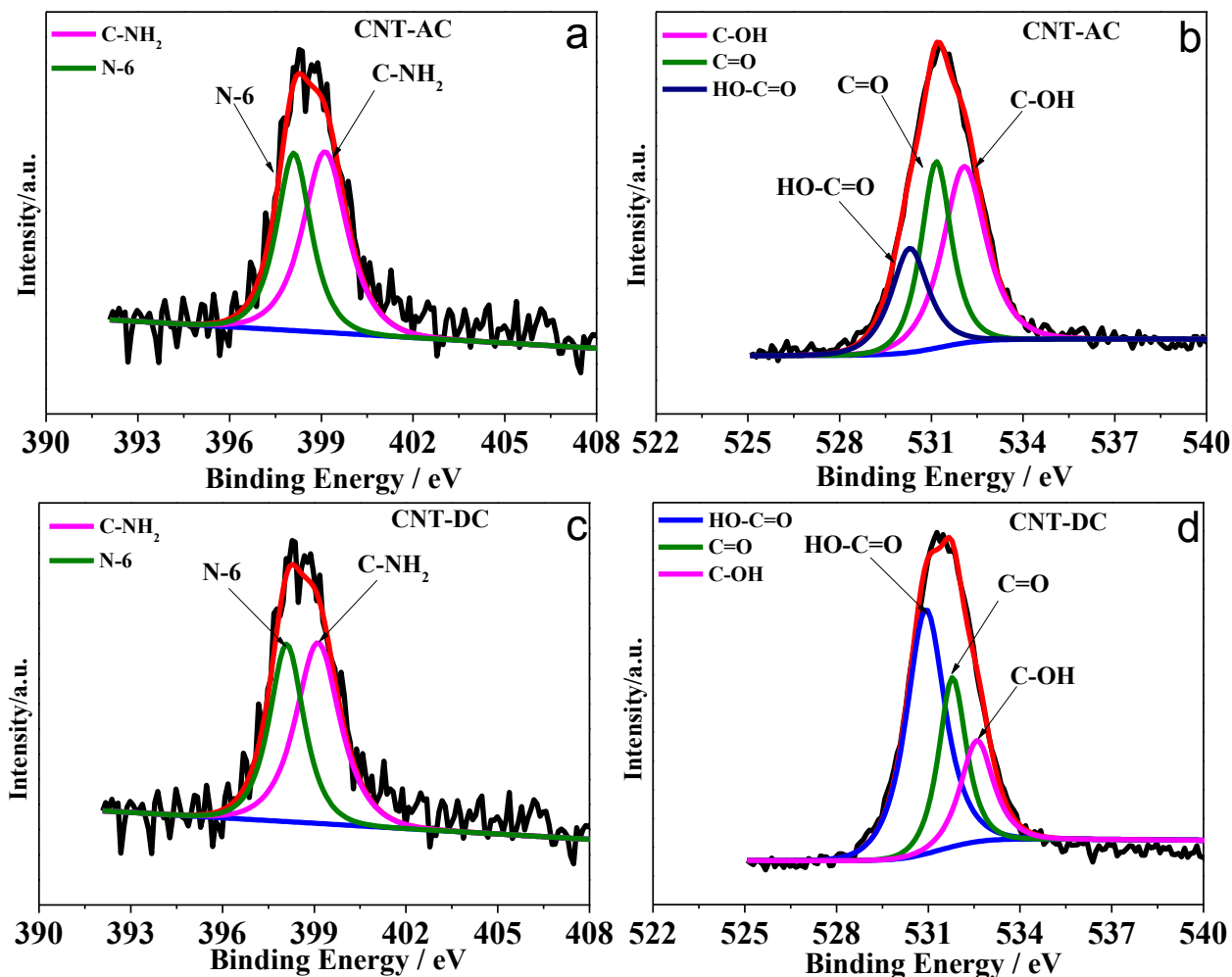


Figure 1. N1s (a, c) and O1s (b, d) spectra of CNT-AC (a, b) and CNT-DC (c, d)

Table 2. Content of nitrogen and oxygen species in the pristine CNTs, CNT-AC and CNT-DC samples.

