Artificial introduction of defects into vertically aligned multiwalled carbon nanotube ensembles: Application to electrochemical sensors

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(Received 29 June 2007; accepted 31 July 2007; published online 28 September 2007)

Carbon nanotubes (CNTs) inevitably contain defects that exert a significant influence on their physical, electrical, and electrochemical properties. In this study, we subject vertically aligned multiwalled CNT ensembles to argon and hydrogen ion irradiation, to artificially introduce defects into the structure. Subsequently, Raman spectroscopy in conjunction with electrochemical analyses was used to characterize the amount and nature of disorder within the CNTs. While an increased disorder with ion irradiation was generally observed, argon and hydrogen exhibit different effects on the Raman intensity spectra. Argon irradiation seems to cause charged defects, e.g., in the form of dangling bonds, and increases the in-plane correlation length (L_a), while hydrogen irradiation passivates residual defects and decreases the L_a . It was noted that hydrogen treated CNTs could serve as electrochemical sensors with quicker response time. © 2007 American Institute of Physics. [DOI: 10.1063/1.2783945]

I. INTRODUCTION

Carbon nanotubes (CNTs) have been extensively studied due to their postulated, remarkable mechanical, thermal, electrical, and chemical properties.^{1,2} A major issue preventing the realization of the theoretically predicted properties is the inevitable presence of defects, 3-5 which can adversely affect their performance. Some examples include the influence of Stone-Wales defects (pentagon-heptagon pairs) in lowering the yield strength of CNTs by a factor of 3,⁶ and divancy defects⁷ significantly reducing the electrical conductivity.⁸ On the other hand, defects are though to be essential in applications involving field emission^{9,10} and electrochemistry,^{11,12} where moieties such as dangling bonds could dominate CNT characteristics. In any case, the sensitivity of CNT properties to the presence of defects is a worthy topic of study for the insights it could offer into the interplay of structure and eventual application. In this paper, we probe the influence of defects through their artificial introduction, using the process of reactive ion etching using both heavy (argon: Ar) and light (hydrogen: H) ions. Our study represents an attempt to introduce defects systematically, to manipulate their influence on multiwalled carbon nanotube (MWCNT) properties. While an earlier work' focused on Ar irradiation to tune the electrical conductivity, we investigate irradiation effects for applications which derive benefit from defects, specifically with reference to electrochemical properties and sensors.

The degree of disorder, in our case, was varied simply by exposing the MWCNT ensembles to irradiation for different lengths of time. The effect of argon and hydrogen exposures, on CNT structure, was characterized extensively through Raman spectroscopy, which has been shown to be sensitive to both structural disorder^{13,14} and charge transfer.¹⁵ Essentially, disorder changes the nature of in-plane bonding of carbon

nanotube sheets, deviating away from intrinsic sp^2 character, to more three-dimensional sp^3 nature.¹⁴ The signature of this change is reflected in the energies and linewidths of the G-peak and the D-peak modes (the G-mode, $\sim 1580 \text{ cm}^{-1}$, refers to the *linear* stretching vibrations of any pair of sp^2 bonded sites and denotes "defect-free" carbon nanotube character, while the D-mode is disorder induced, due mainly to *nonlinear* vibrations, and is present $\sim 1360 \text{ cm}^{-1}$). The ratio of the intensity of the peaks, i.e., I_D/I_G , can be correlated with the relative disorder in the sample and gives a measure of the in-plane correlation length (L_a) , or "grain size," of the carbon nanotube sample, through the Tuinstra-Koenig experiments,¹⁶ as $I_D/I_G = c(\lambda)/L_a$, where $c(\lambda)$ =514.5 nm) is¹³ \sim 4.4 nm. For example, it was seen that as the effective crystallite size is reduced from defect-free graphitic structure to lower order nanocrystalline graphite, the I_D/I_G ratio increases, with a concomitant upward shift of the G-peak. Generally, peak shifts have been associated with charge transfer from/to the graphitic CNT lattice.¹⁵ An electron transfer from the CNT to an acceptor reduces the intraplanar bond lengths, in the CNT, and increases the vibration frequencies contributing to an upshift of the G-peak. A corresponding downshift is observed when electrons are transferred from donor elements to the CNT. Additionally, the width of the peaks is proportional to the amount of variation in systemic order through the samples-a greater linewidth indicating a greater range of stretching frequencies, due to nonuniform bonding. In this paper, we consider the variation of I_D/I_G , both in terms of the G- and D-peak heights $(I_D/I_G)_L$ and integrated peak areas $(I_D/I_G)_A$ to take into account effects due to linewidth variation. We state, at the very outset, that the Raman spectra of argon and hydrogen irradiated CNTs exhibit quite different characteristics and are fascinating topics of investigation. As defects in nanotubes are considered to be integral to the use of CNTs in electrochemistry, e.g., as electrodes with fast electron transfer kinetics,

