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Fluorination of single-wall carbon nanotubes

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Abstract

Purified single-wall carbon nanotubes (SWNTs) were fluorinated at several different temperatures. Product stoichiometries were determined and electron microscopy was used to verify whether or not the fluorination was destructive of the tubes. SWNTs fluorinated at three different temperatures were then defluorinated using hydrazine. Raman spectroscopy and resistance measurements were utilized to verify whether or not the products of the defluorination were in fact SWNTs. It has been determined that the bulk of the SWNTs survive the fluorination process at temperatures up to 325°C and that hydrazine can be employed as an effective defluorinating agent to regenerate the unfluorinated starting material. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

Since the discovery of single-wall carbon nanotubes (SWNTs) [1] there has been a flurry of research activity aimed at understanding their physical properties [2], elucidating their growth mechanisms [3] and developing novel uses for them [4]. Chemistry involving SWNTs is still in its infancy. This is due, in large part, to previous difficulties in obtaining reasonable quantities of highly purified SWNTs.

Progress in the bulk synthesis and purification [5] of SWNTs is now making available high-quality samples in sufficient quantities to begin exploring the chemical modification of this fascinating class of materials. Recently, sono-chemistry was employed to cut the long, intertangled tubes into independent, macro-molecular scale, open tube fragments (50–300 nm long) [6]. In that work, the high reactivity of the dangling carbon bonds at the open tube ends was exploited to tether the tubes to gold particles via thiol linkages.

CHEMICAL PHYSICS

In contrast to the open tube ends, the side-walls of the SWNTs, by virtue of their aromatic nature, possess a chemical stability akin to that of the basal plane of graphite [7]. The chemistry available for modification of the nanotube side-wall (without disruption of the tubular structure) is thus significantly more restrictive.

Using technology developed in the fluorination of graphite [8], we report here on the chemical manipulation of the SWNT side-wall by fluorinating high-purity SWNTs and then defluorinating them. In a

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manner similar to that of fluorinated fullerenes [9], we anticipate that SWNTs, once fluorinated, can serve as a staging point for a wide variety of side-wall chemical functionalizations.

2. Experimental

Single-walled carbon nanotubes were produced by the dual-pulsed laser vaporization of Co/Ni doped graphite rods and purified by techniques described previously [5]. The purification product is a metastable colloidal suspension of SWNT 'ropes' [10] (bundles of hexagonally close-packed tubes ranging from a few to 200 SWNTs) in a 0.2% aqueous solution of Triton X-100 surfactant. Filtering the solution through a PTFE filter membrane and washing with methanol to remove residual surfactant leaves a black film on the surface. If this layer is sufficiently thick (10–75 μ m, as measured by a micrometer) it can be peeled off to form a free-standing film or 'bucky paper' of SWNTs. This form has appreciable mechanical integrity and is convenient for handling, and for electrical conductivity and Raman scattering measurements. It is the fluorination of this 'bucky paper' that we describe here.

In fluorinating the SWNTs, elemental fluorine (Air Products, 98%) was used as the fluorinating agent. HF, being the major impurity in the fluorine, was removed by passing it through an HF trap (Matheson Gas Products) containing sodium fluoride pellets. The fluorine, diluted with helium (Trigas, 99.995%), was then passed through a temperature-controlled Monel flow reactor containing the SWNT sample.

Prior to fluorination, the purified 'bucky paper' was vacuum baked at 1100°C (2×10^{-6} Torr) for several hours in order to desorb any residual surface contaminants. For each reaction a pre-weighed piece of baked 'bucky paper' (being ~ 10 µm thick and weighing 150–200 µg) was used. F₂ and He flow rates for each reaction were 2 and 20 sccm, respectively. In each case the reaction time was 5 h. The only variable was reaction temperature. As the kinetics of inorganic carbon + fluorine reactions are highly temperature dependent [11], several reactions were carried out at the following temperatures: 150, 250, 325, 400, 500, and 600°C. For reaction temperatures

of 325 and 400°C, the fluorination was begun at 250°C and after 1 h, the F_2 flow was stopped and the reactor temperature brought up to the appropriate level after which the F_2 flow was resumed for an additional 4 h. For the reactions at 500 and 600°C, the sample was fluorinated for 1 h at 250°C, 1 h at 400°C and then 3 h at the specified reaction temperature. The rationale behind this 'stepped' reaction temperature procedure was to minimize, as much as possible, the decomposition: $CF_n \rightarrow CF_4$, C_2F_6 , etc., which has been well documented in the fluorination of graphite [12] and fullerenes [13].

