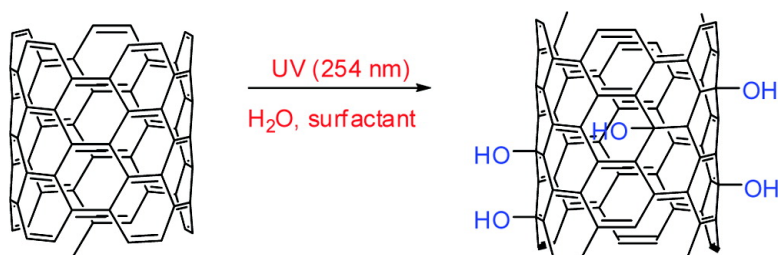Article

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Selective Photochemical Functionalization of Surfactant-Dispersed Single Wall Carbon Nanotubes in Water

Noe T. Alvarez,[†,‡] Carter Kittrell,[†,‡] Howard K. Schmidt,*[,‡,§] Robert H. Hauge,[†,‡] Paul S. Engel,*[,†,‡] and James M. Tour*[,†,‡]

Departments of Chemistry, Mechanical Engineering and Materials Science, and Chemical and Biomolecular Engineering, and The Richard E. Smalley Institute for Nanoscale Science and Technology, Rice University, MS 222, 6100 Main Street, Houston, Texas 77005

Received June 2, 2008; E-mail: hks@rice.edu; engel@rice.edu; tour@rice.edu

Abstract: Ultraviolet (UV) irradiation of single wall carbon nanotubes (SWCNTs) individually dispersed in surfactants leads to diameter and type-selective photohydroxylation of the nanotubes. Photohydroxylation of first semiconductor and then small diameter metallic SWCNTs was confirmed after 254 nm UV irradiation in acidic, neutral, and basic aqueous solutions at ambient and elevated temperatures. The increased oxygen content of the SWCNTs after UV irradiation, as detected by X-ray photoelectron spectroscopy, suggests that SWCNTs were hydroxylated by reaction with water. Attenuated total reflectance Fourier transform infrared analysis provides evidence of hydroxyl functional groups on their surface. This photochemical reaction is impeded by molecular oxygen and appears to involve a reactive intermediate generated in the vicinity of semiconducting SWCNTs. This represents a noncontaminating selective reaction in the liquid phase that uses an intrinsic property of the tubes.

Introduction

Single wall carbon nanotubes (SWCNTs) are one-dimensional molecules that are the subject of much research due to their interesting properties and unique nanoscale dimensions. The potential for use of SWCNTs in sensors, composites, micro-electronics, transparent conductors, energy storage, optoelectronics, molecular filters and many other applications has fostered research in the growth, characterization, dispersion and chemical modification of SWCNTs.[1,2] However, as-produced HiPco[3] SWCNTs comprise about 70 different diameters and chiralities, and, depending on their type, can behave as semiconductors, semimetallics or metallics.[4] SWCNTs produced using the HiPco process contain approximately one-third metallics/semimetallics and two-thirds semiconductors.[4] This diversity of tubes and the extreme difficulty of separating them by type has prevented many applications from being further developed and has hindered research progress in the field.

There are several SWCNT type- and diameter-selective reactions reported in the literature.[5–17] Most show preferential, but incomplete, reactions with either semiconducting or metallic SWCNTs and, when applied for purposes of separation of SWCNTs, have shown mixed success.[14,15,17] Most of them require additional chemical reagents that not only degrade the quality of the dispersed SWCNTs but also require additional treatments to separate the reagents from the nanotubes after reaction. Examples include physisorption and chemisorption processes such as those that use octadecylamine (ODA);[5,6,14] those that use electron transfer reactions such as ozone,[15] nitronium ions,[7] and diazonium salts;[8–10] and others based on

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† Departments of Chemistry and Mechanical Engineering and Materials Science.
‡ The Richard E. Smalley Institute for Nanoscale Science and Technology.
§ Department of Chemical and Biomolecular Engineering.

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thermal[12] and HCl[11] oxidations. Bromine[17] and Fe complexes[18] have shown selective complexation with metallic SWCNTs.

