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CHEMISTRY OF NANOSCALE CARBON MATERIALS:
GAS-PHASE PURIFICATION OF SINGLE-WALL CARBON NANOTUBES,
SYNTHESIS OF NANOSCALE CARBON NITRIDES,
AND NANODIAMONDS IN METEORITE CARBON WITH RELATED DIAMOND
SURFACE CHEMISTRY

by

JOHN L. ZIMMERMAN

A THESIS SUBMITTED
IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE
DOCTOR OF PHILOSOPHY

APPROVED, THESIS COMMITTEE

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ABSTRACT


by

John L. Zimmerman

A unique feature of nanoscale carbon materials is the nature of their surfaces and how their surfaces interact with other species. The carbon materials specifically studied here include single-wall carbon nanotubes, nanoscale carbon nitrides, and a brief study of nanodiamonds from meteorite carbon, and related diamond surface chemistry. These nanometer sized carbon materials often possess curved surfaces. These curved surfaces can result in special structure-property relationships, such as a unique resistance to oxidation in the case of the nanotubes. Also the synthesis of nanoscale structures can be governed by surface interactions with the growth substrate, as shall be demonstrated with the carbon nitrides. The final materials obtained after such chemical treatments, should prove useful in applications such as catalysis, gas storage, chromatography, molecular electronics, high-strength composites, batteries and fuel cells, and abrasives.
Acknowledgments

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Preface

The theoretical performance of nanoscale carbon materials offers many intriguing future applications, including cleaner running vehicles, and fibers stronger than man has ever known. However, the realizations of these theoretical utopias remains to be demonstrated experimentally. The work discussed here shall highlight the steps completed toward applications of such carbon materials. While the studies involved different subsets of carbon materials the systems do have similarities which shall be used to show the unique chemical approach that was required. The first part speaks of a new gas-phase method for single-walled carbon nanotube purification. Part two discusses a route to 3-dimensionaly ordered carbon nitride nanoparticles prepared on quartz. In the final section a brief account of work on nanodiamonds in meteorite carbon, and related diamond surface chemistry is discussed.

The interest in such new materials, and likewise new methods of processing them, is spurred on by a greater need for materials possessing a variety of properties. These properties include, lightweight and high strength which would be useful for transportation, conductive for assembly of electronic devices, hardness for wear resistance, and many others. Also it is sometimes expected that the substance have many of these features simultaneously. Such lofty goals, while seemingly insurmountable at first glance, may become reasonable with innovative materials and processing methods. The application of a gas-phase method for single-wall carbon nanotube purification was thought to be impossible before these experiments. But it will be shown here that it is in fact possible as well as scientifically profitable to carry out such processes. Likewise a unique preparation of spherical carbon nitrides was unheard of until now, and has shown the importance of surface interactions in nanoscale materials. Such materials are truly next generation type materials which may require many years before reaching public markets, but they offer a wealth of
scientific insight today.

These advances in carbon materials chemistry have come about by exploring and exploiting the unique features that are only observable on the very small or nanoscopic length scale. While the exact nature of nanotechnology is still being defined, and its eventual role in the life of everyday people is not determined, the basic chemical processes to control such materials should remain important. Just as chemistry is identified as the "central science", it seems reasonable to expect that the chemical community will play an essential role in shaping the future of nanotechnology. A chemist may act as both a principal investigator as well as a liaison to other fields, since the research endeavors are expected to be very interdisciplinary. In this work the fundamental needs of synthesis, purification, and characterization, of such nanoscale materials have been addressed. Since such ventures are critical to later steps in the development process, this lays the groundwork for future developments and can serve as an example for other investigators.

The procedures used with both the nanotubes and carbon nitrides involved the interaction of gases with solid surfaces. The experiments pertaining to nanotube purification resulted from an attempt to further understand the interaction of chlorine gas with the curved carbon structures only available at nanoscale dimensions. These investigations led to a wealth of both practical and theoretical insights. The unique control over carbon etching afforded with chlorine, water, and hydrogen chloride gives one a way to remove impurities by converting them to a volatile product. Also it led to a variety of mechanistic theories involving nanotube cap protection, charge transfer states, and metal catalysis. For the carbon nitride synthesis, product control was determined by the nature of a variety of solid-solid, and solid-gas interactions. In this case one can generate a new curved carbon structure by the incorporation of
nitrogen. This presence of nitrogen heteroatoms, as well as the incorporation of fluorine into the structure, allows a greater processability for this material.

The experiments involving meteorite carbon demonstrate another application of the nanotube gas purification technique. By applying the chlorine gas mixture one is able to remove impurities that were otherwise inaccessible. This and other observations allows one to see interesting gas to carbon surface interactions with the nanodiamonds contained inside the carbon mixture. The application of such nanodiamond entities for nanotechnology mechanical components was investigated by carrying out specific diamond surface functionalization.
Chapter 1

Gas-Phase Purification of Single-Wall Carbon Nanotubes

1.1 Introduction

1.1.1 General Introduction

Single-wall nanotubes are structurally related to other more common forms of carbon as shown in Figure 1-1. Nanotubes are a combination of a graphite sheet and a fullerene. The graphite sheet is bent around a central axis to form a cylinder, and then the ends of the cylinder are capped by half a fullerene. This creates a closed cage structure without any dangling bonds, a feature unique to fullerene type carbon materials. The tubes are named by the way in which the graphite sheet is rolled up. This results in the assignment of a roll-up vector using an \((n,m)\) notation in which the \(n\) represents the number of hexagonal vertices in the \(x\) direction and the \(m\) represents the number of vertices in the \(-y\) direction.\(^1\) Tubes in which \(n\) and \(m\) are the same number are known as armchair tubes, because the way in which the graphite sheet is rolled up results in the end of the graphite sheet looking as if it is composed of a series of chairs placed side to side. It does not have any relation to the more conventional use of the chair notation for a cyclohexane conformation. As \("n"\) and \("m"\) increase the tube diameter also increases, thus a 10,10 tube is twice the diameter of a 5,5 tube. The tubes with indices \((n,0)\) belong to a general class known as the zigzag tubes because the end of the tube possesses a repetitive triangular tooth pattern. Chiral tubes are those where \(m \neq n\), these have a jagged edge because the graphite sheet is rolled up on an angle not coincident with the graphite lattice. Although this naming system accurately describes all of the carbons in the tube, it does not deal with the atoms in the cap, and there should technically be a separate naming system for tubes with different caps. However, because the carbons on the
Figure 1-1

Structural Comparison

Fullerene (C_{60})

Graphite Sheet

Rolled Up Graphite Plane (End View)

Rolled Up Graphite Plane (Side View)

Single-Wall Carbon Nanotube (End View)

Single-Wall Carbon Nanotube (Side View)
nanotube cap typically make up only a few percent of the total, they are usually neglected. For future use I propose a naming system for the caps be included in describing tube types with a general notation of a(n,m)b where “a” represents the hemifullerene cap on one side of the tube(if it is able to be concluded this would be the cap formed on initiation of the tube) and “b” represents the hemifullerene on the other side of the tube(the cap formed upon termination of growth). Thus for an ideal defect free tube formed from a C₆₀ type cap the complete name would be C₃₀(5.5)C₃₀. Since the variety of tube cap possibilities, as restricted by the isolated pentagon rule, increases with size, this should be particularly useful for larger diameter tubes.

1.1.2 Purification Introduction

A gas-phase purification method for raw nanotube material has been developed which incorporates a chlorine, water, and hydrogen chloride gas mixture to remove unwanted carbon. The evolved gases can be easily monitored by infrared spectroscopy to follow the cleaning process. The quality of the final material was verified by SEM(Scanning Electron Microscopy), TGA(Thermogravimetric Analysis), and VIS-NIR(Visible-NIR Absorption Spectroscopy). The yield of ~15 wt.% indicates a uniquely selective carbon surface chemistry that prevents etching of the nanotubes, which are generally more reactive due to their larger curvature. Although the technique’s usefulness for large-scale purification was not determined, the ability to purify single-wall nanotubes by a gas-phase method has been demonstrated, and a mechanism proposed.

Single-wall nanotubes were first discovered by S. Iijima, and have since been produced by pulsed laser vaporization, arc discharge, chemical vapor deposition, and by high pressure CO disproportionation. The proposed future applications
of this unique material include high-strength composites, molecular electronics, nanoprobe energy storage or conversion, and many others. The research directed at these applications will require pure samples for physical and chemical processing.

The highest synthetic yield, of greater than ~70 vol.% nanotubes, was obtained by the pulsed laser process in a 1" furnace. However, the scale-up of this method to a 4" furnace resulted in lower quality material, and thus a greater need for purification.

The procedures used thus far for single-wall nanotube purification rely on some type of ultra-centrifugation (UCF) or filtration, including microfiltration, ultrasonically assisted filtration, or cross-flow filtration (CFF). The most recently developed technique uses an oxidizing-acid reflux of the raw material, known as felt, followed by UCF. The separation in this case uses the difference in water solubility between the small-oxygenated carbon species and the nanotubes. The other common procedure uses CFF in place of the centrifugation. Although the acid treatment breaks up the unwanted carbon, the actual separation is done by the CFF and is based on physical size and aspect ratio.

Although multi-wall nanotubes can be purified by a variety of gas-phase oxidations, the use of a chemical purification process has not been demonstrated for single-wall nanotubes. Multi-wall nanotubes have been purified by oxygen, a combination of copper and oxygen, or a combination of bromine and oxygen. The copper and bromine are intended to serve as intercalates, and the resulting difference in oxidation rate is used to burn off the unwanted carbon. The difference in oxidation behavior is more pronounced with the intercalate present and results in higher yields. Attempts to use similar procedures for single-wall nanotubes resulted in tube destruction. For example, using the bromine and oxygen system the yield was ~3wt.%. This is related to the amount of curvature experienced by the graphite sheet. Therefore, the oxidation resistance of single-wall nanotubes is less than that of multi-
wall nanotubes, which are in turn less resistant than large carbon fibers. This would seem to preclude chemical purification for single-wall tubes, but we show here that the correct conditions allow for removal of amorphous carbon or onionated particles, with or without metal catalyst inside, while simultaneously protecting the nanotubes.

1.2 Experimental

1.2.1 Materials

The preparation of the felt used for this report was done by the pulsed laser method, and has been described elsewhere. The felt was stored under air in a polyethylene screw cap bottle. Graphite (Aldrich synthetic powder, 1-2µ), and arc-grown single-wall nanotubes (Carbolex, AP Grade), were used as received. Approximately 5mg of material was used for all experiments. Gases used for purification were Chlorine (Scott Specialty Gases, 99.5%), Hydrogen (TRIGAS, 99.99%), Argon (TRIGAS, 99.998%), water from an argon bubbler, and HCl(Fisher, 12.1M) from an argon bubbler. Solvents used include N,N-Dimethyl Formamide(DMF)(ACROS, 99%), and Methanol (Fisher, 99.9%). For infrared analysis the sample holder was a Polyvinyl Chloride gas cell with Potassium Bromide windows. Gases used for infrared quantitation were Carbon Monoxide(TRIGAS, 99%), and Carbon Tetrachloride(Aldrich, 99+%).

1.2.2 Purification and Characterization

The gas ratios used for purification were 7.2ml/min Cl₂, 2.7ml/min H₂, and 3.0ml/min Ar bubbled through water, unless otherwise indicated. The sample was placed in a quartz tube and the system was purged, with the gases mentioned above, for one hour at room temperature. After purging, the sample was lowered into a tube furnace at 500 °C, as measured by a type-K thermocouple. The evolved gases,
including CO, COCl₂, and CCl₄ were collected in the gas cell and monitored by infrared spectroscopy (IRS) (Perkin Elmer, Paragon 1000PC). CO₂ may also be observed at the beginning of a run, due to adsorbed gases. The reaction was carried out until the carbon monoxide partial pressure, as detected by IRS was < 0.5torr, unless noted. The sample was returned to room temperature, then sonicated in a 50:50 mixture of DMF:0.6M HCl to remove metals, and then sonicated in pure DMF. The last step was filtering and methanol washing to form a paper. Alternatively the metals could be removed by sublimation in HCl at a higher temperature. The paper was dried at 160°C, then weighed for yield data. The paper was characterized by SEM (Philips, EL30 ESEM-FEG), TGA (TA-Instruments Inc., SDT2960), and VIS-NIR Absorption (Shimadzu (UV-1601PC)). It should be noted that a toluene reflux and sonication were employed to remove any fullerenes that may be present after purification, but nothing was found. When not being monitored by IRS, the evolved gases were run through an aqueous potassium hydroxide bath to remove chlorine, hydrogen chloride, and phosgene. Although not attempted here, for a larger scale process the carbon tetrachloride can be destroyed before venting, by reaction with alkaline earth metal oxides, or other methods. Special care must be taken when working with both the reagent and product gases due to toxicity hazards; also the chlorine and hydrogen may form explosive mixtures.

