RICE UNIVERSITY

Transition Metal Catalyzed Reactions
of Fullerenes and Carbon Nanotubes

by

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ABSTRACT

Transition Metal Catalyzed Reactions of Fullerenes and Carbon Nanotubes

by

Robin Anderson

Carbon nanomaterials such as fullerenes and single-walled carbon nanotubes (SWNTs) have opened up an exciting new field of research in chemistry. Fullerene research thus far has focused on modification to the outside of the carbon cage to change specific chemical properties, such as solubility or reactivity, to suit a particular target application. Although fullerenes have been shown to undergo facile reduction and to readily react with nucleophiles, oxidation has presented a problem. We have employed a transition metal catalyst to epoxidize fullerenes and create open-caged fullerenes.

We have investigated the reactivity of hydroxyfullerene with a variety of metal salts under ambient aqueous conditions as well as replicating possible environmental exposure. We have proven fullerol reacts irreversibly across a wide pH range with a variety of metal salts to form insoluble cross-linked polymers. It is clear that the interaction of hydroxyfullerenes with metals is an important issue with regard to waste treatment, fullerene exposure in the environment, and fullerene-based pharmaceutical agents.

There is much interest in the development of methods that allow for the synthesis of SWNTs with particular helicities, which determines the electronic properties of SWNTs. It would be desirable to use pre-formed SWNTs as seeds for the growth of longer SWNTs. In order to accomplish this goal, it is necessary that a catalyst particle be preferentially docked to the end of an individual SWNT. Purification and characterization of a suitable iron-molybdenum nanocluster and the methodology for coupling catalyst precursors to a pre-formed SWNT are discussed.
We have discovered a new method of solubilizing SWNTs in organic solvents. This was accomplished by creating a SWNT salt with a crown ether encapsulated sodium counter ion.

Lastly, the effect of carbon nanomaterials on mineral formation was investigated. Water-soluble fullerene and SWNT derivatives produced new and interesting morphologies of calcium carbonate and barium carbonate.
Acknowledgements

At my first conference, my poster was next to a woman’s from a different graduate school. She was telling me about how no one helped anyone else at her school, no one outside of her research group would train her on instruments and everyone thought everyone else was out to steal their data. It made me really appreciate being here at Rice. Everyone here is so willing to help each other, share ideas, and knowledge. I am so glad that I chose to come here.

Of all the people at Rice who have made my time here so enjoyable and productive, none are more responsible for that than my advisor, Andrew Barron. I’d like to thank you for all of the advice and ideas that he’s given me over the last four years. Also I’d like to thank you for being the kind of advisor that knows when to push and when not to.

Everyone in the Barron Lab, past and present, has helped me along the way. I’ve really enjoyed working with you all, especially Doug Ogrin and Liz Whitsitt who have always been there for me when I needed them. I want to thank all the members of the Smalley, Billups and Tour labs for all their persistence and hard work on the SWNTcat project. You’ve made getting up for those 8 am meetings a little easier. I’d like to thank all of those who were in the “Stitch-n-Bitch” and the “Girls Wine Night” groups. Having an opportunity to vent to people who were going through the same things as I was has saved my sanity more than once.

Lastly I’d like to thank my family for your unending support. My mother and father have put up with a lot over the years. It makes me very happy to know that by finishing graduate school I’ve made them proud. My sisters have grown up while I’ve been here in Texas and I’m so glad that we’ve stayed so close even though we’re so far apart. I’d like to thank Eric for his help and support over the last four years. Sometimes not talking about chemistry was all I needed.
Table of Contents

Introduction 1

Chapter 1. Reaction of hydroxyfullerene with metal salts: A route to remediation and immobilization.

Introduction 10

Results and Discussion

Reaction of metal salts with fullerenol 12
Environmental significance of metal-fullerenol cross-linking 23
Competition for fullerenol binding between iron and other metals 30
Cross-linking with nano-C60 31

Conclusions 33

Experimental 34

References 38

Chapter 2. Synthesis and Purification of FeMoC.

Introduction 42

Results and Discussion

Identification and Removal of Impurities 45
Characterization and Purification of FeMoC-EtOH 49
Optimization of FeMoC yield 52
Solution Stability of FeMoC 55

Conclusions 60

Experimental 60

References 65
### Chapter 3. Attachment of Transition Metal Catalysts to SWNTs.

**Introduction** 68

**Results and Discussion**

- Attachment of Catalysts to Dodecylated SWNTs 69
- Attachment of Catalysts to Isophthalic acid SWNTs 75

**Conclusions** 81

**Experimental** 81

**References** 85

### Chapter 4. Epoxidation/Cage-opening of C\textsubscript{60}.

**Introduction** 88

**Results and Discussion**

- Synthesis and Characterization of the Fullerene Epoxide 89
- Optimization of the Synthesis 90
- Discovery of the Open-cage species 97

**Conclusions** 102

**Experimental** 102

**References** 103

### Chapter 5. Sodium Crown Ether Solubilized SWNTs.

**Introduction** 107

**Results and Discussion**

- Synthesis and Characterization of the Sodium Crown Ether SWNTs in toluene 110
- Investigation of Solubility in Alternate Solvents 113

**Conclusions** 116

**Experimental** 119

**References** 120
Chapter 6. Effect of Carbon Nanomaterials on Calcium Carbonate Crystallization.

Introduction

Results and Discussion

- Nucleation of CaCO₃ with C₆₀(OH)ₙ
- Effect of pH on CaCO₃ crystallization
- Effect of Functionalized SWNTs on Crystallization
- Nucleation of BaCO₃ with C₆₀(OH)ₙ

Conclusions

123

124

127

134

137

138

140

145

Conclusions

148

Appendix. Publications and Presentations.