Nonchemical selective processes such as dielectrophoresis[19,20] and photon irradiations[21,22] have shown promising selectivities, although the scalability of these techniques is still under study. Selective photooxidation using high-power-density lasers[21] has been reported where a specific wavelength enhances the resonance of selected SWCNTs, generating chiral-selective reactions. Laser photon-induced selective reaction of metallic SWCNTs with Triton X-100 has also been reported,[22] light assisted oxidations with H_2O_2 exhibit a dependence on the SWCNT diameter and band gap[23,24] and photochemically generated singlet oxygen reacted selectively with metallic SWCNTs.[25] In the solid phase, UV photons induce oxidation of multi wall carbon nanotubes (MWCNTs) and SWCNTs[26,27] and longer UV wavelengths were used to cross-link SWCNTs, leading to improvements in mechanical strength and conductivity.[28,29] Theoretical studies that support and explain photon-induced oxidation have been reported.[30] Also, a recent publication has used a high power Xe lamp (500 W) to selectively destroy the metallic and small diameter SWCNTs in the solid phase.[31]

Here we report a selective and progressive covalent photo-hydroxylation of nearly all detectible semiconducting and eventually some small diameter metallic SWCNTs using 254 nm UV light. The resulting functionalized SWCNTs have increased oxygen content, as determined by X-ray photoelectron spectroscopy (XPS), apparently in the form of hydroxyl (-OH) moieties, as further determined by attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy. Our results show high selectivity for semiconducting SWCNTs and small diameter metallic tubes, with little or no functionalization of the large diameter metallic SWCNTs. This suggests that the pristine metallic and functionalized semiconducting SWCNTs

Scheme 1. Photoreactor Components (Not to Scale)[a]
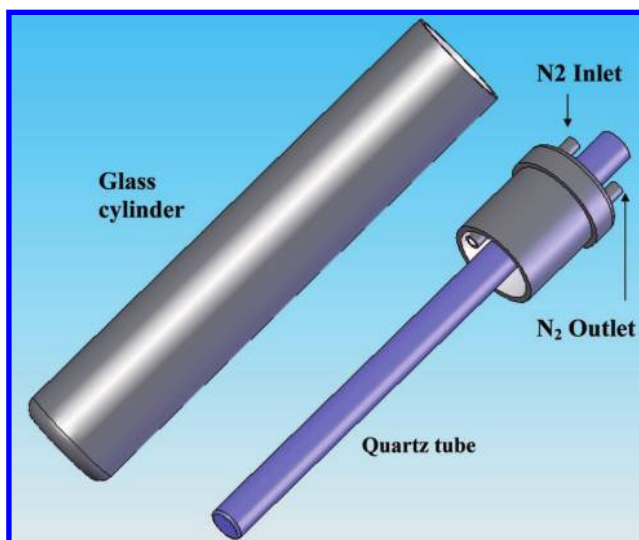
[a] The mercury lamp is inserted into the quartz tube and the glass cylinder holds the reaction solution.

could be physically separated in a simple manner. The reaction appears to be scalable.

Experimental Section

Using a standard protocol reported in the literature,[32] HiPco SWCNTs were dispersed in several surfactants: sodium dodecyl sulfate (SDS), sodium dodecylbenzene sulfate (SDBS), Triton X-400, Pluronic F-108 (BASF 30085465), or Na cholate. Typical UV experiments were performed using a pen-ray 4.4 mW low pressure Hg lamp from UVP (Upland, CA). The SWCNTs/surfactant solution was degassed in a 100 mL homemade glass photochemical reactor that had an inlet and outlet for the N_2 sweeping gas on top. The solution inside of the reactor was degassed with N_2 flow with stirring and heating at 80 °C for 60 min. After degassing the SWCNT/surfactant solution, fluorescence and absorption spectra were collected to ensure the quality of the solution and compare with later spectra of the treated solution. All the surfactants were purchased from Sigma-Aldrich and were used without further purification.

The degassing reactor, Scheme 1 (32 mm ID and 180 mm tall glass), was equipped with a quartz test tube (10 mm ID) that protruded into the SWCNT solution. The 254 nm Hg lamp was placed inside the quartz finger in a coaxial-type configuration ensuring that the light emitting part of the lamp was covered by the solution. The SWCNT/surfactant solution, typically 20 mg/L SWCNTs in 1% SDS was subjected to UV irradiation for various time periods. Samples were collected in quartz cuvettes during irradiation and the progress of the reaction was followed by NIR fluorescence and VIS-NIR absorbance (Nanospectralyzer, model NS1, nanoFluorescence, Houston, TX), and Raman spectroscopy (inVia microRaman Spectrometer, Renishaw, Gloucestershire, UK) in the liquid phase. ATR-FTIR (Nexus 870 FTIR, Thermo Nicolet, Fitchburg, WI) analysis and XPS (Quantera, Physical Electronics, Chahassen, MN) were used for additional characterization. pH measurements were taken with a digital pH/mV/Temperature Meter, model IQ150 equipped with a PH30-GS probe from IQ Scientific Instruments (Carlsbad, CA), pH meter calibration was performed periodically using Buffers at pH 4, 7 and 10 purchased also from

