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# Purification of Single Wall Carbon Nanotubes As a Function of UV Wavelength, Atmosphere, and Temperature

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We investigate the purification of as-prepared single wall carbon nanotubes (SWCNTs) by exposure to pulsed 193 and 248 nm laser light, as well as lamp wavelengths of 254 and 185 nm. Raman spectroscopy before and after laser exposure indicates the removal of non-nanotube material without modification of the distribution of tube diameter for material exposed to a 248 nm laser, while 193 nm laser light does not selectively oxidize carbon impurities. The mechanism of purification is further considered in the context of atmosphere (oxygen, ozone, nitrogen or partial vacuum) and temperature (measured average and calculated maximum). A mathematical model for pulsed laser heating is used to estimate the maximum temperature achieved during laser excitation. We attribute the purification of nanotube samples to photophysical interactions of the pulsed 248 nm photons in resonance with  $sp^2$  carbon.

## Introduction

Scientific research and commercial application of bulk single wall carbon nanotubes (SWCNTs) has been hindered by the lack of material that is free from impurities. As-prepared SWCNTs are typically formed in the presence of catalyst metals and impurities such as amorphous carbon, graphite, nanocrystalline graphite and other nanocarbons. Purification techniques typically require wet acid treatments to remove catalyst metals, and heating to remove functionalized carbon impurities.<sup>1</sup> Achieving the optimal oxidation without damaging or destroying nanotubes is difficult.

Previous work has documented the modification of SWCNTs exposed to continuous-wave (CW) laser light at various wavelengths including 1064,<sup>2</sup> 782,<sup>3</sup> 515,<sup>3</sup> 633,<sup>3,4</sup> and 488 nm,<sup>4</sup> with irradiances in the range of 19 to  $1 \times 10^5$  W/cm<sup>2</sup>. The purification or enrichment of the nanotube material was demonstrated by Raman spectroscopy and attributed to heating effects, whereby tubes of smaller diameter oxidize before larger tubes because of structural strain.<sup>4</sup> In addition, pulsed ultraviolet (UV) laser light has been employed to treat both SWCNT and multiwalled carbon nanotubes (MWCNTs). For example, photodetachment of covalently bonded functional groups has been demonstrated by exposure to 244 and 325 nm lasers.<sup>5</sup> Photo-oxidation of carbon impurities in MWCNT samples has been demonstrated by exposure to a 248 nm laser, after which nanotube tips with sharp edges and clean surfaces were imaged by transmission electron microscopy.<sup>6</sup>

It is well-known that UV light interaction with ambient oxygen generates ozone. Exposure of SWCNTs to ozone can result in functionalization,<sup>7</sup> cutting,<sup>8</sup> purification,<sup>7</sup> and/or destruction of tubes,<sup>9</sup> dependent on experimental parameters including concentration, exposure time, and temperature. Experimental<sup>9</sup> and theoretical<sup>10</sup> work suggests that oxidation by ozone significantly disrupts the conjugated  $\pi$  bonding on the

nanotube sidewall. Raman and X-ray photoelectron spectroscopies have shown an increase in the defect density of SWCNTs exposed to a low-pressure (LP) Hg lamp due to oxidation of the nanotube sidewalls attributed to ozonolysis.<sup>9</sup>

In our previous work, we demonstrated a laser-based purification technique that selectively removed carbon impurities from as-prepared nanotube samples by use of a 248 nm laser in ambient air.<sup>11</sup> It was suggested that such purification was due to the resonance of the incident photons with the  $\pi$  plasmon. The  $\pi$  plasmon is a delocalized network of electrons formed by the hybridization of  $sp^2$  carbon atoms that compose a SWCNT. A broad absorption peak centered at  $\sim 248$  nm is observed due to this collective excitation,<sup>12</sup> and absorption of photons of this energy is therefore resonantly enhanced. The resonance of photons with the  $\pi$  plasmon enables an efficient transfer of energy to the nanotube carbon–carbon bonds, which results in oxidation of the impurities near the SWCNT surface.