150
List of Figures

Introduction

**Figure I.1.** New carbon nanomaterials. 2

**Figure I.2.** Different kinds of SWNTs. 3

Chapter 1

**Figure 1.1.** Photographs of the reaction of Fe(NO₃)₃ with fullerenol at (a) t = 0, (b) t = 10 seconds, and (c) t = 5 minutes. The Fe(NO₃)₃ solution is added to the left and the fullerenol the right of the sample. 13

**Figure 1.2.** UV-visible spectra of (a) Fe(NO₃)₃ (500 mM), (b) fullerenol (46 mM), and (c) the supernatant from the reaction of these two solution. 14

**Figure 1.3.** The SEM images of (a) Fe(NO₃)₃ shows a mostly amorphous solid with a few rhombic features of size 1.3 x 1.1 μm, and (b) fullerenol cross-linked with Fe³⁺ showing similar crystalline features. 16

**Figure 1.4.** SEM image of (a) fullerenol cross-linked with KMnO₄ and (b) KMnO₄ solution evaporated onto carbon tape. 16

**Figure 1.5.** TEM image of an individual particle (150 x 250 nm) of Fe-fullerenol. The scale bar is 50 nm. 18

**Figure 1.6.** TEM image of fullerenol cross-linked with iron showing the non-crystalline nature of the Fe-fullerenol polymer. The scale bar is 200 nm. 18

**Figure 1.7.** Taping-mode AFM image of fullerenol spin-coated on mica from a 46 mM aqueous solution. 19
Figure 1.8. Tapping-mode AFM image of Fe-fullerenol formed from Fe(NO$_3$)$_3$ (500 mM) and fullerenol (46 mM) solutions in 1 minute.

Figure 1.9. Plot of size versus time for aggregate growth as measured from DLS for the reaction of 0.046 M Fe(NO$_3$)$_3$ with 0.5 M fullerenol (blue) and 0.0046 M Fe(NO$_3$)$_3$ with 0.05 M fullerenol (red).

Figure 1.10. The high resolution C1s XPS spectrum of fullerenol (blue) and Fe-fullerenol (red) showing the presence of fullerene-like carbon.

Figure 1.11. XPS spectrum of Fe 2p peak. Fe is present in cross-linked sample and not in fullerenol sample.

Figure 1.12. XPS spectrum of O 1s peak. O 1s peak is shifted, consistent with a change from hydroxide to alkoxide.

Figure 1.13. Raman spectra of (a) Fe-fullerenol, (b) fullerenol, and (c) Fe(NO$_3$)$_3$.

Figure 1.14. Molecular model of Fe(C$_{60}$O$_2$)$_2$ shown as (a) ball and stick, and (b) space filling representations.

Figure 1.15. Calculated molecular structure of the model compound Fe(C$_{60}$O$_2$)$_3$ shown as (a) ball and stick, and (b) space filling representations.

Figure 1.16. UV-visible spectra of various concentrations of Fe(NO$_3$)$_3$ (0.043 mM (red), 0.43 mM (blue), 4.3 mM (brown), and 43 mM (purple) and the supernatant (green) from an iron-fullerenol cross-linking experiment.
Figure 1.17 Graph of UV-visible data to give a molar absorptivity of Fe(NO₃)₃.

Figure 1.18. UV-visible spectrum of (a) 5 mM Fe(NO₃)₃, (b) 5 mM CoCl₂, and (c) centrifuged supernatant after precipitation of M-fullerol.

Figure 1.19. UV/vis spectrum of (a) 0.5 mM Al(NO₃)₃, and (b) the supernatant of M-fullerol. The Al peak is still present, but reduced in absorbance from 0.127 to 0.071.

Chapter 2

Figure 2.1. Computer representation of FeMoC based upon single crystal data showing the ‘cluster-within-a-cage’ structure.

Figure 2.2. UV-visible spectrum of the blue water-soluble fraction (in pH 2 water) formed in the synthesis of FeMoC.

Figure 2.3. ATR of the blue fraction formed in the synthesis of FeMoC.

Figure 2.4. UV-visible spectra of the yellow solid formed in the synthesis of FeMoC (red) and Keplerate (gray), all in pH 2 water.

Figure 2.5. ATR comparison of Keplerate (pink) and the yellow solid formed in the synthesis of FeMoC (red).

Figure 2.6. AFM image and associated height analysis of FeMoC-EtOH showing the features to be about 2 nm tall, the theoretical height is 2.1 nm.

Figure 2.7. UV-visible spectrum of FeMoC-EtOH.

Figure 2.8. ATR of FeMoC-EtOH solid.

Figure 2.9. X-ray photoelectron spectra of (a) C 1s and (b) O 1s for FeMoC-EtOH.
Figure 2.10. $^{31}$P NMR spectrum of FeMoC-EtOH.

Figure 2.11. Plot of FeMoC-EtOH yield as a function of reaction pH.

Figure 2.13. Plot of concentration versus time for FeMoC in aqueous solution at pH 2 (●), 3 (○), 4 (●) and 5 (○).

Figure 2.14. Plot of concentration versus time of FeMoC in MeOH (○), MeOH/H$_2$O 1:1 (●), and H$_2$O at pH 4.5 (■) at room temperature.

Figure 2.15. TGA of FeMoC-EtOH under different atmospheres.

Chapter 3

Figure 3.1. AFM image of dd-SWNTs.

Figure 3.2. AFM image of ddp-SWNTs.

Figure 3.3. AFM images of FeMoC-EtOH attachment to ddp-SWNTs.

Figure 3.4. AFM image of SWNT-cat functionalization with 1-hexadecane thiol.

Figure 3.5. AFM image of 1:4 ddp-SWNTs:FeCl$_2$ in CHCl$_3$.

Figure 3.6. AFM image of 1:4 ddp-SWNTs:FeCl$_3$.

Figure 3.7. AFM image of 1:4 ddp-SWNTs:Fe(NO$_3$)$_3$.

Figure 3.8. AFM image of ddp-SWNTs:Fe$_3$O(O$_3$CMe)$_6$(H$_2$O)$_3$.

Figure 3.9. IR spectrum of Fe$_3$(CO)$_{12}$ attachment to ddp-SWNTs.