Once fluorinated, SWNTs were defluorinated with anhydrous hydrazine (Aldrich, 98%). To the pieces of 'bucky paper', fluorinated at 250, 325, and 400°C, was added 5 ml of hydrazine under an inert atmosphere at room temperature. The SWNTs were allowed to sit in the hydrazine for 1 h prior to filtering and washing with water.

Product stoichiometries as a function of reaction temperature were obtained both gravimetrically (TA Instruments TGA-DTA 2960 microbalance) and via electron microprobe analysis (Cameca SX-50). Infrared spectroscopy (Perkin-Elmer Paragon 1000 FT-IR) was used to confirm the presence of covalently bound fluorine. Transmission electron microscopy (JEOL model 2010 TEM using 100 keV beam energy) was used to determine if, and at what temperature the tubes were being destroyed (i.e., 'unzipped') by the fluorination. Raman spectroscopy (Jobin Yvon-Spex model HR460 monochrometer coupled with an ISA Spectrum ONE series CCD detector and using a 532 nm Nd:YAG laser excitation source), scanning electron microscopy (JEOL model JSM-6320F field emission SEM using 5 keV beam energy), and two-point resistivity measurements were used to analyze the untreated, fluorinated, and defluorinated SWNT samples.

Table 1

Reaction product stoichiometries determined by both gravimetric and electron microprobe analysis

	Reaction temperature (°C)					
	150	250	325	400	500	600
Gravimetric Microprobe	CF _{0.114} CF _{0.097}	CF _{0.521} CF _{0.458}	CF _{0.495} CF _{0.554}	CF _{0.565} CF _{0.647}	(^a) CF _{0.815}	(^a) CF _{0.996}

^aNo determination at these temperatures.

3. Results

Infrared spectroscopy (KBr pellet method) confirmed the presence of covalently bound fluorine (peaks in the 1220–1250 cm⁻¹ region) in the samples fluorinated at temperatures of 250°C and higher. No C–F stretching frequency was seen for the sample fluorinated at 150°C, and its two-point resistance (5 mm apart) was ~ 100 Ω which therefore precludes large amounts of fluorine being covalently bound to the SWNT side-wall. Product stoichiometries of the fluorination reactions are shown in Table 1. Discrepancies between the gravimetric and microprobe analyses can be attributed to product decomposition as described above, especially at the higher temperatures.

Fig. 1A shows a TEM image of the purified, unreacted SWNT material. Fig. 1B shows a TEM image of SWNTs fluorinated at 325°C. As can be seen from the image, the tubes remain largely intact



Fig. 1. (A) TEM image of pure, unreacted SWNTs. (B) TEM of SWNTs after being fluorinated at 325°C. (C) TEM of SWNTs after being fluorinated at 500°C. (D) Another TEM of SWNTs fluorinated at 500°C showing the formation of MWNTs.

after treatment under these conditions. Fig. 1C is a TEM image of SWNTs fluorinated at 500°C. Here it would appear that the tubes are essentially all destroyed. However, a fair number of nested tube-like graphitic structures reminiscent of multiwall carbon nanotubes (MWNTs) seem to have been generated as a result of the high-temperature reaction. These structures are shown in Fig. 1D.

The fluorination of MWNTs has been reported previously [14]. This was done at two temperatures: 25 and 500°C. The room temperature reaction was done with a F_2 , HF, and IF_5 mixture, and yielded an intercalated type compound. The reaction carried out at 500°C was done with F_2 , and was determined to have destroyed the tube structure to yield a graphite fluoride compound of stoichiometry CF. In light of this, it is not too surprising that we observe destruction of the SWNTs at 500°C, but somewhat surprising that MWNT-like structures are formed.

Not unexpectedly, the electronic properties of the fluorinated tubes differ dramatically from those of their unfluorinated counterparts. While the untreated SWNTs are good conductors (10–15 Ω two-probe resistance across the length of the ~ 10 × 3 mm × 30 μ m bucky paper samples), the tubes fluorinated at

temperatures of 250°C and above are insulators (two-probe resistance > 20 M Ω).

We have found that, once fluorinated, SWNTs can be defluorinated with anhydrous hydrazine via the following reaction: $CF_n + \frac{1}{4}nN_2H_4 \rightarrow C + nHF$ $+\frac{1}{2}nN_2$. As the Raman spectroscopy of SWNTs has been well developed both theoretically [15] and experimentally [16], we utilize it here to examine the results of both the fluorination and subsequent defluorination of the SWNTs. Fig. 2 shows the Raman spectrum of the pure, unadulterated SWNT material. The smaller peak at 186 cm^{-1} is due to a characteristic breathing mode of the SWNTs. Raman spectra of SWNTs fluorinated for 5h at reaction temperatures of 250, 325, and 400°C are shown in Fig. 3. Trace A, corresponding to the reaction at 250°C, shows only two broad peaks centered around 1340 and 1580 cm^{-1} and a broad band fluorescence. The Raman peaks correspond to sp^3 and sp^2 carbon stretching modes, respectively. At higher reaction temperatures, yielding high F to C ratios, these peaks disappear and the fluorescence is attenuated. As C-F bonds are not very polarizable, it is understandable that they are not seen in the Raman spectra presented here.



