

Tailoring the Electrochemical Behavior of Multiwalled Carbon Nanotubes Through Argon and Hydrogen Ion Irradiation

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As carbon nanotubes (CNTs) inevitably contain defects, it is of interest to investigate the possibility of artificially introducing defects to tune their properties. This is especially important for applications in electrochemistry and field emission. We report on the electrochemical behavior, through cyclic voltammetry measurements, of multiwalled CNT samples with different defect densities induced through exposure to hydrogen and argon irradiation. Ar exposure leads to CNT charging and reversible/quasi-reversible electron-transfer kinetics, while hydrogen irradiation yields irreversible kinetics. Correlation with Raman spectroscopy implies the termination of residual dangling bonds in CNTs by hydrogen, causing an elimination of reactive sites. © 2008 The Electrochemical Society. [DOI: 10.1149/1.2834929] All rights reserved.

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Since their discovery,¹ carbon nanotube (CNT)-based systems have been investigated² to exploit their, theoretically predicted, remarkable electronic, mechanical, thermal, and electrochemical properties. For example, in electrochemistry, both multiwalled CNTs (MWCNTs) and single-walled CNTs have been found to exhibit fast electron-transfer kinetics³ and high electrocatalytic activity,^{4,5} presumably due to their large surface-to-volume ratio, making CNTs sensitive to chemical or environmental interactions. Combined with high electronic conductivity,⁶ these aspects make CNTs attractive for electrodes as well.

From a structural point of view, CNTs are generally grown openended in most chemical vapor deposition (CVD) processes.⁷ The open ends of CNTs have been compared to the edge plane and the tube walls to the basal plane of highly-ordered pyrolytic graphite.³ Then, a defect-free, basal plane-dominated surface of CNTs would display slow electron-transfer kinetics due to the absence of reactive sites. The enhanced electrochemical properties of CNTs could then be a consequence of the available reactive sites at the tips and defects present along the tube walls. Such a conclusion could be drawn through the similar responses in cyclic voltammetry (CV) of both CNT film modified basal plane graphite electrodes and bare edge-plane pyrolytic graphite electrodes.⁵ However, the inevitable pres-ence of defects^{9,10} even along the edge plane and through the vol-ume of the CNTs¹¹ has also been widely acknowledged⁶ and seems to be integral to their performance in various technologies such as nanoelectronics,¹² field-emission devices, electrodes in electrochemistry, supercapacitors, etc. It has also recently been reported⁵ that defects mimicking the edge-plane/edge-plane-like sites of graphite are relevant for explaining the electrochemical activity of CNTs. These defects are responsible for fast electron-transfer reactions, with up to nine orders of magnitude larger⁵ value of the electrontransfer rate constant (k^{0}) , enhancing the applicability of CNTs for high-efficiency electrodes.

It would be interesting to examine if the number of defects in a particular CNT ensemble could be manipulated, so as to obtain tunable physical and chemical properties. In the present study, argon and hydrogen ions were introduced in a controllable manner into MWCNTs, through ion irradiation, to influence the degree of disorder. Raman spectroscopy was used for structural characterization. The irradiated MWCNTs were then used as working electrodes in CV to yield insight into the influence of argon and hydrogen on the electrochemical properties. It was seen that exposure to argon has the effect of charging the nanotubes and preserving reversible/quasireversible electrochemical behavior, while hydrogen seems to passivate the electrodes and promotes irreversibility in the CV characteristics. Our study has the broad implication that controlled in

troduction of impurities can be used to tune MWCNT electrode properties for various applications in which defects are posited to play a major role.

Experimental

Vertically aligned MWCNTs were synthesized by the thermal CVD method described by Deck et al.¹³ Briefly, silicon substrates were coated, through E-beam evaporation, with an iron catalyst 5–10 nm thick. 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 Ar mixed with 200 sccm ammonia. The reaction chamber was held at 850°C. Well-aligned MWCNTs ~40 to 50 μ m in length, with radii between 20 and 30 nm and separated by ~200 nm, were synthesized. Figure 1 shows a scanning electron micrograph of the as-grown MWCNTs.