Figure 3.10. IR spectrum of Ni(CO)$_4$ attachment to ddp-SWNTs.

Figure 3.11. AFM image of IPA-SWNTs from water.

Figure 3.12. AFM image of 1:40 IPA-SWNTs:FeMoC solution, incubated for 4 h. at 50 °C.

Figure 3.13. AFM image of 1:40 IPA-SWNTs:Fe-trimer solution, incubated for 4 h. at 50 °C.

Figure 3.14. AFM image of 1:40 IPA-SWNTs: Fe(NO$_3$)$_3$. 
Figure 3.15. AFM image of 1:40 IPA-SWNT:Fe(acac)$_3$.  
Figure 3.16. AFM image of 1:10 IPA-SWNTs:$\alpha$-D-glucose.  
Figure 3.17. AFM image of 1:10 IPA-SWNTs:L-lysine.

Chapter 4

Figure 4.1. Representative mass spectrum of C$_{60}$(O)$_n$ formed from the catalytic epoxidation of C$_{60}$ at 60 °C using an olefin:peroxide: catalyst ratio of 1:4:0.4.  
Figure 4.2. IR spectra of C$_{60}$ (bottom) and C$_{60}$(O)$_n$ (top) formed from the catalytic epoxidation of C$_{60}$ at 60 °C using an olefin:peroxide:catalyst ratio of 1:4:0.4.  
Figure 4.3. UV-visible spectra of C$_{60}$ and C$_{60}$(O)$_n$ formed from the catalytic epoxidation of C$_{60}$ at 60 °C using an olefin:peroxide: catalyst ratio of 1:4:0.4.  
Figure 4.5. $^{13}$C NMR of heated sample with an olefin:peroxide: catalyst ratio of 1:4:0.4 in toluene-d$_8$.  
Figure 4.5. Graph of data showing epoxide formation dependence on time of reflux, taking relative abundance into account.  
Figure 4.6. Graph of data concerning the dependence of relative abundance of epoxides on catalyst concentration.  
Figure 4.7. Graph of data concerning the dependence of relative abundance of epoxides on peroxide concentration.  
Figure 4.8. Graph of data concerning the dependence of relative abundance of epoxides on temperature.  
Figure 4.9. HPLC trace of a reaction mixture from the MoO$_2$(acac)$_2$ catalyzed epoxidation of C$_{60}$ sample.
Figure 4.10. UV-visible spectrum taken at (b) 9.2 min, (c) 5.5 min and (d) 4.1 min.

Figure 4.11. Mass spectrum of epoxidized sample showing open-cage fullerene peaks.

Figure 4.12. Calculated structure of $C_{54}O_3$ formed by the oxidative removal of one $C_6$ ring and the generation of three furan groups.

Figure 4.12. Graph of $C_{60}(O)_n$ and open-cage fullerene relative abundance as a function of catalyst concentration.

Figure 4.13. Proposed creation of the rational design for an endohedral fullerene.

Chapter 5

Figure 5.1. AFM images of the products from the reaction of Na/Hg amalgam, dibenzo-18-crown-6, and (a) raw or (b) purified SWNTs in toluene. The AFM of dibenzo-18-crown-6 from toluene solution is shown for comparison (c).

Figure 5.2. AFM image of the products from the reaction of Na/Hg amalgam, dibenzo-18-crown-6, and purified SWNTs in toluene after removing excess dibenzo-18-crown-6 by centrifugation.

Figure 5.3. Raman spectra of toluene (blue) and $[Na(dibenzo-18-crown-6)]_n[SWNT]$ complex in toluene (pink).

Figure 5.4. ATR-IR spectra of (a) raw SWNTs and (b) $[Na(dibenzo-18-crown-6)]_n[SWNT]$ complex.

Figure 5.5. MALDI-MS of $[Na(dibenzo-18-crown-6)]_n[SWNT]$ complex.

Figure 5.6. TGA of (a) $[Na(dibenzo-18-crown-6)]_n[SWNT]$ complex and (b) dibenzo-18-crown-6.
Figure 5.7. AFM image of the products from the reaction of Na/Hg amalgam, dibenzo-18-crown-6, and purified SWNTs in toluene after extraction into EtOH.

Figure 5.8. UV-visible spectrum of the $[\text{Na(dibenzo-18-crown-6)}]_m[\text{SWNT}]$ complex in (a) toluene and (b) EtOH.

Chapter 6

Figure 6.1. ESEM image of CaCO$_3$ precipitation at (a) 30 °C and (b) 50 °C.

Figure 6.2. Powder XRD spectrum of CaCO$_3$ precipitation at (a) 30 °C and (b) 50 °C.

Figure 6.3. ESEM image of CaCO$_3$ precipitated in the presence of fullerenes.

Figure 6.4. ESEM images of the various morphologies formed for the growth of CaCO$_3$ in the presence of fullerensols.

Figure 6.5. Powder XRD data for CaCO$_3$ (pink) and CaCO$_3$ precipitated in the presence of fullerensols (blue).

Figure 6.6. ESEM images of CaCO$_3$ formed in the presence of fullerensols after evaporation of the solution.

Figure 6.7. Graph of change in pH during crystallization of CaCO$_3$ at 30 °C.

Figure 6.8. ESEM image of CaCO$_3$ precipitated in the presence of NaOH (1.25 mM) at a pH of 8.

Figure 6.9. Powder XRD spectrum of CaCO$_3$ precipitation with NaOH.
Figure 6.10. ESEM image of CaCO₃ precipitation with (a) SDS and (b) SDS-C₆₀.

Figure 6.11. ESEM images of CaCO₃ precipitated in the presence of HO-SWNTs.

Figure 6.12. ESEM images of CaCO₃ precipitation with isophthalic acid SWNTs.

Figure 6.14. Powder XRD spectrum of CaCO₃ precipitation with hydroxylated SWNTs.

Figure 6.14. ESEM images of BaCO₃ precipitation at 30 °C.