In this work, we further investigate the interaction between UV light and the  $\pi$  plasmon and consider the laser wavelength, fluence, atmosphere and temperature. We also consider the interaction of CW UV photons with carbon nanotube samples and comment on the purification mechanism.

## Experimental Section

The nanotube samples were prepared by dispersing commercially available arc-generated SWCNTs (Carbolex<sup>13</sup>) in chloroform and sprayed by air-brush onto a quartz substrate. The samples were then exposed to different sources of UV light, including excimer lasers and gas lamps. One laser was a 248 nm excimer laser operating with a pulse width of approximately 20 ns and a pulse repetition frequency of 10 Hz, as well as a 193 nm laser operating in the range of 10 to 20 ns. Both laser systems operated at an average power of 200–800 mW/cm<sup>2</sup>. The frequency of the 193 nm laser was adjusted in the range of 10–50 Hz in order to achieve comparable average power. The beam exiting each laser was spatially homogenized by means of two lenses in series, where each lens consisted of an array of cylindrical lenselets with the cylindrical axis of the first lens

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perpendicular to that of the second. At the plane of the sample exposure, the beam in each instance was an unpolarized homogeneous square area of approximately  $1 \times 1 \text{ cm}^2$ , as measured by a pyroelectric array detector. The duration of each laser exposure was defined by opening a shutter for 30 s. For each exposure to the laser, the average power was measured with a thermopile-based detector, calibrated by means of an isoperibol calorimeter.

The nanotube samples were also exposed separately to UV light from two different LP Hg grid lamps. An ozone-producing lamp emitting at 185 and 254 nm, and a nonozone-producing lamp with a phosphor coating that emitted at 254 nm were employed. The irradiance of each lamp at 254 nm was  $7 \text{ mW/cm}^2$ , as specified by the manufacturer.

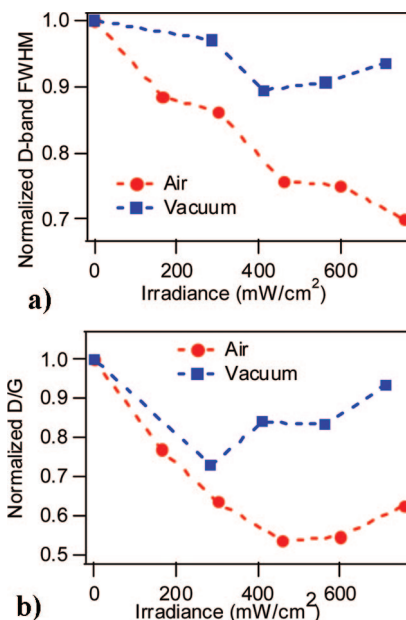
The nanotube samples were exposed to UV light within a local enclosure that controlled the atmosphere. Experiments with the 248 nm laser were performed in vacuum ( $10^{-5}$  Torr), or in ambient air. The experiments at 193 nm were performed in air or pure nitrogen. The entire 193 nm laser system was necessarily enclosed in pure  $\text{N}_2$  atmosphere to avoid attenuation of the 193 nm beam by ambient oxygen in the atmosphere. The 193 nm exposures in air were achieved by placing the nanotube sample in a box with a fused silica window that allowed transmission of the light source. Air flowing over the sample ( $\sim 100 \text{ sccm}$ ) was vented outside the nitrogen-purged laser system. All irradiance losses through the silica window were accounted for by measuring the power transmitted through the window.

Raman spectroscopy was used to characterize the nanotube samples after irradiation. The system operated in a backscattering configuration by use of  $\sim 10 \text{ mW}$  of an argon ion laser providing 488 nm (2.54 eV) excitation. A 55 mm telephoto lens was employed both to focus the beam to an  $\sim 0.25 \text{ mm}^2$  area and to collect the Raman-scattered light. The scattered light was analyzed with a 0.27 m grating spectrometer equipped with a liquid-nitrogen-cooled charge-coupled detector and a holographic notch filter. For this study, three 30 s snapshots were averaged to obtain each Raman spectrum.