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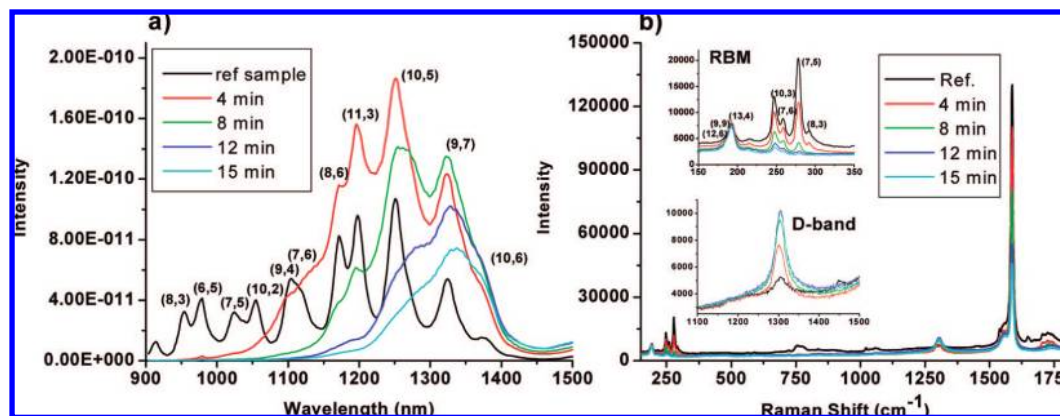
Figure 1. Effect of 254 nm UV irradiation on SWCNTs solution at different time intervals: (a) Fluorescence at 785 nm excitation wavelength during the 15 min UV irradiation. All fluorescence was quenched after 30 min irradiation (not shown) and (b) 633 nm Raman spectra on liquid samples collected during the irradiation process.

same manufacturer. AFM images were taken with a Nanoscope IIIa (Veeco Instruments, Plainview, NY).

Results and Discussion

Photohydroxylation reactions were set up by first degassing the SWCNT/surfactant dispersion. In order to determine the consistency of the reaction in different surfactants, screening reactions were performed using all the surfactants above, however for reasons discussed later, only the results from reactions done with SWCNT/SDS are reported here. The degassing method is similar to that reported by Dukovic et al.[33] which detailed a simple method to desorb O_2, CO_2 and endoperoxide from the solution and the surface of SWCNTs. Solutions degassed in this manner remain fluorescent in acidic conditions (pH 3) demonstrating that the vast majority of the O_2 has been removed from the solution. It has been suggested that direct protonation of SWCNTs at low pH was the cause of fluorescence quenching and absorption bleaching.[32,34] That assumption was confirmed and further detailed by Dukovic et al. that O_2 is necessary for absorption bleaching and fluorescence quenching by H^+.[33]

Degassing the SWCNT/surfactant solution increases its fluorescence intensity, as was observed by Dukovic et al.[33] Even though the temperature used here for degassing is 18 °C less than that used by Dukovic, a similar fluorescence recovery was observed when these nanotube solutions were degassed at low pH. An acidified sample with almost no fluorescence at pH 3.2 fully recovers its original (pH 6.5) fluorescence intensity as the solution was heated to 80 °C for 60 min under nitrogen purge. The 80 °C temperature was determined by heating the SWCNT/SDS solution at different temperatures and registering the stability of the micelle by changes in SWCNT fluorescence. At temperatures higher than 80 °C the fluorescence intensity of the SWCNTs started decaying, possibly due to micelle disturbance and bundle formation.[35] For a typical SWCNT/SDS decant, the fluorescence intensity and pH (8.5−9.5) after

degassing were higher than of the original near-neutral (pH 6.5) solution exposed to air.

The selectivity of the photohydroxylation reactions was monitored in the solution phase by near IR fluorescence (Figure 1a) and Raman spectroscopy (Figure 1b). After 4 min of UV irradiation the fluorescence intensity of (8,3), (6,5), (7,5) and (10,2) semiconducting tubes was quenched almost completely while the fluorescence of larger diameter SWCNTs remained, becoming more intense in some cases (Figure 1a). Typically, it took almost 30 min of irradiation to quench all fluorescence of SWCNTs, as observed when excited at either 785 or 660 nm. The Raman spectra obtained from liquid samples at different irradiation times are strong evidence of covalent functionalization of the SWCNT surface. As observed in Figure 1b, the radial breathing mode (RBM) intensities of semiconducting SWCNTs that resonate at 633 nm decreased as the reaction progressed with no effect on the bands <200 cm^{-1}. In order to avoid characterization and interpretation errors of the Raman spectra, all the Raman data were collected from samples in the liquid phase. Previous studies in our laboratories have advised about interpretation errors due to changes in morphology of the samples on analysis by Raman in the solid state.[10] Also it can be observed that the D-band increases with time, suggesting covalent bond formation on the surface of the affected tubes.[36] The D-band increase accompanied by ordered fluorescence decay, led by the small-diameter SWCNT, as the reaction progresses is strong evidence that selective photoreaction has occurred. It has been demonstrated that covalent functionalization of the SWCNT surface destroys the electronic band structure.[36,37] Therefore, those nanotubes that were functionalized will no longer be resonance enhanced.[38,39] The fact that after 30 min of UV irradiation the RBM of the metallic SWCNTs has not changed while all the semiconductor SWCNTs were nearly gone is particularly notable.