0021-8979/2007/102(6)/064306/6/\$23.00

102, 064306-1

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FIG. 1. SEM micrograph of aligned multiwalled carbon nanotube ensembles grown by thermal chemical vapor deposition (Ref. 21).

supercapacitors,¹⁸ and biochemical sensors,¹⁹ we focus on the electrochemical properties of irradiated CNTs in terms of their responsivity to chemical detection. The efficiency of charge transfer at the irradiated nanotubes was monitored through a cyclic voltammetry²⁰ (CV) technique where the ion-irradiated CNT electrodes serve as electrodes. It was seen that even nonfunctionalized, but defected, CNTs can exhibit remarkable chemical detection sensitivity.

II. EXPERIMENT

Vertically aligned MWCNT ensembles (Fig. 1) were synthesized by a thermal chemical vapor deposition (CVD) method as described in detail elsewhere.²¹ Initially, silicon substrates were coated, through e-beam evaporation, with an iron catalyst 5–10 nm in thickness. A benzene source was used to introduce carbon into the reaction chamber at about 0.1 mL/min along with a slow stream of 500 SCCM (SCCM denotes cubic centimeter per minute at STP) Ar mixed with 200 SCCM ammonia. The reaction chamber was held at 850 °C. Well aligned MWCNTs ~40–50 μ m in length with radii ranging between 20 and 30 nm, and separated by ~200 nm were synthesized. Figure 1 shows a scanning electron microscopy (SEM) micrograph of the as-grown MWCNTs.

Subsequent to growth, the samples were placed in a dry etch chamber [Trion reactive ion etching (RIE)/inductively coupled plasma (ICP)], where argon and hydrogen ion based plasmas were introduced. The effect of reaction with the carbon nanotubes over a range of different process parameters, such as background pressure and flow rate, was studied. In this paper, we report on one specific study which yielded significant effects vis-a-vis structure and electrochemical properties. Here, the reactive ion etching was set to occur at a power of 300 W, a flow rate of 10 SCCM, and a pressure of 10 mTorr, of the argon and hydrogen process gases. These parameters yielded reliable and reproducible results over six tested samples, and the structural damage, as a function of time, was quantified through Raman spectroscopy analyses. While the CNTs seem to be relatively stable up to 60 min of



FIG. 2. (Color online) (a) The Raman spectra for the as produced and argon irradiated carbon nanotubes. The spectra for samples treated for 3, 30, and 60 min, along with the positions of the *D*-peak and *G*-peak are shown. (b) An example of the deconvolution process performed to yield Lorentzian *D*-peak and *G*-peak of the Raman spectra. Both the peak heights and integrated intensities are used in the analyses.

exposure to argon ions, it was seen that hydrogen ion exposure of just ~10 min, results in a significant removal (noticeable with the naked eye) of the nanotubes from the substrate. Hydrogen is known to selectively etch graphitic planes, which explains the enhanced sensitivity. Subsequently, Raman spectroscopy analysis was performed on the as-prepared and treated samples, using a 514.5 nm Ar ion laser (Renishaw) at a power of 1.49 mW. A study of the shape and variation of the Raman spectra with irradiation time allows for the systematic investigation of time-dependent defect formation, induced due to ion exposure. Multiple spectra were taken at different regions of each nanotube sample to ensure accurate structural characterization of the MWCNT sample as a whole. Concomitantly, the ion-irradiated CNTs were investigated for their electrochemical properties, through amperometric response measurements, by placing them as working electrodes in cyclic voltammetry²⁰ experiments.