Figure 6.15. ESEM images of BaCO₃ precipitated in the presence of C₆₀(OH)ₙ.

Figure 6.16. Powder XRD spectra of BaCO₃ precipitation and BaCO₃ precipitation with fullerol.
List of Tables

Chapter 1

Table 1.1. Reaction of metal salts with fullerenol. 15

Table 1.2. Particle size as a function of reaction time as measured by DLS. 20

Table 1.3. Dependence of time to precipitation on concentration of reactants. 27

Table 1.4. Competition for fullerenol binding between Fe\(^{3+}\) (5 mM) and various metal salts (5 mM) with fullerenol. 32

Table 1.5. Reaction of metal salts with n-C\(_{60}\) (100 µL). 32

Chapter 2

Table 2.1. XPS elemental ratio analysis for the yellow byproducts from FeMoC synthesis. 47

Table 2.2. XPS elemental ratio analysis for the products from FeMoC synthesis. 52

Table 2.3. Product yield as a function of reagent ratio. 54

Table 2.4. Fe:Mo ratio as determined by XPS for FeMoC-EtOH thermal decomposition products under air, argon, and hydrogen atmospheres. 59

Chapter 4

Table 4.1. Data collected from mass spectra of samples taken at different reaction time at 110 °C. 93

Table 4.2. Data collected from mass spectra of samples taken at different temperatures after 24 h. 96
Chapter 5

Table 5.1. The concentration of Na/dibenzo-18-crown-6 solubilized purified SWNTs in various solvents. 119

Chapter 6

Table 6.1. pH of solutions used for precipitation of CaCO₃. 131
# Abbreviations

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Å</td>
<td>angstrom, 10⁻¹⁰ m</td>
</tr>
<tr>
<td>AFM</td>
<td>atomic force microscopy</td>
</tr>
<tr>
<td>atm</td>
<td>atmosphere (101, 325 Pa)</td>
</tr>
<tr>
<td>ATR-IR</td>
<td>attenuated total reflection- IR</td>
</tr>
<tr>
<td>avg.</td>
<td>average</td>
</tr>
<tr>
<td>tBu</td>
<td>tert-butyl, -C(CH₃)₃</td>
</tr>
<tr>
<td>C₆₀</td>
<td>buckminsterfullerene, fullerene</td>
</tr>
<tr>
<td>C₆₀(OH)ₙ</td>
<td>polyhydroxylated fullerene, fullerol</td>
</tr>
<tr>
<td>cm</td>
<td>centimeter</td>
</tr>
<tr>
<td>ca.</td>
<td>circa, approximately</td>
</tr>
<tr>
<td>CVD</td>
<td>chemical vapor deposition</td>
</tr>
<tr>
<td>°C</td>
<td>degrees centigrade</td>
</tr>
<tr>
<td>dd-SWNT</td>
<td>dodecyl functionalized SWNTs, dodecylated SWNTs</td>
</tr>
<tr>
<td>ddpy-SWNT</td>
<td>pyridine ended, dodecylated SWNTs</td>
</tr>
<tr>
<td>DLS</td>
<td>dynamic light scattering</td>
</tr>
<tr>
<td>DMF</td>
<td>dimethyl formamide</td>
</tr>
<tr>
<td>DTA</td>
<td>differential thermal analysis</td>
</tr>
<tr>
<td>δ</td>
<td>delta, chemical shift (NMR)</td>
</tr>
<tr>
<td>ε</td>
<td>epsilon, extinction coefficient, dielectric constant</td>
</tr>
<tr>
<td>Eq.</td>
<td>equation</td>
</tr>
<tr>
<td>EtOH</td>
<td>ethanol</td>
</tr>
<tr>
<td>eV</td>
<td>electron volt</td>
</tr>
<tr>
<td>et al.</td>
<td>et alia, and others</td>
</tr>
<tr>
<td>FeMoC</td>
<td>([H_xPMo_{12}O_{40}\subset H_4Mo_72Fe_{30}(O_2CMc)<em>{15}O</em>{254}(H_2O)_{98}] (x = 1 \text{ or } 2))</td>
</tr>
<tr>
<td>Fe₂O</td>
<td>compounds of the general formula ([Fe_3(\mu_3-O)(\mu-O_2CR)_6(L)_3])</td>
</tr>
</tbody>
</table>
g  grams
h  hour
HPLC  high performance liquid chromatography
Hz  hertz
i.e.  *id est*, that is (to say)
IPA-SWNT  isophthalic acid functionalized SWNTs
IR  infrared spectroscopy
λ  lambda, wavelength
L  liters
LPD  liquid phase deposition
MS  mass spectroscopy
MALDI-MS  matrix assisted laser desorption ionization-MS
m  meters
mg  milligram(s), $10^{-3} \text{ g}$
MeOH  methanol
μm  micrometers, $10^{-6} \text{ m}$
mL  milliliters, $10^{-3} \text{ L}$
min  minutes
M  molar
mol  moles
mmol  millimole(s), $10^{-3} \text{ mol}$
MW  molecular weight
MWNT  multi-walled carbon nanotube
nm  nanometer, $10^{-9} \text{ m}$
NMR  nuclear magnetic resonance spectroscopy
py  pyridine
Raman  Raman spectroscopy
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>rpm</td>
<td>revolutions per minutes</td>
</tr>
<tr>
<td>s</td>
<td>second</td>
</tr>
<tr>
<td>SDS</td>
<td>sodium dodecylsulfate</td>
</tr>
<tr>
<td>SEM</td>
<td>scanning electron microscopy</td>
</tr>
<tr>
<td>SWNT</td>
<td>single-walled carbon nanotube</td>
</tr>
<tr>
<td>TEM</td>
<td>transmission electron microscopy</td>
</tr>
<tr>
<td>TGA</td>
<td>thermogravimetric analysis</td>
</tr>
<tr>
<td>THF</td>
<td>tetrahydrofuran</td>
</tr>
<tr>
<td>UV-vis</td>
<td>ultraviolet-visible spectroscopy</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffractometry</td>
</tr>
</tbody>
</table>
Glossary

agglomerate: clustering of small particles through electrostatic attraction to form larger particles

amorphous: lacking crystallinity

composite: a complex solid mixture of two or more components; one component comprises the majority of the mass and acts as the primary host matrix for the other components.