## Results and Discussion

First, we compare our previous results for as-prepared SWCNTs exposed to a 248 nm laser in air<sup>11</sup> to those from samples exposed to the same laser exposure conditions in vacuum. In order to qualitatively measure changes in the carbon-based purity of the nanotube material, we consider two carbon nanotube characteristic peaks in the Raman spectrum; the G-band at  $1590 \text{ cm}^{-1}$ , and the D-band at  $1350 \text{ cm}^{-1}$ . The G-band arises due to the in-plane vibrations of the carbon atoms in the curved graphite sheet, while the D-band at  $1350 \text{ cm}^{-1}$  is attributed to symmetry lowering defects. The width of the D-band may be used as a relative measure of the amount of carbon impurities, where a narrow D-band is consistent with highly purified nanotubes.<sup>14</sup> Figure 1a shows the full width at half-maximum (fwhm) of the D-band normalized to the fwhm of the as-prepared sample as a function of laser fluence in both air and vacuum. (The original fwhm of the as-prepared materials was  $40 \text{ cm}^{-1}$ ). For laser exposure in air, the width of the D-band continues to narrow throughout the entire range of irradiances, which is consistent with the elimination of carbon impurities. However, in vacuum, exposure of the nanotubes to the 248 nm laser produces a much smaller decrease in the fwhm, of only  $\sim 10\%$  at  $400 \text{ mW/cm}^2$ . At greater irradiance in vacuum, the D-band fwhm begins to slightly increase.

Calculating the ratio of the intensity of the D-band to the intensity of the G-band (D/G ratio) is commonly used to

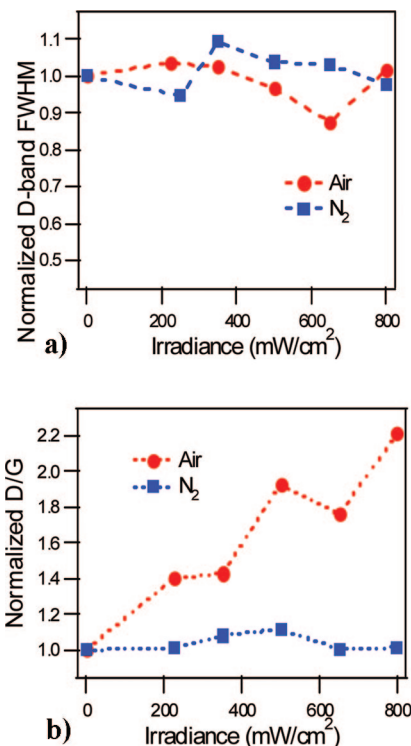


**Figure 1.** Normalized (a) D-band fwhm and (b) D/G for nanotube samples exposed to 248 nm laser as a function laser irradiance in air (circles) and vacuum (squares).

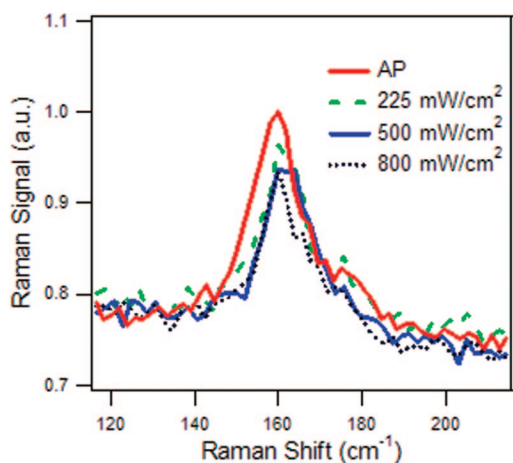
compare the relative measure of the amount of defects in a nanotube sample.<sup>15</sup> Figure 1b compares the D/G ratio for samples exposed to the 248 nm laser in air or in vacuum, for which the data are normalized by the D/G ratio for as-prepared material (0.039). In air, the D/G ratio decreases with increasing irradiance up to  $450 \text{ mW/cm}^2$ , while at irradiance greater than  $450 \text{ mW/cm}^2$ , the D/G ratio increases. This indicates that the defect density in the sample initially decreases, and then at higher irradiance, defects are incorporated into the sample. Also, since exposure in air to irradiances greater than  $450 \text{ mW/cm}^2$  causes the fwhm of the D-band to continue to narrow, it is likely that defects are created in the nanotubes themselves. Changes in the D/G ratio for exposure to the 248 nm laser in vacuum are less evident than those resulting from exposure in an air atmosphere. This suggests that the higher concentration of oxygen facilitates the removal of carbon impurities, while the lower concentration of oxygen limits the degree of photo-oxidation.