1.3 Results and Discussion

The felt produced by the laser vaporization process contains mostly other forms of carbon besides the nanotubes, including amorphous carbon and a large amount of onionated particles as shown in Figure 1-2. After purification the material shows predominately nanotube ropes. Figure 1-3 shows the “sponge” type material after the gas-phase treatment, showing that the purification is a direct result of the
Figure 1-2: SEM of Raw Nanotube Material (a.k.a. Felt)
Figure 1-3: SEM of Gas-Purified Nanotube Material (a.k.a. Sponge).
gaseous chemistry and not the treatments that followed. The bright metal particles, originally cobalt and nickel catalyst, visible after the gas treatment can be removed by the DMF:HCl wash. The final paper obtained appears to be high quality single-wall nanotube material, see Figure 1-4. The difference in material quality can also be seen via VIS-NIR Absorption spectroscopy, as shown in Figure 1-5, where the unique electronic structure of the nanotubes becomes much more apparent after purification. Also the VIS-NIR spectrum indicates that the nanotubes are not significantly altered chemically by the purification process, and that they are electronically similar to tubes obtained by other purification techniques. The suspension of gas-purified tubes in DMF is limited to lower concentrations than acid-purified tubes, due to increased rope strength from the high temperature treatment and/or residual impurities. TGA in air, Figure 1-6, indicated a combustion onset temperature of \( \sim 400^\circ \text{C} \) for the purified tubes, versus \( \sim 360^\circ \text{C} \) for the felt. The TGA also indicates that the purified material contains \( \sim 11 \) wt% of an unknown substance with a burning onset of \( \sim 235^\circ \text{C} \).

It is important to note the exact gas mixture that allows for purification of the nanotubes, see Table 1. Among the single component gases, chlorine is the most effective at etching carbon, as shown by the 21\% weight decrease after 6hrs. There is an additional 21\% weight loss when the material is subsequently washed in DMF:HCl and then filtered. The large weight loss seen with chlorine treatment is not a result of direct reaction between carbon and chlorine, but rather the combined affect of chlorine and adsorbed air, given that the partial pressure of carbon monoxide is two orders of magnitude greater than carbon tetrachloride. The weight of the material after gas-phase water or gas-phase hydrogen chloride(aq) treatment shows no change, due to physical and chemical adsorption offsetting the small amount of carbon etched. Therefore, the IR data for the samples are needed to get a better understanding of the
Figure 1-4: SEM of Gas-Purified Nanotube Material in Paper Form
Figure 1-5: Visible-Near IR Absorption spectra of Gas-Purified Nanotubes and Felt in DMF
Figure 1-6: TGA of Gas-Purified Nanotubes in Air, 5°C/min to 900°C, with 1 hour hold at 200°C, 100ml/min.
chemical processes responsible for carbon etching. Ultimately no single gas was found to offer any purification, or more specifically, chlorine, hydrogen chloride, or water separately do not remove carbon at a useful rate. Of the dual gas mixtures, only chlorine and water were found to remove carbon quickly. However, there is no preferential removal of unwanted carbon with just chlorine and water, and thus no purification results. The unwanted carbon is selectively removed only if hydrogen chloride is added to the chlorine and water mixture. This observation also implies that the source of hydrogen chloride needs to be separate from the water in order to get individual control of the gas ratios, as done in this study.

It was found that the progress of the reaction could be followed by infrared spectroscopy of the effluent gas. This allows in-situ investigation of gas-phase chemistry and the ability to follow carbon etching without exposure of the sample to air. Figure 1-7 shows the IR spectra of the gas purification products. One can clearly see the CO stretch for carbon monoxide at $2170\text{cm}^{-1}$, and the CCl stretch for phosgene at $850\text{cm}^{-1}$, and the antisymmetric CCl stretch for carbon tetrachloride at $792\text{cm}^{-1}$.17 As changes are made to the composition of the gas purification mixture, the results can be followed by infrared spectroscopy. The ultimate ratio of reactant gases present is determined by equation 1.

$$\text{Cl}_2 + \text{H}_2\text{O} = 2\text{HCl} + 1/2\text{O}_2$$

Equation 1

The gases introduced into the system include chlorine, water, and hydrogen chloride, which therefore determines the amount of oxygen and the overall oxidation potential toward carbon etching. The influence of water on the oxidation potential was determined for both rate of reaction and the final yield of nanotubes. Table 2 presents the results from variation of the water bubbler flow rate. With a low oxidation potential the yield of nanotubes is maximized. With inclusion of the TGA data, these values would mean 15.6% and 14.5% nanotubes respectively, which agrees well with
Table 1: Summary of Control Purification Experiments for SWNT Felt.

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<th>Weight Change (+/-%) After Wash and Filter</th>
<th>Total Weight Change (+/-%)</th>
<th>Purification Observed (Y/N)</th>
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<td>-77</td>
<td>-83</td>
<td>-96</td>
<td>Y</td>
</tr>
</tbody>
</table>

All reactions were for 6hrs at 500C and flow rates 10ml/min unless indicated.

a. Secondary water supply.
b. Bubbler flow rate=3ml/min
c. No carbon material recoverable.

Table 2: Nanotube Yields and Reaction Times.

<table>
<thead>
<tr>
<th>Conditions*</th>
<th>Time (hrs)</th>
<th>Yield (wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>tla(L.O.P.)</td>
<td>11</td>
<td>17.5</td>
</tr>
<tr>
<td>tlb(L.O.P.)</td>
<td>10</td>
<td>16.3</td>
</tr>
<tr>
<td>2(H.O.P.)</td>
<td>8.5</td>
<td>7.6</td>
</tr>
<tr>
<td>3(S.O.P.)</td>
<td>8</td>
<td>11.7</td>
</tr>
</tbody>
</table>

*Flow rate of argon water bubbler was varied to change oxidation potential.
L.O.P. = Low Oxidation Potential, flow rate=3.0ml/min.
H.O.P. = High Oxidation Potential, flow rate=5.5ml/min.
S.O.P. = Stepped Oxidation Potential, flow rate = started at 3.0ml/min and stepped up to H.O.P. after 2 hours.
Figure 1-7: Infrared Spectra of Product Gases. a) Carbon Monoxide b) Phosgene (C-Cl Region) and Carbon Tetrachloride
the 10-20wt.% expected. However, this yield comes with a slow carbon etch rate and a long run time. If the oxidation potential is increased the rate of reaction can be improved, but the final yield is compromised. It was found that a stepped oxidation potential offered a little better yield and reaction rate. One explanation for this behavior is that at a high oxidation potential the heat of reaction from other carbon forms may be sufficient to cause etching of nanotubes. With a stepped oxidation potential, one allows more of the unwanted carbon to be removed before proceeding to the next level. In this case however, it seems to indicate the need for sufficient time to remove adsorbed gases from the felt or an induction period for the establishment of the intended gas-surface interactions.

The presence of the cobalt/nickel metal catalyst in the felt could have a detrimental influence on the nanotubes. Transition metals are known to catalyze the gasification of carbon. Although the exact mechanism of metal catalyzed oxidation has been debated, as to whether gas-metal or metal-carbon interactions dominate, both interactions should be impeded by the formation of a metal chloride phase. Given that the metal catalyst is contained in a carbon shell, the interaction between the metal and the bulk of the material is not expected to be important until later in the purification process when the metals can become mobile on the surface. Also the ability of chlorine on platinum to impede the catalyzed oxidation of graphite has been shown, and it is expected that the chlorine will have a similar influence on the cobalt and nickel. With the ability to form a mixed metal oxychloride phase by the gases used, interaction with the metal may become important for larger scale purification in which longer reaction times may be needed, or whenever a higher temperature is used.

Also of interest is the behavior of other carbon materials in the gaseous purification environment. Arc grown single-wall nanotubes could not be purified by
the same method used for the laser-grown material. The rate of carbon etching was found to drop dramatically after three hours to a rate that was negligible. This is due to the higher density of the arc-grown material, ~0.33 g/cm$^3$ for arc material vs. ~0.03 g/cm$^3$ for laser material, and thus a limited ability for the gases to get to reactive sites. Observation of the material after the treatment, however, did show an enrichment of nanotubes on the particle surface. Perhaps a high-pressure gas system could overcome the problem of decreased reaction rate. Graphite is essentially unaffected, in that there is no weight loss and the evolution of carbon gases stops completely after one hour. This shows that the conditions used favor edge attack or defect sites for a perfectly unstrained aromatic system.

Of foremost importance in explaining the mechanism of purification is the experimental observation that hydrogen chloride is required for selective removal of unwanted carbon. As demonstrated earlier, the correct gas ratios yields a reactant mixture of low oxidation potential, which is seen to remove the impurity carbon, while leaving the nanotubes unharmed. These conditions are similar to those used by the more conventional acid-purification of nanotubes, where the oxidation potential is controlled by acid concentration. However, the partial pressure of oxygen is still high enough for gasification of the nanotube into carbon monoxide. Even more interesting is the ability of some of the nanotubes to withstand further increases in oxidation potential. Although the nanotubes are more reactive because of the increased curvature of the graphite sheet, they do have structural features that should be of benefit, under the correct conditions. Unlike the majority of other carbon forms in the felt, the single-wall nanotubes have more perfect sidewalls, and a lack of edges due to the presence of caps. Although the caps are more reactive than the sidewall, the cap structure seems important for the nanotube survival in the gas purification environment. Figure 1-8 show the plausible interactions of the chlorine gas mixture
Figure 1-8: Reaction Schemes for Cap Chemistry

Scheme 1

\[ \text{SWNT} \xrightarrow{\text{Cl}_2, \text{H}_2\text{O}} \text{SWNT} \]

Scheme 2

\[ \text{SWNT} \xrightarrow{\triangle} \text{SWNT} \]

CO + HCl
with the nanotube cap. Figure 1-8a indicates the formation of a hydroxy-chloride functionalized nanotube cap as already demonstrated in the reaction with water and carbon nanotubes and as shown in the chlorination of $C_{60}$.\textsuperscript{23,24} These reactions illustrate the particular need for hydrogen chloride in the gas-phase purification mixture. Without the hydrogen chloride present in Figure 1-8b, any hydroxyl groups that form on the nanotube cap would be deprotonated, leading to the eventual breakup of the cap structure, and exposure of the strained graphitic edge. Thus the function of the hydrogen chloride would seem to be the protection of the more reactive caps. by shifting such reactions in the reverse direction.

The various mechanisms of attack, for etching of carbon materials, offer further clarification for the survival of the more highly strained single-wall nanotubes in the purification environment. Typically the addition of a heteroatom such as oxygen, to a graphite sheet, first involves attachment at the edge, followed by desorption of the product gas. This is because the aromaticity of the basal plane does not allow attachment to the interior carbons. Likewise, the etching of a diamond also occurs at the edge of a crystal. In this case however, it is not so much the difference in reactivity of the surface carbons in relation to the bulk, but simply that the dense packing of atoms does not allow gas species to reach the interior. Thus the etching of diamond allows one to see the effect on reaction rate as the nature of the surface changes. The formation of a hydroxyl group on a diamond surface has been shown to offer a significant impediment to the etching rate of diamond.\textsuperscript{25} In this case, the formation of a hydroxyl serves to block the etching of an oxygen environment by filling up reactive sites on the diamond surface. Because of the unique closed-cage structure of nanotubes the formation of a hydroxyl group on the nanotube cap should also serve to protect it from oxygen attack. Unlike a planar graphite sheet with edges, a nanotube with caps only allows front-side attack, similar to diamond. This means
that filling the reactive sites for front-side attack should similarly impede the action of oxygen on a nanotube. Given that the nanotube sidewall will not react under these conditions, protection of the cap means preservation of the entire tube.

1.4 Summary

Although this method has not yet been used on a large scale, the basic nature of gas-phase reactions should lead to a fully automated and perhaps scalable system. With the ability to volatilize the unwanted carbon and metal chloride impurities, such a gas-phase purification represents the ultimate one step method, allowing raw material to be produced in a quartz tube and then after some time the pure nanotube "sponge" removed. The ability to preferentially remove unwanted carbon, in the presence of the more highly strained nanotubes, represents a new manner of thinking for structure-property relations of this unique material. The necessity for hydrogen chloride, in the purification gas mixture, indicates that a protection mechanism may be involved. Further work is currently underway to develop a better understanding of the role of the nanotube caps.

1.5 System Optimization and Mechanistic Considerations

1.5.1 Introduction

Although the studies mentioned above were very useful in demonstrating the applicability of a gas-phase purification, there was still much more that could be done. The need to further the understanding of the protection mechanism is obvious and there is also some impetus to increase the efficiency of the process. This required a variety of experiments be undertaken with various theories in mind, which could
then be tested. To do this it was also considered necessary to update the experimental setup.

1.5.2 New Reaction Setup

The use of corrosive and toxic gases requires special considerations when designing a reaction system. The chlorine and hydrogen chloride used in the purification can be particularly harmful to system components. Normally it is only recommended that one use Teflon tubing, fittings and etceteras. But the softness and temperature limits of Teflon can also cause problems. As a way to circumvent these problems a new reaction system incorporating a special inert gas purge and vacuum was built, see Figure 1-9. Separating the other gases from the water helps reduce the corrosion normally seen on metal components in moist environments: also the gases are dried immediately after exiting the tank and in other key places within the system. Also, the gases are premixed to a diluted concentration of 10 wt.%. As a final precaution a vacuum pump with Fomblin, a fluorinated oil, was incorporated. For handling product gases a potassium hydroxide bath was used as well as a secondary furnace for carbon tetrachloride decomposition. With such a setup working appropriately the only effluent gases are carbon monoxide and carbon dioxide. Also, the water bath can be neutralized prior to disposal, making the entire system relatively environmentally friendly.

