Cutting single-walled carbon nanotubes

This article has been downloaded from IOPscience. Please scroll down to see the full text article.
2005 Nanotechnology 16 S539
(http://iopscience.iop.org/0957-4484/16/7/031)

View the table of contents for this issue, or go to the journal homepage for more

Download details:
IP Address: 171.67.216.21
The article was downloaded on 11/09/2011 at 06:00

Please note that terms and conditions apply.
Cutting single-walled carbon nanotubes


Department of Chemistry, Center for Nanoscale Science and Technology, Rice University, Houston, TX 77005, USA

E-mail: res@rice.edu

Received 30 November 2004, in final form 24 April 2005
Published 2 June 2005
Online at stacks.iop.org/Nano/16/S539

Abstract

A two-step process is utilized for cutting single-walled carbon nanotubes (SWNTs). The first step requires the breakage of carbon–carbon bonds in the lattice while the second step is aimed at etching at these damage sites to create short, cut nanotubes. To achieve monodisperse lengths from any cutting strategy requires control of both steps. Room-temperature piranha and ammonium persulfate solutions have shown the ability to exploit the damage sites and etch SWNTs in a controlled manner. Despite the aggressive nature of these oxidizing solutions, the etch rate for SWNTs is relatively slow and almost no new sidewall damage is introduced. Carbon–carbon bond breakage can be introduced through fluorination to $\sim C_2F$, and subsequent etching using piranha solutions has been shown to be very effective in cutting nanotubes. The final average length of the nanotubes is approximately 100 nm with carbon yields as high as 70–80%.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Single-walled carbon nanotubes (SWNTs) have unique electronic and mechanical properties making them attractive for many materials science and electronic applications [1, 2]. The synthesis of nanotubes typically results in average lengths ranging from hundreds of nanometres to several micrometres depending on the reaction conditions. However, the availability of single-walled carbon nanotube samples of uniform length is essential for many specialized applications. For example, in biological imaging and sensing applications shorter length nanotubes (20–100 nm) will be required to penetrate cells and to serve as biological markers. Short nanotubes will also be important for the integration of SWNTs into electronic devices where nanotubes of a specific band gap and precise length must be placed in a well-defined location on a substrate.

To meet these demands, some researchers have begun to explore methods aimed at cutting long, entangled, as-produced nanotube ropes into short individual nanotubes. The first attempt at cutting nanotubes used concentrated 3:1 $H_2SO_4:HNO_3$ mixtures to cut the highly entangled long ropes of SWNTs into short, open-ended pipes [3]. Other approaches have focused on the use of sonication [4–6] with additives such as diamond, lithographic techniques [7], or ball-milling [8]. These processes have shown the ability to cut nanotubes to lengths of several hundred nanometres but do not appear to be able to achieve lengths below 100 nm. Shorter length nanotubes have been achieved by fluorination of the nanotubes followed by pyrolysis [9]. In this process, fluorine atoms tend to form fluorinated bands around the circumference of the nanotube sidewall [10] which when heated to 1000 °C in Ar are pyrolysed off leaving short, cut SWNTs with average lengths of approximately 40 nm. The problem with this method, however, is that the nanotubes tend to coalesce into intractable aggregates, possibly due to cross-linking of the ends. It is likely that the high temperatures (>500 °C) in pyrolysis are sufficient to overcome the activation energy required for cross-linking of the open nanotube ends. Therefore, any high-temperature approach will not be feasible for cutting, requiring the development of more benign approaches.

The general approach to cutting nanotubes described here is based on a two-step process shown in figure 1. The first step requires the introduction of carbon–carbon bond breakage in the lattice (sidewall damage) while the second
step is aimed at exploiting these damage sites by locally etching the lattice to create short, cut nanotubes. A process capable of consuming the damaged sites combined with a controlled means of introducing carbon–carbon bond breakage will allow the controlled cutting of SWNTs into short pristine segments. An important aspect to consider in the second step is the etch rate. Strong acid solutions heated to 40–70 °C have been previously shown to create short nanotubes from long SWNTs [3]. These aggressive solutions are good at creating short length nanotubes; however, they typically result in significant losses due to fast etch rates. While this type of processing will indeed achieve short lengths, it does so by consuming the product from the ends. For example, if 100 nm length nanotubes were desired from a nanotube sample that has an average length of 1000 nm, then 90% of all the carbon has to be destroyed to obtain the desired product. Clearly this is not an efficient means to achieve short nanotubes. Cutting strategies should therefore attempt to achieve minimal carbon loss. Finally, these processes should not induce significant oxidation which may ultimately affect the electrical properties and usefulness of the SWNTs [11].

