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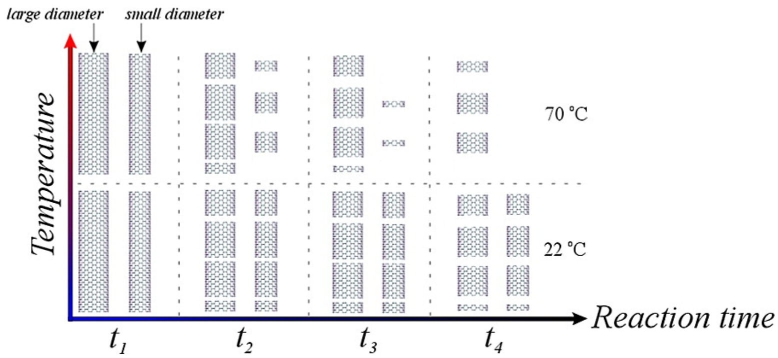

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Controlled Oxidative Cutting of Single-Walled Carbon Nanotubes

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Contribution from the Department of Chemistry, Center for Nanoscale Science and Technology, Rice University, Houston, Texas 77005

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Abstract: The oxidation reaction of piranha solutions with purified HiPco carbon nanotubes was measured as a function of temperature. At high temperatures, piranha is capable of attacking existing damage sites, generating vacancies in the graphene sidewall, and consuming the oxidized vacancies to yield short, cut nanotubes. Increased reaction time results in increasingly shorter nanotubes. However, significant sidewall damage occurs as well as selective etching of the smaller diameter nanotubes. On the other hand, room-temperature piranha treatments show the capability of cutting existing damage sites with minimal carbon loss, slow etch rates, and little sidewall damage. Combined with a method of introducing controlled amounts of damage sites, these room-temperature piranha solutions have the potential to yield an efficient means of creating short, cut nanotubes.

Introduction

Since the discovery of single-walled carbon nanotubes (SWNTs), they have attracted much attention due to their unique electronic and mechanical properties.[1,2] Before these properties can be manipulated for materials science applications and electronic devices, however, several technical hurdles must be overcome. Nanotubes are typically synthesized with polydisperse micrometer lengths where they are bound into macroscopic entangled ropes. Many applications, however, will require short undamaged individual nanotubes 20−100 nm in length. For example, the introduction of SWNTs into electronic devices will clearly require the ability to place SWNTs of a specific band gap and precise length in a well-defined location on a substrate.

The use of oxidation reactions has been vital to SWNT processing. These processes are often utilized in cleaning raw SWNT material of metals and fullerenes[3−8] and for the chemical "shortening" of SWNTs.[9,10] Our research group[9] reported the first use of concentrated 3:1 H_2SO_4/HNO_3 mixtures to cut the highly entangled long ropes of SWNTs into short, open-ended pipes. As a result of chemical oxidation, the ends and often the sidewalls of the nanotubes are covered with oxygen containing groups[11,12] which has important implications for the electronic properties of these materials.[13]

Nonoxidizing cutting strategies have also been explored. It has been shown that fluorine atoms tend to form fluorinated bands around the circumference of the nanotube sidewall.[14] When heated to 1000 °C in Ar, these bands are pyrolyzed off leaving short, cut SWNTs with lengths between 20 and 300 nm.[15] However, this method tends to result in nanotube ends that have coalesced into intractable aggregates. Recently, other researchers have focused on the use of sonication in a monochlorobenzene solution of poly(methyl methacrylate)[16] or the use of diamond particles to act as an abrasive during sonication.[17,18] Lustig et al.[19] have developed a lithographic technique which embeds the SWNTs in a photoresist and uses

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ion etching to cut exposed nanotubes. These processes, however, often involve difficulties in separating the nanotubes from the other additives and typically do not have lengths shorter than several hundred nanometers.

Many cutting processes can be viewed as a two-step process: (i) introduction of sidewall damage and (ii) consumption or cutting of damaged sites. While many processes have been shown capable of inducing sidewall damage, there have been few scaleable processes capable of consuming the damaged sites without also inducing further sidewall damage. Such a process, however, when combined with a controlled means of introducing damage sites will allow the controlled cutting of SWNTs into short pristine segments. Here we describe an efficient, scaleable means of achieving the second step in a cutting strategy, i.e., consumption of damaged sites on the sidewalls of SWNTs without increased sidewall damage. It is shown that 4:1 (vol/vol 96% H_2SO_4/30% H_2O_2) piranha solutions cooled to room temperature are capable of attacking existing damage sites in the nanotube sidewall and induce cutting of SWNTs. However, these room-temperature reactions are incapable of introducing new damage sites into the sidewall. In addition, these room-temperature reactions have minimal carbon loss and slow etch rates preserving the original diameter distribution of nanotubes, whereas high-temperature piranha solutions etch away the smaller diameter nanotubes.