This system allows a certain amount of automation and unattended use. The mass flow controllers constantly monitor and adjust the gas outlet to compensate for differences in pressure and keep the flow constant. The furnace incorporates a timer
Figure 1-9: New Reaction Design for Gas-Phase Experiments
which ramps the furnace at a prescribed rate, holds for a given time and then shuts itself off. The system also uses an automatic purge with argon following an experimental run.

1.5.3 Gas Quantitation

As mentioned earlier, the product gases can be observed by infrared spectroscopy. Thus it was necessary to determine which product gas, carbon monoxide, carbon tetrachloride, or phosgene, was responsible for removing most of the carbon. A set of standards was prepared of both carbon monoxide and carbon tetrachloride at known pressures, in a sample holder designed for gas monitoring. Figure 1-10 shows the standard curve for carbon monoxide. From this figure one can determine that the carbon monoxide partial pressure was typically around 5 Torr at the beginning of the reaction and then decreased (for more information regarding monitoring of the IR signal for determination of reaction completion see section 1.5.6). Also, given that the entire range of peak areas seen during the experiment was covered by the calibration curve, the quantitation of carbon monoxide can be considered applicable. The quantitation of the other product gases was much more difficult but yet still informative. The calibration curve of the carbon tetrachloride is not included because of difficulty preparing samples of low enough pressure accurately. The manometer used only gave readings to 0.02 Torr, and to prepare samples in the correct range would require a better vacuum system. With a standard sample of 4 Torr and an area of 0.6 the amount of carbon tetrachloride present at the beginning of the purification is approximately 0.06 Torr. This excludes carbon
Figure 1-10

Calibration Curve for Carbon Monoxide

$R^2 = 0.9977$
tetrachloride from consideration as an important carbon removal gas. Although one could theoretically calculate the phosgene contribution by subtracting out the amount of carbon removed by the other gases, this was obviously hindered by the inaccuracies in the carbon tetrachloride quantitation as well as other problems (see section 1.5.6). Thus it was determined, after much consideration of the hazards, that phosgene standards would need to be prepared. The use of phosgene is VERY dangerous in terms of toxicity. The Threshold Limit Value (TLV), the amount of toxin one can be exposed to in an eight hour period without adverse affects, is 0.1 ppm. To put this in perspective this value indicates that phosgene is ten times more toxic than fluorine and one hundred times more toxic than hydrogen cyanide. Thankfully, the one good aspect of phosgene is that it easily reacts with water to give carbon dioxide and hydrogen chloride. Thus, after use the gas can be run through a water bubbler for decomposition before venting into the hood. Analysis of phosgene standards, see Figure 1-11, indicated that although phosgene is formed at a lower concentration than carbon monoxide, it is still a significant etch gas with the pressure at startup of 0.4 Torr. This indicates that carbon monoxide is ~10x more abundant than phosgene and ~100x more abundant than carbon tetrachloride.

1.5.4 Role of Individual Gases

The complexity of the original gas mixture used to purify the nanotubes warrants further analysis. As shown earlier in equation 1, the overall oxidation potential was controlled by the relative amounts of chlorine, water, and hydrogen chloride. As the oxidation potential increased so did the rate of carbon gasification.
Figure 1-11

Calibration Curve for Phosgene Gas

\[ R^2 = 0.9786 \]
This led to an investigation as to the exact role each gas plays in the purification process, and an attempt to find if certain gases could be removed, or substituted.

The observation that most of the carbon etched was released in the form of carbon monoxide indicates that an oxygen containing gas is the most important etching gas. Since the oxygen is introduced in the form of water the transformation to carbon monoxide involves several steps. Equations 2 and 3 demonstrates the gas-phase reaction between chlorine and water in more detail.\textsuperscript{26,27}

\begin{equation}
\text{Cl}_2 + \text{H}_2\text{O} \rightleftharpoons \text{HCl} + \text{HOCl}
\end{equation}

\begin{equation}
2\ \text{HOCl} \rightleftharpoons 2\ \text{HO}^- + 2\ \text{Cl} \rightleftharpoons 2\ \text{HCl} + \text{O}_2
\end{equation}

These reactions demonstrate that the hypochlorous acid intermediate may be an active oxygen transfer agent. Although the system would stop at equation 2 with liquid water, this is not the case in the gas phase. The lack of solvation possibilities in the gas phase does not allow normal acid dissociation which would stabilize the system. To further test the importance of the gas-phase interactions between reactants, equilibrium calculations were carried out using the TEQWORKS program.\textsuperscript{28} The equilibrium partial pressures of all oxygen containing gases is shown in Figure 1-12. Please note that no value is included for a partial pressure lower that $5\times10^{-6}\text{(atm)}$. At the 500\degree C operating temperature, the amount of HOCl present is $\sim10^{-5}\text{atm}$. This value is particularly low and it would appear that the hypochlorous acid is not important in the overall scheme of oxygen transfer, and thereby is not responsible for carbon etching. Also, it has been demonstrated that chlorine and carbon tetrachloride are effect inhibitors of oxygen(O\textsubscript{2}) gasification of graphite.\textsuperscript{29} Therefore, if a graphite model is appropriate for the nanotube felt, it would also seem that molecular oxygen
Figure 1-12: Equilibrium Composition of Oxygen Containing Gases
is not involved in the transfer of oxygen to the nanotube felt, and that only the surface interaction of chlorine and water on the felt causes formation of carbon monoxide.

To investigate the role of oxygen at very low levels, an experiment was run with a 0.03% Oxygen in Argon mixture. This level of oxygen is the percentage indicated by the equilibrium calculations of Figure 1-11. The TGA of this low level Oxygen run at 500C, shows a final weight of 46% after 11 hours. The temperature was ramped quickly to 500C so that the conditions would simulate the gas-phase purification method. The TGA shows an initial quick weight loss as the sample comes up to temperature, similar to what was seen during nanotube purification. Then once the sample reaches the ascribed temperature the TGA indicates a single constant rate of weight loss. The material present at the end of the run shows no selectivity to etching of unwanted carbon.

1.5.5 Metal Interactions

1.5.5.1 Surface Chemistry Introduction

Further considerations to the above mentioned gaseous interactions are the changes resulting from metal catalyzed chemistry. Absolute determination of the role of the metal catalyst present during purification is difficult if not impossible. The removal of metals from the felt without adversely changing the properties of the carbon is not possible because acid treatments necessary to remove the metal will also react with the carbon. Likewise, introduction of more metal into the system can not be done so that it accurately mimics the metal inside the carbon onions present in the
felt. In short, the inability to prepare control experiments for questions of metal interactions makes only speculative conclusions possible.

The observations, shown in Table 2, regarding the change in nanotube yield as a function of oxidation potential may be a result of metal catalysis. Equation 4 shows

$$\text{MO} + \text{HCl} \rightarrow \text{M} - \text{OH}$$

(4)

the adsorption of hydrogen chloride by a surface metal oxide to form a hydroxy substituent. Thus an alternate method, to that shown in scheme 2, for forming a hydroxyl group on the end of the nanotube is the transfer of such species from a metal surface. Both mechanisms agree with the observation that a low oxidation potential is needed at the beginning of the purification, perhaps to allow formation of such protective hydroxyl groups before increasing the nature of the gas ratios to a more vigorously etching mixture.

1.5.5.2 Carbon Gasification

Since the nickel and cobalt used for growth of the nanotubes are known active catalysts one needs to consider if they are also active in a carbon gasification cycle. Studies of cobalt and nickel catalyzed oxidation of graphite have been rather extensively explored by McKee at General Electric. In one study, McKee determined the ignition temperature of graphite in a pure oxygen environment with or without metal catalyst. Without metal present the ignition temperature was 740°C. With nickel added the ignition temperature drops to 613°C, while for cobalt the effect was more dramatic with an ignition temperature of 525°C. Given the proximity of the
cobalt ignition temperature to the purification operating temperature, it was necessary to examine the case of cobalt more carefully.

First of all, one must realize that the metals introduced in this study were in the form of the oxide. Thus they are markedly different from the reduced form believed to be present in the nanotube felt. However, it has been demonstrated, in the case of water particularly, that the active form of the metal is the reduced form. Thus if one wishes to use water as the source of oxygen it must be done in a net reducing environment, otherwise the metal is rather inactive. With this in mind it is easy to see why cobalt shows such a lower ignition temperature. It is because of cobalt’s ability to shuttle between the +2 and +3 oxidation states that makes it more active in the pure oxygen environment. In this case however, the gases present do not serve as the reductant but rather the carbon itself is the reducing agent. This demonstrates that only the catalyst surface is important in the catalytic cycle. Thus, one can imagine that if oxygen were able to reach the surface of the cobalt particle in the nanotube felt, the cobalt could serve as an active carbon gasification site. However, because of the temperature and large amount of oxygen used in McKee’s experiment, the possibility of cobalt catalyzed gasification in the purification environment seems unlikely. The oxidation potential used in McKee’s experiments were on the opposite side of the scale compared to the conditions used in the nanotube experiments. Specifically, in McKee’s case it was 100% oxygen, versus approximately 0.03% in the nanotube work reported here. This low level of oxygen also helps explain the slow carbon removal rate and the need for several hours of reaction to remove just a few milligrams of material.
Also of interest is whether the cobalt or nickel can aid in the gasification of carbon by interaction with the water vapor. As mentioned earlier, McKee demonstrated that the active form of the metal catalyst was the reduced form, when water serves as the oxidant. These requirements for a net reducing environment are closer to the characteristics of the gases used for nanotube felt purification. McKee found that a wet hydrogen mixture initiated carbon gasification with nickel at 650°C and with cobalt at 600°C. Without the hydrogen present no activity was observed between 800°C-1000°C.

Both theoretical ideas and experimental observations argue that the metals are not involved in the purification. The temperature of operation indicates that metal catalyzed gasification is not possible. Likewise, the observation that the etching rate decreases with time insinuates that the release of the metals during the reaction is not accompanied by a metal catalyzed gasification.

1.5.6 Monitoring by Infrared Spectroscopy

Another interesting feature of the gas-phase purification is the ability to investigate the chemistry occurring inside the reaction chamber by monitoring the product gases by infrared spectroscopy. Figure 1-13 shows the change in product gas pressure over time for phosgene and that for carbon monoxide is shown in Figure 1-14. The large drop in phosgene pressure between nine and thirteen hours gives a good indication of the completion of the purification. This drop is also most pronounced for the low oxidation potential reaction, see Figure 1-15. Comparatively the changes in carbon monoxide near the end of the reaction time is less well
Figure 1-13: Infrared Monitoring of Phosgene Product Gas Pressure over Time

\[ R^2 = 0.8372 \]
Figure 1-14: Infrared Monitoring of Carbon Monoxide Product Gas Pressure over Time

\[ R^2 = 0.6743 \]
Figure 1-15: Change in Phosgene Formation as a Function of Oxidation Potential
defined. This results from the weak strength of the CO vibrational transition; and thus the low height combined with the large width of the carbon monoxide peak, makes determination of differences in peak areas difficult at the end of the reaction.

Keeping in mind the instrumental limitations of quantitation, as well as the limitations listed above, one can use the infrared data to see the amount of carbon removed over time. Using the calibrated values for carbon monoxide and phosgene the peak areas observed by IR spectroscopy were converted into moles using the gas law PV=nRT. Figure 1-16 shows the moles of carbon monoxide over time while the data for phosgene is shown in Figure 1-17. Also shown are the best fit curves to the raw data. Integration of this curve with respect to time indicates the formation of ~2x10^{-4} moles of carbon monoxide.\(^{33}\) It must be noted that this value was obtained by first shifting the curve in Figure 1-10 to have a y-intercept of zero. The y-intercept for the raw data of Figure 1-10 indicates that there is either a non-linear relationship between peak area and pressure, at pressures close to zero; or more likely that the manometer used requires calibration using a diffusion pump or other high vacuum apparatus. The integration reveals that ~70% of the unwanted carbon was removed in the form of CO. Likewise the integration of the phosgene signal gives ~10^{-5} moles of COCl\(_2\), accounting for ~5% of the carbon eliminated from the felt.

This ability to monitor the progress of the purification by Infrared Spectroscopy is a unique and potentially sensitive tool for examining the chemistry occurring in situ. As demonstrated in Figure 1-15 changes in low concentration species can be easily discerned and related to experimental parameters. These features are unavailable in all other purification methods. To make such
Figure 1-16: Moles of Carbon Monoxide Product Gas Formed Over Time

\[ y = 4 \times 10^{-5}x^2 - 1 \times 10^{-6}x + 2 \times 10^{-5} \]

\[ R^2 = 0.6743 \]
Figure 1-17: Moles of Phosgene Product Gas Formed over Time

\[ y = -9 \times 10^{-3} x^3 + 1 \times 10^{-8} x^2 - 5 \times 10^{-8} x + 1 \times 10^{-6} \]

\[ R^2 = 0.8372 \]
determinations with the acid purification method would require further disruption of
the process. The gas-phase IR method offers many opportunities for computer
assisted monitoring and optimization of purification parameters.