morphology: the characteristic shape of contour of a surface

Piranha acid: a solution that is 50% H₂SO₄, 10% 30% H₂O₂, and 40 % H₂O

seeded growth: particle size growth than occurs as a result of a small particle acting as a nucleation site rather than through simple agglomeration of particles

superacid: any acid stronger than 100% sulfuric acid

supernatant: the liquid solution that remains after suspended particles or precipitation is removed from a mixture

surfactant: a surface active agent

SWNT-cat: a pre-formed SWNT seed in which a metal particle catalyst has been attached to an end
Introduction

Carbon nanomaterials such as fullerenes and single-walled carbon nanotubes (SWNTs) have opened up an exciting new field of research in chemistry. Combining the rich chemistry of organic compounds and exhibiting many new properties, these nanomaterials are expected to find applications in such diverse fields as medical agents, molecular electronics, and high performance composites. For all its promise, nanotechnology, like any emerging field, is not without its stumbling blocks. For instance, solubility is a major obstacle for both materials. Water solubility will be essential for any biological applications to be realized. Functionalization has become a key focus of research and a major challenge to implementation of applications.

**Fullerenes.** Fullerenes have attracted a great deal of attention since their discovery in 1985 by Kroto, Curl and Smalley, who later won the Nobel Prize for their discovery of this third allotrope of carbon in 1996. Krätschmer and co-workers produced the first macroscopic quantities of solid fullerenes in 1990. The fullerene archetype is made up of 60 carbon atoms arranged in spherical cage that resembles a soccer ball (Figure I.1). There are also other higher fullerenes, such as C$_{70}$, C$_{80}$, and single-walled carbon nanotubes, which share some of the properties of C$_{60}$. These higher fullerenes can be imagined as the result of stretching C$_{60}$ along one axis. Much of the fullerene research that has followed their discovery has been focused on modification to change specific chemical properties. Functionalization of fullerenes is made relatively easy by its strained structure. The reactivity of the fullerene is enhanced by the strained sp$^2$ carbons. Functionalization can occur at either to [6,6] or [5,6] ring junctions, but usually are found at the [6,6] ring junction where the breaking of a carbon-carbon double bond allows for easiest formation of a new bond with the incoming functional group. Functionalizing the outside of a fullerene can allow the structure to remain essentially intact, while changing properties such as solubility or allowing for attachment of a pharmaceutical agent.
Proposed applications of functionalized fullerenes include drug delivery,\textsuperscript{8} MRI contrast agents,\textsuperscript{9} nanocomposites,\textsuperscript{10,11} and superconductors.\textsuperscript{12} While there has been a great deal of excitement generated from these proposals, only one product, the Nanodesu\textsuperscript{®} bowling ball,\textsuperscript{13} has been brought to market using $C_{60}$.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig1.png}
\caption{New carbon nanomaterials.\textsuperscript{14}}
\end{figure}

Another reason for desiring chemical modification to fullerenes and SWNTs is to minimize their potential toxicity.\textsuperscript{15} For instance, selected cytotoxicological studies on the water-soluble n-$C_{60}$ aggregate with human skin (HDF) and liver carcinoma (HepG2) cells\textsuperscript{16} and large mouth bass,\textsuperscript{17} have revealed pronounced toxicity prompting concerns about possible release into the environment. In contrast, functionalized water-soluble fullerenes, including hydroxyfullerene [fullerenol, $C_{60}(OH)_n$], carboxylated fullerenes [$C_{60}[C(COOH)_2]_{10}$], and dendrofullerenes (octadecaacid dendritic methano[60]fullerene monoadduct) were shown to have negligible toxicity.\textsuperscript{9,18,19,20} Finding a simple method of fullerene functionalization would therefore be most desirable.

**Single-walled carbon nanotubes.** Discovered in 1991 by Iijima,\textsuperscript{21} multi-walled carbon nanotubes (MWNT) can be thought of as rolled graphene cylinders nested within
each other. In 1993, single-walled carbon nanotubes (SWNT) were discovered. They have become a cornerstone of nanotechnology research due to their high aspect ratio, Young's modulus, tensile strength, low density, and electrical properties. SWNTs can be either metallic or semi-conducting, depending on their diameter and chirality (n,m values).

![Diagram of SWNTs](image)

**Figure 1.2.** Different kinds of SWNTs.

An armchair SWNT has an n,m value such that (n − m) is divisible by 3 and it is metallic. All other SWNTs are semi-conducting, such as a zigzag SWNT, and has an n,m value such that (n − m) is not divisible by 3. The availability of gram quantities of carbon nanotubes of one type or the other is necessary to the implementation of proposed applications, such as nanotubes high performance composites and molecular electronics. There is much interest in the development of methods that allow for the synthesis of SWNTs with particular helicities.

The n,m values of the produced SWNTs are affected by the metal catalyst used in their synthesis. A variety of transition metal catalysts and alloys have been studied.
metals most commonly used for SWNT growth are iron, cobalt, nickel, molybdenum, and various bimetallic alloys of these metals.\textsuperscript{27} Iron species, such as iron oxides,\textsuperscript{28} iron nitrates,\textsuperscript{29} Fe(CO)\textsubscript{5}\textsuperscript{30} and ferrocene,\textsuperscript{31} have been reported as active catalysts. The current methods of SWNT synthesis, including electric-arch discharge,\textsuperscript{32} HiPCO,\textsuperscript{33} CVD,\textsuperscript{34} and laser-arch ovens,\textsuperscript{35} employ metal catalysts of various sizes and shapes that produce a mixture of nanotubes with a range of sizes, shapes, and properties. Attempts to separate gram quantities of one type of nanotube from another have thus far been unsuccessful. However, small amounts of a specific type have been isolated with some success.\textsuperscript{36} If this small amount could be amplified, then it would be of major advantage to carbon nanotube research.