Experimental Section

HiPco[20,21] single-walled carbon nanotubes (lot 120.2) were purified using wet-air oxidation as described by Chiang et al.[8] The metal content after purification was measured by TGA analysis in air (TA instruments) and was determined to be approximately 6 wt %. Piranha solutions (4:1, vol/vol 96% H_2SO_4/30% H_2O_2) were prepared immediately prior to use to maintain their activity. The solution was then either heated or cooled to the desired temperature prior to use. Once the piranha solution reached the reaction temperature, it was added to the nanotubes (1 mL piranha/1 mg of nanotubes). A hot plate was used to maintain the temperature for reactions at 70 °C. The nanotube/piranha mixture was stirred with a PTFE stir bar and immediately formed suspensions. The reactions proceeded for 15 min to 9 h and showed the evolution of gas. The reaction temperature was continuously monitored. CAUTION: piranha solutions are very aggressive, corrosive solutions, and appropriate safety precautions should be utilized including the use of acid resistant gloves and adequate shielding. After completion, the oxidation reaction (~100 mL) was quenched by adding the suspension to approximately 2 L of NanoPure (Barnstead International, Dubuque, IA) water. The solution was then filtered through 0.1 μm polycarbonate membranes (GE Osmonics) and washed with deionized water until pH neutral and then washed with a small amount of ethanol. The samples were then dried under vacuum at 50 °C for 30−60 min. The piranha treatment reduced the metal content in the nanotubes to 3 wt %.

For analytical purposes, a small portion of the nanotube sample was then functionalized to analyze the lengths of individual nanotubes. Prior to functionalization, the nanotubes reacted with piranha were treated with H_2 (Matheson) in a horizontal quartz tube oven (Lindberg/Blue, Asheville, NC). The nanotubes were placed in a ceramic boat near the center of the oven and heated to 500 °C for 1 h. The pressure of H_2 was 1 atm, and the flow rate was approximately 20 sccm. These nanotubes were then functionalized[22,23] with dodecyl chains through a Birch reaction in liquid ammonia. The addition of the lithium is found to intercalate the nanotube ropes allowing the efficient reaction of the alkyl chains with the nanotube sidewall. Typically, the degree of functionalization was approximately 1 chain per 20−30 C atoms.[22] After functionalization, complete suspension of these nanotubes were prepared by sonicating ~1 mg of the dried powder in 15 mL of chloroform for ~1 min yielding a clear, lightly colored solution. These dilute suspensions were then spin-coated onto freshly cleaved mica substrates yielding a high quantity of individual nanotubes. AFM images were obtained on a Digital Instruments Nanoscope IIIA. The nanotube lengths were determined using SigmaScan software. Typically, 500−1000 nanotubes were measured to obtain statistically meaningful results.

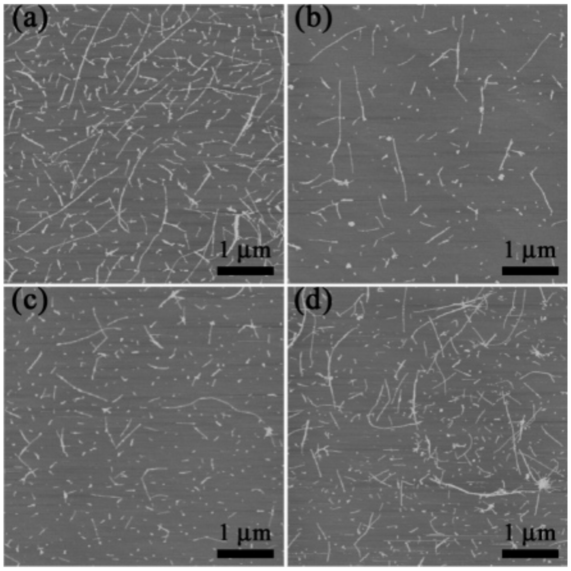

Figure 1. AFM images of (a) purified SWNTs and SWNTs after piranha treatment at 22 °C for (b) 1 h, (c) 3 h, and (d) 9 h.