1.5.7 Cap Chemistry

1.5.7.1 Fullerene Model

According to the mechanism of protection depicted in Schemes 1 and 2, one
would also expect fullerene type molecules to survive the purification environment.
In other words, any closed cage carbon structure should behave similar to the
nanotubes. To test this idea a 5mg portion of C₆₀ was subjected to the same
conditions as the nanotube felt. After two hours the weight of the material at the
bottom of the reaction vessel was reduced to 3mg. However, analysis of the effluent
gases by IRS, revealed that less than 1% of the carbon had been removed in the form
of phosgene or carbon tetrachloride, and that no carbon monoxide was formed. The
2mg of material which vaporized was simply due to the volatility of C₆₀ (EI-MS
revealed the presence of C₆₀ in significant quantity). Analysis of the remaining
material by EDAX(Energy Dispersive X-Ray Analysis, performed on carbon tape)
indicated the presence of both oxygen and chlorine, and extrapolation of this data
would give the rough formula C₆₀O₃Cl. Figure 1-18 shows the Infrared spectrum of
this compound. The peak at ~798cm⁻¹ agrees well with published C-Cl stretch for
chlorinated fullerenes and the peak at 1091cm⁻¹ can be assigned to the C-O bond of
an alcohol group, while the peak at ~3400cm⁻¹ is consistent with an OH group. This
formation of a chloro-hydroxylated fullerene is further evidence of the proposed
Figure 1-18: Infrared Spectrum of $C_{60}O_3Cl$. A: C-Cl and C-O Region. B: OH Region.
protection mechanism. Also seen in the IR spectra was a peak at 1260 cm\(^{-1}\), which agrees with the position for an ether structure, which may have formed from the interaction of two neighboring hydroxyl groups.

Figure 1-19 and 1-20 shows the TEM of gas purified nanotubes. This image shows the high quality of the tubes. The metal particles remaining in the gas-phase purified material also exhibit a multi-fullerene type cage, see Figure 1-21, as opposed to the amorphous coating seen by other methods. The amount of metals removed, based on the level found in 5 mg of raw material, would represent an 87% reduction in metal content. These figures are based on indirect metal quantitation by TGA analysis of felt and gas purified nanotubes and have a uncertainty of ~5%. Direct elemental analysis of cobalt and nickel levels is still required given that the metal level is below the limit of detection of the EDAX.

1.5.7.2 Oxidation and Annealing

Experimental observation of the oxidation of nanotube caps has only been done for multiwall nanotubes, while studies for single wall nanotubes focus on theoretical issues.\(^{34,35}\) The work by Yao et. al. shown the direct observation of the oxidation of a 19.2° conical multi-wall tube by high-resolution TEM. By fitting the TEM data to computer models Yao was able to identify the particular pentagonal face which was the first portion of the nanotube attacked by the gas treatment. Similarly, all theoretical work on single wall nanotubes have shown that caps are more reactive towards oxidation due to the curvature and electronic effects of the incorporated pentagons.
Figure 1-19: Transmission Electron Micrograph of Gas Purified Nanotubes
Figure 1-20: Transmission Electron Micrograph of Gas Purified Nanotubes
Figure 1-21: Transmission Electron Micrograph of Metal Particle in Carbon Cage
In a recent report by Luzzi et. al. the possibility of closing an opened tube was demonstrated.\textsuperscript{36} The interesting feature of this study was the apparent low temperature anneal of \textasciitilde 550C needed to close the nanotubes. This makes one consider whether the closing phenomenon was occurring during the gas-phase purification. Although the possibility of a hydrogen chloride assisted nanotube closing can not be completely ruled out it seems unlikely given the operating conditions. The study by Luzzi was conducted under an inert atmosphere. This inert atmosphere should favor the closed nanotube due to the entropy gained by formation of gaseous CO or CO2. If a tube were opened during the gas-phase purification, the oxidatively active environment should favor an opened tube with oxygen, hydrogen, or chlorine termination. Such questions could potentially be answered by AFM(Atomic Force Microscope), STM(Scanning Tunneling Microscopy), and TEM. Microscopy studies however are hindered by difficulties in obtaining a large enough sampling which would be particularly troublesome for nanotube caps. The compression of large diameter nanotubes on microscope substrates more than small diameter tubes may increase the reactivity of the nanotube sidewalls. This interaction of tubes with microscope substrates may change the tube reactivity to the point where they are reversed relative to tubes free of substrate effects.

1.6 Concluding Remarks

1.6.1 Material Production Types

The properties of the raw nanotube material being used will certainly determine the applicability of the gas-phase purification method. As discussed
earlier, the material grown by the arc method is not able to be efficiently purified by
the gas-phase method. The most recently developed HiPCO (high pressure gas-phase
carbon monoxide) method for nanotube growth should be compatible with the gas-
phase purification. First, they both use gaseous reagents so they both require similar
apparatus for control and monitoring. Secondly, the major component formed by
etching of the unwanted carbon by the gas-phase purification is carbon monoxide.
This carbon monoxide could be recycled into the growth apparatus for growth of
more nanotubes. Finally, the ability to remove metals is particularly important for the
HiPCO process, in which a significant portion of the material is iron. The ability to
form volatile iron chloride is another unique feature of the gas-phase purification
method. The gas-phase purification thus has the opportunity to volatilize the
unwanted carbon and fullerenes as well as the metal catalyst, making it the most
comprehensive purification to be carried out in a single step. These features, as well
as those mentioned earlier (see section 1.5.2), indicate that the gas-phase purification
method can give a sustainable and environmentally friendly process, which can be
fully integrated with the nanotube growth system.

1.6.2 Comparison to Other Methods

The major difference between the gas-phase purification method and the
more conventional acid treatment is the scale on which the acid method is used. The
acid method has been applied to quantities as high as ~60g of raw material which is
well beyond what is practical for the gas-phase method. However, the acid treatment
method also requires greater than 13 steps to reach the final material.
Another method which has recently been developed, for laser grown single-wall carbon nanotubes, is acid treatment followed by burning in air for 30 minutes at 550°C. In this process the ability to remove the unwanted carbon is made possible by physical factors, since it has already been shown that oxygen exhibits no selectivity towards etching of unwanted carbon. The authors propose that a 16hr treatment in 3M nitric acid produces a uniform coating of oxygenated PAH (polyaromatic hydrocarbon) substances around the nanotubes. The subsequent step of burning in air then removes the PAHs because they are more exposed to the gases than the nanotubes. This treatment was repeated for laser grown felt made here at Rice. The material did exhibit an enrichment in the quantity of nanotubes, as viewed by SEM. However, the material was also found to have a very high oxygen content of 27 weight % by EDAX. Also it was unable to be suspended in dimethyl formamide or aqueous Triton-X.

Note: Please consult appendix for further information which may have been added during the final preparation of manuscript.
Chapter 2
Synthesis of Nanoscale Carbon Nitrides

2.1 Introduction

2.1.1 General Introduction

While a large variety of carbon materials are now available, the ability to alter the properties of such materials by incorporation of other elements has not been well explored. The diversity of carbon materials has been growing since the discovery of C\textsubscript{60} in 1985.\textsuperscript{41} Following this discovery the related forms of single-wall nanotubes, multi-wall nanotubes, hyperfullerenes, tori, and nano-cages were produced. While the amount of carbon materials has increased their application has still not come to fruition. Because of the applications intended for these materials, the properties needed can not be realized with a pure carbon substance. The properties wanted for future applications such as processability and greater interaction with composite matrices require the presence of other atom types besides carbon. Thus many researchers perform functionalization of these materials to incorporate other properties, as done previously in this group.\textsuperscript{42,43,44} An alternative to such an approach is direct incorporation of heteroatoms into the carbon framework.

One key question is what should be the other element chosen to be added to the carbon materials in order to gain the needed properties. Although one must accept a lose of some of the best qualities of an all carbon material, the choice of heteroatom should offer new benefits which compensate. The element which best
seems to fit these criteria is nitrogen. In a recent study Gaub et. al. calculated the rupture force for several bond types as shown in Figure 2-1. From this study it was shown that C-C and C-N bonds require very similar rupture forces, of approximately 4nN, making a nitrogen atom substitute promising for composite applications. Another important aspect of this study was the observation of the relative weakness of the Si-C bond, thus demonstrating that the silicon atom would not be an appropriate choice for many of the intended uses of carbon materials.

The method of heteroatom incorporation described here was developed while preparing graphite like carbon nitrides. Carbon nitride research is generally directed at making the diamondoid cubic form, for which the graphite form is expected to serve as a precursor. The formation of a stronger than diamond material has been intensely sought after since 1980, when Cohen suggested it was possible to make an extended carbon nitride network possessing such properties, with a formula of C$_3$N$_4$. Since then many researchers have reported various types and phases of carbon nitrides, but no one has definitively produced a significant quantity of the elusive ultra-hard carbon nitride. The variety of synthetic methods used has resulted in a vast array of material types with varying properties, as well as spectral differences which makes comparisons difficult. Although this current state of affairs is daunting it can also be informative. Reviewing what others have done, and seeing what can be changed or improved, may assist in the ultimate understanding of experimental parameters. After discussing various productions types, there will be an explanation of the new bulk scale synthetic method that has allowed investigation of catalytic surface interactions and how this led to the synthesis of a new nanoscale
Figure 2-1: Rupture Force of Several Bonds
carbon nitride.

2.1.2 Production Types

The production of carbon nitrides has been dominated by thin film growth methods. A recent study by Kouvetakis et. al. is particular interesting, in that he reported the growth of films on (100)Si, graphite, beryllium and SiO$_2$ using a unimolecular carbon/nitrogen precursor, C$_3$N$_3$F$_2$(SiMe$_3$)$_2$, which is similar to the bimolecular components used here for the preparation of nanoscale carbon nitrides. However, Kouvetakis did not observe the formation of any spherical nanoparticles. The precursor he used was proposed to result in a structure like that shown in Figure 2-2. This structure, which is shown in planar 2-dimensional format, is obviously not an accurate depiction of reality. How inaccurate is this model? One would expect that the 3-coordinate bridging nitrogen would have a similar trigonal pyramid geometry as found in ammonia, because of the lone electron pair. As an additional problem, the steric interaction of the rings should change the overall structure. In order to better access the hypothetical geometry, of such an extended carbon nitride network, a few molecular modeling experiments were performed. Figure 2-3 shows the minimized energy configuration for a single bridging nitrogen with three triazine rings attached, using a molecular mechanics method. As expected, the central nitrogen is pyramidal and the neighboring triazine rings stagger their conformation so as to reduce steric interactions. It is perhaps more difficult to predict how this structure might change as more nitrogen bridges and rings are added. For this task, a large molecule containing nine nitrogen bridges and ten triazine rings were used. The resulting minimized structure is quite informative, see Figure 2-4. As the size of the
Figure 2-2: Fragment of a Graphitic Like Carbon Nitride
(Dotted triangle indicates portion of structure used in Figure 2-3.
entire structure used in Figure 2-4)
Figure 2-3: Optimized Structure of Small Carbon Nitride Fragment  
(Portion Taken from Figure 2-2 and terminated with fluorines, and lone pairs added)
Figure 2-4: Optimized Structure of Large Carbon Nitride Fragment (Structure Taken from Figure 2-2 and terminated with fluorines, and lone pairs added)
molecule increases the geometry about the bridging nitrogens dominates resulting in a shallow bowl structure. This curvature of the plane is caused by the inability of the triazine rings to rotate as they become linked to more than one nitrogen bridge. This curvature was not seen in the work of Kouvetakis, but was exhibited by a unique method developed here for nanoscale particle assembly. More detail regarding the conformation model calculations, and the mechanism of curved nanoparticle synthesis will be given later. However, with this precursor Kouvetakis was able to produce material having the intended C$_3$N$_4$ stoichiometry, which others had difficulty doing by CVD with other precursors.

The use of dissociation of gaseous molecules was also used by Benard et. al. for preparation of films on diamond, silicon carbide, or gallium nitride surfaces.$^{48}$ The molecule primarily used was cyanogen azide, NCN$_3$, along with cyanogen, NCCN, or cyanogen halides, XCN. In this study it was found that the crystalline nature of the carbon nitride film was dependent on the substrate used. In the case of the diamond substrate amorphous films resulted, while with the silicon carbide, and gallium nitride, the films possessed a crystalline nature.

Another common synthetic method is the use of self-propagating reactions.$^{49,50}$ Often solid state reactions can be hindered by diffusion problems, lack of contact between reactants, and high activation energy barriers. With an appropriate choice of reactants some of these problems can be avoided. For self-propagating reactions the heat evolved from product formation is great enough to keep the reaction going until all of the reagent is consumed. With this type of
reaction it is only necessary to supply heat to the system for a few seconds, which is
often done by a resistively heated wire.