The effect of photon wavelength over the same range of average irradiance was considered by exposing a set of SWCNT samples to a 193 nm laser. Figure 2a shows that the fwhm of the D-band is largely unchanged for exposure to 193 nm laser in either air or  $\text{N}_2$  atmospheres over the entire range of fluences. A small decrease in the width of the D-band is observed at  $650 \text{ mW/cm}^2$  for exposure in air, yet at  $800 \text{ mW/cm}^2$  the fwhm returns back to its original width. Figure 2a, which depicts the D/G ratio as a function of irradiance level, indicates that the D/G ratio remains constant for exposure in  $\text{N}_2$  atmosphere, yet irradiation of nanotube samples in air causes the D/G ratio to more than double at  $800 \text{ mW/cm}^2$ . Increases in the D/G ratio while the D-band fwhm largely remains unchanged suggests that exposure to greater irradiance at 193 nm in air may be creating defects in the nanotubes.

The radial breathing modes (RBMs) in the range of  $100\text{--}300 \text{ cm}^{-1}$ , are representative of the diameters of nanotubes, where the frequency of the Raman peak is inversely proportional to diameter of the nanotube.<sup>14</sup> We have previously reported no changes in the RBM distribution for 248 nm laser exposure in air.<sup>11</sup> Here we also show that the diameter distribution of



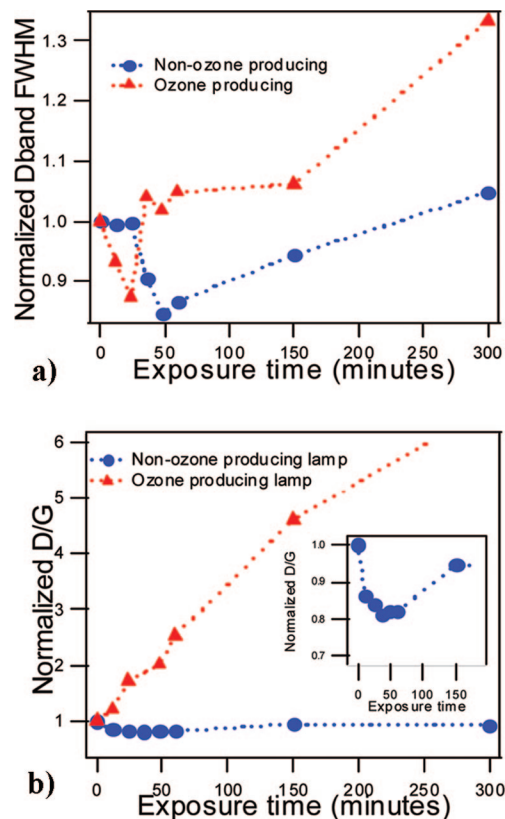
**Figure 2.** (a) Normalized D-band fwhm for SWCNT exposed to 193 nm laser in air (circles) and N<sub>2</sub> (squares), and (b) normalized D/G in air (circles) and N<sub>2</sub> (squares).



**Figure 3.** Normalized radial breathing modes shown for nanotube samples exposed to 193 nm laser at various fluences in air.

nanotubes exposed to the 193 nm laser does not change as a function of laser irradiance in air (Figure 3). The RBM signals, however, become weaker and more difficult to resolve after exposure to higher intensity excitation in air; this suggests nonselective damage or destruction of the tubes.