In addition to the issue of producing a large quantity of a specific kind of tube, the poor solubility of SWNTs is another obstacle that must be overcome to implement these applications and exploit the unique characteristics of nanotubes. Some applications, such as composites that would like to use the SWNTs to provide greater strength to the host material, do not require one type of tube or another. Fullerene and SWNT based organic-inorganic nanocomposites for applications such as nonlinear optics and photoelectrochemistry are very promising.\textsuperscript{37} In the past they have been prepared using porous inorganic oxides\textsuperscript{38} or aerogels.\textsuperscript{39} SWNTs are not soluble in any common solvent, only in superacids\textsuperscript{40} or with strong sonication.\textsuperscript{41} Additionally the strong van der Waals attractive forces (\textit{ca.} 500 eV per \textmu m of tube contact\textsuperscript{42} ) between the tubes results in roping or bundling. The issue here is functionalizing the tube so that it is an individual and so that it can bond strongly with the host material. Current methods of solubalization include fluorination,\textsuperscript{43} free radical chemistry,\textsuperscript{44} surfactants,\textsuperscript{45} and polymer wrapping.\textsuperscript{46}
References


http://www.smalltimes.com/document_display.cfm?section_id=45


It should be noted that the mechanism of n-C60 toxicity effects is yet to be established since proposals that reactive oxygen generation are involved are suspect since fullerenols have been shown to produce both singlet oxygen and superoxide. See, K. D Pickering, and M. R. Wiesner, Environ. Sci. Technol., 2005, ACS ASAP.


Chapter 1

Reaction of hydroxyfullerene with metal salts:
A route to remediation and immobilization

Introduction

There has recently been much publicity given to both the potential toxicity\(^1\) and physiological benefit\(^2\) of fullerenes and their derivatives. With regard to toxicity interest has focused on the water-soluble aggregate nano-C\(_{60}\) formed by either the partial hydrolysis of C\(_{60}\)\(^3,4\) sonication\(^5\) or the water extraction of a C\(_{60}\)-solvent clathrate from organic solvents.\(^6,7\) Cytotoxicological studies on the water-soluble nano-C\(_{60}\) aggregate with human skin (HDF) and liver carcinoma (HepG2) cells\(^8\) and large mouth bass,\(^9\) have suggested toxicity, prompting concerns about possible release into the environment. However, some controversy surrounds these studies. In contrast, functionalized water-soluble fullerenes, including hydroxyfullerene [fullerenol, C\(_{60}\)(OH)\(_n\)], carboxylated fullerenes C\(_{60}\)[C(COOH)\(_2\)]\(_{10}\) and dendrofullerenes (octadecaacid dendritic methano[60]fullerene monoaaduct) were shown to have negligible toxicity.\(^9,10,11,12\) Encouraged by reports of the low toxicity of functionalized fullerenes, many different applications have been proposed utilizing fullerene's unique characteristics. Functionalized fullerenes could find applications in fields such as HIV protease inhibition,\(^13\) neuroprotection,\(^14\) photodynamic antimicrobial and anti-cancer activity,\(^15\) biochemical probes,\(^16\) and transport of radioactive metals for imaging or therapeutic applications in nuclear medicine.\(^12,17\) Based upon the lower toxicity of hydroxyfullerene than that of fullerenes, a pathway to environmental remediation of fullerenes can be envisaged based upon an oxidation/hydrolysis protocol.

It is appreciated that toxicity is just one issue that must be considered with regard to the environmental impact of nanoparticles. The transport of the nanomaterials in the
environment is also of great importance. Wiesner and co-workers\textsuperscript{18} have addressed this issue by assessing nanoparticle release in porous media, simulating their response to water treatment plant filters and groundwater aquifers. They have reported that nano-C\textsubscript{60} has a very low mobility in aqueous medium (lower than other nanomaterials in the study such as SWNTs and silica); conversely, hydroxyfullerenes are very mobile. Thus the fullerene material with the lowest observed toxicity would appear to have the highest mobility in aqueous environments, and that with the highest toxicity the least mobile.\textsuperscript{18} Despite the apparent low toxicity of C\textsubscript{60}(OH)\textsubscript{n} there are still concerns that its ease of transport may allow accumulation in the environment.

The fulleranol, C\textsubscript{60}(OH)\textsubscript{n}, used in the study is made by the reaction of C\textsubscript{60} with NaOH/\textsuperscript{m}Bu\textsubscript{4}NOH. Studies have shown an average chemical formula of Na\textsubscript{n}[C\textsubscript{60}O\textsubscript{x}(OH)\textsubscript{y}]\textsuperscript{n-} (where $n = 2 - 3$, $x = 7 - 9$, and $y = 12 - 15$).\textsuperscript{19}

Wilkerson and co-workers have shown metal ions to be cross-linking agents for marine mussel proteins, specifically 3,4-dihydroxyphenylalanine (DOPA).\textsuperscript{20} The affinity of iron for DOPA and other hydroxyl containing ligands, such as catechol, is well established.\textsuperscript{21} Since catechol (I) is a hydroxylated aromatic molecule, we propose that polyhydroxylated fullerenes (II) may act in an analogous manner towards ligation of transition and main group metals.

\begin{figure}[h]
\centering
\includegraphics[width=0.4\textwidth]{diagram1.png}
\caption{Diagram 1.1.}
\end{figure}
In this Chapter we investigate the reactivity of hydroxyfullerene with a variety of metal salts under ambient aqueous conditions as well as replicating possible environmental exposure.