The reaction bleaches the E_{11} semiconductor (900 to 1600 nm) and E_{22} semiconductor (550 to 900 nm) electronic transitions of the SWCNTs in the absorption spectra after different periods of UV irradiation (Figure 2a). As expected, covalent bond formation on the SWCNT surface broadens the van-Hove singularities in general (Figure 2a). The spectroscopic evidence

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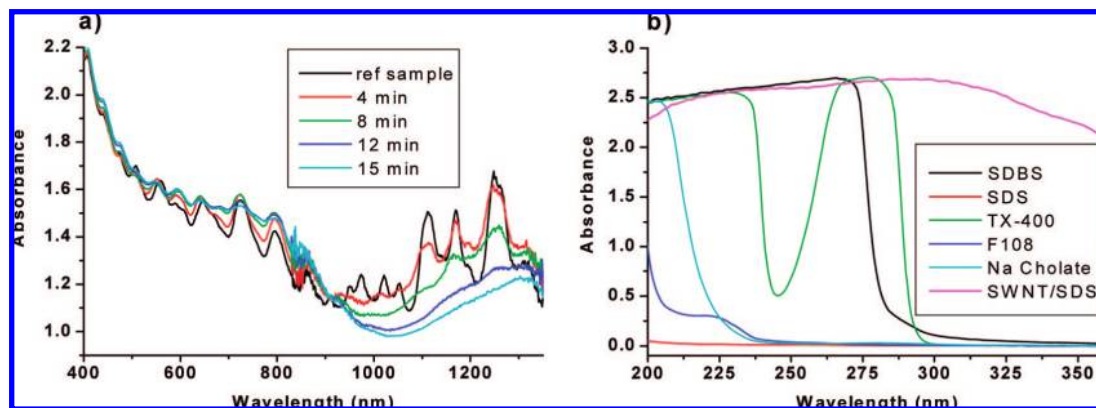(39) Banerjee, S.; Wong, S. S. *J. Phys. Chem. B* **2002**, *106*, 12144–12151.

Figure 2. Absorption spectra of: (a) SWCNT/SDS after different periods of UV irradiation that shows the progress of the photohydroxylation versus time and (b) UV-absorbance of different surfactants that shows SDBS as the only surfactant that strongly absorbs 254 nm UV light.
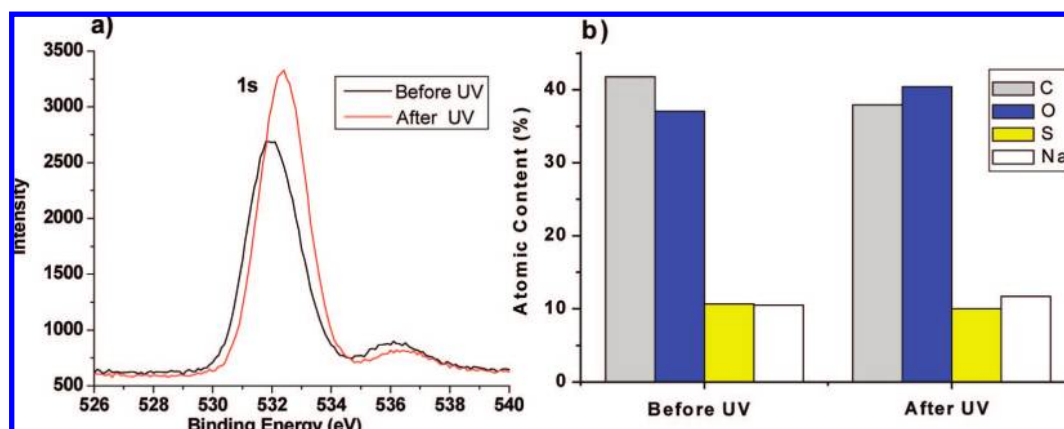