The doping of materials such as nanotubes and fullerenes with nitrogen has
been attempted as a route to carbon nitride. Iijima used a nitrogen atmosphere in a
laser ablation of graphite, with the ideas of putting substitutional nitrogen into the
tube structure, but found that the nitrogen was only present in the amorphous
carbon.\textsuperscript{51} In this case, the relatively high gas pressure of 500 Torr is expected to
reduce the ability of nitrogen to be incorporated into the tubes. After ablation from
the target, the large concentration of carbon atoms and clusters in the immediate
expansion zone results in a greater possibility for carbon-carbon collisions than
carbon-nitrogen collisions. Thus nitrogen is only bonded to carbon in the cooler zone
of the plasma plum, in which nanotube growth is already finished. Experiments using
buckminsterfullerene were more fruitful. Ion bombardment of C\textsubscript{60} films resulted in
formation of an amorphous carbon nitride, with use of high energy, 50eV-3000eV.
N\textsubscript{2}\textsuperscript{+} ions.\textsuperscript{52} In another study, the formation of the heterofullerene C\textsubscript{59}N\textsuperscript{+} was realized
by mass spectroscopy analysis of an originally external nitrogen fullerene adduct.\textsuperscript{53}
The most successful process for nitrogen incorporation into the fullerene cage seems
to be the introduction of nitrogen species into the graphite arc apparatus.\textsuperscript{54} In this
work, allowing small amounts of nitrogen gas into the normal synthesis apparatus,
resulted in the presence of a C\textsubscript{59}N\textsubscript{6} in the mass spectrum of the toluene extracted
product. However, C\textsubscript{60} was still the dominate species present. If ammonia was used
instead of nitrogen the results were much better. By leaking ammonia into the system
and performing chromatographic separation of the product, they were able to isolate
quantities of nitrogen containing nitrogen substituted fullerenes. The products contained species such as C$_{69}$N as well as fullerenes with as many as six nitrogens. Although the authors were not able to verify if the nitrogen is substituted into the cage or just bonded to the outside, the appearance of such "magic" numbers like C$_{69}$N supports the idea of nitrogen substitution into a C$_{70}$ cage.

There are several factors involved in determining the final properties of carbon nitride materials that can be summarized. As seen by others experimentally, the choice of reagents allows control of Carbon/Nitrogen ratio. The choice of linker reagent should also result in control of the 3-dimensional orientation, but this has not been seen yet. Substrate interactions can result in improved crystallinity. Selecting chemistry with appropriate energetic stabilities can help speed up reaction time. Finally, use of active nitrogen species or precursors with C-N bonds already present works better than incorporation of nitrogen into an already formed pure carbon material.

2.1.3 New Bulk Scale Method

The development for the reaction reservoir went through many different stages before the final design. The first prototype was a stainless steel cylinder with a NiChrome ignition wire, see Figure 2-5. This cylinder is basically an adaptation of that used for making potassium bromide pellets. In this case however, there is the added feature of allowing an ignition wire to run through the solid. This assembly was then suspended inside a conventional bomb calorimeter. By applying a voltage to the ignition wire one could start the reaction. However, depending on the reactants
involved one may need to assure better contact with the wire over a larger area, otherwise only that portion of sample in contact with the wire would react. This is obviously not the best setup for a more widely applicable reaction design. The second generation reaction vessel used a large threaded stainless steel tube, see Figure 2-6. In this setup the added vertical extension rod on the top allowed attachment to a vibratory reactor. This allows constant agitation of the tube contents and is particularly useful for solid state reactions. However, the sealing of the vessel was not sufficient and contents would leak out when the temperature was raised.

Finally, with the idea of creating large quantities of material a new reaction method was initiated. This method involved a sealed reaction tube that could be lowered into a furnace such that the entire vessel is heated. Figure 2-7 shows a schematic of the reaction setup. This setup is sealed with a gas tight Con-Flat seal, allowing one to use volatile reactants. The ability to vary the reagents used, the quantities of those reagents, and their temperature and pressure, makes this system a rather versatile setup. As an additional modification other substrates or catalysts were also introduced into the sealed tube. Given that the system is completely sealed one can run a reaction with a particular set of parameters, and then transfer the entire vessel to a glove box to observe the resulting products. If the reaction did not start or if additional reagent is needed, one can reseal the chamber without exposure to the laboratory atmosphere, and then place the vessel back in the furnace for further heating.

With this apparatus a variety of materials were made and characterized. The reagents used were typically lithium nitride and cyanuric fluoride or chloride. The
Figure 2-5: Schematic For Stainless Steel Pellet Type Sample Holder With Ignition Wire

Figure 2-6: Schematic For Stainless Steel Threaded Type Sample Holder With Vertical Bar For Vibratory Mixing
Figure 2-7: Schematic of New Stainless Steel Sealed Tube Design for Carbon Nitride Synthesis
carbon nitrides prepared in this chamber exhibited mostly an amorphous structure as seen by X-ray Diffraction (XRD) and Scanning Electron Microscopy (SEM), see Figure 2-8 and 2-9. However, the material made did exhibit the correct stoichiometry of C₃N₄ needed for use as a high pressure precursor. Although one would ideally like to heat the sample while applying pressure, this can only be done to a limited extent with carbon nitride due to formation of volatile decomposition products. Figure 2-10 shows the thermogravimetric analysis of a typical sample in an air atmosphere, with significant weight loss exhibited after ~300°C. Upon pressurization to several GPa, and heating to 400°C the sample appears to become more ordered while retaining the correct Carbon/Nitrogen ratio, see Figure 2-11. This order can be viewed by the occurrence of graphitic like planes in the micrograph. If the sample is heated to a temperature higher than ~400°C, nitrogen is lost and the sample converts to graphite, see Figure 2-12. The conversion to graphite is also seen by the presence of a sharp peak at 3.34 Angstroms in the XRD powder pattern, see Figure 2-13. Thus we now have a better idea of what treatment conditions can be used in pursuit of the ultra-hard cubic C₃N₄, and further work in this area is still in progress.

2.2 Synthesis of Nanoscale Carbon Nitrides

2.2.1 Introduction

While the synthesis of the high pressure precursor was making progress an investigation of substrate influence on particle morphology was launched. It had been known from previous studies that the nature of the carbon nitride formed can be affected by substrate catalysis. In such instances the interplay between chemical
Figure 2-8: Powder X-Ray Diffraction Pattern For Bulk Type Carbon Nitride
Figure 2-9: Scanning Electron Microscope Image of Bulk Type Carbon Nitride
Figure 2-10: Thermogravimetric Analysis of Bulk Type Carbon Nitride Decomposition in Air
Figure 2-11: Scanning Electron Microscope Image of Low Temperature Treated Bulk Type Carbon Nitride
Figure 2-12: Scanning Electron Microscope Image of High Temperature Treated Bulk Type Carbon Nitride
Figure 2-13: Powder X-Ray Diffraction Pattern For High Temperature Treated Bulk Type Carbon Nitride
factors such as reactant decomposition and physical factors such as surface area can lead to differences in the connectivity, shape, and size of the species produced.

The variation in substrate, or likewise the type of reaction container, was found to produce profound difference in the products obtained. One of the first substrates used was a Monel, or nickel/copper alloy, film. This was inserted into the stainless steel tube during the reaction and resulted in an explosion in which the bottom welded portion of the stainless steel tube was ruptured. Obviously this indicates that metals can be very effective catalysts for decomposition of the reactants and formation of volatile products. Given that the objective of these experiments was to create solid materials, it was decided that other reaction vessels should be investigated to reduce decomposition. Such studies led to a unique type of carbon nitride produced by interaction with a quartz surface.

2.2.2 Experimental

2.2.2.1 Synthesis

The general reaction used for nanoscale carbon nitride synthesis is depicted in Figure 2-14, and demonstrates the formation of a single C$_3$N$_4$ unit. The cyanuric fluoride or chloride is added in slight excess to reduce the amount of lithium termination in the final product. Continued reaction of these fragments leads to formation of a nanoscale particle. Fiber type substrates resulted in the most efficient reaction preparation and the best particle characteristics. The incorporation of an alternative substrate into the apparatus in Figure 2-7, was initially attempted by putting a large quartz test tube inside, and adding pieces of graphite foil to serve as
Figure 2-14: General Reaction For Nanoscale Carbon Nitride Synthesis
gaskets which would not break the quartz. However, this was not effective in forming a gas tight seal and reactants leaked out into the surrounding tube at reaction temperatures, and were thus unable to react with the nonvolatile reactants still inside. It was found that a wad of the appropriate fibers could be placed directly inside the stainless steel tube without the need for further surrounding by the quartz tube. In this method solid reactants, such as lithium nitride or cyanuric chloride, were encased in the fiber wad and liquid reactants were simply squirited on top, see Figure 2-15.

After loading, the sample was then heated to 500°C in a vertical tube furnace for one hour. Unless noted the time required to ramp up to 500°C was 1 hour, giving a two hour total reaction time. In some cases the time and temperature programming was changed, for reasons which will be discussed later. The sample was then removed from the furnace with fiberglass gloves and allowed to cool in the hood.

2.2.2.2 Materials

The materials used for nanoscale carbon nitride preparation include, Lithium Nitride(Aldrich, 80 mesh), Cyanuric Chloride(Aldrich, 99%), and Cyanuric Fluoride(Alfa-Aesar, 99%). All reagents were stored in a nitrogen purged glove box, and the Cyanuric Chloride and Cyanuric Fluoride were placed in the refrigerator inside the glove box. Solvents include 200 Proof Ethanol(Pharmco Products Inc.), and in house distilled water supply. Quartz Wool and Carbon Fiber (Wales Apparatus), were used as received.
Figure 2-15: Assembly of Reaction System for Nanoscale Carbon Nitride Synthesis
2.2.2.3 Purification

After the stainless steel reaction tube is cooled to room temperature it is opened and the quartz wool removed. At this point the quartz, or whatever fiber may have been used, is colored yellow because of the presence of the nanoscale carbon nitride particles. The fibers are washed with distilled water and the supernatant liquid filtered through a 0.45 micron Teflon filter. After this treatment the lithium halide salt is removed, but a large quantity of short quartz fibers remain. To remove the quartz fibers centrifuging in absolute ethanol proved effective, whereby the relatively large fibers are forced to the bottom of the tube due to increased gravitational forces, while the nanoscale carbon nitrides interaction with the solvent is able to overcome the g-forces.

2.2.2.4 Results and Discussion

The manner in which starting material associates with the amount of surface present was shown to be very important in determining material properties. Figure 2-16 shows the product obtained by running the reaction with a low surface area quartz microscope slide. It can be seen that a few spherical particles are produced, on the order of ~20 microns. However, the dominant product is more amorphous carbon nitride film. With this observation it was expected that one could increase the number of spherical particles formed by simply increasing the surface area of the substrate. Thus the quartz microscope slide was replaced with quartz wool, and the amount of spherical particles increased immensely. Also, the increase in surface area allowed for a greater number of nucleation sites and thus smaller particles in the
Figure 2-16: Scanning Electron Microscope Image of Large Carbon Nitride Sphere
Figure 2-17: Scanning Electron Microscope Image of Micro/Nanoscale Carbon Nitrides
~1 micron to ~200nm range were produced as the dominant product on the quartz wool, see Figure 2-17.\textsuperscript{57} Investigation of this material with TEM(Transmission Electron Microscopy) revealed that the particles are mostly spherical with a hollow center, see Figure 2-18.\textsuperscript{58} It could also be seen that the interior space of the particles varied, along with the exterior. Some particles with exteriors as small as ~50nm and interior dimensions of ~10nm where also found, see Figure 2-19. Although there seemed to be a relatively high concentration of these found during the TEM investigation, this is undoubtedly because the sampling method favors small particles. The dispersion of the sample in an alcohol favors small particles because of the greater solvent interaction for small particles, which have a high surface area and low mass. Given the very small size of these particles one wonders what is the limit to size reduction. By extrapolating the curvature observed in the optimized structure of Figure 2-4, a size of ~2.5nm is found to be the smallest spherical structure possible.

2.3 System Optimization and Investigation

2.3.1 Substrate Interactions

An important factor in determining the nature of the final material is the substrate used. Although the formation of the carbon nitride nanospheres was discovered with a quartz substrate the quartz may not be the best material available. Figure 2-20 shows the powder X-Ray Diffraction pattern of carbon nitride prepared on quartz wool, while carbon nitride made with a carbon fiber substrate gives the pattern seen in Figure 2-21. The peak located at a 2Theta of approximately 28 degrees can be ascribed to the 002 type reflection from a graphitic material. While
Figure 2-18: Transmission Electron Microscopy Image of Hollow Nanoscale Carbon Nitride Particles
Figure 2-19: Transmission Electron Microscopy Image of Nanoscale Carbon Nitride Particle With Small Inner Diameter
Figure 2-20: X-Ray Diffraction Pattern for Nanoscale Carbon Nitride Prepared on Quartz Wool
Figure 2.21: X-Ray Diffraction Pattern for Nanoscale Carbon Nitride Prepared on Carbon Fiber
the peak at 42 degrees can be assigned to a 101 reflection. Both types of substrates result in material with these peaks, but the quartz material also has several other peaks visible. These peaks can be indexed in terms of intensity and position to be lithium fluoride. While the presence of lithium fluoride could be attributed to inadequate washing, it appears that this lithium fluoride could be trapped inside the center of some of the carbon nitride spheres which appear solid, see Figure 2-22. While the presence of lithium fluoride is detrimental it is not necessarily a reason to abandon the use of quartz. However, the observation that the quartz is melted or decomposed during the reaction indicates that the carbon fiber would be a better substrate for highly exothermic reactions.