Species	Binding energy [eV]	Content [at. %]		
		CNTs	CNT-AC	CNT-DC
N-6	398.1	--	0.407	0.282
C-NH <sub>2</sub>	399.1	--	0.453	0.368
HO-C=O	530.8	0.275	0.452	1.187
C=O	531.8	0.557	0.657	0.586
C-OH	532.6	0.428	0.882	0.416

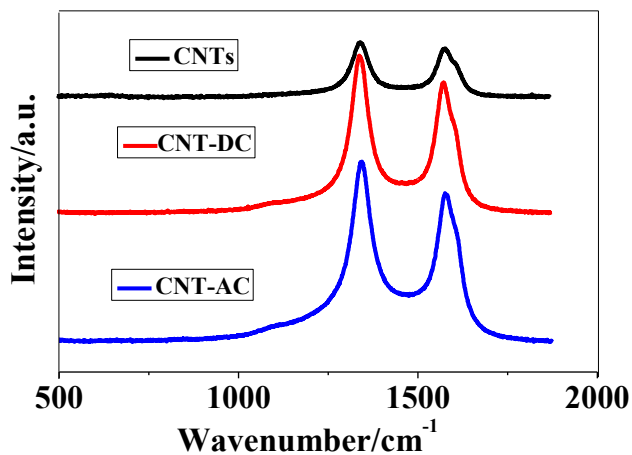


Figure 2. Raman spectra of the pristine CNTs, CNT-DC and CNT-AC samples.

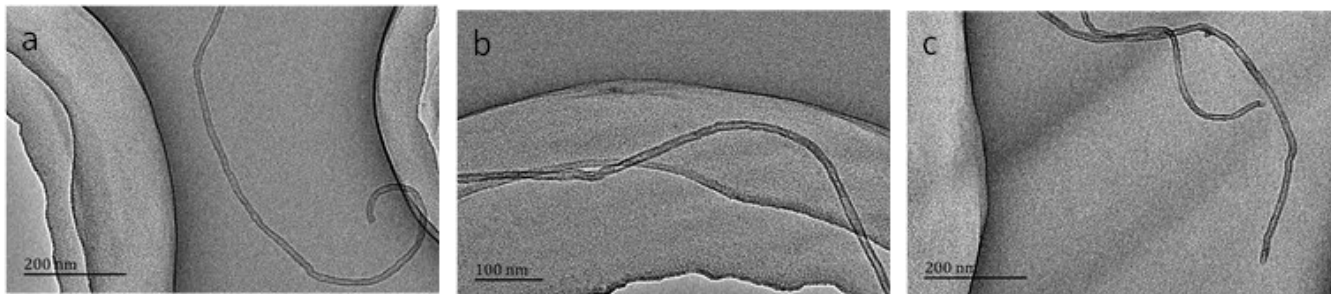


Figure 3. TEM images of the pristine CNTs, CNT-DC and CNT-AC samples.