2. Experimental details

Purification of nanotubes

HiPco [12, 13] single-walled carbon nanotubes were purified using wet-air oxidation as described by Chiang et al [14] or using SF6/O2 oxidation as described by Xu et al [15]. The metal content after purification was measured by TGA analysis in air and was determined to be approximately 5–6 wt% for the wet-air oxidized cleaning while the SF6/O2 oxidized cleaning typically resulted in 1–2 wt%. The wet-air purified SWNTs were utilized for the study on cutting nanotubes with piranha solutions because the purification process induces small amounts of sidewall damage in the lattice structure. The recent advance of SF6/O2 purification minimizes sidewall damage by deactivating the metal catalyst during oxidation. Therefore, these nanotubes were utilized to study the introduction of bond breakage.

Piranha and ammonium persulfate reactions

Piranha reactions with SWNTs were previously described [16] and are briefly described here with some slight changes. 4:1 (vol/vol 96% H2SO4:30% H2O2) piranha solutions were prepared immediately prior to use to maintain their activity. The solution was then added to the nanotubes (1 ml piranha: 1 mg of nanotubes) once the solution was either cooled or heated to the desired temperature. Ammonium persulfate solutions were prepared by dissolving 4 g of the salt in 50 ml of 96% H2SO4. The persulfate solution was then added to the nanotubes (1 ml solution: 1 mg of nanotubes). Caution: these oxidant solutions are very aggressive, corrosive solutions and appropriate safety precautions should be utilized, including the use of acid-resistant gloves and adequate shielding.

The nanotubes readily dispersed in the oxidant mixture with magnetic stirring. When the desired exposure was reached, the reaction was quenched by diluting the suspension with approximately five times the amount of NanoPure (Barnstead International, Dubuque, IA) water, resulting in a rapid rise in temperature. The solutions were quickly cooled to room temperature in an ice bath. This solution was then added to a separation funnel with a small amount of hexane. Ethanol (200 proof) was then slowly added, occasionally with shaking, until the nanotubes were extracted into the hexane layer. The addition of too much ethanol, however, would result in the apparent expansion of the hexane layer, making the separation of the aqueous phase more difficult. The two-phase mixture was allowed to settle for approximately 30 min and then the aqueous layer was drained from the funnel. After the initial separation, NanoPure water could be added to the funnel with the SWNTs remaining in the hexane layer. The nanotubes were then washed multiple times (4–5) until the pH was neutral. The remaining hexane solution was then filtered through 0.1 μm polycarbonate membranes (GE Osmonics) and dried under vacuum at 50 °C for 30–60 min.

Fluorination of SWNTs

The fluorination of nanotubes was done in a similar manner to previously published approaches [9, 17]. The nanotubes were exposed to a 10% F2 in He gas mixture at approximately 150 °C for 8–12 h. The carbon to fluorine ratio was determined by XPS to be ~C2:F. Defluorination was achieved by suspending the fluorinated nanotubes in isopropanol and reacting them with 35% hydrazine in water for 1–2 h. Typically, after defluorination the nanotubes were reduced to ~C10F. The defluorinated SWNTs were then reacted with room-temperature piranha solutions as described above. The fluodore content in the final cut nanotubes was below the detection limit.

Characterization

For analytical purposes, the SWNTs were functionalized at various steps to analyze the nanotube lengths outlined in detail elsewhere [18]. The functionalization is based on a Birch reaction, resulting in the addition of dodecyl groups to the sidewall, and has been shown to achieve a high degree of functionalization [18–20]. Tapping mode AFM images were obtained on a Digital Instruments Nanoscope IIIA. The nanotube lengths were measured using the Nanotube

Figure 1. Generalized approach to cutting single-walled carbon nanotubes. The first step involves the introduction of carbon–carbon bond breakage into the sidewall of the nanotube while the second step exploits these damaged sites for cutting.
Length Analysis package of SIMAGIS software (Smart Imaging Technologies, Houston, TX). Typically, the lengths of 500–2000 nanotubes were measured to obtain statistically meaningful results. Multiple Raman spectra (7–10) were recorded on a Renishaw Raman microscope with 780 nm excitation, normalized to the G band, and averaged to give a comprehensive snapshot of the material. SWNT powder was pressed onto 0.5 mm thick soft indium foil, and XPS data were collected on a PHI Quantera SXM Scanning X-ray Microprobe with monochromatic Al Kα x-radiation (1486.6 eV). Thermogravimetric analysis (TA Instruments) was utilized to determine the metal content in the purified nanotubes by pyrolysing the SWNTs in air to 1000 °C. The residual weight was attributed to iron oxide and converted to a metal concentration.

3. Results

The first step in the generalized cutting scheme shown in figure 1 is to introduce carbon–carbon bond breakage. However, the ability to quantify the number or distribution of carbon–carbon bond breakage is limited to labor-intensive techniques such as STM. Therefore, the processes utilized to introduce bond breakage described below were measured by the ability to exploit these sites with the etching step. For this reason, the etching of nanotubes will be discussed first, followed by processes which can introduce bond breakage within the carbon lattice.