An ozone monitor measured the concentration of ozone during exposure in air to be 0.01 and 0.7 ppm for the 248 and 193 nm lasers, respectively. We note that the uncertainty of the monitor was 0.01 ppm, as specified by the manufacturer; therefore, the concentration is seen to be negligible for the 248 nm laser. The absence of purification and the increase in defect density for samples exposed to the 193 nm laser is most plausibly attributed to the oxidation of the nanotube sample by ozone. Within the experimental parameters in this study, ozone is not desired for the purification for nanotube material. The presence of oxygen in the ambient atmosphere, however, is important for the photoassisted oxidation of impurity carbons.



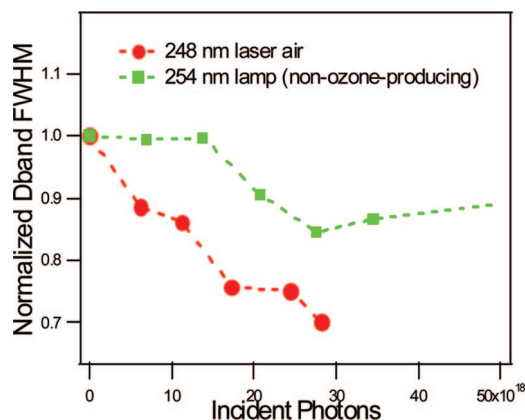
**Figure 4.** Analysis of Raman spectra for nanotube samples (a) normalized fwhm of the D-band and (b) the normalized ratio of the D and G bands exposed to an ozone-producing (triangles) and nonozone-producing (circles) UV lamp. The inset data are expanded to see detail.

The effect of coherence was investigated by utilizing CW UV light either from an ozone-producing lamp, or, from a nonozone-producing LP Hg lamp to irradiate nanotube samples. For the ozone-producing and nonozone producing LP Hg lamps, the measured ozone concentrations were 2.0 and 0.01 ppm, respectively. The Raman analysis of exposed samples is shown in Figure 4a and b; a magnified view of the D/G ratio for the nonozone-producing lamp is inset in Figure 4b.

Upon short exposure periods (no greater than 30 min), the ozone producing lamp reduced the non-nanotube carbon content depicted by the decrease in the fwhm of the D-band. However, for exposure periods greater than 30 min, the fwhm of the D-band increases, as does the D/G ratio. The RBMs of samples exposed to the ozone-producing lamp (not shown here), became more difficult to resolve at longer exposure time, thus indicating the nonselective destruction of SWCNTs. The ozone-producing lamp created similar trends in the data to similar to that of exposure to the 193 nm laser in air. In both cases, the concentration of ozone during light exposure was high, and is thus responsible for the nonselective oxidation of nanotube material.

Purification (in terms of the width of the D-band and in the magnitude of the D/G ratio) of nanotube samples is observed for exposure to the nonozone-producing lamp for less than 50 min. This is attributable to resonant photon absorption at the  $\pi$  plasmon; however, it is less prominent than that observed by the 248 nm laser. For longer exposure periods, (greater than 50 min), the width of the D-band and the magnitude of the D/G ratio returns to the value of the as-prepared material. No changes in the RBMs were observed for samples exposed to the nonozone-producing lamp.





**Figure 5.** Normalized fwhm of the nanotube D-band for UV exposure in air to a 254 nm lamp and a 248 nm pulsed laser versus the number of incident photons.

**TABLE 1: Heat Transfer Properties of Carbon Species Cited from the Literature**

	thermal conductivity $k$ (W/(m·K))	diffusivity $D$ (m <sup>2</sup> /s)
SWNTs	75 <sup>20</sup>	$1.74 \times 10^{-5}$ <sup>21</sup>
amorphous carbon	$\sim 5.15$ <sup>22</sup>	$1.0 \times 10^{-6}$ <sup>22</sup>
graphite	12.65 <sup>23</sup>	$1 \times 10^{-6}$ <sup>24</sup>