Results and Discussion

Based upon the efficacy of Fe\(^{3+}\) as a cross-linking metal for 3,4-dihydroxyphenulalnine, we have chosen Fe(NO\(_3\))\(_3\) for our initial studies. In a typical reaction, the addition of an aqueous solution of Fe(NO\(_3\))\(_3\) (0.5 M) to a homogeneous solution of C\(_{60}\)(OH)\(_n\) (46 mM) results in the precipitation within 1 h of all the fullerol and the formation of an Fe-fullerol complex (Figure 1.1). The presence of a reaction is confirmed by UV-visible spectroscopy from the loss of the peak at 220 nm due to C\(_{60}\)(OH)\(_n\) (Figure 1.2) UV-visible spectroscopy indicates that unreacted Fe\(^{3+}\) is the predominant species in supernatant solution. The use of an excess of the fullerol results in removal of the metal ion from solution.

According to Wilker and co-workers,\(^{22}\) other metal salts should display similar cross-linking reactivity. Based upon the similarities of these ligand systems we chose additional metal salts for study. Wilker and co-workers have shown that for the cross-linking of marine mussel adhesive the effectiveness of cross-linking is heightened by the use of oxidizing metal ions (MnO\(_4^-\) and Fe\(^{3+}\)).\(^{20}\) However, in the present case while oxidizing species are active, so are non-redox metals, i.e., Zn\(^{2+}\), Al\(^{3+}\), and Ca\(^{2+}\), suggesting that the fullerol acts as a chelate ligand to the metal ions.\(^{23}\) Solutions of nitrates of aluminum and silver, chlorides of calcium, cobalt, copper and zinc, potassium permanganate, and boric acid were investigated as cross-linking agents. The choice of boric acid was based upon prior work in the Barron Group on the cross-linking of saccharide with boric acid.\(^{24}\) As may be seen from Table 1.1, red-brown precipitate was produce from fullerol solutions reacted with aluminum nitrate, calcium chloride, cobalt chloride, cupric chloride, silver nitrate and zinc chloride. Upon visual
Figure 1.1. Photographs of the reaction of Fe(NO₃)₃ with fullerenol at (a) t = 0, (b) t = 10 seconds, and (c) t = 5 minutes. The Fe(NO₃)₃ solution is added to the left and the fullerenol the right of the sample.

inspection, the precipitate looked consistent with that observed in the reaction with Fe³⁺. The reaction with potassium permanganate was too dark in color to see if any precipitate formed.

Interestingly, no precipitate was formed from the reaction with boric acid. Wilker suggests that cross-linking of his marine muscles with boric acid occur most readily at a pH of 8.5. Additional reactions were undertaken adjusting the boric acid solution to pH 8, 8.5 and 9 with 1 M NaOH prior to reaction with fullerenol. No precipitate formed in any of the trials. However, boric acid has been found to be a poor cross-linking reagent in a number of systems.
Figure 1.2. UV-visible spectra of (a) Fe(NO₃)₃ (500 mM), (b) fullerol (46 mM), and (c) the supernatant from the reaction of these two solution.

The M-fullerol cross-linked polymers have been characterized by SEM, TEM, IR and Raman spectroscopy, and XPS. The physical appearance of the precipitates is similar. Where an excess of the metal salt is employed the cross-linked samples have an amorphous appearance. SEM images do not show any definitive structure, although in several samples small crystals are observed that are similar to those for the metal salts, see Figures 1.3 and 1.4. As may be seen from Figure 1.3, the SEM image of the
precipitate formed from the reaction between Fe$^{3+}$ and C$_{60}$(OH)$_n$ are shown to consist of a textured unstructured material, however, the rhombic crystals (Figure 1.3b) are most likely excess Fe(NO$_3$)$_3$ (Figure 1.3a). In contrast, the SEM image of the precipitate formed from the reaction of fullerenol with KMnO$_4$ (Figure 1.4b) shows significantly smaller features than for KMnO$_4$ (Figure 1.4a). It is possible to suggest that the cross-linked polymers form small aggregates that then act as numerous small nucleation sites for the excess KMnO$_4$ in the solution to nucleate around.

TEM samples of Fe-fullerenol were prepared by reacting an excess of iron nitrate with fullerenol and after mixing well placing the solution on a copper coated carbon TEM grid prior to the observation of any precipitation from solution. Thus, the TEM images

**Table 1.1. Reaction of metal salts with fullerenol.**

<table>
<thead>
<tr>
<th>Metal source</th>
<th>$[\text{M}^{n+}]$ (mM)</th>
<th>[fullerenol] (mM)</th>
<th>Observation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(NO$_3$)$_3$</td>
<td>500</td>
<td>46</td>
<td>red-brown precipitate</td>
</tr>
<tr>
<td>Al(NO$_3$)$_3$</td>
<td>500</td>
<td>46</td>
<td>red-brown precipitate</td>
</tr>
<tr>
<td>CaCl$_2$</td>
<td>500</td>
<td>4.6</td>
<td>red-brown precipitate</td>
</tr>
<tr>
<td>CoCl$_2$</td>
<td>500</td>
<td>4.6</td>
<td>red-brown precipitate</td>
</tr>
<tr>
<td>CuCl$_2$</td>
<td>500</td>
<td>4.6</td>
<td>red-brown precipitate</td>
</tr>
<tr>
<td>KMnO$_4$</td>
<td>500</td>
<td>4.6</td>
<td>dark solution</td>
</tr>
<tr>
<td>AgNO$_3$</td>
<td>500</td>
<td>4.6</td>
<td>red-brown precipitate</td>
</tr>
<tr>
<td>ZnCl$_2$</td>
<td>500</td>
<td>4.6</td>
<td>red-brown precipitate</td>
</tr>
<tr>
<td>B(OH)$_3$</td>
<td>500</td>
<td>4.6</td>
<td>no precipitate</td>
</tr>
</tbody>
</table>
enable a view of the cross-linked material prior to precipitation from solution. Figure 1.5 shows an individual aggregate (150 x 250 nm) formed when a drop of solution was allowed to cross-link and dry onto a TEM grid. It may be clearly seen that there is no defined structure to the aggregate and no evidence of a periodic lattice. These small aggregates form larger agglomerates as may be seen in Figure 1.6.