Subsequent to growth, the samples were placed in a dry-etch chamber (Trion RIE/ICP) where argon- or hydrogen-based plasmas could be independently introduced. The effect of the ion irradiation in the plasma with the CNTs over a range of different process parameters, such as background pressure and flow rate, was studied. In this paper, we report on one specific process condition, conducted on several MWCNT samples, which yielded significant effects vis-á-vis structure and electrochemical properties. In this case, the reactive ion irradiation was set at a power of 300 W, a flow rate of 10 sccm, and a background pressure of 10 mTorr. These parameters yielded reliable and reproducible results over six tested samples, and the structural disorder, as a function of irradiation time, was quantified



Figure 1. SEM micrograph of aligned MWCNT ensembles grown by thermal CVD. $^{\rm 13}$

through Raman spectroscopy (from Renishaw Inc., using a 514.5 nm Ar ion laser at 1.49 mW) analyses. A study of the shape and variation 14,15 of the Raman spectra with irradiation time allows for the systematic investigation of time-dependent defect formation due to argon/hydrogen exposure. While the CNTs were relatively stable up to 60 min of 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. Concomitantly, the ionirradiated CNTs were investigated for their electrochemical properties, through amperometric response measurements, by placing them as working electrodes in CV experiments¹⁶ using a PCI4-300 potentiostat from Gamry Instruments Inc. The potentiostat was configured to have a current range of 3 nA to 300 mA and a voltage range ± 11 V, with a resolution of 1 fA and 1 μ V, respectively. A threeelectrode setup, in a 1 M KCl supporting electrolyte solution containing various concentrations (1-10 mM) of K₃Fe(CN)₆, was employed with a (i) MWNT working electrode, (ii) platinum wire counter electrode, and a (iii) saturated calomel reference electrode. All the CV experiments were conducted at room temperature. The MWCNT working electrode was fabricated, using conducting epoxy (H20E from Epotek, Inc.) to attach a copper wire to the back of the silicon substrate on which the vertically aligned MWCNTs were grown. Care was taken to ensure that neither the copper wire nor the epoxy contacted the electrolyte solution. It was also verified, through control experiments, that neither the silicon nor the epoxy displayed any electrochemical activity in the voltage window (-0.35 to 0.8 V) used for the CV measurements. We also took care to eliminate the possibility of hexacyanoferrate complex adsorbate formation on the electrodes, which could affect electrochemical kinetics, through a careful choice of the voltage scan range and by using freshly prepared (<2 h old) $Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$ solutions.¹⁷ Experiments were carried out at different scan rates (1 mV/s-1 V/s).

Results and Discussion

The MWCNT working electrode in our experiments is really made up of multiple nanotubes (~2000/cm²), each acting as an individual electrode. Assuming a diffusion coefficient¹⁸ (*D*) of ~ 6.3×10^{-6} cm²/s, for K₃Fe(CN)₆ in KCl, we calculate a diffusion layer thickness, which is scan-rate dependent, to be in the range of 150–700 µm, which is much larger than the spacing between the individual nanotubes (~200 nm). Consequently, due to the overlap of the individual diffusion layers, a macroelectrode-like behavior could be obtained.