III. RESULTS AND DISCUSSION

A. Reactive ion etching with Ar

The Raman spectra for the as-prepared and aligned MWCNT samples subject to Ar ion irradiation for several times (t=3, 30, and 60 min) are shown in Fig. 2(a). The

Ar exposure time (min)	G-peak (cm ⁻¹)	D-peak (cm ⁻¹)	$(I_D/I_G)_L$	$(I_D/I_G)_A$	G-peak FWHM (cm ⁻¹)	D-peak FWHM (cm ⁻¹)
0	1578.1±1.4	1355.2 ± 1.4	0.79 ± 0.01	1.77±0.03	89.8±0.8	198.2±5.5
3	1586.4 ± 1.4	1358.4 ± 1.6	0.83 ± 0.02	1.42 ± 0.01	82.1 ± 1.1	146.3 ± 2.5
30	1597.4±2.7	1354.3 ± 2.6	0.86 ± 0.02	1.25 ± 0.12	134±6	188.5 ± 5.6
60	1600.7 ± 4.2	1354.9 ± 2.5	0.89 ± 0.03	1.16 ± 0.14	83.0±3.2	108.5 ± 6.9

TABLE I. Summary of Raman spectra for the as-prepared and argon treated MWCNTs.

presence of the CNT intrinsic *G*-peak and the disorder induced *D*-peak, indicative of inherent disorder, was observed even in the as-prepared samples. The low synthesis temperature (~850 °C), which is far below the ~2000 °C necessary²² for the development of long range crystalline order, is presumably responsible. It was also noted²¹ that the CNTs generally grow open ended, and the tube ends would contribute to enhanced defect density.¹² The Raman spectra were then analyzed by deconvoluting the spectrum, in the range of 1100–1700 cm⁻¹, to fit the *G*-peak and the *D*-peak with two Lorentzian peak functions [Fig. 2(b)]. The Lorentzian is generally considered to be a good fit for disordered CNTs,²³ which have not been subject to extensive amorphization. The following equation was used for fitting the intensity (*I*) with the Raman shift (*f*, in cm⁻¹) as follows:

$$I = \frac{2A}{\pi} \frac{w}{4(f - f_c)^2 + w^2}.$$
 (1)

Here, A is the area under the curve, w is the full width at half maximum (FWHM) of the curve, and f_c the abscissa of the peak. The summary of the data for Raman spectra for the Ar irradiated samples is listed in Table I.

Analysis of the data, and Fig. 2(a), indicates several interesting features. First, there is a significant shift $[\sim 22 \text{ cm}^{-1}, \text{ Fig. 3(a)}]$ in the position of the *G*-peak indicative of charge transfer. Second, a decrease [Fig. 3(b)] in the D- and G-peak area intensity ratio, i.e., $(I_D/I_G)_A$ with increasing Ar etch time is seen. As Ar ion exposure was intended to disorder the nanotubes, this is quite contrary to expectation. However, the D- and G-peak line intensities, i.e., $(I_D/I_G)_L$, do increase as expected [Fig. 3(c)]. To account for the $(I_D/I_G)_A$ variation, the linewidths of the peaks must also be taken into account-a detail that is not often followed in literature.²³ From Table I, while the *G*-peak linewidth is relatively constant for the as-prepared sample (FWHM $\sim 90 \text{ cm}^{-1}$) and the sample irradiated with Ar for 60 min (FWHM \sim 83 cm⁻¹) there is a significant sharpening of the linewidths of the D-peak (as-prepared sample $\sim 198 \text{ cm}^{-1}$ and the 60 min irradiated sample $\sim 109 \text{ cm}^{-1}$).

While the decrease in $(I_D/I_G)_A$ with exposure to Ar was confusing, this can be understood by examining the effects of etching on the *G*-peak and *D*-peak individually. Increasing the amount of disorder in the MWCNT sample increases the intensity of the *D*-peak while decreasing the *G*-peak intensity. On the other hand, the *D*-peak linewidth decreases, while no significant broadening is observed for the *G*-peak. As a result, the reduction in area resulting from the sharpening of the *D*-peak outweighs the area increase caused by the increased intensity of the *D*-peak (relative to that of the *G*-peak), causing an $(I_D/I_G)_A$ decrease.

The integrated intensity ratio was then used to calculate the in-plane correlation length (L_a) , using the Tuinstra-



FIG. 3. (a) Plot of the Raman shift of the *G* band as a function of the Ar irradiation time. The error bars in all the measurements were calculated from the average of six runs. (b) The ratio of the integrated *D*-peak area intensity to the *G*-peak area intensity decreases as a function of exposure to argon. Note that this graph takes into account both the variation in linewidth and peak intensity. (c) The ratio of the *D*-peak line intensity to the *G*-peak line intensity decreases as a function of exposure to argon.