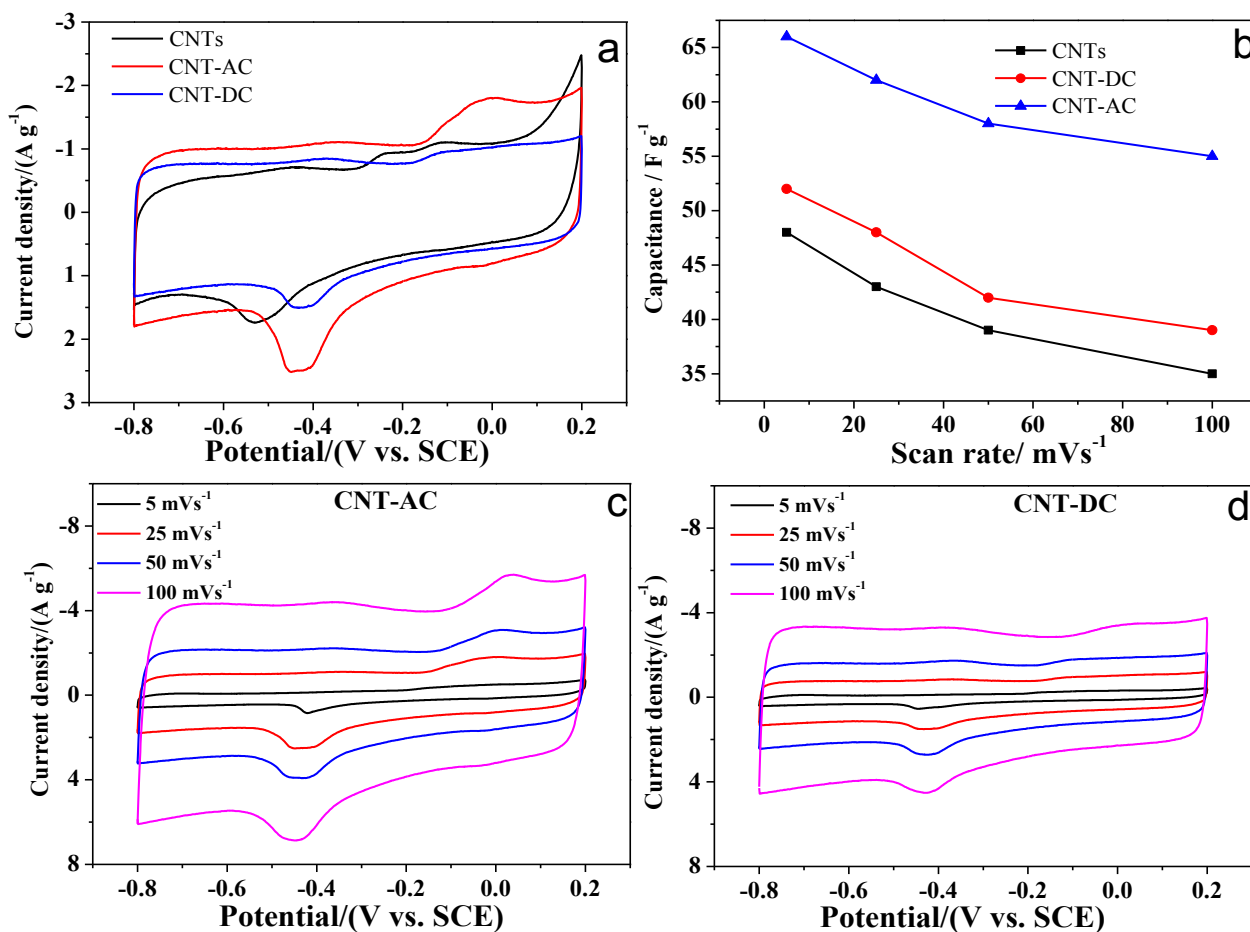


Figure 4. CV plots of the pristine CNTs, CNT-DC and CNT-AC samples at the scan rate of  $25 \text{ mV s}^{-1}$  (a), capacitance as a function of scan rate (b), CV plots of CNT-AC (c) and CNT-DC (d) at different scan rates.

of  $25 \text{ mV s}^{-1}$ , in which the redox currents of the CNT-AC and CNT-DC are obviously larger than the pristine CNTs, accompanied with the more positive reduction peak potentials, these phenomena suggest the positive effect of the incorporation of heteroatoms. It is reported that the N-5, N-6 and oxygen groups can contribute to the pseudocapacitance of CNTs electrodes, which could increase the pseudocapacitance<sup>[21-22]</sup>. Fig.4b further illustrate that the larger redox currents result in the capacitance increments, where the ca-

pacitances of the pristine CNTs, CNT-DC and CNT-AC electrodes at  $5 \text{ mV s}^{-1}$  are measured as  $48 \text{ F g}^{-1}$ ,  $52 \text{ F g}^{-1}$  and  $66 \text{ F g}^{-1}$ , respectively. In addition, the sequence (CNT-AC > CNT-DC > pristine CNTs) remains unchanged as the scan rate increasing, although the specific capacitances of all materials decrease. Fig.4c and 4d shows the CV curves of CNT-AC and CNT-DC at variant scan rates spanning from  $5 \text{ mV s}^{-1}$  to  $100 \text{ mV s}^{-1}$ , where the former exhibits larger redox currents than the latter at every scan rates, but the shape of