Etching with Caro’s acid

The wet-air purification of nanotubes can be expected to introduce a small amount of sidewall damage. These nanotubes were utilized to study the effect of temperature on the etching at these damage sites [16]. Piranha solutions consist of a mixture of sulfuric acid and hydrogen peroxide (4:1 vol/vol 96% H₂SO₄:30% H₂O₂) and have been extensively utilized in the semiconductor industry to remove organic contaminants. The mixture of the two results in the formation of the strong oxidant H₂SO₅ (Caro’s acid):

\[ \text{H}_2\text{SO}_4 + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{SO}_5 + \text{H}_2\text{O}. \]

Figure 2(a) shows the average nanotube length determined from the histograms for nanotubes reacted with room-temperature (22°C) and high-temperature (70°C) piranha solutions. The average nanotube length of the high-temperature piranha solutions shows a decrease in length as the exposure time increases. After a 9 h treatment at 70°C, the average length is less than half of the original length. The average length for the room-temperature treatment on the other hand shows an initial decrease and then small changes in length after a longer exposure to piranha. The weight loss associated with these reactions also shows a similar pattern, as seen in figure 2(b). Nanotubes treated with high-temperature piranha initially lose a significant amount of weight and then continually decrease, reaching a weight loss of ~55% after 9 h. The weight loss of nanotubes treated with room-temperature piranha, however, plateau at approximately 10–15% after only 1 h.

The weight loss during piranha exposure clearly indicates that some of the nanotubes are consumed in the reaction. This etching can occur at the ends of the nanotubes or at sites where bond breakage has occurred. As seen in figure 2, the room-temperature piranha reactions indicate that the nanotubes have length changes of approximately 30% with only a 10% weight change. These data suggest that these strong oxidizing solutions are capable of etching at damage sites. The plateau in the length distribution of room-temperature reactions suggests that the etching rate has been considerably slowed at room temperature, having a rate of the order of 1–5 nm h⁻¹, whereas high-temperature piranha solutions have an etch rate of the order of 15–20 nm h⁻¹. The
Figure 4. Raman spectra of the radial breathing modes (RBMs) as a function of piranha reaction time at (a) 70 °C and (b) 22 °C. Note that the RBMs are inversely proportional to the nanotube diameter. Therefore, the decrease at ~267 cm⁻¹ indicates a decrease in the population of the smallest diameter nanotubes. Reproduced with permission from J. Am. Chem. Soc. 2005, 127, 1541 [16]. © 2005 Am. Chem. Soc.

etch rates for graphite have been described as constant over the entire reaction [21–23], and SWNTs can be expected to behave similarly. Therefore, the initial change in the length distribution of over 100 nm in 1 h for room-temperature piranha reactions confirms that etching has occurred at damage sites. Etching from the nanotube ends is still occurring at these reaction conditions but because of the slow etch rate this process will not induce significant changes in the length. In addition, high-temperature piranha solutions were shown to increase the amount of sidewall damage, while room-temperature solutions had almost no increase in sidewall damage as determined by Raman spectra before and after the reaction.

At this point, it is clear that both room- and high-temperature piranha solutions are capable of etching at damage sites with high-temperature piranha solutions creating more sidewall damage. The significant advantage of room-temperature piranha solutions is that it does not induce significant changes in the length. Furthermore, high-temperature piranha solutions are shown to preferentially etch away smaller diameter nanotubes. The Raman radial breathing modes (RBMs) shown in figure 4(a) are inversely dependent on the SWNT diameter [24–26] and clearly show that smaller diameter nanotubes are being consumed or etched away at high temperatures, as might be expected due to the higher lattice strain [14, 27, 28]. On the other hand, the RBMs of room-temperature piranha solutions shown in figure 4(b) show no signs of selective etching after piranha treatment. UV–vis–NIR spectra on the room- and high-temperature piranha treatments also confirm that lower temperatures preserve the initial length distribution.