TABLE II. In-plane correlation length (L_a) for the Ar treated MWCNTs, calculated using integrated D/G-peak intensity ratios.

Argon exposure time (min)	L_a (nm)		
0	2.49		
3	3.10		
30	3.52		
60	3.80		

Koenig relationship,¹⁶ $L_a(\text{nm}) = 4.4(I_D/I_G)_A^{-1}$, and is listed in Table II. L_a could be used as an approximate measure of the length over which the CNT is *defect-free*, and indicates increased order by ~50% due to argon exposure.

To provide a physical picture on the effects of argon irradiation, we hypothesize that Ar is being inserted into the graphitic lattice of the MWCNTs. Charged Ar⁺ ions could be intercalated¹³ into the CNTs, resulting in the formation of acceptor-like defects, causing a contraction of the intraplanar sp^2 bond lengths and an upshift of frequency. The *D*-peak position is relatively constant (~1355 cm⁻¹, Table I), implying that the defects created, due to Ar irradiation, have the same energy as in the as-prepared MWCNTs. However, the linewidth (FWHM) sharpening is indicative of decreased sp^2 or enhanced sp^3 character, which is promoted by interaction of the planar, graphitic, phonon modes with the introduced argon. Note that the Raman scattering cross section for sp^2 bonded carbon atoms is ~50 times greater than that for sp^3 bonded carbons.

B. Reactive ion etching with H₂

The Raman spectra for the as-prepared and aligned MWCNT samples subject to hydrogen ion irradiation for several times (t=1, 3, and 10 min) are shown in Fig. 4(a). The Raman spectra were deconvoluted into Lorentzian peaks as described in the previous section. Table III provides a summary of these spectra.

No frequency shift of the G peak was observed in this case [Fig. 4(b)]. Both the $(I_D/I_G)_L$ and $(I_D/I_G)_A$ ratios increase with increased exposure to hydrogen, as expected from increased disorder. A comparison of the linewidths of the as-prepared sample with the 10 min hydrogen treated sample (Table III) indicates a significant broadening for the $G(\sim 25\%)$ and the D-peak ($\sim 50\%$). The above observations could be explained on the basis of relative affinity between the hydrogen and the carbon atoms. It has been shown²⁴ that hydrogen can terminate any residual dangling bonds (e.g., at the CNT ends) and stabilize sp^3 bonding. The lower bond enthalpy of the C—H bond (~340 kJ/mol) compared to the C—C bond ($\sim 600 \text{ kJ/mole}$) is the primary reason.²⁵ In contrast with Ar, very little charging of the MWCNTs occurs due to exposure to hydrogen irradiation due to the passivation effect. Consequently, no peak shift was observed [Fig. 4(b)]. In one sense, exposure to hydrogen is self-healing for the nanotube.

An increasing hydrogen exposure [Figs. 4(a), 4(c), and 4(d)] correlates with diminished sp^2 bonding in the CNTs, as H saturates the C==C bonds, converting sp^2 carbons into sp^3 =CH₂ sites.¹⁴ The broadening of the *D*-peak and *G*-peak,



FIG. 4. (Color online) (a) The Raman spectra for the as produced and hydrogen irradiated carbon nanotubes. The spectra for samples treated for 1, 3, and 10 min, along with the positions of the *D*-peak and *G*-peak are shown. (b) Plot of the Raman shift of the *G* band as a function of the hydrogen etching time. (c) The ratio of the integrated *D*-peak area intensity to the *G*-peak area intensity increases, as expected, as a function of exposure to hydrogen. (d) The ratio of *D*-peak line intensity to *G*-peak line intensity as a function of hydrogen etching time.

along with the absence of any peak shifts, leads us to hypothesize increased disorder associated with hydrogen ion implanted nanotubes.¹³ The broadening of the *G*-peak seen with hydrogen treatment (but absent in Ar) most likely occurs due

TABLE III. Summary of Raman spectra for the as-prepared and hydrogen treated MWCNTs.