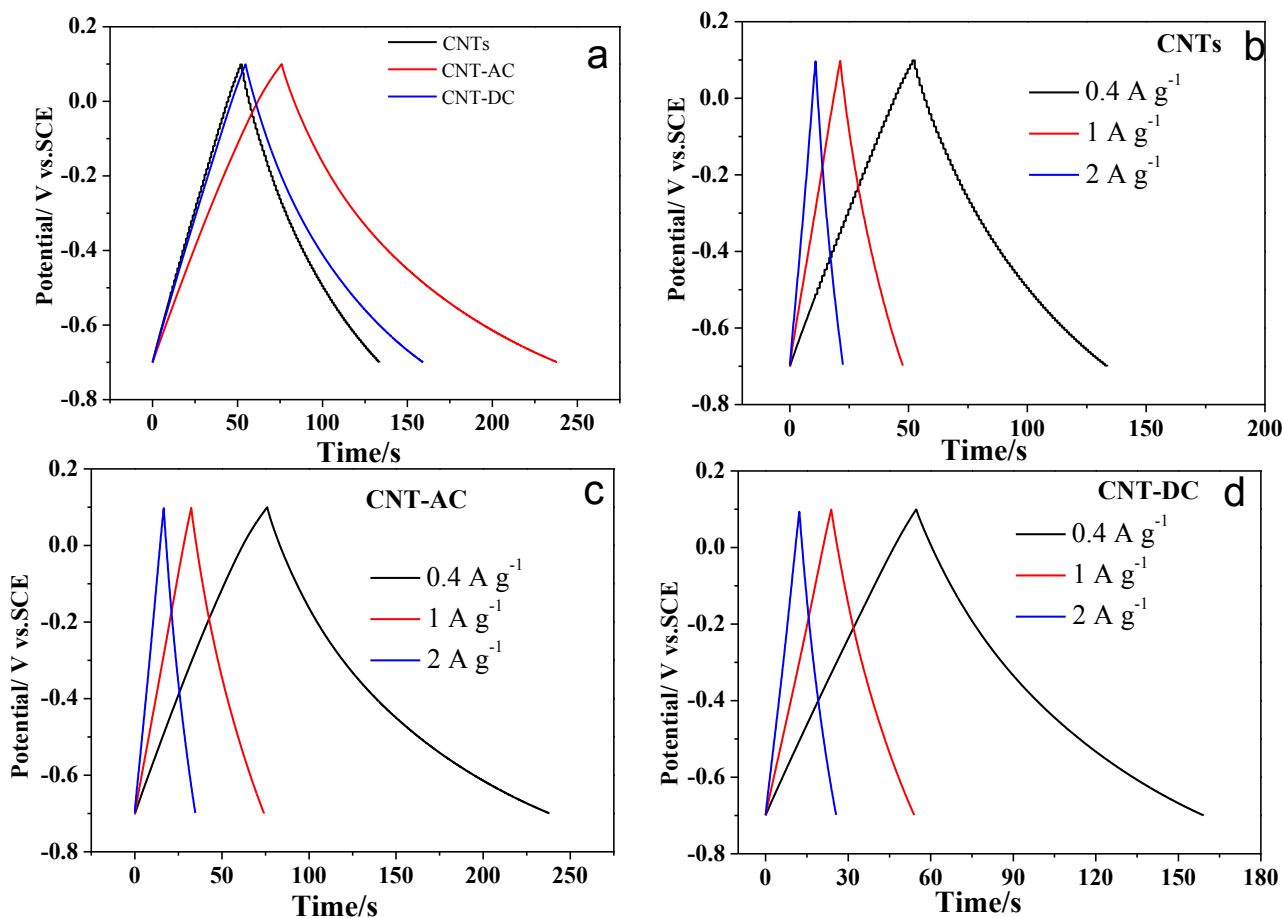


Figure 5. Charge-discharge curves of CNTs, CNT-AC and CNT-DC at  $0.4 \text{ A g}^{-1}$  (a), Charge-discharge curves of CNTs (b), CNT-AC(c) and CNT-DC (d) at different scan rate.

both CV plots is almost unchanged with the rise of scan rate, indicative of the good conductivity of the treated CNTs.