Argon-irradiated MWNT Electrodes

The CV spectra for the as-prepared and aligned MWCNT sample electrodes subject to argon irradiation for increasing times (t = 3,30, and 60 min) are shown in Fig. 2 and summarized in Table I. The as-produced MWCNT electrode has a cathode-anode peak potential difference $\Delta E_{\rm p}(=E_{\rm pc}-E_{\rm pa}) \approx 35.9$ mV, which is less than the 59 mV characteristic of a reversible redox system.¹⁹ This could presumably be due to the adsorption of electroactive species onto the MWCNT electrode. Because $\Delta E_{\rm p} = 0$ mV for adsorbed species (if the oxidized and reduced form adsorbed with the same affinity),¹² a mixed contribution from both adsorbed species and species in solution would lead to intermediate values between 0 and 59 mV. It is further observed that the $\Delta E_{\rm p}$ increases with Ar irradiation time, indicating diminished electron-transfer kinetics.^{16,19} The shift in $\Delta E_{\rm p}$ and the individual peak potentials, cathodic ($E_{\rm pc}$) and anodic (E_{pa}) , are more explicitly indicated in Fig. 2b and c, respectively. The E_{pc} shifts to increasingly positive potentials, while E_{pa} moves negatively with increased argon exposure, which seems to be indicative of MWCNT charging (as demonstrated by Raman spectroscopy,²⁰ see Fig. 3). A more positive potential is required to initiate the reduction of $Fe(CN)_6^{3-}$ to $Fe(CN)_6^{4-}$ (the cathodic reac-



Figure 2. (Color online) (a) Cyclic voltammograms [6 mM K₃Fe(CN)₆ in 1 M KCl, with a scan rate of 20 mV/s] for MWCNT electrodes exposed to argon irradiation for 0 (as produced), 3, 30, and 60 min. (b) The cathodic–anodic peak potential difference (ΔE_p) as a function of Ar irradiation time (the error bars were calculated from the average of three runs). (c) The individual anodic (E_{pa}) and cathodic (E_{pc}) peak potentials as a function of Ar irradiation time irradiation time.

tion) to compensate. Concomitantly, smaller anodic (negative) potential is needed to initiate the oxidation of $Fe(CN)_6^{4-}$ to $Fe(CN)_6^{3-}$. In spite of the increase in ΔE_p , however, the electrode reactions remain reversible/quasi-reversible, as indicated by the ratio of the cathodic peak current density to the anodic peak current density

Table I. Summary of data taken from the cyclic voltammograms of vertically aligned MWCNT electrodes exposed to argon for 0 (as produced),3, 30, and 60 min.Electrode treatmentAs produced3 min30 min60 min

Electrode treatment	As produced	3 min	30 min	60 min
$i_{\rm pa} ({\rm mA/cm^2})$	-0.91 ± 0.02	-0.66 ± 0.01	-0.40 ± 0.01	-0.58 ± 0.00
$i_{\rm pc} ({\rm mA/cm^2})$	0.91 ± 0.06	0.67 ± 0.06	0.38 ± 0.00	0.55 ± 0.02
$\dot{E}_{\rm pa}~({\rm mV})$	217.1 ± 0.1	205.1 ± 0.7	200.1 ± 0.6	196.1 ± 0.8
$E_{\rm pc}$ (mV)	253.0 ± 0.0	261.0 ± 1.4	267.1 ± 1.4	278.2 ± 1.6
$\Delta E_{\rm p} ({\rm mV})$	35.9 ± 0.1	55.9 ± 0.7	67.0 ± 0.8	82.1 ± 0.8
$ \dot{i}_{\rm p,c}/\dot{i}_{\rm p,a} $	1.0 ± 0.1	1.0 ± 0.1	0.95 ± 0.01	0.95 ± 0.03

 $(i_{p,c}/i_{p,a})$, which is close to 1. (In Table I the values for $i_{p,c}$ and $i_{p,a}$ were carefully determined through the procedures outlined by Bard and Faulkner.¹⁶)

The previous results indicate that argon treatment does not alter the electron transfer characteristics of the MWNT electrodes, but only changes the effective available electrode surface, which is manifested through a change in the peak potentials ($E_{\rm pc}$ and $E_{\rm pa}$). The notion of quasi-reversibility and efficient electron-transfer kinetics is noted in Table I, where the stability of $E_{\rm pc}$ and $E_{\rm pa}$ (± 1 mV) vis-à-vis both the concentration of the redox agents and scan rate, dV/dt, is observed. The cyclic voltammograms for all the argonexposed MWCNTs show similar behavior. A linear dependence of



