Surface functionalization of vertically-aligned carbon nanotube forests by radio-frequency Ar/O₂ plasma

Bin Zhao, Lei Zhang, Xianying Wang, Junhe Yang *

School of Materials Science and Engineering, University of Shanghai for Science and Technology, Shanghai 200093, China

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ABSTRACT
Vertically-aligned carbon nanotube (CNT) forests were modified using radio-frequency Ar/O₂ plasma. The effect of plasma parameters on surface morphology, atomic composition and structure of CNT forests were studied. Functionalized CNT forests preserved vertical alignment and showed dramatic change in surface morphology, and bundle-like patterns were observed from scanning electron microscopy examination. X-ray photoelectron spectroscopy and Raman analyses reveal that the amount of sp²-hybridized graphite-like carbon bond in CNTs decreased significantly and oxygen-containing functionalities like C–O and O–C=O groups were introduced after treatment. And the functionalization occurred exclusively on outer surface of CNT forests. Ar/O₂ plasma was found to be more efficient than pure Ar plasma for oxygen functionalization.

1. Introduction
When carbon nanotubes (CNTs) are efficiently grown by chemical vapor deposition (CVD) from catalysts deposited on a substrate, the subsequently grown nanotubes align vertically into a bulk material called a CNT forest [1–5]. Nanotubes within the CNT forest possess excellent alignment, high surface area, high carbon purity, good electrical conductivity, and long length. As such, possessing these important properties, CNT forests have been shown to be advantageous for numerous applications spanning from high power and density supercapacitors [6], highly sensitive electrochemical sensors [7], field-emitters in flat-screen displays [8], low-voltage actuators [9], nanofiltration membrane [10], and gecko tape [11].

However, in order to fully explore the potential for these applications, further modification to CNT forests is often requisite. For example, CNT sidewall opening are necessary to achieve high specific capacitance and energy density for supercapacitor application [12]. For sensing applications, the surface of the CNT tip needs to be properly functionalized with chemical groups to obtain tuned electrical and chemical properties while preserving the intrinsic properties of the CNT forests [13]. Among various strategies, plasma treatment could be a promising way for functionalizing CNT forests, since it could well maintain the vertically alignment of CNT forests compared with wet chemical manipulation [14]. Furthermore, plasma etching can also purify vertically-aligned CNTs by removing the amorphous carbon layer on CNTs [15]. Although extensive research has been performed on plasma modification of CNTs [16–18], controlled functionalization of vertically-aligned CNT forests by plasma has not be studied in great detail.

In this work, radio-frequency (RF) Ar/O₂ plasma treatment was performed on millimeter-long CNT forests efficiently grown by water-assisted chemical vapor deposition [2,3]. The effects of plasma treatment parameters, specifically work pressure, gas flow ratio and plasma power, on surface morphology and chemical composition of CNT forests were investigated.

2. Experimental
Vertically-aligned CNT forests were synthesized in a 1-inch tube furnace by water-assisted CVD at 800 °C using ethylene...
(99.9%) as carbon source. Al₂O₃ (~30 nm)/Fe (1.5 nm) bilayer films were evaporated on Si(100) substrate as catalyst. Pure Ar (99.999%) with H₂ (99.999%) (total flow 600 sccm) was used as a carrier gas at one atmosphere. A small and controlled amount of water vapor was employed as a catalyst preserver and enhancer and was supplied by passing a portion of the Ar carrier gas through a water bubbler [3,6]. Typical CVD growth was carried out with ethylene (30–50 sccm) and a water concentration of 100–200 ppm for 10 min. Millimeter-long CNT forests composed with nanotubes of 6–11 nm in diameter were synthesized and utilized as-grown.