The absorption spectrum of the  $\pi$  plasmon in the SWCNTs is known to be a broad peak that overlaps both 248 and 254 nm; therefore, each wavelength is resonantly enhanced.<sup>12</sup> To compare these similar wavelengths, we consider purification of carbon nanotubes initiated by exposure to pulsed versus CW light by normalizing on the basis of the number of photons. The number of photons per exposure was calculated from the irradiance and exposure time. Figure 5 shows the normalized fwhm of the D-band for SWNT material exposed to roughly the same wavelength of pulsed (248 nm) versus CW light (254 nm) on this basis. The decrease in the fwhm of the nanotube D-band is greater for light from the 248 nm laser than that from the 254 nm lamp, indicating that the carbon impurities are more efficiently removed by the pulsed light than by the CW for the same number of photons in ambient air. This also suggests that the purification mechanism is not attributable solely to a photochemical process, which is typically a function of irradiance, but also to photothermal effects.

The absorption of photons may be manifested by either bulk excitation or the direct excitation of carbon impurities or nanotubes. From the dependence of our study on photon wavelength, we believe that resonance of the  $\pi$  plasmon is relevant. It is well-known that photon absorption is greater in  $sp^2$  carbon materials in the region of the  $\pi$  plasmon; hence the photon absorption is resonantly enhanced at 248 nm. The resonant plasmon excitation energy may be dissipated through electron–phonon coupling interactions of the nanotubes and cause heating. We have measured the bulk average temperature of the sample during exposure to be 343 K, where oxidation of non-nanotube carbon is minimal;<sup>1</sup> therefore, we dismiss a bulk thermal heating mechanism as the dominant mechanism. We were unable to measure the instantaneous (maximum) temperature, however, it may be estimated mathematically by use of a heat transfer model and knowledge of laser pulse and material properties.

We approximate the temperature increase for amorphous carbon, graphite and SWCNTs exposed to a pulsed laser excitation at 248 nm based the development by Piglmayer et

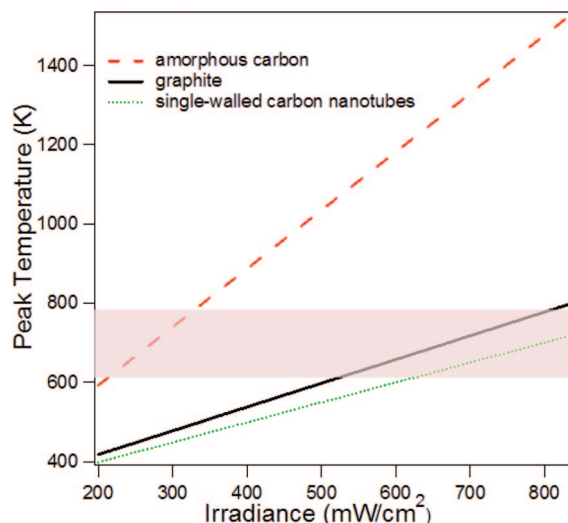
al.<sup>16</sup> With this approximation, we simply attempt to demonstrate the relative difference in temperature rise for each carbon constituent. In the limit of one-dimensional heat diffusion, the laser-induced temperature rise can be described by

$$\Delta T = \frac{A\phi}{\alpha K \tau_i} \left( \frac{2}{\sqrt{\pi}} (D\alpha^2 \tau_i)^{1/2} + \exp(D\alpha^2 \tau_i) \operatorname{erfc}[(D\alpha^2 \tau_i)^{1/2}] - 1 \right) \quad (1)$$

where  $A$  is the absorptivity,  $D$  is the diffusivity,  $\tau$  is the pulse length,  $\phi$  is the fluence,  $\alpha$  is the absorption coefficient, and  $K$  is the thermal conductivity of the material. We approximate  $\alpha = (4\pi k/\lambda)$  at  $\lambda = 248$  nm, where the extinction coefficient is assumed to be a constant for a random network of graphitic material, with  $k = 0.712$  from Palik,<sup>17</sup> and the absorptivity as constant  $A = 0.89$  according to Piglmayer et al.<sup>16</sup>

Differences in the thermal properties of the constituent carbon species in the impure nanotube samples create disparities in the temperature increase of each material. Table 1 lists experimentally measured thermal conductivities and thermal diffusivities of amorphous, graphite and SWNTs cited from the literature. These transport properties are much greater for carbon nanotubes compared to those of graphite and amorphous carbon. Hence, energy is more efficiently transferred in a nanotube than in either carbon impurity.