Figure 3. XPS spectra of SWCNT/SDS: (a) Increase in the O_2 content after UV irradiation, (b) Atomic concentration of C, O, S and Na before and after UV irradiation.
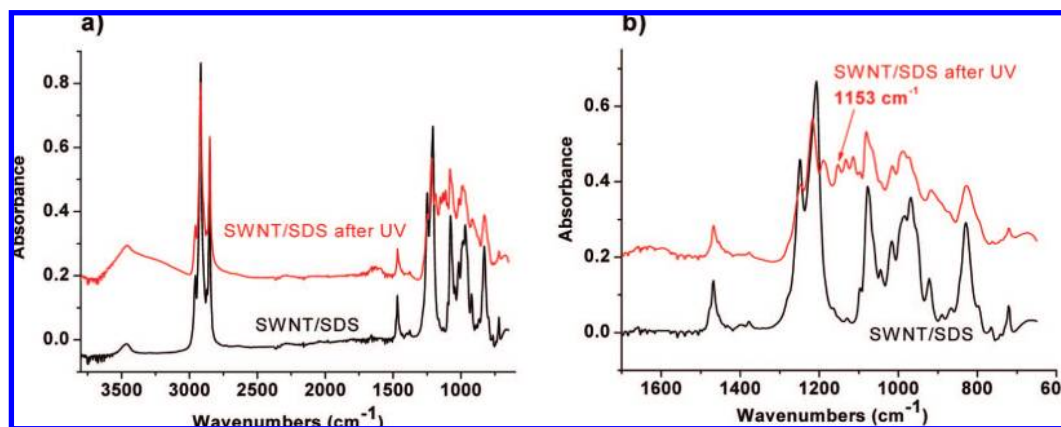

Figure 4. ATR-FTIR spectroscopy of SWCNT/SDS before and after UV irradiation: (a) full spectrum and (b) IR fingerprint region.

collected suggests that the photoreaction is driven by SWCNT absorption of UV light; if this assumption is correct, the fluorescence quenching should be independent of the surfactants used, the pH of the reaction mixture as well as the temperature. In fact, that is what has been observed. The UV irradiation reactions on SWCNTs dispersed in different ionic and nonionic surfactants (SDS, Na Cholate, Pluronic F-108 and Triton X-400) proceeded in a similar fashion. However, even after 5 h of irradiation, no reaction was detected by spectroscopic means in SDBS. This is evidently due to strong absorption by SDBS at wavelengths below 275 nm, while the other studied surfactants

are transparent at 254 nm (Figure 2b). SDS is clearly the surfactant of choice due to its minimal absorption in the region of interest and the efficacy with which it forms SWCNT decants.

XPS (Figure 3) and ATR-FTIR (Figure 4) results show that the oxygen content of the photofunctionalized SWCNTs increases substantially, and that this oxygen is present in the form of hydroxyl groups. The oxygen content increase on the SWCNT surface is striking because the solution is low in O_2 before irradiation and the only sources of additional oxygen are SDS and H_2O. The XPS spectra were collected from samples before

and after irradiation and were prepared in a similar manner: spin-coating then drying the samples in the oven for 60 min prior to XPS analysis in order to remove H_2O from the spin-coated sample. Four separate samples from different reactions show higher oxygen content after UV irradiation, with increases from 20 to 40%. The IR spectrum in Figure 4 shows a significant broadening of the peak at 3400 cm^{-1} which is indicative of OH content, and three peaks at 1153, 1131 and 1115 cm^{-1} are located in the region where C−O stretches are expected for a tertiary alcohol.

Based on the abundance of oxygen on the functionalized material, it is likely that H_2O is directly involved in the reaction. Note that the energy provided by 254 nm photons, 112.3 kcal/mol, is barely sufficient to homolytically dissociate the O−H bonds of H_2O molecules (110 kcal/mol[40]). Since water is essentially transparent at this wavelength, the SWCNTs themselves are the only good absorbers available. It is interesting to note that precipitating SWCNTs from UV irradiated solutions requires twice as much acetone as nonirradiated solutions. Furthermore, irradiation in D_2O requires more time to achieve similar fluorescence quenching than irradiations in H_2O, indicating a significant isotope effect. These observations are consistent with the idea that the reaction involves water and results in hydroxylated SWCNTs.

The overall process is termed a photohydroxylation because the SWCNT photolysis product is hydroxylated. In this type- and diameter-selective reaction, the term 'photooxidation' would imply that the reaction step that drives selectivity extracts electrons from the SWCNT. Oxidative processes involving organic acceptors at high oxidation potentials have been convincingly shown to react preferentially with the large diameter (or small band gap) SWCNTs first, then progressively attack the smaller diameter SWCNTs.[41] Studies in our laboratory using inorganic species[18] show similar trends for inorganic oxidizing species, and demonstrate that reducing agents preferentially attack small diameter (large bandgap) semiconducting SWCNT. This results in an inverted order of fluorescence quenching compared to oxidizers. It is quite clear from Figure 1a that the small diameter tubes are quenched first, indicating that the key selective reaction behaves like a reductive process. However the initial step of this reaction is the production of a SWCNT excited-state, and electron transfer from the SWCNT may be a reaction of a highly excited-state with a very short lifetime that is dependent on the band gap of the particular SWCNT. Until the reaction mechanism involved in this reaction is determined, we will describe the process as a photohydroxylation so as to not connote any particular mechanism.