Raman spectra were obtained using a Renishaw MicroRaman with a 780.6 nm diode laser. Multiple spectra (7−10) were obtained, normalized to the G band, and averaged to give a comprehensive snapshot of the material. For UV−vis−NIR absorbance spectra, the piranha treated nanotubes were treated with H_2 and then dispersed in 1 wt % SDS solutions. These solutions were sonicated in a bath sonicator for approximately 30 min, and the absorbance spectra were measured on a Shimadzu UV-3101PC spectrometer.

Results

Typically, piranha solutions are heated (70−150 °C) to create an aggressive environment for the oxidative attack of organic species. These strong oxidative solutions have been previously shown to create short nanotubes from long SWNTs.[9] While heated piranha solutions are good at creating short length nanotubes, it typically results in a significant loss of the nanotubes. To further understand the oxidation of SWNTs, the nanotubes were reacted at 70 °C and 22 °C (hereafter called high and room temperature, respectively) for varying lengths of time to determine the effect of temperature on the oxidative attack of SWNTs.

Figure 1 shows AFM images for room temperature piranha reactions and Figure 2 shows the corresponding length distributions of the purified SWNTs before and after piranha treatment at high and room temperature. Initially, the SWNTs have a very broad length distribution. After 1 h of high temperature piranha

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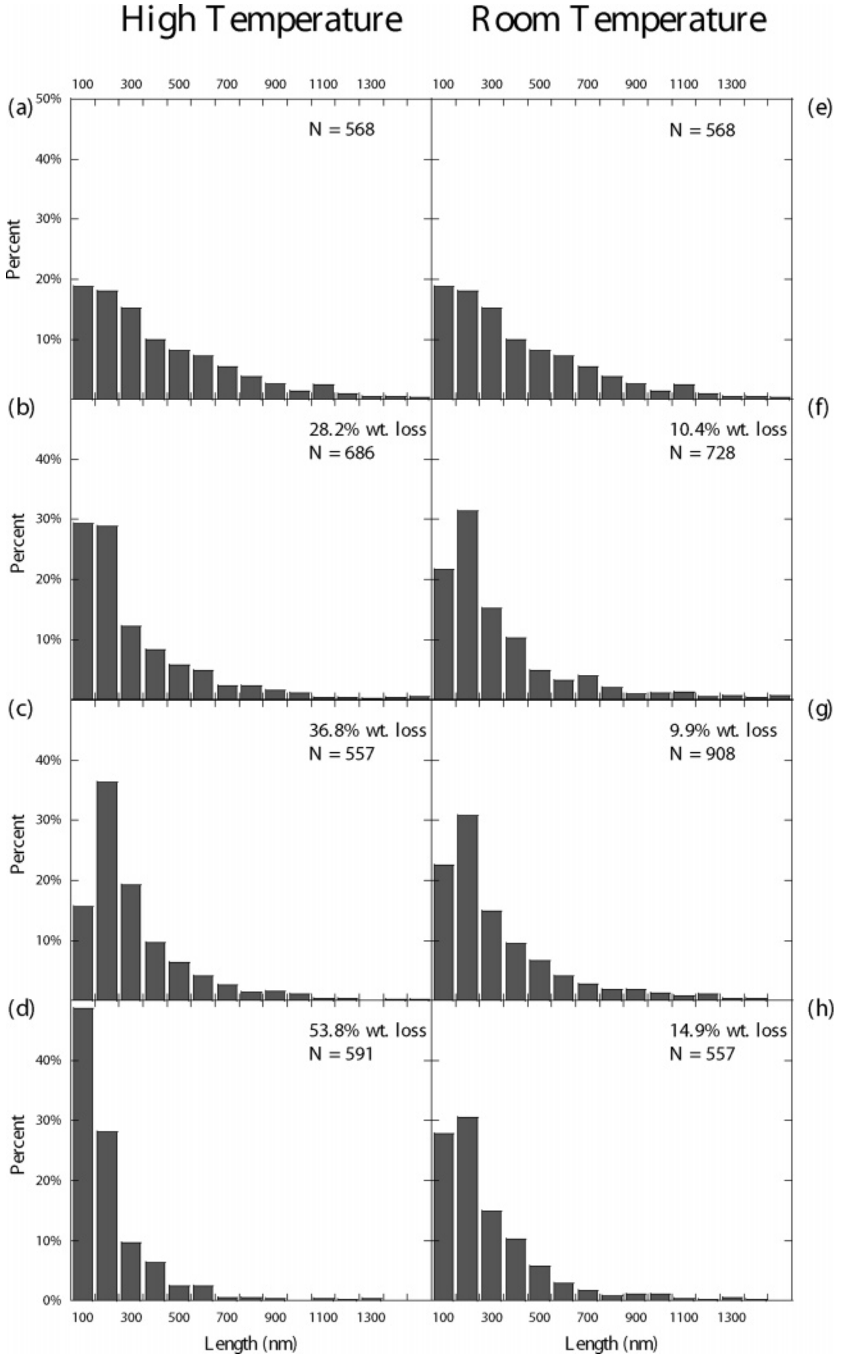