Fig.5a shows the galvanostatic charge-discharge curves of the pristine CNTs, CNT-AC and CNT-DC. The non-linear discharge curves indicate of the existence of pseudocapacitance for all the three CNTs electrodes, among which the CNT-AC exhibits the longest discharge duration, corresponding to the largest capacitance over the CNT-DC and pristine CNTs. Fig.5b, 5c and 5d illustrates that the charge and discharge durations of the pristine CNTs, CNT-AC and CNT-DC decrease which means that the capacitances decay with the increase of current density, but the CNT-AC still exhibits the longest discharge duration at each current density, followed by CNT-DC and the pristine CNTs.

The long-life stability of the pristine CNTs, CNT-AC and CNT-DC is investigated by cyclic voltammetry at the scan rate of  $25 \text{ mV s}^{-1}$ . As Fig.6 shows, the capacitances of all the three samples follow the same trend: They decline rapidly at the first 100 cycles and end up with the different plateaus of retention capacitance, in other words, 90.8 %, 85 % and 94.1 % of the initial capacitances are kept up to 2000 runs for the pristine CNTs, CNT-DC and CNT-AC, respectively.

The ionizable group of  $-\text{NH}_2$  donates electron to the aromatic

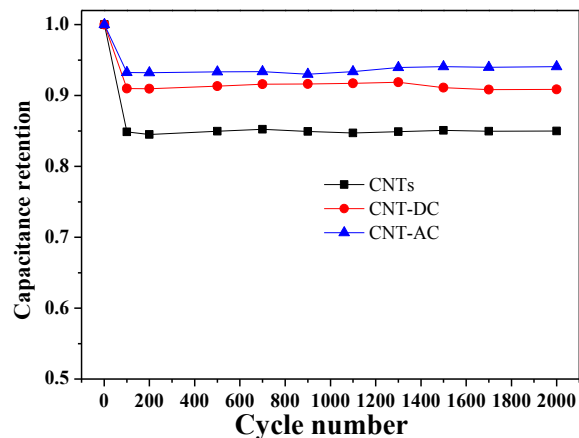


Figure 6. Cycling stability of CNTs, CNT-DC and CNT-AC.

ring of CNTs, which generated pseudocapacitance and improved the wettability<sup>[23]</sup>. Nitrogen doping (N-6) improve the conductivity and catalyze the oxygen reduction reaction of CNTs. The C=O and

C-OH are also in close association with the pseudocapacitance in the charge-discharge cycles, and C-OH facilitates the transportation of ions to the internal surface in the charge/discharge process<sup>[22,24]</sup>. The increased nitrogen and oxygen groups lead to higher pseudocapacitance for the functionalized CNTs, possibly due to the beneficial N-6, -NH<sub>2</sub>, C=O and C-OH groups is incorporated. While the carboxyl group (-HO-C=O) is believed to be detrimental to the stability of carbon materials, which causes chemical degradation in charge-discharge cycles.

#### 4. CONCLUSIONS

Nitrogen and oxygen atoms are introduced into the CNTs by the non-thermal plasma treatment of NH<sub>3</sub>/air mixture excite either by AC or DC currents under atmospheric condition. XPS, TEM and Raman analyses indicate that the functional groups are in the form of N-6, -NH<sub>2</sub>, as well as the HO-C=O, C=O and C-OH, and no apparent destructive to the CNTs are observed. The electrochemical measurement demonstrates that the pseudocapacitance of the functionalized CNTs is improved, and the carbon materials treated by non-thermal plasma is potential catalytic materials towards oxygen reduction, further efforts are needed to improve the method to the increase the doping amount of heteroatom.

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