AFM images, taken on spin coated (3.5 K rpm) SWCNT samples on mica before (Figure 5a) and after (Figure 5b−d) UV irradiation show significant differences. Samples after UV irradiation exhibit unusual aggregations completely different from the side by side aggregation normally seen in SWCNT bundling. Figure 5b is a typical image collected after UV irradiation where aggregations of tens of tubes have shapes that are distinct from the common side-by-side bundling. Other aggregations, Figure 5c and d, that are more drastically different from the common ropes were also observed and may have come, in part, from the spinning solvent-based evaporation forces or they were ropes before UV irradiation and as a result of the

photoreaction they have accumulated more tubes on their surface. These images are a representative summary of hundreds collected during these studies. Overall, this effect is consistent with photohydroxylation of the SWCNT. SDS surfactant molecules would be unlikely to form a micelle monolayer on the polar functionalized SWCNT surface. Indeed, a densely hydroxylated surface would be expected to enable aggregation, as observed, via intertube hydrogen bonding.

Longer periods of irradiation (up to 100 min) were performed to further test and confirm the selectivity of the technique. As is observed in Figure 6, normalized Raman spectra of the liquid phase from samples after 100 min irradiation provide important highlights. The 514 nm Raman spectra (Figure 6a) shows mostly metallic SWCNTs. In fact, it is observed that the RBMs of small diameter metallic ones also disappear, however the D/G$^+$ band ratio is much smaller compared to ratios observed at 633 nm. Additionally, 633 nm Raman spectra (Figure 6b) supports the statement that after 100 min the RBMs of metallic SWCNTs remain, even when all the Raman features observed at 785 nm (Figure 6c) were gone. More surprisingly, the semiconductor SWCNTs that resonate at 785 nm lose all their Raman features after 100 min UV irradiation. The D/G$^+$ ratios calculated from Figure 6 spectra (after baseline correction) are shown in Table 1. The results demonstrate that large diameter metallic SWCNTs have not reacted since they still resonate at 633 nm, and are therefore nearly unreactive in this overall photohydroxylation process.

Prior work with 254 nm UV irradiation of SWCNTs was reported to have caused photodesorption of O_2 from the SWCNT surface in the liquid[34] and solid/gas phases[42] while Parekh et al. used this wavelength to effect SWCNT photooxidation in the solid phase.[27] The discrepancy between whether the SWCNTs will be degassed or photooxidized may arise from the different photon irradiance, also called intensity and fluence, of the UV sources used in each case. It is likely that lower total photon flux leads only to photodesorption of O_2 from the SWCNT surface, while higher intensities cause the photohydroxylation reported here. The apparatus used in our experiments ensures that most of the emitted photons from the Hg lamp impinge on the SWCNT solution. The theoretical report by Grujicic et al.[30] serves as the basis for an understanding of O_2 adsorption on the SWCNT surface. The calculations indicate that 7−5−5−7 and Stone-Wales defects on the SWCNTs have a higher likelihood of adsorption than the defect-free surface. However Grujicic's results were based on an O_2 environment in contrast to the present experiments where most of the oxygen was removed from solution. Surprisingly, Grujicic et al. found that there is no significant difference in the interaction of O_2 with different types and chiralities of SWCNTs. His calculations were supported by experimental evidence reported by Savage et al.[26]

Although the mechanism of this photoreaction is not yet understood, it is thought that radicals are generated during the irradiation process. This assumption is supported by experimental evidence when irradiations were performed in air- or oxygen-saturated rather than degassed solutions. O_2 is a well-known radical scavenger,[43] so in the presence of O_2 from air the reaction rate should be suppressed, as it nearly completely was, by capture or scavenging of radical reactive intermediates.