Figure 2. Length distribution for (a,e) purified SWNTs and SWNTs after piranha treatment for (b) 1 h at 70 °C, (c) 3 h at 70 °C, (d) 9 h at 70 °C, (f) 1 h at 22 °C, (g) 3 h at 22 °C, and (h) 9 h at 22 °C.

treatment, the histograms show a decrease in the number of longer nanotubes and an increase in the number of shorter nanotubes. Then the length distribution sharpens and shifts to longer lengths after 3 h. After 9 h of piranha treatment time, the length distribution moves to substantially shorter nanotubes with nearly 50% shorter than 100 nm in length. Interestingly, the nanotube length distributions of room temperature piranha solutions do not have significant changes after 1 h. The length distributions are nearly identical for 1, 3, and 9 h treatment times.

Figure 3 summarizes the average nanotube length determined from the histograms and the corresponding weight loss for room- and high-temperature piranha reactions. The average nanotube length and weight loss of the high-temperature piranha solutions show a continual decrease with reaction time. After a 9 h treatment at 70 °C, the average length is less than half of the original length with a weight loss of 53.8%. The average length and weight loss for the room temperature reactions on the other hand show an initial decrease and then plateau after a 1 h piranha treatment. In addition, the average length is longer and the weight loss significantly less than the high-temperature piranha reaction for the same reaction time.

Discussion

The chemical oxidation of SWNTs can be described by several processes:[10,24−27] (i) oxidative attack of existing active

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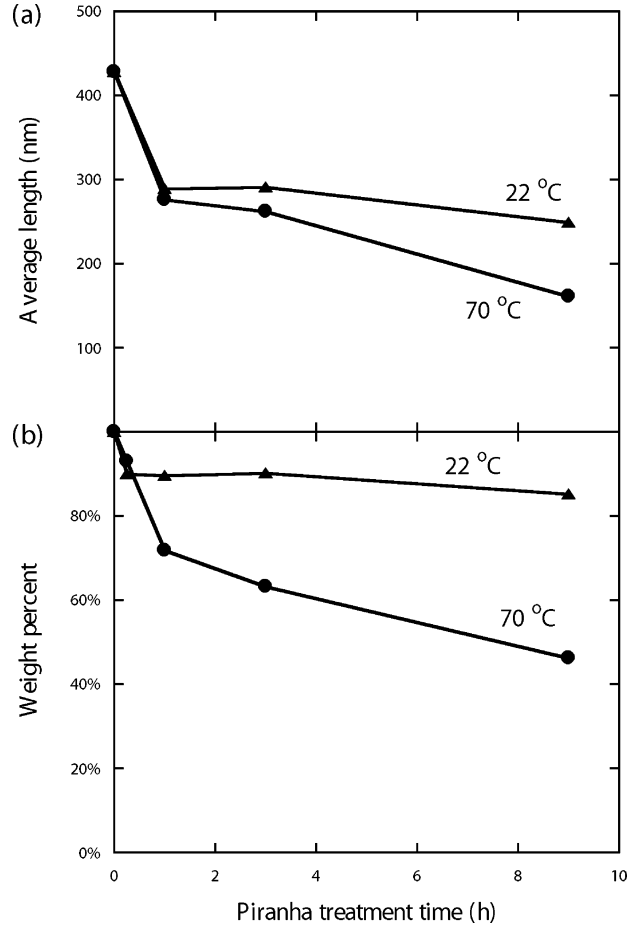

Figure 3. (a) Average nanotube length and (b) weight loss as a function of piranha treatment time for reactions at 22 °C and 70 °C.