Fig. 2. Raman spectrum of pure, unreacted carbon SWNTs.



Fig. 3. Raman spectra of SWNTs fluorinated at: (A) 250°C; (B) 325°C; and (C) 400°C.

Raman spectra of the defluorinated products of the SWNTs originally fluorinated at 250, 325, and 400°C are shown in Fig. 4. Traces A, B, and C correspond to the material originally fluorinated at 250, 325, and 400°C, respectively. As can be seen in traces A and B, the characteristic breathing mode at 186 cm⁻¹ returns upon defluorination. This is not true in trace C, indicating that the tubes are largely destroyed at 400°C. Additionally, the peak at 1340 cm⁻¹ grows relative to the characteristic SWNT peaks with increasing fluorination temperature. This can be attributed to one or both of the following factors: (1) tubes are being 'unzipped' much more readily at the higher temperatures; and (2) at higher



Fig. 4. Raman spectra showing the defluorination of the nanotubes originally fluorinated at: (A) 250°C; (B) 325°C; and (C) 400°C.

reaction temperatures, a greater amount of decomposition of the type: $CF_n \rightarrow CF_4$, C_2F_4 , C_2F_6 , etc., is occurring.



Fig. 5. (A) SEM of pure, unreacted SWNTs. (B) SEM of SWNTs after having been fluorinated at 325°C for 5h. (C) SEM of SWNTs fluorinated at 325°C and then defluorinated in hydrazine.

SEM images and two-point resistivity measurements were obtained on a single piece of 'bucky paper' after each of the following stages: purification, fluorination at 325°C, and defluorination in hydrazine at room temperature for 1 h. Fig. 5A shows the purified starting material. Fig. 5B shows the same piece after having been fluorinated at 325°C for 5h. The image shows excessive charging due to its insulating nature, but the 'rope-like' structure of tubes is still evident. Finally, Fig. 5C shows the same piece of 'bucky paper' after having been defluorinated in hydrazine. The two-point resistance of the purified starting material is $15-16 \Omega$ measured 5 mm across the surface of the 'bucky paper'. Identical measurements on the fluorinated and defluorinated 'bucky paper' yielded a resistance of > 20M Ω and 125–130 Ω , respectively. It is interesting to note that the defluorinated material recovers most. but not all of its original conductivity.

4. Conclusions

We have demonstrated via gravimetric and electron microprobe analysis that large amounts of fluorine can be added to SWNTs. Resistance measurements along with vibrational spectroscopy (Raman, IR) confirm the formation of new chemical bonds to the nanotube superstructure. Contributions of adsorbed molecular fluorine to the overall fluorine uptake are precluded at these temperatures [11]. We conclude, therefore, that fluorine is being covalently attached to the side-wall of the SWNTs.

TEM studies have shown that at fluorination temperatures as high as 325°C, the majority of the fluorination product maintains a tube-like structure. These studies also indicate that at 500°C, the singlewall tubular structure does not survive the fluorination process and that some MWNT-like structures are being formed.

From the product stoichiometries, resistance measurements and IR spectra we conclude that reaction temperatures in excess of 150°C are necessary to covalently add significant amounts of fluorine to the tube wall. The small amount of fluorine that does show up in the product of the 150°C fluorination reaction could be attributed to a combination of adsorbed fluorine and fluorination of the end caps of the SWNTs.

We have also demonstrated that fluorine can be effectively removed from the SWNTs using anhydrous hydrazine and that the rejuvenated product is in fact a SWNT. From the results of these defluorination experiments and the Raman and SEM studies associated with them, we would conclude that a majority of the tubes are destroyed at fluorination temperatures of around 400°C, whereas only a slight amount of tube destruction occurs at 250°C.

We believe that for reactions in which only the outside of the tube is being fluorinated (the SWNTs used in this study are closed at the ends), that there is a limiting stoichiometry of C_2F for which the fluorinated tube can still maintain its tube-like (albeit puckered) structure. This is supported by the product stoichiometries we have obtained via elemental analysis and the evidence of significant tube destruction at fluorination temperatures greater than 325°C. Further addition of fluorine would then lead to the breaking of carbon–carbon bonds and, hence, destruction of the tube.

Efforts to conceptualize a structure consistent with this C_2F stoichiometry are ongoing and will be presented shortly.

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