Plasma treatment for CNT forests was performed in a home-made cylindrical vacuum chamber with a diameter of 40 cm and a height of 30 cm. Electrode distance from cathode to anode was 5 cm. A 13.56 MHz RF power supply (CESAR 136) was used to generate plasma. Ar (99.999%) and O₂ (99.999%) were employed as feed gas and the O₂ concentration in feed gas was 0 (pure Ar), 25% and 50%, respectively. Background vacuum of the equipment was 1·10⁻⁴ Pa and three pressure levels during plasma treatment were employed, which were 30, 60 and 100 Pa, respectively. Three plasma power levels were utilized for treatment, which was 50, 100 and 200 W, respectively. For all samples, the plasma treatment was performed for 30 min. Table 1 lists the typical parameters used for plasma treatment and etching rate in different conditions. The CNT forest thicknesses were measured using a high-accuracy digital measuring instrument (Mitutoyo Litematic VL-50A). And the error in the evaluation of etching rate came from the CNT forest thickness measurement, which was estimated to be around ± 1 μm.

Surface morphology of pristine and plasma-treated CNT forests was examined by field-emission scanning electron microscope (FE-SEM, FEI, Quanta FEG 450) operated at 20–30 kV. X-ray photoelectron spectroscopy (XPS, PHI, 5000C ESCA) was carried out to evaluate chemical state and composition of CNT forests using a Mg Kα source (1253.6 eV). Raman spectroscopy (PerkinElmer Ramanstation 400) with 785-nm excitation wavelength was performed to characterize the crystallinity of CNT forests.

### 3. Results and discussion

#### 3.1. SEM examination

Fig. 1a shows a side-view SEM image of a pristine CNT forest grown by water-assisted CVD. Dense and vertically aligned CNTs with average height of 1200 μm can be observed. SEM examination on a cleaved forest sample after plasma functionalization (O₂ concentration of 50%, 100 W and 60 Pa) shows that the vertical alignment was not destroyed by the plasma treatment, as shown in Fig. 1b.

Fig. 2 demonstrates top-view SEM images of the pristine CNT forest and the plasma-treated samples in different conditions. The untreated sample presents a typical morphology of vertically-aligned CNT forests with spaghetti-like surface, as shown in Fig. 2a. After plasma treatment, the CNT forests show significant change in their surface morphology. Randomly-distributed small bundles were observed with nanotube tips agglomerated together. Fig. 2b–d are the SEM images of the plasma-treated samples.
images of plasma-treated CNT forests as a function of O₂ concentration in feed gas. Although the O₂ concentration was quite different, the three samples demonstrated similar feature in their morphology, indicating that the O₂ concentration in feed gas has little effect on surface morphology of CNT forests. During plasma treatment, the surface energy of CNTs can be increased by the defects and the functional radicals introduced by plasma physically or chemically; this can cause the CNTs’ tip coalescent and form into CNT bundles as a result of reducing the surface energy \[18–20\]. As the work pressure during plasma treatment raised, dimension of the bundles on CNT forest surface increased distinctly, and some volcano-like patterns were observed from Fig. 2e. Increasing plasma power exhibited the same effect on surface morphology as work pressure (Fig. 2f). Generally, high work pressure and high discharge power will result in more charged ions and electrons in plasma, suggesting a high plasma density \[21,22\]. Therefore, it might be the high-density plasma that caused the coalescence of CNTs in large area and formation of large-size bundles on CNT forests.

3.2. XPS analysis

To characterize the change in the atom composition before and after plasma treatment, XPS analysis was performed. Fig. 3 shows XPS survey spectra of the pristine CNT forest and the samples treated by plasma at 60 Pa, 100 W and different O₂ concentrations. All spectra reveal the distinctive presence of carbon and oxygen.

Moreover, the oxygen peaks become stronger and the carbon peaks weaken after plasma treatment, indicating the formation of oxygen-containing functional groups upon plasma. Table 2 shows the normalized C and O atomic composition of different samples. For pristine CNT forest, the oxygen come from air contamination oxidation on the nanotube surface, which is about 7.2 at.%. And the oxygen content increased
significantly to above 20 at.% after plasma treatment. Functionalization from plasma of Ar/O2 mixture gas is more effective than pure Ar in terms of the amount of oxygen-containing groups.