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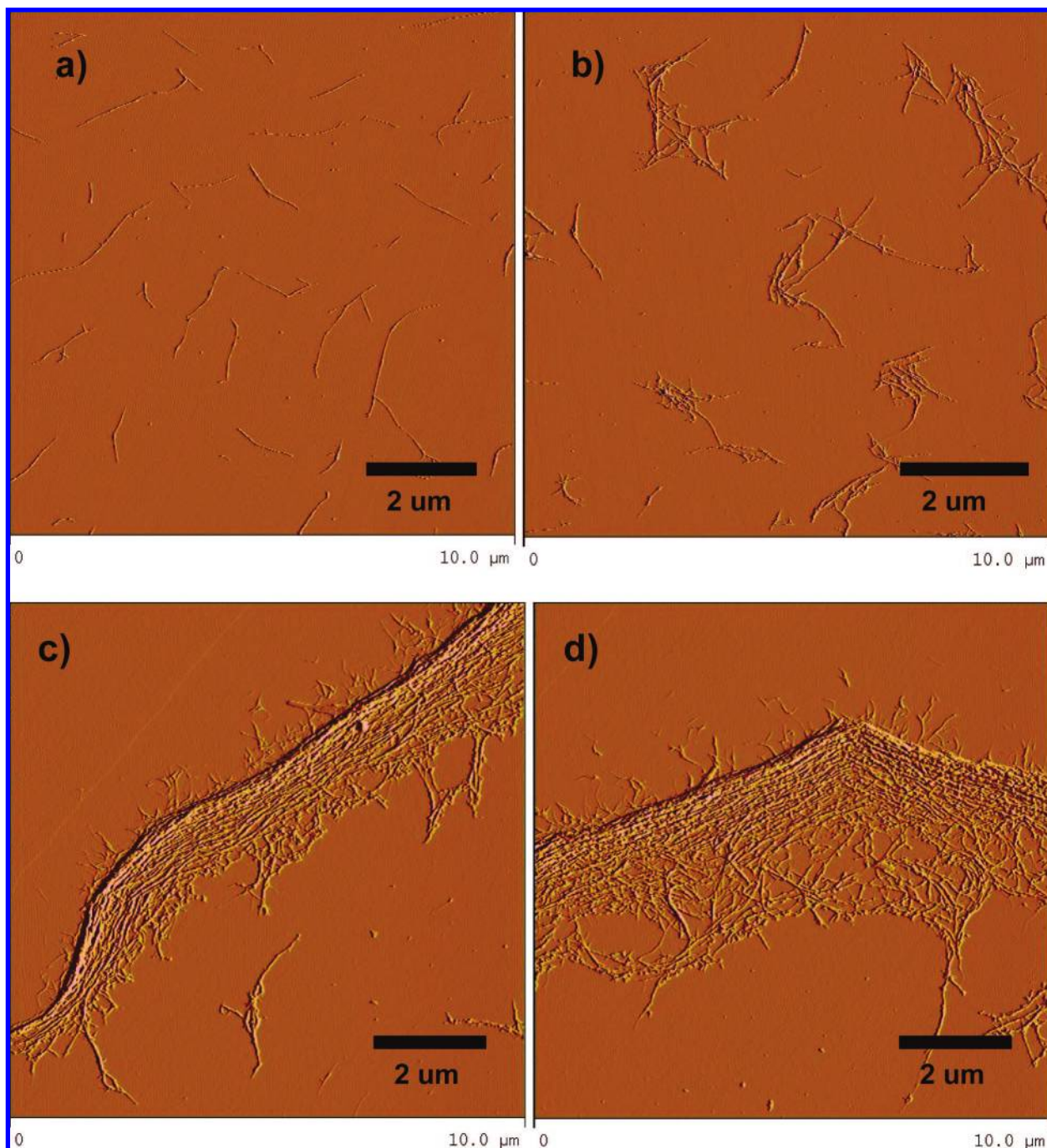(43) Turro, N. J. *Modern Molecular Photochemistry*; University Science Books: Sausalito, CA, 1991.

Figure 5. AFM images of SWCNTs spin coated on mica: (a) a typical image before UV irradiation, (b) a typical image after UV irradiation, (c) and (d) additional images observed after UV irradiation.

It was found that CO_2 saturated solutions proceeded at essentially the same rate as degassed solutions.

A potential candidate for this reactive intermediate is the hydroxyl radical, which has been implicated in some previous reports. It was reported, for instance, that SWCNT oxidation in H_2O_2 was enhanced using 488 and 515 nm laser light,[24] leading to selective elimination (burn out) of specific SWCNTs to generate CO and CO_2. A decrease of certain RBM peaks was provided as evidence for the selective reaction, although H_2O_2 dissociation at 488 and 515 nm is unlikely because H_2O_2 does not absorb light at either of these wavelengths. The same authors in a later work proposed light assisted oxidation of SWCNTs in H_2O_2[23] and it was suggested that weak fluorescence