Ammonium persulfate in 96% sulfuric acid has also been utilized for the cutting of SWNTs. This salt dissociates to form H₂SO₄ and H₂SO₅ (Caro’s acid) similar to piranha solutions. As can be seen in figure 5, the distribution of the cut SWNTs is nearly identical for piranha and ammonium persulfate solutions. The average measured length of the cut SWNTs varied by less than 10 nm. These ammonium persulfate solutions offer additional advantages over piranha solutions. These ammonium persulfate solutions maintain their oxidative strength better than piranha, making the reactions easier to control. In addition, SWNTs can be stirred for long periods of time in H₂SO₄ where the acid is able to intercalate the nanotube ropes [29] before the addition of the oxidant. The dispersion of individual nanotubes ensures that all of the SWNTs will react with the oxidant. The addition of H₂O₂ (piranha solutions), however, would cause a significant temperature rise due to the heat of mixing (to 50–70 °C) which results in significant carbon loss, increased sidewall damage, and selective etching of the small diameter nanotubes, while the addition of ammonium persulfate can be maintained at ambient temperatures.
Cutting single-walled carbon nanotubes

Fluorination

De-fluorination

Etching

**Figure 6.** Cutting scheme using fluorination to induce carbon–carbon bond breakage.

Room-temperature Caro’s acid solutions offer the ability to exploit sites where carbon–carbon bond breakage has occurred in the nanotube sidewall in a controlled manner without counterproductive destruction of the nanotubes. In conjunction with methods used to induce controlled amounts of carbon–carbon bond breakage, these room-temperature Caro’s acid solutions have the potential to yield an efficient means of creating short, cut nanotubes useful for many electronic, biological, and materials applications.

**Fluorination-based carbon–carbon bond breakage**

Recently, STM analysis of the pyrolysis of fluorinated nanotubes showed that as the fluorine was slowly removed from the nanotube during pyrolysis some defect sites remained behind [30, 31]. As the temperature was increased, pyrolysis occurred at these defect sites, resulting in cut nanotubes. These data suggest that the fluorination of the nanotubes at elevated temperatures results in some carbon–carbon bond breakage during fluorination. It is believed that thermal fluctuations during fluorination will create hot spots that have sufficient activation energy to form CF₄ and leave a vacancy in the nanotube sidewall. Indeed, fluorination at very high temperatures has been shown to completely destroy the nanotubes [17]. In order to eliminate the coalescence problem associated with high-temperature pyrolysis, these nanotubes were reacted with Caro’s acid to exploit the vacancies. The complete cutting strategy is depicted in figure 6. The fluorination is carried out until ~C₂F is achieved. Prior to the reaction with Caro’s acid the fluorine had to be removed from the nanotubes to make the nanotubes wettable with piranha. Defluorination of the SWNTs is achieved by reacting the fluorinated nanotubes with hydrazine which has been previously shown to remove a majority of the fluorine [17]. After fluorine removal, the vacancies

**Figure 7.** AFM image and corresponding histogram for defluorinated C₂F nanotubes (a), (c) before and (b), (d) after Caro’s acid treatment.
created during fluorination have been exposed and can now be exploited using room-temperature Caro’s acid solutions.

Figure 7 displays the AFM images and corresponding histograms for the nanotubes before and after Caro’s acid treatment. Prior to the Caro’s acid reaction, the defluorinated nanotubes show no apparent damage sites and have an average length of 300 nm. After ~1 h of room-temperature Caro’s acid treatment, however, the average nanotube length has decreased to ~100 nm. Unfluorinated control samples give an average length of ~275 nm (not shown), indicating that damage sites are introduced through the fluorination process. Recall that these room-temperature Caro’s acid solutions have a very slow etch rate of the order of 1–5 nm h⁻¹. This slow etch rate suggests that a significant amount of vacancies were created during the fluorination process and subsequently exploited with Caro’s acid. The fluorination-based cutting process has been shown to be a very efficient process, with an overall carbon yield of 70–80%.

4. Conclusions

The fluorination-based cutting strategy has been shown to be an effective, controlled process with a high yield of short, cut nanotubes. The process involves fluorination to C₂F₃ which creates carbon–carbon bond breakage in the form of sidewall vacancies. These vacancies can then be exploited through the use of a strong oxidizing solution. However, it is important to maintain the reaction temperature near ambient conditions to minimize carbon loss and sidewall damage. Room-temperature Caro’s acid solutions are shown to exploit vacancies in the nanotube sidewall in a controlled manner without counterproductive destruction of the nanotubes to achieve short, cut nanotubes. The overall carbon yield for the fluorination cutting strategy is typically 70–80%, and the final average length of the nanotubes is approximately 100 nm. While the fluorination-based route is effective, there is concern about the safety of scale-up and the presence of terminal fluorine on the nanotube ends. Terminal fluorine may hinder the reactivity of the ends which may be required for molecular-scale electronics where metal nanocrystals [3] or conducting linker molecules [32] may be utilized to connect SWNT segments. Therefore, alternative approaches are being investigated that will allow efficient introduction of sidewall damage.

Acknowledgments

We gratefully acknowledge financial support from the National Science Foundation, the Office of Naval Research, the Robert A Welch Foundation, the Center for Biological and Environmental Nanotechnology, and the Air Force Office of Scientific Research.

References


[27] Haddon R C and Raghavachari K 1996 Tetrahedron 52 5207