2.3.2 Nanoscale Carbon Nitride Identification

Several characterizations were performed to determine the identifying characteristics of the nanoscale carbon nitride particles. Figure 2-23 shows the laser desorption mass spectrum of the carbon nitride nanospheres. The 337 nm nitrogen laser used causes a mild ablation of the material into smaller fragments, which are then detected by a time of flight mass spectrometer. Although one is not able to assign the fragments to particular species the presence of peaks differing by 28 m/z units indicates the loss of several N₂ molecules. Also seen are peaks differing by 26 m/z units which serves as evidence for loss of CN. The presence of such large molecular weight species as 550 m/z indicates that these carbon nitrides could be used as interesting target material for laser ablation synthesis of other carbon nitride films. Figure 2-24 gives the TGA of the nanospheres in argon, indicating that
Figure 2-22: Transmission Electron Micrograph of Solid Carbon Nitride Particle
Figure 2-23: Laser Desorption Mass Spectrum of Nanoscale Carbon Nitride
Figure 2-24: Decomposition of Nanoscale Carbon Nitride in Argon
temperatures above 400°C will cause significant decomposition. The thermal stability of the nanospheres is much lower than a pure carbon graphitic material because of the tendency to form N₂. The Infrared spectrum of cyanuric fluoride derived nanospheres in Figure 2-25 is more informative of the chemical structure. The peaks at 807 cm⁻¹ and 1574 cm⁻¹ can be assigned to triazine ring modes. The peaks in the region ~1300 cm⁻¹ to 900 cm⁻¹ can be attributed to C-N stretching. The presence of these two features is evidence of the structure proposed in Figure 2-2. However, it must also be noted that interference from oxygen groups in this region could also be possible. The elemental analysis of the nanospheres by EDAX indicated a weight % carbon of 31% (39% calc.) and a weight % nitrogen of 58% (61% calc.). Also found was 10 weight % oxygen. The carbon nitrides are easily suspended in alcohol, which is a feature of their nanoscopic length scales.

2.3.3 Self-Assembly Process

An important consideration in the synthesis of nanoscale carbon nitrides is how the material achieves such an interesting spherical form. The observation of these spherical particles has not been seen prior to the experiments listed here and must be a result of experimental parameters that were previously unexplored. The major difference between the experiments which form non-distinct shapes, and those which result in nanospheres seems to be the nature of the low molecular weight carbon nitride monomers or oligomers which cross link to form the final material. In the experiments mentioned in section 2.1.3 these monomers would have been
Figure 2-25: Infrared Spectrum of Nanoscale Carbon Nitride
confined in the solid state while the monomers present in the nanosphere reaction would have been free flowing gaseous species.

The decreased mobility of the solid state leads to a disordered material. An appropriate species for investigating the mobility of carbon nitrides may be triphenylamine (N(C₆H₅)₃), which would have a similar structure to the carbon nitride fragment shown in Figure 2-3. A study involving triphenylamine by Yip et. al. demonstrated the increased mobility of the gas state relative to the condensed phase.⁵⁹ By studying the twist angle of the phenyl rings relative to the nitrogen, Yip indicated that the phenyl ring was more able to move in the gas phase due to decreased steric hindrance, while the rings are less able to move in the solid state because of interaction with close lying neighbor molecules.

The experimental setup for the synthesis of nanoscale carbon nitrides utilizes gaseous carbon nitride oligomers. The carbon nitride nanospheres form on the large fiber surface area above the lithium nitride, see Figure 2-15. In order for the nanospheres to form in this zone of the reactor they must have been assembled from small gaseous species. These gaseous monomers or oligomers should have a greater conformational and translational mobility. This mobility allows the gas phase species to migrate to a reaction site and rotate to form the preferred conformation with the growing nanoparticle. The oligomers in the solid state are much more constrained by steric hindrance and result in the formation of a rumpled graphitic structure instead of the ordered sphere.

2.3.4 Size and Shape Control With SiO₂ Template
A critical factor in controlling the properties and applicability of the carbon nitride nanoparticles is the capability to determine their size and shape. Although most of the particles seen by SEM and TEM are spherical, some particles form other shapes, such as the bean shape seen in Figure 2-26. Obviously the self-assembly process which makes the nanospheres is not perfect resulting in defective structures. In order to reduce these defects a directed self assembly process was developed to assist in the formation of the nanospheres. This method uses silica as a template for the growing carbon nitride nanospheres. The silica spheres were ~330nm spheres arranged into a crystalline array. Several pieces of the silica template (~2mm x 1mm x 0.5 mm) were placed in the reaction chamber above the carbon fiber. Using the silica template the carbon nitrides form almost monodisperse ~350nm spheres, see Figure 2-27. After the synthesis step the silica arrays were removed and rinsed in HF (hydrofluoric acid). The HF treatment removes the silicon by conversion to SiF₄. EDAX analysis verified that the silica is removed while the spherical shape of the carbon nitride remains intact.

2.4 Concluding Remarks

The preparation of carbon nitride nanospheres gives the opportunity for many applications. There use as lubricants, hole transport materials for electroluminescent displays, drug delivery agents, gas storage, and precursors for an ultrahard material are being investigated. The direct incorporation of nitrogen into a graphitic network offers further opportunities for functionalization and more extensive characterization.

Note: Please consult appendix for further information which may have been added during the final preparation of manuscript.
Figure 2-26: Transmission Electron Micrograph of Non-Spherical Carbon Nitride
Figure 2-27: Scanning Electron Microscope Image of Carbon Nitride Nanospheres on Silica Template
Chapter 3

Nanodiamonds in Meteorite Carbon With Related Diamond Surface Chemistry

3.1 Introduction

Using diamondoid structures for mechanical components in nanotechnology devices has recently been proposed by Drexler. In this work Drexler claims that in order to have a gear, or shaft, or other mechanical device on the nanometer scale it should be made of diamond in order to be stable and rugged enough to last. An example of a nanoscale bearing structure is shown in Figure 3-1. Although this structure is composed of four coordinate carbon atoms it does not take on the normal physical appearance of a diamond crystal. The most common structure for a diamond crystal is an octahedron. Other forms are also seen such as the cube and dodecahedron seen in Figure 3-2. Although rounded structures can be seen on natural diamond crystals from etching, intentionally rounded diamond structures, such as the torus shaped bearing proposed by Drexler, have never been seen at these length scales. This is because the rigidity of the diamond structure resists distortion. Thus the only reasonable method of assembling such devices seems to be the attachment of very small diamonds of known shapes into more complex arrangements.

Perhaps the best known formation of nanometer scale diamonds is that which naturally occurs in meteorites. These nanodiamonds are typically ~5nm in size. Also, often present in these meteorites are chlorine and metals such as iron and chromium, and unique levels of isotopically enriched inert gases. Thus the use of the same gas-phase purification technique used for the nanotubes offered an interesting
Figure 3-1: Space Filling Model of Drexler’s Hypothetical Diamondoid Bearing Structure.
Outer Diameter = 45 Angstroms
Figure 3-2: Idealized Diamond Crystal Shapes. (from left to right an octahedron, cube, cubo-octahedron, macle twin, and dodecahedron)
option to separate the nanodiamonds from the other carbons present. Also the interaction of gaseous components with the diamond surface can lend insight into the opportunities for assembly of nanoscale mechanical components.

3.2 Preparation of Meteorite

The removal of most of the non-carbon species from the Allende meteorite was performed by Dieter Heymann. The preparation uses an acid wash to remove the metals and then rinsing with Nanopure water and drying. Following the acid treatment a toluene wash was used to remove sulfur. This results in a residue of mostly carbon with a few metal impurities, which are apparently inaccessible due to a carbon overcoating.

3.3 Gaseous Treatment of Meteorite Carbon

A ~48mg sample of the meteorite carbon was treated to the same chlorine, water, and hydrogen chloride treatment used in the nanotube purification, at 500°C. This was reduced over a few hours to ~34mg, of which 3mg was removed, and then the rest was returned to the furnace for further treatment. This was again exposed to the gas purification mixture until the carbon weight was 20mg.

3.4 Results and Discussion

The treatment of the meteorite carbon caused a portion of light yellow crystals to condense in the cold region of the quartz tube above the furnace. Analysis of these crystals revealed them to be iron and chromium chloride. This demonstrates the
usefulness of the chlorine gas mixture to remove metals which are not accessible by acid treatment.

The analysis of the remaining carbon yielded insight into the carriers of the various inert gas components. It was shown by Anders et. al. that most of the inert gases contained in meteorite samples are found in a small portion rich in carbon, and perhaps chromite. The exact nature of the sample containing such gases is unknown and is thus designated as the letter Q. Thinking that Q may be a closed cage type carbon structure, the purification of the meteorite carbon was hoped to reveal the identity of Q. Also the isotopic ratios of the gases can be compared to others to determine if they are planetary or cosmogenic in nature.

If the carbon remaining after the gas treatment was the carrier of the inert gases one would expect a two fold increase in the amount of inert gases. Mass spectroscopic analysis of the remaining carbon revealed an increase in the Helium(4He) amount by a factor of 1.7 and that of Neon (20Ne) by a factor of 1.5. Although this is a substantial increase it is not at the level expected and furthermore many of the Q related gases decreased. These increase in the Helium and Neon gases however, can be attributed to the nanodiamonds. This is supported by the increase in the Xenon isotopic ratios for 124Xe and 126Xe, which are known to occur with the nanodiamonds. Thus the gas treatment revealed the superior resistance of the nanodiamonds to etching atmospheres and that the meteorite carbon did not contain defect free cage structures similar to fullerenes. The occurrence of such large gases as Xenon with the nanodiamonds is a surprising observation, since conventional diamond doping of atoms much smaller than Xenon is difficult to achieve. This may
be a result of an expansion of the diamond lattice by radiation damage and the presence of a near surface bound Xenon.

3.5 Diamond Surface Chemistry

Since diamond is composed of greater than 99% carbon, this leads to the unique characteristic that all chemistry takes place at the surface. Thus the study of diamond growth mechanisms as well as many applications of diamond films, such as heat dissipaters and emission cathodes for flat panel displays, require an intimate knowledge of surface characteristics, and the ability to tailor these characteristics to the specific purpose. Research efforts on diamond, involved thin film synthesis as well as chemical functionalization, and development of a specialized Raman technique for characterization.

3.6 Diamond Thin Film Synthesis

The apparatus shown in Figure 3-3 was constructed to allow synthesis of diamond films from methane-hydrogen mixtures. The filament used was a tantalum (99.99%) wire, and the substrate was molybdenum (99.95%) foil. Typical reaction conditions use a filament temperature of 2100°C, and a substrate temperature of 800°C, with a gas composition of 0.8% methane in hydrogen. The films produced varied in color from white to gray depending on thickness. Although natural diamond is clearer than the films produced, the polycrystalline nature and the existence of small amounts of graphitic like carbon at grain boundaries, leads to absorption of
Figure 3-3: Hot Filament Chemical Vapor Deposition Apparatus for Diamond Films
visible light, and thus slight discoloration. The most transparent diamond films are
produced by the microwave-plasma technique\textsuperscript{66}. The films created here, by the hot
filament technique, do exhibit properties of high quality diamond, as shown in the
SEM and Raman spectrum of Figures 3-4 and 3-5.

Based on the known scattering efficiency of graphite being fifty times greater
than diamond, the above Raman spectrum can be used to determine the purity of the
diamond film.\textsuperscript{67} Using the formula described by Wada, the Raman spectrum
indicates a film that is 90.8\% diamond. This purity is close to the highest value
obtainable for the hot filament method. Polo et. al. was able to prepare films via the
microwave plasma method with purities greater than 97\% by adding small amounts of
boron, as seen in Figure 3-6.\textsuperscript{68} However, without boron doping, diamond made by
the hot filament method is of much greater quality than the microwave technique.

3.7 Surface Enhanced Raman Spectroscopy

3.7.1 Introduction

A technique that may become very useful for nanoscale carbon chemistry is
known as Surface Enhanced Raman Spectroscopy (SERS). This method allows
detection of species on the surface which are of too low a concentration to be seen by
normal Raman. Usually the method uses colloidal metal particles or thin films of
gold or silver, on to which the species of interest is adsorbed, but in recent years this
geometry has been reversed, so that the metal is deposited as a very thin film on top
of the component being investigated. Although the mode of enhancement depends on
the particular system under investigation, it is worth mentioning the basic principles
Figure 3-4: Scanning Electron Microscope Image of Diamond Film
Figure 3-5: Raman Spectrum of CVD Diamond Film

Figure 3-5: Diamond Purity Dependence on Boron Doping. Squares: Microwave Plasma CVD, Circles: Hot Filament CVD.
of Raman scattering, in order to see the factors involved. In a classical sense, the intensity of Raman scattering is proportional to the square of the electric field-induced dipole moment $\mu$.

$$\mu = \alpha \cdot E$$  \hfil (1)

Where $\alpha$ is the polarizability, and $E$ is the electric field. From equation (1) it can be seen that in order to increase the signal intensity, either the polarizability of the molecule must increase or the electric field experienced by the molecule must be magnified. For a more in depth look at the theoretical considerations of SERS the reader is referred to the article by Garrell. It is worth noting the reason why normal Raman will not suffice for surface characterization. Figure 3-7 shows the energy level diagram for Raman spectroscopy. The dominant process occurring, shown by the thickness of the lines, is Rayleigh scattering, in which the incident radiation is unchanged. Such low level signals are thus many magnitudes lower, for components of low concentration.