Figure 3. (Color online) (a) Raman spectra for the as-produced and argonirradiated CNTs. The spectra for samples treated for 3, 30, and 60 min, along with the positions of the D and G peaks, are shown. (b) Plot of Raman shift of the G band as a function of Ar irradiation time. The error bars in all the measurements were calculated from the average of six runs.

the peak current density (i_p) on the concentration and the square root of the scan rate, $(dV/dt)^{1/2}$ as predicted by the Randles–Sevcik equation for the reversible/quasireversible system,¹⁹ is also seen. A relative decrease in the peak current density with increased Ar irradiation was observed, which could be correlated to the negative charging of the nanotubes, hindering the diffusion of species to the MWCNT electrodes. A modified effective electrode area does not seem to be responsible for the larger current density in the asproduced MWCNT electrode, as is seen later in the paper. The notion of MWCNT charging due to argon exposure was confirmed through Raman spectroscopy, which is sensitive to both structural disorder^{14,15} and charge transfer,²¹ by analyzing the positions and linewidths of the G- and D-peak modes (Fig. 3). While increased disorder causes the width of the peaks to increase, electron transfer from/to the nanotube is manifested in an up-/downshift of the G peak,¹⁴ respectively. Such an upshift was indeed seen in the variation of the G peak (Fig. 3b), and more detailed analysis, which has been published elsewhere,²⁰ confirms charging of MWNTs due to argon.

Hydrogen Irradiated MWNT Electrodes

The CV spectra for the as-prepared and aligned MWCNT sample electrodes subject to hydrogen irradiation for several lengths of time (t = 1, 3, and 10 min) are shown in Fig. 4 and summarized in Table II. This system exhibits irreversible electron transfer characteristics. The large increase in ΔE_p with increasing hydrogen exposure time from 35.9 (as produced) to 237.0 mV (after 10 min) is much greater than that for the argon-exposed MWCNTs. Additionally, a marked deviation of $i_{p,c}/i_{p,a}$, from an ideal ratio of 1, by ~23%, is seen. We tentatively ascribe the gradual deviation from reversible electron-

As produced 8 Current Density x 10⁴ (A/cm²) 1 min Inc. hydrogen 3 min 4 10 min 0 4 -8 0.2 -0.2 0.0 0.4 0.6 0.8 -0.4 Voltage (V)

Figure 4. (Color online) Overlay of cyclic voltammograms [6 mM $K_3Fe(CN)_6$ in 1 M KCl, with a scan rate of 20 mV/s] for MWCNT electrodes exposed to hydrogen irradiation for 0 (as produced), 1, 3, and 10 min.

Table II. Summary of data taken from the cyclic voltammograms of vertically aligned MWCNT electrodes exposed to argon for 0 (as produced), 1, 3, and 10 min.

Electrode treatment	As produced	1 min	3 min	10 min
$i_{\rm p,a}~({\rm mA/cm^2})$	-0.91 ± 0.02	-0.92 ± 0.00	-0.89 ± 0.00	-073 ± 0.06
$i_{\rm pc}$ (mA/cm ²)	0.91 ± 0.06	0.77 ± 0.01	0.73 ± 0.06	0.57 ± 0.02
\dot{E}_{pa} (mV)	217.1 ± 0.1	170.0 ± 0.8	141.9 ± 0.8	101.9 ± 1.4
$E_{\rm pc}$ (mV)	253.0 ± 0.0	287.9 ± 0.8	316.0 ± 4.2	338.9 ± 15.6
$\Delta E_{\rm p} ({\rm mV})$	35.9 ± 0.1	117.9 ± 1.6	174.1 ± 3.4	237.0 ± 17.0
$\left i_{\rm p,c}/i_{\rm p,a}\right $	1.0 ± 0.1	0.83 ± 0.01	0.82 ± 0.06	0.77 ± 0.04

transfer kinetics to be caused by the tendency of hydrogen to terminate reactive sites, such as dangling bonds, irradiation-induced defects, or even amorphous carbon species.⁷ The primary motivation for hydrogen termination is the lower energy of the C–H bonds compared to C–C bonds.²² With fewer active sites, the kinetics would be adversely affected and the electrochemical properties of the MWCNTs would begin to resemble those of basal plane graphite, with ΔE_p approaching large values (>200 mV) for the $(CN)_6^{3-}/(CN)_6^{4-}$ redox system.²³