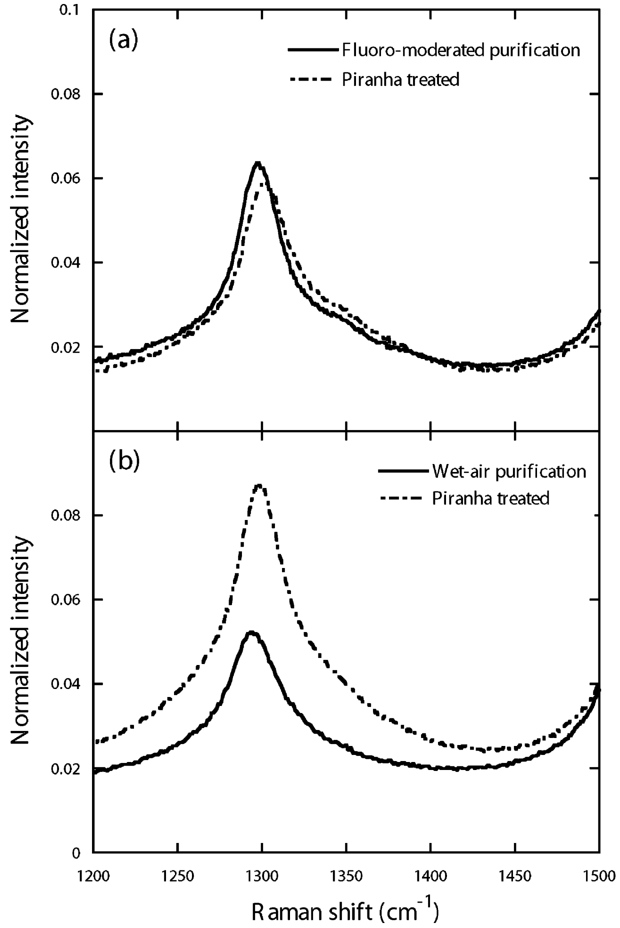

Figure 4. D-band Raman spectra (780 nm excitation) of dried SWNT powder before and after 15 min of high-temperature piranha treatment for (a) fluoro-moderated purification of SWNTs and (b) wet-air purification of SWNTs.

sites such as sidewall functional groups or Stone–Wales defects; (ii) generation of additional active sites (sidewall damage); (iii) generation of a vacancy in the graphene layer; and (iv) consumption of the graphene sidewall around the vacancy or nanotube end. The consumption process can occur along the circumferential or axial direction of the nanotube and is the only process that affects length. Circumferential consumption will induce cutting of the nanotube and appears to preferentially leave an exposed armchair edge,[28] while axial consumption will induce shortening of the nanotube.

To investigate the oxidative attack of existing damage sites, high-temperature piranha solutions were reacted with nanotubes with varying degrees of sidewall damage. Most SWNT cleaning processes induce some oxidative sidewall damage[29,30] which can be active sites for cutting by chemical oxidation processes such as piranha. Fluoro-moderated purification[31] is expected to induce less sidewall damage to the nanotubes by having fluoride interact with the exposed metal catalysts hindering the oxidation of the nanotubes. As can be seen in Figure 4, after 15 min of high-temperature piranha treatment, the fluoro-purified nanotubes show a minimal increase in the D band (Figure 4a), while wet-air purified nanotubes show a larger increase in the D band (Figure 4b). The Raman spectra, therefore, suggest that the piranha solutions are attacking the existing damage sites located on the sidewall of the SWNTs.

Raman spectra of the SWNTs were also measured as a function of reaction time to investigate the effect of piranha on the nanotube sidewall. As seen in Figure 5a, the disorder band (D) at 1300 cm^{-1} for high-temperature piranha treatments rises and stabilizes, whereas the D band of room-temperature piranha treatments in Figure 5b shows a slow gradual increase with reaction time. It is important to note, however, that reaction times beyond 1 h at room temperature offer no additional length changes. Therefore, 1 h of reaction time is sufficient to induce all length changes where the Raman spectrum shows no significant increase in the D band. It is apparent from the D band Raman spectra that high-temperature piranha solutions are capable of generating new sidewall damage, while room-temperature piranha solutions induce little sidewall damage.