3.7.2 Surface Enhanced Raman Spectroscopy of Carbon Materials

A few studies have been published in recent years applying SERS to C$_{60}$ and C$_{70}$. Mo et. al. used SERS to follow photochemical degradation of C$_{70}$ to amorphous carbon. In this study, about 2 monolayers of C$_{70}$ were deposited onto a silver island film, and then the sample was exposed to high laser power of $5 \times 10^4$ W/cm$^2$, over time. Figure 3-8 shows the SER spectra obtained. After 25 minutes, spectrum c shows a 1004 cm$^{-1}$ peak, as well as others, which indicate the formation of phthalic anhydride.
Figure 3-7: Scattering Process Energy Level Diagram
Figure 3-8: Surface Enhanced Raman of C\textsubscript{70} Degradation. Starts with a) and ends up as e)
This is a result of reaction with air, which eventually leads to the complete
destruction of C\textsubscript{70} and the formation of amorphous carbon after 80 minutes, see
spectrum e. Zhang et al. studied reduction and symmetry effects of C\textsubscript{60} and Ir-C\textsubscript{60} on
a gold electrode\textsuperscript{72}. They found that the uniquely symmetric structure of C\textsubscript{60} leads to a
relaxation of selection rules upon adsorption onto gold. Allowing the infrared active
bands to also be seen in the Raman. Likewise, the Ir-C\textsubscript{60} complex shows a reduction
in symmetry caused by the iridium metal, which removes the fivefold degeneracy of
the H\textsubscript{8} modes. This can be seen in Figure 3-9, where four additional bands are seen in
the range 774-790\textsuperscript{cm\textsuperscript{-1}}. Finally, they were able to discern by comparison of multiple
spectra, that the extra electron from the reduction, resides mainly on the C\textsubscript{60} cage and
not on the iridium metal. Siu et al. was able to form Langmuir-Blodgett films by
mixing C\textsubscript{60} with stearic acid on silver.\textsuperscript{73} The most prominent feature of the spectra
obtained in this manner is the large increase in intensity for the pentagonal pinch
mode at 1468\textsuperscript{cm\textsuperscript{-1}}, seen in figure 3-10. This mode is easily affected by the local
environment around the C\textsubscript{60}, indicating in this case that the fullerene is rather strongly
bound to the surface.

SERS can be used to determine the quality of a carbon material production.
Ishida et al. used the method of depositing the silver on top of the sample, to
determine the surface characteristics of highly oriented pyrolytic graphite (HOPG) and
carbon fibers.\textsuperscript{74} The HOPG shows no SER effects, with the normal graphite peak
observed to be unaffected, because of the high quality of such materials. If one uses
a carbon fiber however, SERS allows the detection of an increased concentration of
amorphous carbon on the surface. Figure 3-11 shows the normal and SER spectra of
Figure 3-9: Surface Enhanced Raman of Ir-C\textsubscript{60} on Gold

Figure 3-10: Surface Enhanced Raman of C\textsubscript{60} Langmuir Blodgett Film. Inset Shows SER of Weakly Bonded C\textsubscript{60} Film
Figure 3-11 Carbon Fiber Silver Surface Enhanced Raman
a. Control  b. 51 Angstrom Silver  c. 106 Angstrom Silver
a carbon fiber. The application of silver is seen to produce an increase in the sp$^3$ hybridized carbon signal at 1350cm$^{-1}$, and the occurrence of a polyene peak at 1140cm$^{-1}$. With an argon ion etching of HOPG, the surface can be deformed to exhibit similar characteristics. Figure 3-12 shows the SER spectra of argon etched HOPG. The resulting surface changes are depicted in Figure 3-13, with the unique peak at 1000cm$^{-1}$ being assigned to the trigonal breathing mode of polyaromatic species.

3.8 Diamond Surface Functionalization

3.8.1 Introduction

With the idea of creating gear type structures as mentioned by Drexler, a new assembly method was envisioned, as shown in Figure 3-14. This gear would be made of octahedral nanodiamonds held together by the chemical interaction of there surfaces. In order to access the possibility of assembling very small nanodiamond crystals into a larger structure, a series of reactions were run on a diamond surface and investigated by Surface Enhanced Raman Spectroscopy.

3.8.2 Results and Discussion

Figure 3-15 shows the cross-sectional view of a scratch made in a sputter deposited silver film, obtained by Atomic Force Microscopy (AFM). As indicated by Ishida, a silver film of 6nm thickness, exhibits a SER effect on etched diamond surfaces. Although the sputter technique was able to produce films of this type, the reproducibility was only around ± 1nm. This level of control however did not
Figure 3-12: Surface Enhanced Raman of Argon Etched HOPG

Figure 3-13: Surface Characteristics of Etched HOPG
Figure 3-14: Proposed Diamond Nanogear Assembled from Octahedral Crystals. Top = Idealized Shape. Bottom = Space Filling Model
Figure 3-15: Atomic Force Microscope Image of Silver Film Cross Section

Vert distance 5.998 nm
present a limitation to demonstrating the SER effect on a graphitized diamond surface. The normal Raman of a diamond that was heated to 1200°C is shown in Figure 3-16. After depositing a 6nm silver film on this diamond, see Figure 3-17, the graphitic type carbon that is formed on the surface can now be seen by the occurrence of a broad peak around 1550cm⁻¹. This layer has been shown to be the thickness of only three graphite basal planes.

With the possibility of using SER for characterization, a series of reactions was performed on a diamond in order to functionalize the surface. Since the initial functionalization of diamond by halogens, in order to understand growth processes, it has now grown to include, subsequent reaction with nucleophiles such as ammonia and methylamine, reactions with oxygen and water, as well as reducing reactions with hydrogen. The initial reaction carried out was hydrogenation at 900°C. The hydrogenation is necessary to insure the largest amount of chlorine attachment possible, which is the second reaction. The hydrogen helps remove certain oxygen functionalities which are the hardest surface species to remove. Following the chlorine attachment, is reaction with 1,6-hexamethylene diamine in a hexane solution. Finally, complexation with the amine is performed by trinitro-benzene sulfonic acid (TNBS). The end result is depicted in Figure 3-18.

The use of the TNBS is intended to serve two purposes. Its reaction with amines is known to give quantitative yields, and it has a high polarizability. Although one can not confirm the presence of the above complex, evidence for the presence of the nitro groups, is seen in Figure 3-19. A SER of a functionalized diamond single
Figure 3-16: Normal Raman of Oxidized Diamond

Figure 3-17: Silver Surface Enhanced Raman of Oxidized Diamond
Figure 3-18: Proposed Structure of Diamond Surface Functionality

Figure 3-19: Silver Surface Enhanced Raman of Functionalized Diamond Surface
crystal shows a peak at 790 cm$^{-1}$, and what is believed to be the corresponding mode in the unreacted TNBS is at 820 cm$^{-1}$.

With the attachment of such functionalities to the diamond surface one could carry out various reactions for assembly of mechanical type nanoscale components. Obviously the incorporation of a trinitrobenzene derivative may allow some type of “nanoexplosion” synthesis, where by heating of the diamond powder in a vibratory reactor the diamond crystals would adhere to one another forming larger clusters. Although this may be useful in creating larger structures it is probably limited in its ability to make well ordered structures. To make more ordered structures it is proposed that two or more sets of diamond powder be made with differing surface groups. These groups would be chosen to be reactive with one another, so that the interaction between surface groups would bind the crystals together. Along with this idea the nitro groups of the trinitrobenzene species could be reduced to the amine for interaction with an acid group on another diamond. This would result in the formation of an amide linkage between the diamonds. Of course the reaction of the surface functionalities is going to be particularly hindered by the steric bulk of the diamond, thus the reactive group should be removed from the surface by some sort of linker, as attempted here with the 1,6-hexamethylene diamine. Another useful aspect of the amide linkage is that it is reversible, and can be broken by pH changes to give the original amine and acid groups back
Chapter 4

Future Directions

The main impedance to the commercialization of a gas-phase nanotube purification method for laser grown nanotube material is the slow rate of carbon etching. This low rate of carbon removal may make scale up to larger sample sizes impractical, but this remains to be proven by experimental trials. While the chlorine, water, and hydrogen chloride gas mixture proved useful, there may be other unknown mixtures which can serve the requirements of oxygen transfer and nanotube protection. The need to remove such a large quantity of carbon is likely to be decreased for the HiPCO process and thus the rate of carbon removal by the gas-phase method should not be a hindrance.

The self-assembly of spherical carbon nitride particles helps explain the difficulty in obtaining the ultrahard cubic $C_3N_4$ phase. The formation of large crystalline carbon nitride samples proposed by Cohen remains an unattained goal, and may be a result of the tendency to form such curved structures. The initial theoretical predictions should be reevaluated with this newly obtained experimental evidence. Likewise, by applying the advanced computer modeling used for the cubic phase carbon nitride, the knowledge of the all too often neglected graphitic phase should be greatly enhanced. In fact, it is perhaps this oversight of the graphitic phase which has caused so much trouble to synthetic researchers. The eventual application of the carbon nitride nanospheres will require larger scale synthesis.

The formation of nanoscale diamond mechanical components is yet to be experimentally realized. However, the assembly of such systems by surface
functionality still seems the most profitable approach, and is encouraged by recent increased interest in diamond surface chemistry.\textsuperscript{76,77} Surface Enhanced Raman Spectroscopy has exhibited a unique ability to characterize surface species, with a widely applicable method. It also gives particular information about chemical structure, which is absent in conventional surface techniques like XPS, AES, and SIMS. Future work may also lead to quantitative capabilities and increased detection limits. Whether one is interested in raw materials production quality, or more exotic chemical attachment to the surface, SERS could have a key role in the application of nanoscale carbon materials.
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Appendix

1.5.7.1 Fullerene Model Continued

The analysis of the fullerene material treated in the purification environment gives direct evidence of the hydroxy-chloride functionalization. Although previous investigation indicated the presence of C-Cl bonds and C-OH bonds in the fullerene treated material, there was no direct evidence of the attachment of such groups to the fullerene cage. This is because simple electron ionization mass spectroscopy (EIMS) causes removal of the species attached to the fullerene and only bare C₆₀ with a mass/charge ratio of ~720 is detected. Also the cleavage of functional groups to form bare C₆₀ is favored relative to volatilization of the functionalized fullerene. If however, a matrix assisted laser desorption ionization (MALDI) technique is used, the functionalized fullerene can be identified, although still in low concentration compared to C₆₀. Figure 1-22 shows the MALDI spectrum of the treated C₆₀ in a sulfur matrix. Peaks corresponding to C₆₀OH, C₆₀O₂, C₆₀OCl, and C₆₀OHClO can be identified within 0.2m/z. These results conclusively show the formation of hydroxy-chloride groups and the simultaneous survival of the cage structure, as predicted by the protection mechanism proposed. Also, it indicates that the transfer of a hydroxy substituent from a metal particle is not required as discussed in section 1.5.5.1.

1.5.8 Charge Transfer Protection

An alternative explanation for the protection of the nanotubes in the purification environment may be related to a charge transfer mechanism. Charge transfer complexes
Figure 1-22: MALDI Spectrum of Treated $C_{60}$
for graphite are separated into acceptor and donator types. In acceptor phases, such as those formed with the halogens, the intercalate accepts an electron from the graphite sheet. For donor intercalates, such as the alkali metals, the intercalating species donates electrons to graphite. Single-wall nanotubes are typically more pronged to charge transfer than graphite, presumably due to increased curvature and greater availability to donate the aromatic electrons to acceptor compounds.\(^7\) Thus one might expect that a transfer of electrons away from the nanotube to create a positively charged tube would decrease its tendency to be further oxidized.

The nature in which the intercalate species interacts with the various carbon structures found in nanotube felt has not been established. In the multi-wall nanotube system, it was proposed that a bromine intercalation was more favored for the unwanted carbon forms than for the MWNT.\(^13\) Exfoliation of the bromine treated material was proposed to cause more damage to the unwanted carbon forms and thus allowed for purification in an oxygen environment. However, X-ray analysis was unable to show the formation of an intercalate phase. As mentioned earlier, attempts to use a bromine and oxygen treatment for single-wall nanotubes was unable to give a useful purification.

In the case of graphite, the formation of a defined intercalate phase is accompanied by a charge transfer; but the charge transfer complex for single-wall nanotubes is much more spontaneous and no distinct crystalline intercalate has been demonstrated. Single-wall nanotube felt was treated to determine if a charge transfer mechanism is responsible for the survival of the nanotubes over the other carbon forms. A portion of felt was placed in a glass tube with shut off valves on both sides, and evacuated with a rough pump. Following chlorine exposure at room temperature, the
glass tube was sealed and Raman analysis indicated a shift in the tangential mode to higher frequency, as seen for the case of bromine. However, treatment of the nanotube felt with both chlorine and hydrogen chloride did not show any further shift in the tangential mode.