emission of SWCNTs at the near-IR wavelength where H_2O_2 absorbs is the origin of H_2O_2 dissociation. The dissociation of H_2O_2 generates OH radicals that oxidize the SWCNT surface. The authors did not mention the possibility of SWCNT excited states being formed as a result of the irradiation wavelength employed in any of these mechanisms. We also performed a comparison experiment, irradiating SWCNTs in H_2O_2 at 254 nm. Upon initial addition of H_2O_2, SWCNT fluorescence is partially quenched, with preferential suppression of large-diameter SWCNT emission. UV irradiation of H_2O_2/SWCNT/SDS solutions (1.5%, 7.5% and 15% H_2O_2 by volume) demonstrated that the reaction proceeds in a manner similar to the reaction without H_2O_2, although the quenching appeared to
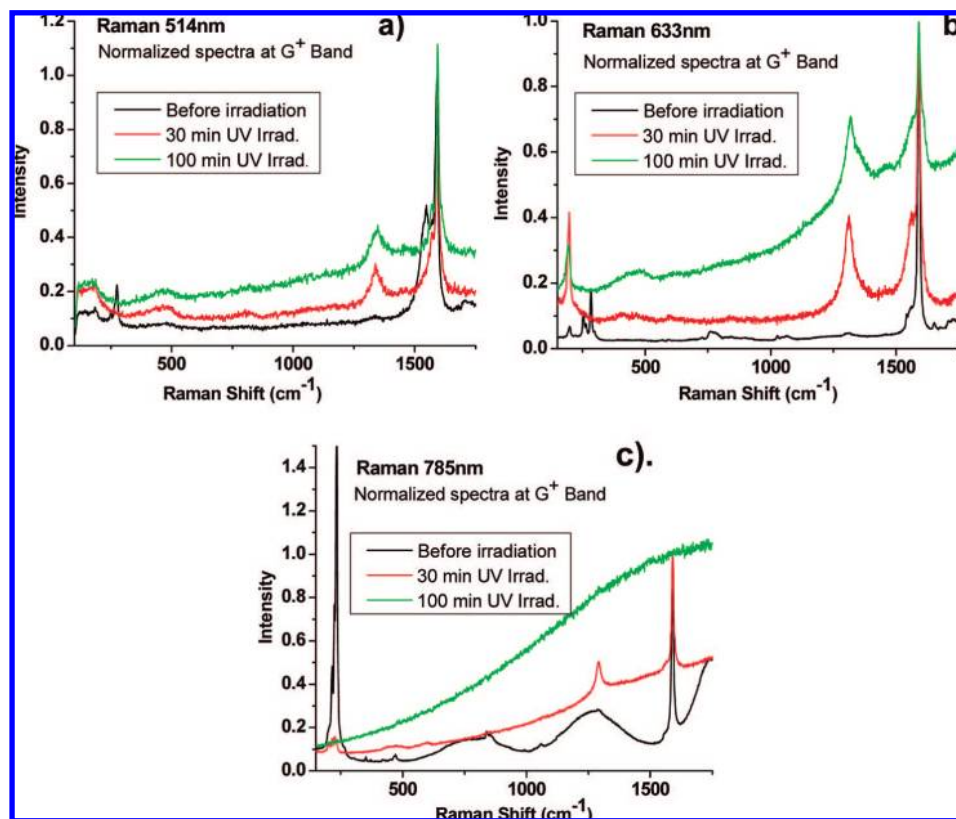
Figure 6. Raman spectra of SWCNT/SDS solutions before and after 30 and 100 min UV irradiations. (a) 514 nm excitation shows relatively lower D to G ratios compared to (b) 633 nm excitation. (c) Excitation at 785 nm preferentially shows semiconductor SWCNTs. The spectra after 100 min of irradiation shows no RBMs nor G^+ peaks, indicating that all the semiconductor SWCNTs were heavily functionalized.

Table 1. D/G^+ Ratios after 30 and 100 min UV Irradiation

	514 nm	633 nm	785 nm
0 min	2%	3%	NA
30 min	31%	63%	80%
100 min	46%	100%	NA

be slower as the H_2O_2 concentration increased. After 30 min of UV irradiation, the fluorescence of many SWCNTs was still intense. When H_2O_2 was degassed prior to addition to the degassed SWCNT/SDS solution, higher fluorescence quenching was observed for the same periods of UV irradiation.

Overall, these results indicate that the reaction is initiated by the SWCNT photon absorption, leading to the generation of an excited-state which thereafter activates small molecules, likely water, in their close surroundings. Semiconducting SWCNTs would be good candidates for the specific sensitizers initiating the process. While a broad range of excited-state lifetimes are reported in the literature, metallic tubes are consistently found to have two or 3 orders of magnitude shorter lifetimes (femtosecond range) than semiconducting species (picosecond range).[44−47] This physical property gives the semiconducting tubes enough time to react with the molecules in their surroundings and produce selective reactions, while metallic

SWCNT should be essentially unreactive toward photohydroxylation. Reactive intermediate molecules generated in the vicinity of semiconducting SWCNTs would presumably have a finite lifetime of their own, and would have to diffuse to metallic SWCNTs to react. To our knowledge, this is the first noncontaminating selective reaction in the liquid phase that uses an intrinsic property of the tubes and can be scalable; current experiments use 100 mL solutions. Current efforts are focused on physical separation of the functionalized semiconducting tubes to establish a reliable separation method, as well as efforts to elucidate the reaction mechanism.

Conclusions

Evidence has been provided for a photochemical reaction initiated and dependent on the SWCNT absorption as well as the selectivity of the reaction toward semiconducting and small diameter SWCNTs. The selectivity of the reaction is supported by Raman and fluorescence spectroscopy as well as absorption in the liquid phase. Experimental evidence demonstrates a significant increase in the oxygen content via OH attachment on SWCNT surfaces. The reported photohydroxylation requires no additional reactants; therefore; type-separation efforts of SWCNTs should be easier, providing cleaner samples. Overall, this seems to be a promising approach for developing separation processes and selective functionalization chemistries.

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