Although active sites are attacked by piranha solutions, it does not guarantee a vacancy will be generated in the graphene layer. The generation of vacancies, however, will be important for any cutting strategy. Without the formation of vacancies, the nanotube is simply consumed from the ends in an oxidative environment to create shorter pieces. The generation of vacancies in the sidewall combined with their consumption allows amplification of the number of nanotubes which is essential for

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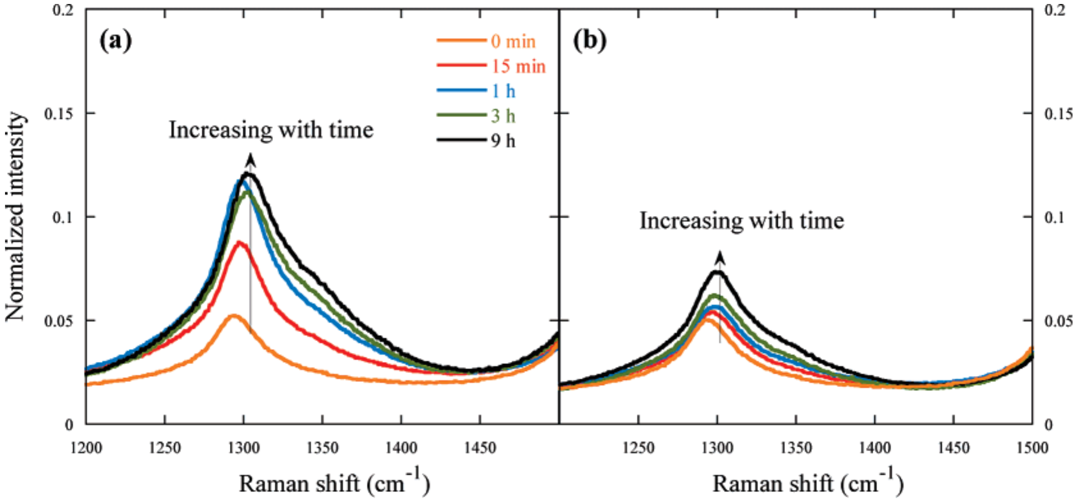

Figure 5. D-Band Raman spectra (780 nm excitation) of dried SWNT powder as a function of piranha reaction time at (a) 70 °C and (b) 22 °C.

the use of cut nanotubes in seeded growth. The changes in the length distributions after piranha reactions clearly indicate that consumption of the sidewall occurs. However, this consumption could be from the existing open ends of the nanotubes (etching) or from vacancies generated in the graphene layer (cutting). Room temperature reactions show little changes after 1 h suggesting that the consumption rate has been considerably reduced at these conditions. Therefore, assuming that the consumption rate will be constant over the entire reaction,[25−27] circumferential consumption or cutting of the nanotubes has to occur at generated vacancies to achieve substantial changes in the length distribution. Axial consumption or etching is still occurring at these reaction conditions but will not induce significant changes in the nanotube lengths. The weight loss data of room temperature piranha treatments also suggest that the dominant consumption process is cutting. The weight loss after 1 h only shows a reduction of 10%. If the weight loss was primarily due to etching of the nanotube ends, the average length should only decrease by 10%. However, the change in the average length after 1 h is 32%. Furthermore, this difference is highlighted in the length distributions where etching would only be expected to shift the length distributions (by 10%) to shorter lengths. However, the shift is more than 10% and also shows a change in the shape of the distribution after piranha treatment. Therefore, the changes in length distribution at lower temperatures must be due to consumption around oxidized vacancies in the sidewall.

At higher temperatures, an increased rate of consumption yields increasingly shorter nanotubes due to both cutting and etching of the nanotubes as witnessed by the Raman spectra for piranha treated nanotubes after H_2 treatment. The H_2 treatment resulted in significant reduction of the disorder band caused by the oxidizing piranha environment minimizing the effect of resonance changes and allowing the ability to probe the effect of piranha on the SWNTs. The radial breathing modes (RBM), located between 150 and 300 cm^{-1}, are inversely dependent on the SWNT diameter[32−34] and are shown in Figure 6 for high- and room-temperature piranha solutions, respectively. The RBMs shown in Figure 6a show that the peak at ∼267 cm^{-1} shows substantial decreases in relative intensity as the reaction time increases. This decrease in intensity suggests that smaller diameter nanotubes are being consumed or etched away under these reaction conditions. Indeed, it is expected that the smaller diameter nanotubes should be more reactive due to the