References


Gas-Phase Purification of Single-Wall Carbon Nanotubes

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A gas-phase purification method for raw nanotube material has been developed which incorporates a chlorine, water, and hydrogen chloride gas mixture to remove unwanted carbon. The evolved gases can be easily monitored by infrared spectroscopy to follow the cleaning process. The quality of the final material was verified by SEM (scanning electron microscopy), TGA (thermogravimetric analysis), and UV–vis (ultraviolet and visible absorption spectroscopy). The yield of ~15 wt % indicates a uniquely selective carbon surface chemistry that prevents etching of the nanotubes, which are generally more reactive due to their larger curvature. Although the technique’s usefulness for large-scale purification was not determined, the ability to purify single-wall nanotubes by a gas-phase method has been demonstrated, and a mechanism proposed.

Introduction

Single-wall nanotubes, which are graphitic tubes approximately a nanometer in diameter, were first discovered by S. Iijima, and have since been produced by pulsed laser vaporization, arc discharge, or chemical vapor deposition.1-4 The proposed future applications of this unique material include high-strength composites, molecular electronics, nanoprobes, energy storage or conversion, and many others.5 The research directed at these applications will require pure samples for physical and chemical processing. The highest synthetic yield, of greater than ~70 vol % nanotubes, was obtained by the pulsed laser process in a 1 in. furnace. However, the scale-up of this method to a 4 in. furnace resulted in lower quality material, and thus a greater need for purification.

The procedures used thus far for single-wall nanotube purification rely on some type of ultracentrifugation (UCF) or filtration, including microfiltration, ultrasonically assisted filtration, or cross-flow filtration (CCF).6,7 The most recently developed technique uses an oxidizing-acid reflux of the raw material, known as felt, followed by UCF. The separation in this case uses the difference in water solubility between the small-oxygenated carbon species and the nanotubes.8 The other common procedure uses CFF in place of the centrifugation. Although the acid treatment breaks up the unwanted carbon, the actual separation is done by the CFF and is based on physical size and aspect ratio.9

Although multiwall nanotubes can be purified by a variety of gas-phase oxidations, the use of a chemical purification process has not been demonstrated for single-wall nanotubes. Multiwall nanotubes have been purified by oxygen, a combination of copper and oxygen, or a combination of bromine and oxygen.10-13 The copper and bromine are intended to serve as intercalates, and the resulting difference in oxidation rate is used to burn off the unwanted carbon. The difference in oxidation behavior is more pronounced with the intercalate present and results in higher yields. Attempts to use similar procedures for single-wall nanotubes resulted in tube destruction. For example, using the bromine and oxygen system the yield was ~3 wt %. This is related to the amount of curvature experienced by the graphite sheet. Therefore, the oxidation resistance of single-wall nanotubes is less than that of multiwall nanotubes, which are in turn less resistant than large carbon fibers. This would seem to preclude chemical purification for single-wall tubes, but we show here that the correct conditions allow for removal of amorphous carbon or ionothermal particles, with or without metal catalyst inside, while simultaneously protecting the nanotubes.

Experimental Section

Materials. The preparation of the felt used for this report was done by the pulsed laser method, and has been described elsewhere. The felt was stored under airtight polyehtylene screw cap bottle. Graphite (Aldrich synthetic powder, 1–2 μm), and arc-grown single-wall nanotubes (Carbolex, AP Grade), were used as received. Approximately 3 mg of material was used for all experiments. Gases used for purification were chlorine (Scott Specialty Gases, 99.5%), hydrogen (TRIGAS, 99.99%), argon (TRIGAS, 99.998%), water from an argon bubbler, and HCl (Fisher, 12.1 M) from an argon bubbler. Solvents used include N,N-dimethylformamide (DMF) (ACROS, 99%), and methanol (Fisher, 99.8%). For infrared analysis the sample holder was a polyvinyl chloride gas cell with potassium bromide windows. Gases used for infrared quantitation were carbon monoxide (TRIGAS, 99%) and carbon tetrachloride (Aldrich, 99+%).

Purification and Characterization. The gas ratios used for purification were 7.2 mL/min Cl₂, 2.7 mL/min H₂, and 3.0 mL/min Ar bubbled through water, unless otherwise indicated. The sample was placed in a quartz tube and the system was purged, with the gases indicated above, for 1 h at room temperature. After purging, the sample was lowered into a tube furnace at 500 °C, as measured by a type-K thermocouple. The evolved gases, including CO, COCl₂, and CCl₄ were collected in the gas cell and monitored by infrared spectroscopy (IRS) (Perkin-Elmer, Paragon 1000PC). CO₂ may also be observed at the beginning of a run, due to adsorbed gases. The reaction was carried out until the carbon monoxide partial pressure, as detected by IRS was < 0.5 Torr, unless noted. The sample was returned to room temperature, then sonicated in a 50:50 mixture of DMF:H₂O to remove metals, and then sonicated in pure DMF. The last step was filtering and methanol washing to form a paper. Alternatively the metals could be removed by sublimation in HCl at a higher temperature. The paper was dried at 180 °C and then weighed for yield data. The paper was characterized by SEM (Philips, XL30 ESEM-PGC), TGA (TA-Instruments Inc., SDT2960), and UV−vis (Shimadzu UV-1601PC). It should be noted that a toluene reflux and sonication was employed to remove any fullerences that may be present after purification, but nothing was found. When not being monitored by IRS, the evolved gases were run through an aqueous potassium hydroxide bath to remove chlorine, hydrogen chloride, and phosgene. Although not attempted here, for a larger scale process the carbon tetrachloride can be destroyed before venting, by reaction with alkaline earth metal oxides, or other methods. Spectral care must be taken when working with both the reagent and product gases due to toxicity hazards, also the chlorine and hydrogen may form explosive mixtures.

Results and Discussion

The felt produced by the laser vaporization process contains mostly other forms of carbon besides the nanotubes, including amorphous carbon and a large amount of sonicated particles as shown in Figure 1. After purification, the material shows predominantly single-wall nanotube ropes. Figure 2a shows the "sponge" type material after the gas-phase treatment, showing that the purification is a direct result of the gaseous chemistry and not the treatments that followed. The bright metal particles, originally cobalt and nickel catalyst, visible after the gas treatment can be removed by the DMF:HCl wash. The final paper obtained appears to be high-quality single-wall nanotube material; see Figure 2b. The difference in material quality can also be seen via UV–vis–NIR spectroscopy, as shown in Figure 3, where the unique electronic structure of the nanotubes becomes much more apparent after purification. Also the UV–vis–NIR spectrum indicates that the nanotubes are not significantly altered chemically by the purification process, and that they are electronically similar to tubes obtained by other purification techniques. The suspension of gas-purified tubes in DMF

is limited to lower concentrations than acid-purified tubes, due to increased rope strength from the high-temperature treatment and/or residual impurities. TGA in air, Figure 4, indicated a combustion onset temperature of $\sim 400 ^\circ C$ for the purified tubes, versus $\sim 360 ^\circ C$ for the felt. 9 The TGA also indicates that the purified material contains $\sim 11$ wt. % of an unknown substance with a burning onset of $\sim 235 ^\circ C$.

It is important to note the exact gas mixture that allows for purification of the nanotubes, see Table 1. Among the single component gases, chlorine is the most effective at etching carbon, as shown by the 21% weight decrease after 6 h. There is an additional 21% weight loss when the material is subsequently washed in DMF: HCl and then filtered. The weight of the material after gas-phase water or gas-phase hydrogen chloride (aq) treatment shows no change, due to physical and chemical adsorption offsetting the small amount of carbon etched. Therefore, the IR data for the samples are needed to get a better understanding of the chemical processes responsible for carbon etching. The large weight loss exhibited with chlorine is not a result of...
direct carbon to chlorine reaction but rather the combined effect of chlorine and adsorbed air, given that infrared analysis shows that a typical carbon tetrachloride pressure is 2 orders of magnitude lower than the carbon monoxide pressure. Ultimately no single gas was found to offer any purification, or more specifically, chlorine, hydrogen chloride, or water separately do not remove carbon at a useful rate. Of the dual gas mixtures, only chlorine and water were found to remove carbon quickly. However, there is no preferential removal of unwanted carbon with just chlorine and water, and thus no purification results. The unwanted carbon is selectively removed only if hydrogen chloride is added to the chlorine and water mixture. This observation also implies that the source of hydrogen chloride needs to be separate from the water to get individual control of the gas ratios, as done in this study.

It was found that the progress of the reaction could be followed by infrared spectroscopy of the effluent gas. This allows in situ investigation of gas-phase chemistry and the ability to follow carbon etching without exposure of the sample to air. Figure 5 shows IR spectra of the gas purification products. One can clearly see the CO stretch for carbon monoxide at \(\approx 2170 \text{ cm}^{-1}\), and the CH stretch for phosgene at \(\approx 850 \text{ cm}^{-1}\), and the anti-symmetric CCl stretch for carbon tetrachloride at \(\approx 792 \text{ cm}^{-1}\). As changes are made to the composition of the gas purification mixture, the results can be followed by infrared spectroscopy. The ultimate ratio of reactant gases present is determined by

\[
\text{Cl}_2 + \text{H}_2\text{O} \rightarrow 2\text{HCl} + \frac{1}{2}\text{O}_2
\]

The gases introduced into the system include chlorine, water, and hydrogen chloride, which therefore determines the amount of oxygen and the overall oxidation potential toward carbon etching. The influence of water on the oxidation potential was determined for both rate of reaction and the final yield of nanotubes. Table 2 presents the results from variation of the water bubbler flow rate. With a low oxidation potential the yield of nanotubes is maximized. With inclusion of the TGA data, these values would mean 15.6% and 14.5% nanotubes respectively, which agrees well with the 10–20 wt% expected. However, this yield comes with a slow carbon etch rate and a long run time. If the oxidation potential is increased the rate of reaction can be improved, but the final yield is compromised. It was found that a stepped oxidation potential offered a little better yield and reaction rate. One explanation for this behavior is that at a high oxidation potential the heat of reaction from other carbon forms is sufficient to cause etching of nanotubes. With a stepped oxidation potential, one allows enough of the unwanted carbon to be removed before proceeding to the next level. In this case, however, it seems to indicate the need for sufficient time to remove adsorbed gases from the felt or an induction period for the establishment of the intended gas–surface interactions.

The presence of the cobalt/nickel metal catalyst in the felt could have a detrimental influence on the nanotubes. Transition metals are known to catalyze the gasification of carbon. Although the exact mecha-
nism of metal-catalyzed oxidation has been debated, as to whether gas–metal or metal–carbon interactions dominate, both interactions should be impeded by the formation of a metal chloride phase. Given that the metal catalyst is contained in a carbon shell, the interaction between the metal and the bulk of the material is not expected to be important until later in the purification process, when the metals are able to become mobile on the surface. Also the ability of chlorine on platinum to impede the catalyzed oxidation of graphite has been shown, and it is expected that the chlorine will have a similar influence on the cobalt and nickel.\textsuperscript{20} With the ability to form a mixed-metal chloride–oxide phase by the gases used, interaction with the metal may become important for larger scale purifica-

![Graph](image)

**Figure 5.** (a) IR Spectrum of carbon monoxide product gas and (b) IR spectrum of phosgene and carbon tetrachloride product gases.

Also of interest is the behavior of other carbon materials in the gaseous purification environment. Argon-grown single-wall nanotubes could not be purified by the same method used for the laser-grown material. The rate of carbon etching was found to drop dramatically after 3 h to a rate that was negligible. This is due to the higher density of the arc-grown material, \(0.33\) g/cm\(^3\) for arc material vs \(0.03\) g/cm\(^3\) for laser material, and thus a limited ability for the gases to get to reactive sites. Observation of the material after the treatment however did show an enrichment of nanotubes on the particle surface. Perhaps a high-pressure gas system could overcome the problem of decreased reaction rate. Graphite is essentially unaffected, in that there is no

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weight loss and the evolution of carbon gases stops completely after 1 h. This shows that the conditions used favor edge attack or defect sites for a perfectly unstrained aromatic system.

Of foremost importance in explaining the mechanism of purification is the experimental observation that hydrogen chloride is required for selective removal of unwanted carbon. As demonstrated earlier, the correct gas ratio yields a reactant mixture of low oxidation potential, which is seen to remove the impurity carbon, while leaving the nanotubes unharmed. These conditions are similar to those used by the more conventional acid purification, where the oxidation potential is controlled by acid concentration. However, the partial pressure of oxygen is still high enough for gasification of the nanotube into carbon monoxide. Even more interesting is the ability of some of the nanotubes to withstand further increases in oxidation potential. Although the nanotubes are more reactive because of the increased curvature of the graphite sheet, they do have structural features that should be of benefit, under the correct conditions. Unlike the majority of other carbon forms in the felt, the single-wall nanotubes have more perfect sidewalls, and a lack of edges due to the presence of caps. Although the caps are more reactive than the sidewall, the cap structure seems important for the nanotube survival in the gas purification environment. Schemes 1 and 2 show the plausible interactions of the chlorine gas mixture with the nanotube cap. Scheme 1 indicates the formation of a hydroxy–chloride–functionalized nanotube cap as already demonstrated in the reaction with water and carbon nanotubes and as shown in the chlorination of C_{60}. These reactions illustrate the particular need for hydrogen chloride in the gas-phase purification mixture. Without the hydrogen chloride present in Scheme 2, any hydroxyl groups that form on the nanotube cap would be deprotonated, leading to the eventual breakup of the cap structure, and exposure of the strained graphitic edge. Thus, the function of the hydrogen chloride would seem to be the protection of the more reactive caps, by shifting such reactions in the reverse direction.

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