The temperature increases for the carbon allotropes calculated by eq 1, from the material properties listed in Table 1, are shown in Figure 6. The estimated peak temperature for the three different carbon allotropes shows a linear relationship between irradiance and instantaneous peak temperature. Oxidation of carbon occurs in the range of 625 to 775 K according to kinetic and thermodynamic influences of varying material composition and structure. This region is highlighted in red in Figure 6. The temperature of amorphous carbon upon irradiation by pulsed light is greater than the threshold temperature for oxidation at low values of irradiance; however, up to approximately 600 mW/cm<sup>2</sup>, the temperatures of graphite and SWCNTs are below the oxidation temperature. This correlates well with the data shown in Figure 1, where the minimum D/G ratio occurs at  $\sim 600$  mW/cm<sup>2</sup>. Therefore up to the point where irradiance is greater than 600 W/cm<sup>2</sup>, the amorphous carbon may be selectively oxidized due to transient heating. At greater irradi-



**Figure 6.** Approximated peak temperature at 248 nm excitation associated with amorphous carbon, carbon nanotubes, and graphite as a function of fluence, (assuming a constant absorptivity and extinction coefficient for each carbon material). The highlighted area denotes the temperature of carbon oxidation

ance levels, where the D/G ratio starts to increase, graphite begins to oxidize, and defects are created in the SWCNTs.

Resonantly enhanced absorption of the  $\pi$  plasmon can also create hot electrons, which in turn create unstable and reactive moieties. Chen et al. described a dramatic decrease in the conductance of SWCNTs in ambient atmosphere caused by UV photoinduced oxygen desorption from the nanotube surface.<sup>18</sup> UV excitation of carbon nanotubes results in collective electron oscillations in nanotubes that de-excite into single-particle hot-electron excitations. Chen et al. suggest that part of the plasmon excitation energy is dissipated through breaking of molecule–nanotube binding, producing desorption.<sup>18</sup> This same effect may also be manifested by the removal of carbon impurities, where bond breaking results in photo-oxidation and purification of nanotube materials. A pulsed laser beam incident upon a van der Waals bonded carbon impurity complex excites the conduction-band electrons, thus creating a highly nonequilibrium distribution of hot electrons. These hot electrons undergo the equivalent of inelastic resonance scattering from the adsorbed molecule and form a temporary negative ion.<sup>19</sup> If the temporary hot electron results in a new set of forces on the atoms composing the localized surface complex, such that the combined kinetic and potential energy of the atoms associated with the bonded adsorbate exceed the bond energy, a desorbed or carbon anion may preferentially react with the surrounding oxygen. Alternatively, the energy from hot carriers may undergo a variety of scattering processes and be transformed into lattice phonons, resulting in heat. In such a surface photochemical process, the excited electrons that heat the nanotubes increase the local temperature, which leads to the oxidation.

We suggest that the purification process is a photophysical process in which both thermal and nonthermal contributions directly contribute to the mechanism. Future measurement and analysis of the reaction rate will present insight into the distinction and influence of purely photochemical and photo-thermal contributions.

## Conclusion

We have demonstrated the importance of wavelength and atmosphere for the purification of as-produced SWCNTs by UV photons. Excitation of the collective electron oscillations of the  $\pi$  plasmon in nanotubes leads to the photo-oxidation of carbon impurities. We suggest that the plasmon excitation energy may be dissipated through electron–phonon coupling interactions that result in resonant transient surface heating and/or generation of hot electrons. We are currently undertaking ab initio studies to model such interactions.

Excimer laser-treatment of as-prepared carbon nanotube material exploits the differences in thermal transport between carbon nanotubes and the carbon impurities, and provides a pathway for purification or functionalization of carbon nanotubes in an efficient method suitable for bulk materials.

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