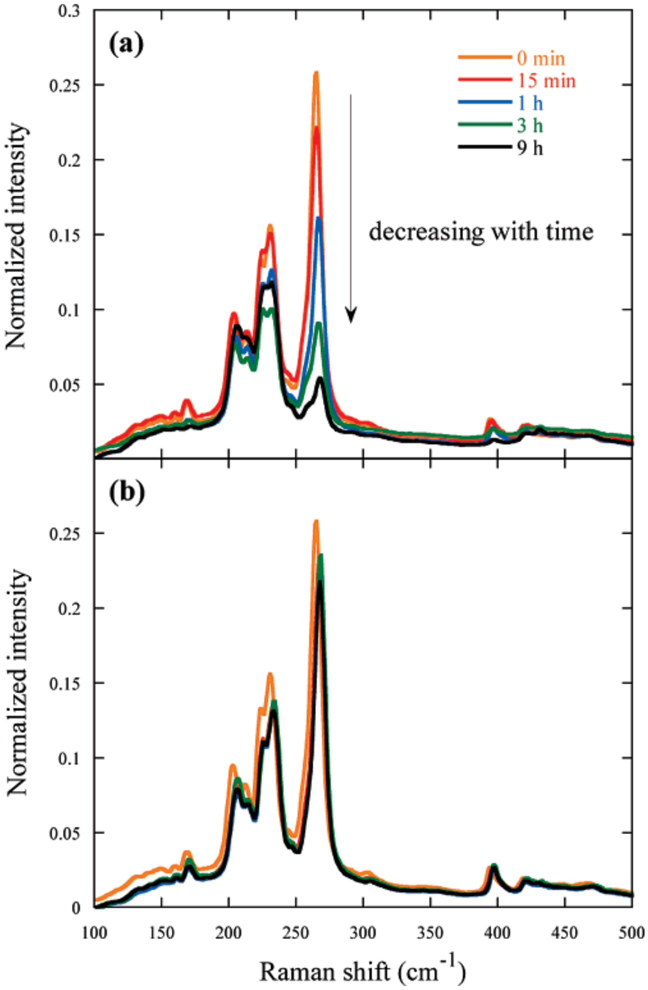

Figure 6. RBM Raman spectra (780 nm excitation) of dried SWNT powder after H_2 treatment as a function of piranha reaction time at (a) 70 °C and (b) 22 °C.

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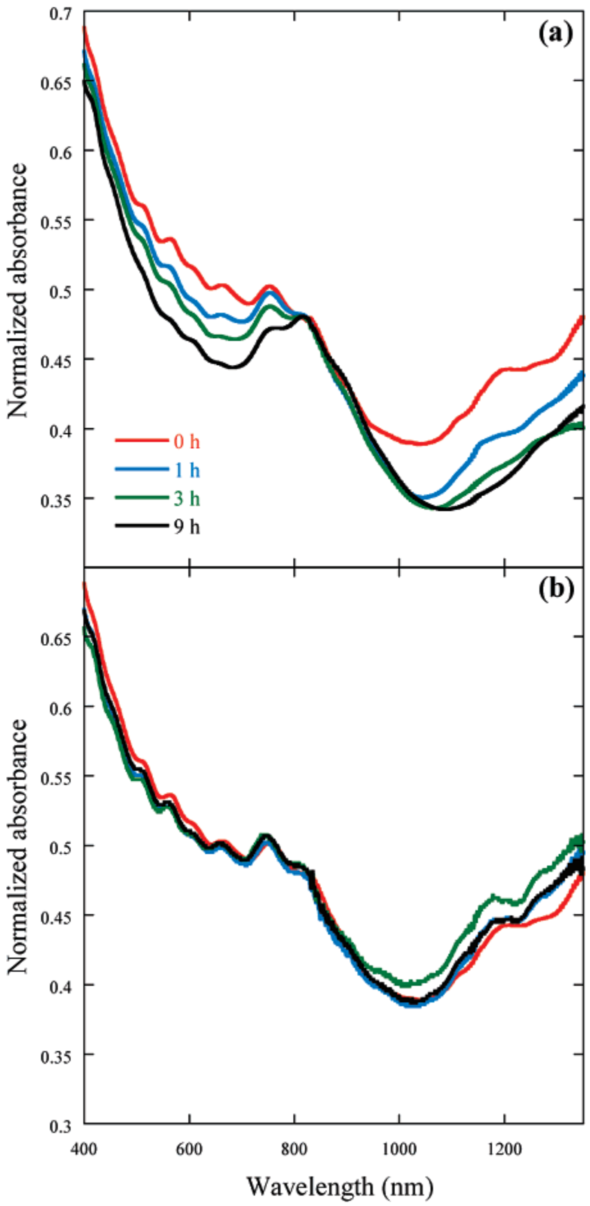

Figure 7. UV−vis−NIR specta after H_2 treatment for nanotubes treated in piranha at (a) 70 °C and (b) 22 °C at different reaction times.

higher strain induced on the lattice.[8,35,36] However, the RBMs of room-temperature piranha solutions in Figure 6b show virtually no relative changes in the spectra after piranha treatment.