More information on the nature of the functional groups on CNT surface may be obtained by high-resolution XPS analysis. Fig. 4 shows high-resolution C 1s and O 1s spectra for the pristine CNT forest and the functionalized samples at 60 Pa, 100 W, and different O2 concentrations.

Deconvolution of the C 1s peak of the pristine CNT forest (Fig. 4a) show a main peak at 284.9 eV, which was attributed to the graphite structure (C=\text{C}) [23]. Peak 2 centered at 286.2 eV was related to sp3-hybridized carbon atoms (C–C) [24]. And the peak at 287.7 (peak 3) and 289.4 eV (peak 4) correspond to C–O (e.g., alcohol and ether) and O–C=C=O (e.g., carboxylic and ester) functionalities, respectively [25]. The peak 5, commonly related to the n–π transition levels (free electrons of the graphitic plane) is observed at 291.5 eV [23,17]. Therefore, radicals are believed to generate firstly on the amorphous carbon might have been removed by plasma.

The effect of O2 concentration and plasma power on functionalized CNTs was further investigated by XPS analysis. Table 2 demonstrates the detailed composition of the five components forming the XPS C 1s spectra. Obviously, when the work pressure of the feed gas is constant, the change of O2 concentration from 50% to 25% (corresponding to different partial pressure of each gas) did not influence the surface chemistry of CNT forests greatly. The fractions of C–O and O=C=O groups showed almost no change. This phenomenon suggests that there is a saturation state for surface oxidation, for which the surface cannot accept new oxygen species from the plasma environment due to the oxidation level and molecular steric hindrance. Chen et al. also found presence of the similar saturation state with regard to plasma treatment time [24]. At O2 concentration of 25%, it is believed that the oxidation level on the surface of CNT forests reaches or approaches this saturation state after 30 min plasma treatment.

![Fig. 3 – XPS survey spectra of (a) pristine CNT forest, (b) sample A, and (c) sample B.](image)

### Table 2 – XPS analysis of CNT forests before and after plasma treatment.

<table>
<thead>
<tr>
<th>Sample group</th>
<th>C (%)</th>
<th>O (%)</th>
<th>sp2 (%)</th>
<th>sp3 (%)</th>
<th>C–O (%)</th>
<th>O=C=O (%)</th>
<th>n–π Transitions (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine CNTs</td>
<td>92.8</td>
<td>7.2</td>
<td>52.4</td>
<td>27.9</td>
<td>12.6</td>
<td>3.7</td>
<td>3.4</td>
</tr>
<tr>
<td>A</td>
<td>79.1</td>
<td>20.9</td>
<td>31.1</td>
<td>25.3</td>
<td>24.8</td>
<td>15.7</td>
<td>3.1</td>
</tr>
<tr>
<td>B</td>
<td>66.6</td>
<td>33.4</td>
<td>27.8</td>
<td>21.5</td>
<td>28.6</td>
<td>21.1</td>
<td>1.0</td>
</tr>
<tr>
<td>C</td>
<td>65.1</td>
<td>34.9</td>
<td>26.2</td>
<td>21.3</td>
<td>30.8</td>
<td>20.8</td>
<td>0.9</td>
</tr>
<tr>
<td>D</td>
<td>63.2</td>
<td>36.8</td>
<td>26.8</td>
<td>20.2</td>
<td>30.3</td>
<td>21.4</td>
<td>1.3</td>
</tr>
</tbody>
</table>
treatment. Therefore, further increase of the \( \text{O}_2 \) concentration in feed gas cannot obviously change the surface functionalities. This is important when choosing appropriate \( \text{Ar}/\text{O}_2 \) gas ratio to realize effective functionalization on CNT forest surface. Besides, when the plasma power was decreased to 50 W from 100 W while keeping other parameter constant, the surface composition of the treated CNT forest showed only slight change, indicating that plasma of 50 W might have been enough for efficiently grafting of oxygen-containing species onto CNT surface.