H exposure time (min)	G-peak (cm ⁻¹)	D-peak (cm ⁻¹)	$(I_D/I_G)_L$	$(I_D/I_G)_A$	G-peak FWHM (cm ⁻¹)	D-peak FWHM (cm ⁻¹)
0	1583.0±2.6	1355.9 ± 2.9	0.82±0.03	1.34±0.05	74.4±1.0	125.5±1.7
1	1581.4 ± 1.9	1354.5 ± 1.5	0.83 ± 0.02	1.35 ± 0.02	74.6±0.8	124.9 ± 2.8
3	1584.4 ± 1.4	1355.7 ± 2.4	0.87 ± 0.01	1.54 ± 0.01	83.7±1.4	151.3 ± 2.9
10	1583.7 ± 3.9	1358.2 ± 3.2	0.89 ± 0.02	1.88 ± 0.22	93.4±7.9	193.8 ± 35.3

to hydrogen bonding to dangling carbon bonds, thus affecting individual intraplanar bonds and causing a large variation in bond length/energy. The *D*-peak linewidth could also be correlated to a greater span of disorder associated bond lengths.

The in-plane correlation length (L_a) , which measures the translational symmetry of the CNTs, was calculated from the intensity ratio and is listed in Table IV. In contrast to the Ar case, the net disorder increases with increased hydrogen irradiation.

We note that our experiments are typical of stage I of the amorphization of carbon as defined by Ferrari and Robertson,²³ incorporating the transition from perfect graphite to nanocrystalline graphite. We have crudely estimated, from the geometry of the nanotubes and process conditions, an average energy of 1-10 eV/at. for $\sim 10 \text{ min of exposure}$, which is sufficient to cause atomic displacements and rearrangement. This corresponds to a progressive reduction in L_a along the nanotube while the aromatic rings are still maintained. Consequently, we have shown that different degrees of disorder can be obtained in CNTs through exposure to Ar and H irradiation. We next investigate the electrochemical application of these *defect tuned* structures.

The chemical response of the treated CNT electrodes was investigated through amperometric measurements in a CV experiment, where the variation of electrochemical cell current with time, at a constant voltage, was monitored. The details of the experiments will be published elsewhere.²⁶ The response of the as-prepared [Fig. 5(a)], 3 min argon treated [Fig. 5(b)] and 10 min hydrogen treated [Fig. 5(c)] CNT ensembles to 1 ml additions of 5 mM glucose (every 20 s) is illustrated. From the experiments, it was evident that all CNT electrodes are sensitive to chemical addition, with an average current density change of $38.8 \pm 6.6 \ \mu \text{A/cm}^2$ (as prepared), $29.3 \pm 10.0 \ \mu \text{A/cm}^2$ (Ar treated), and $67.3 \pm 8.8 \ \mu \text{A/cm}^2$ (hydrogen treated). The enhanced sensitivity for the hydrogen exposed CNT electrode could be due to the passivating effects of hydrogen as delineated earlier, which minimizes charging and associated capacitive effects. The similar responses for the as-prepared and argon treated samples are

TABLE IV. In-plane correlation length (L_a) for the hydrogen treated MWCNTs, calculated using integrated D/G-peak intensity ratios.

Hydrogen exposure time (min)	L_a (nm)		
0	3.28		
1	3.26		
3	2.86		
10	2.34		

symptomatic of charged nanotubes, which could contribute a significant capacitive (non-Faradaic) component to the detected current.

IV. CONCLUSIONS

We have shown that exposure of CNTs to argon and hydrogen ion irradiation can be used to controllably intro-



FIG. 5. Amperometric measurements, of aligned MWCNT ensemble electrodes in the (a) as produced, (b) 3 min argon irradiated, and (c) 10 min hydrogen irradiated conditions. The arrows indicate 1 ml additions of 5 mM glucose to 25 ml of a 0.1M, pH 7.4 phosphate buffer, every 20 s. The voltage was fixed at -0.2 V.

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duce defects and tune the electrochemical properties for sensors and other applications. A detailed analysis using Raman spectroscopy showed that the disorder could be related to intercalation and CNT charging, in the case of Ar ions. Hydrogen irradiation had the effect of passivating defects and primarily results in a broadening of the Raman peaks. The Raman intensities were correlated to the in-plane correlation length (L_a), which provides a semiquantitative measure of the degree of disorder. The implications of this study extend to a better understanding of the nature of defects in CNTs and to applications where defects are of primary importance, e.g., electrochemistry and field emission.

ACKNOWLEDGMENTS

We gratefully acknowledge support from the National Science Foundation (Grant Nos. ECS-05-08514, ECS-06-43761, and DMI-0304019) and the Office of Naval Research (Award No. N00014-06-1-0234). We are thankful to Professor Frank Talke's group at the Center for Magnetic Recording Research (CMRR) at UC, San Diego for help with the Raman spectroscopy.

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