UV−vis−NIR spectra on the room- and high-temperature piranha treatments after H_2 treatment, shown in Figure 7, also suggest that lower temperatures preserve the initial distribution of nanotube diameters in the sample. The 1-D nature of SWNTs results in diameter dependent van Hove maxima in the density of states resulting in sharp interband transitions associated with the singularities. The van Hove frequencies are diameter dependent with smaller diameter nanotubes having frequencies at lower wavelengths. The first van Hove frequencies of the high-temperature piranha solutions (Figure 7a) show substantial changes with reaction time in the absorption spectra at 1000 and 1200 nm which correspond to diameters of approximately 0.8 and 0.96 nm, respectively.[8] The second van Hove frequencies show similar changes in the intensities of the smaller diameter nanotubes confirming that selective oxidative etching of small diameter nanotubes is occurring at these reaction conditions. The UV−vis−NIR spectra of room-temperature piranha solutions (Figure 7b), however, confirm that no selective etching occurs at these reaction conditions. It should be noted that these spectra do not show the same intensity often observed in raw SWNT samples for two reasons. First, these solutions are not centrifuged; therefore, a substantial amount of bundles will be present that will effect the observed optical spectra. Second, oxidation of SWNTs through purification processes or cutting processes is known to have an effect on the electrical properties and, hence, optical spectra. For this reason, the samples were exposed to H_2 in an attempt to reduce the damage created by oxidation. While reduction can recover some of the optical spectra, it does not return the nanotubes to the pristine state observed prior to purification. The complete recovery of the SWNTs to their pristine state is currently being investigated. Nonetheless, the spectra observed in Figure 7 combined with the Raman data in Figure 6 strongly suggest that the smallest diameter nanotubes are being etched away at higher temperatures.

The selective etching of the nanotubes under high-temperature piranha conditions may also explain the apparent loss of short length nanotubes after 3 h (Figure 2c) yielding higher average lengths than might be expected. The smaller diameter nanotubes that are being etched away will also be the most probable nanotubes to be cut due to the increased strain in the lattice and, therefore, chemical activity.[8,35,36] Therefore, under this strong oxidizing environment these nanotubes can be expected to make up the majority of the nanotubes at shorter lengths. As these smaller diameter nanotubes are etched away (Figures 6 and 7), the length distribution could be expected to shift toward the remaining larger diameter nanotubes and, therefore, longer lengths witnessed at 3 h (Figure 2). Increased reaction times under this strong oxidizing environment eventually cut and etch the larger diameter nanotubes resulting in a substantial amount of short nanotubes.

Conclusions

Purified HiPco nanotubes were treated with piranha solutions at 70 and 22 °C to study the chemical oxidation process on SWNTs. At high temperatures, piranha is capable of attacking existing damage sites and consuming the oxidized vacancies to create cut nanotubes. The SWNTs in these high-temperature reaction conditions become increasingly shorter in length with an increase in reaction time. However, half of the starting material is lost to achieve these short length nanotubes. In addition, Raman and UV−vis−NIR spectra show that these reaction conditions result in the selective oxidative etching of the smaller diameter nanotubes. Room-temperature piranha treatments also show the capability of attacking vacancies in the sidewall to achieve cut nanotubes. However, contrary to high-temperature piranha solutions, there is minimal carbon loss, no new sidewall damage, and no selective etching of the nanotubes. Therefore, room-temperature piranha solutions offer the ability to exploit active damage sites in the sidewalls of the

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nanotube in a controlled manner without counterproductive destruction of the nanotubes. In conjunction with methods used to induce controlled amounts of damage sites, these room-temperature piranha solutions have the potential to yield an efficient means of creating short, cut nanotubes useful for many electronic, biological, and materials applications.

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Supporting Information Available: AFM images of high-temperature piranha reactions and complete Raman spectra of SWNTs after H_2 treatment of the piranha reactions. This material is available free of charge via the Internet at http://pubs.acs.org.

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