Considering possible electromagnetic shielding of CNTs [26], plasma may not penetrate thick CNT forests to functionalize the nanotubes inside the forests. To clarify this, a CNT sample treated under the B condition (60 Pa, 100 W, 50% \( \text{O}_2 \)) was partially detached from Si substrate and XPS analysis was performed on newly-cleaved cross-section of the CNT forest. Carbon composition was found to be as high as 95.2 at.%, indicating that less functionalization occurred inside the forest even after treating for 30 min. Analysis from deconvolution of the C 1s and O 1s peaks (Fig. 5) reveals that the \( \text{sp}^2 \)-hybridized \( \text{C}–\text{C} \) component is about 54.5 at.%, and \( \text{C}–\text{O} \) and \( \text{O}–\text{C}–\text{O} \) components are 8.3 at.% and 6.4 at.%, respectively. Compared with the results for pristine CNT forests (top surface), it is obvious that the interior nanotubes in the forest were not modified and oxygen-containing functional groups were not grafted successfully even be treated for long time by \( \text{Ar} + \text{O}_2 \) plasma. In fact, it is also noticed that CNT coverage area on Si substrate shrinked after plasma treatment. Therefore, it is reasonable to believe that plasma etching and functionalizing effects for thick CNT forests act primarily from the outer surface. Uniform functionalization throughout a sample might only be possible for thin CNT forest, since plasma treatment may induce the formation of CNT bundles on CNT forest surface as demonstrated by Fig. 2.
3.3. Raman analysis

The information about structure properties of CNTs could be obtained from Raman spectroscopy. Fig. 6 presents the Raman spectra on CNT forest surface before and after plasma treatment as a function of gas flow ratio and work pressure. The G band at 1590 cm\(^{-1}\) is associated with the \(E_{2g}\) in-plane stretching vibration mode in the basal plane of graphite, which indicates the presence of crystalline graphitic carbon in CNT samples. And the peak at 1309 cm\(^{-1}\) (D band) is assigned to the imperfections on nanotubes and amorphous carbon. The intensity ratio between G band \(I_G\) and D band \(I_D\) is sensitive to chemical modification and is an index of the defects on CNTs [27]. From Raman analysis, the \(I_G/I_D\) ratio was determined to be 2.57 for the pristine CNTs, suggesting good crystallinity of the CNT forests grown by water-assisted CVD. It is obvious that a reduction in the G band intensity occurred, with a simultaneous rise in the D band intensity after plasma treatment. Although the CNTs were treated using different plasma parameters, the \(I_G/I_D\) ratio showed little difference, which was around 0.5. The decreased \(I_G/I_D\) ratio after plasma treatment may be interpreted by change in the structure of nanotubes and the increased oxygen content on the forest surface [24]. Compared to the pristine CNTs, the blue shift of G band and D band for the treated samples took place, which may be ascribed to the increased disorder and defect density in the treated CNTs [28,29].

To investigate the influence of plasma treatment on the interior CNTs in a forest, Raman analysis was performed on the fresh cross-section of the forest sample before and after plasma treatment (under the B condition). As show in Fig. 7, no distinctive change is found in terms of the Raman shift and the \(I_G/I_D\) ratio. This fact suggests that the CNT structure and the chemical composition for the interior nanotubes
were not varied after Ar + O$_2$ plasma treatment, which agrees well with the XPS analysis.

4. Conclusions

Oxygen-containing functional groups were introduced onto vertically-aligned CNT forests by using Ar/O$_2$ RF plasma treatment. SEM examination demonstrates that vertical alignment was preserved for nanotubes and bundle-like morphology formed on the surface of CNT forests after plasma treatment. XPS analysis indicates that the amount of sp$^2$-hybridized C was preserved for nanotubes and bundle-like morphology. Ar/O$_2$ RF plasma treatment is an efficient approach to achieve the oxygen functionalization to CNT forest surface.

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