In contrast to a reversible electrode system (i.e., as-prepared and argon-treated MWCNTs), the $\Delta E_{\rm p}$ for the hydrogen-irradiated MWCNT electrodes increases linearly with both K₃Fe(CN)₆ concentration and scan rate (Table II). The increase in $\Delta E_{\rm p}$ could be correlated to the concentration gradients in the solution. Here, the electron transfer kinetics cannot keep up with the enhanced diffusion of the $(CN)_6^{3-}/(CN)_6^{4-}$ species to the electrode, and this lag could be responsible for the irreversibility. $E_{\rm pc}$ shifts to increasingly more positive potentials, while E_{pa} shifts negatively, with the magnitude of the shift dependent on the exposure of the MWCNTs to hydrogen. In contrast to the argon-irradiated case, it was determined through Raman spectroscopy that nanotube charging was not involved. In the Raman spectra (Fig. 5a), no peak shifts symptomatic to charging were seen (Fig. 5b), but the G and D peaks broaden, pointing to the sp³ bonding tendency and the passivating effect of hydrogen. Increasing passivation, due to the hydrogen, of reactive electrocatalytic sites could cause diminished reversibility.

Table II further demonstrates the irreversibility, through recorded cyclic voltammograms, as a function of concentration and scan rate for the hydrogen-irradiated MWCNT electrodes. Also, for the peak current density vs concentration and vs scan rate, a linear dependence, characteristic of the Randles–Sevcik equation¹⁹ is not obtained. All the above characteristics indicate that an irreversible electrochemical system is obtained when MWCNTs are irradiated with hydrogen.^{16,19}

Our study indicates that ion treatment of CNTs could be utilized for tuning their electrochemical response. For example, argon exposure, which creates charged defects, could mimic nanotube functionalization, while hydrogen treatment of MWCNT electrodes, which has been shown to be effective for nanotube passivation, could be considered for minimization of capacitive effects.²⁴ In preliminary experiments, we have investigated the chemical response of the argon- and hydrogen-treated CNT electrodes through amperometric measurements where the variation of electrochemical cell current with time, at a constant voltage, was monitored. The details of the experiments are published elsewhere,²⁰ and verified the above conclusions. It was evident that the hydrogen exposed CNTs exhibit lower charging-related effects, while the as-prepared and argontreated MWCNT electrodes contribute a significant capacitive (nonfaradaic) component.

Conclusions

We have shown that exposure to argon and hydrogen ion irradiation can be used to controllably introduce defects or passivate MWCNTs. While the argon treatment leads to nanotube charging, the electrochemical characteristics as measured through CV show quasireversibility. While the peak potential difference ΔE_p gradually increases from 36 to 82 mV with increasing argon exposure, the peak current ratio $i_{\rm p,c}/i_{\rm p,a}$ remains close to 1, indicating quasireversible kinetics. Hydrogen irradiation had the effect of passivating the nanotubes and irreversible kinetics was observed. A large increase of $\Delta E_{\rm p}$ to ~237 mV, on exposure to hydrogen for 10 min, was observed, along with a reduction of $i_{\rm p,c}/i_{\rm p,a}$ from 1 to 0.77. Raman spectroscopy analysis of the peak shifts and broadening was used to indicate MWCNT charging, in the case of Ar irradiation, and passivation, for hydrogen exposure. Our work lays the foundation for a better understanding of defects in nanotubes and can be applied for tuning the electrochemical properties of MWCNT-based electrodes, e.g., in chemical sensors.



Figure 5. (Color online) (a) Raman spectra for the as-produced and hydrogen-irradiated CNTs. The spectra for samples treated for 1, 3, and 10 min, along with the positions of the D and G peaks, are shown. (b) Plot of the Raman shift of the G band as a function of hydrogen irradiation time.

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