![Image](a) (b)

**Figure 1.3.** The SEM images of (a) Fe(NO₃)₃ shows a mostly amorphous solid with a few rhombic features of size 1.3 x 1.1 μm, and (b) fullerol cross-linked with Fe³⁺ showing similar crystalline features.

![Image](a) (b)

**Figure 1.4.** SEM image of (a) fullerol cross-linked with KMnO₄ and (b) KMnO₄ solution evaporated onto carbon tape.

Atomic force microscopy (AFM) revealed a marked difference in the appearance of the cross-linked polymer (e.g., Fe-fullerol) versus the fullerol alone. Unreacted
fullerenol solution spin-coated on mica consists of spherical features 0.6 - 1.2 nm in height, and 30 - 80 nm in diameter (Figure 1.7). This is consistent with small aggregates of the fullerenol formed during the drying process. It is also possible that fullerenols form small aggregates in solution. The height of the features is consummate with that of the fullerenol itself. In contrast, AFM images of cross-linked product suspended in water spin-coated on mica show large textured aggregates 1.4 – 3.0 nm in height and 700 - 1100 nm in diameter (Figure 1.8).

Based upon SEM images Fe-fullerenol forms an amorphous extended structure once precipitation is allowed to occur. TEM and AFM images show that the size of the aggregates is significant even within the first few minutes of reaction. In an effort to follow the formation of the aggregates formed in solution during the cross-linking reaction, a dynamic light scattering (DLS) study was attempted on cross-linked samples. However, this was ultimately only of partial success. The problem arose from the fact that at concentrations that are considered suitable for detection by the instrument, the aggregates form too rapidly and are too large for detection. At dilute concentrations, where the particle sizes are smaller, the detector is not considered reliable. It would have been useful to have data on how rapidly aggregates form. Samples were made immediately prior to data acquisition. When equal volumes of fullerenol (0.46 mM) and Fe(NO₃)₃ (5 mM) were reacted together, particles of 243 - 359 μm were observed during the first 12 minutes, then no more data could be obtained. When the cuvette was removed from the instrument, it was observed that all of the precipitate had fallen out of solution and was settled at the bottom of the cuvette out of the range of the detector. Further runs were performed with successively diluted solutions. Table 1.2 shows the average particle size versus reaction time formed from a range of solution concentrations. The data from the more dilute runs are shown graphically in Figure 1.9. As may be expected from a condensation type polymerization reaction the particle size increases exponentially with reaction time. An additional observation from Figure 1.9 is that the rate of particle size
Figure 1.5. TEM image of an individual particle (150 x 250 nm) of Fe-fullerenol. The scale bar is 50 nm.

Figure 1.6. TEM image of fullerenol cross-linked with iron showing the non-crystalline nature of the Fe-fullerenol polymer. The scale bar is 200 nm.

growth is dependent on the reagent concentration. This variation of particle growth and hence subsequent particle precipitation has an impact on the environmental implications of the cross-linking reaction, *vide infra*. From DLS solution data and microscopy characterization it appears that the reaction of a metal salt with fullerenol is typical for a
condensation polymerization process, however, we are interested in the coordination chemistry of the cross-linked polymer with regard to the metal and fullerol. In this regard, the M-fullerol materials have been characterized by XPS, UV-visible and Raman spectroscopy.

Figure 1.7. Taping-mode AFM image of fullerol spin-coated on mica from a 46 mM aqueous solution.

Figure 1.8. Tapping-mode AFM image of Fe-fullerol formed from Fe(NO₃)₃ (500 mM) and fullerol (46 mM) solutions in 1 minute.
Table 1.2. Particle size as a function of reaction time as measured by DLS.

<table>
<thead>
<tr>
<th>[Fe$^{3+}$] (mM)</th>
<th>[fullerenol] (mM)</th>
<th>Reaction time (min.)</th>
<th>Particle size (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.46</td>
<td>12</td>
<td>243 – 359</td>
</tr>
<tr>
<td>0.5</td>
<td>0.046</td>
<td>1</td>
<td>0.250</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.5</td>
<td>0.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.5</td>
<td>12</td>
</tr>
<tr>
<td>0.05</td>
<td>0.0046</td>
<td>14</td>
<td>0.20</td>
</tr>
<tr>
<td></td>
<td></td>
<td>16</td>
<td>2.7</td>
</tr>
</tbody>
</table>

Figure 1.9. Plot of size versus time for aggregate growth as measured from DLS for the reaction of 0.046 M Fe(NO$_3$)$_3$ with 0.5 M fullerenol (blue) and 0.0046 M Fe(NO$_3$)$_3$ with 0.05 M fullerenol (red).
XPS data were collected on fullerenols (shown in blue in XPS spectra below) and Fe-fullerenol (red) samples. The XPS of both samples show the presence of fullerene-like carbon (Figure 1.10) and, as expected, only the Fe-fullerenol shows the presence of iron (Figure 1.11). In the sample whose spectra are shown in Figure 1.10 and 1.11, the Fe:C ratio is consistent with ca. three iron atoms per C_{60} unit. The optimum Fe:fullerenol ratio has been investigated and discussed below. The O 1s peak shows a significant change in chemical speciation during the reaction of fullerenol and Fe^{3+} (Figure 1.12). There is a distinct shift in the O 1s peak from 535 eV to 530 eV upon addition of Fe^{3+} consistent with the formation of alkoxide oxygen from a hydroxide oxygen. Thus, we propose that the condensation polymerization reaction is consistent with the coordination of the fullerenol to the metal centers in an analogous manner to that of a 1,2-diol or catechol.

The Raman spectra of M-fullerenol (Figure 1.13a) do not show bands that are readily assignable, however, the spectra show that the sample generally retains the

![Figure 1.10. The high resolution C1s XPS spectrum of fullerenol (blue) and Fe-fullerenol (red) showing the presence of fullerene-like carbon.](image-url)
character of the fullerenol spectrum (Figure 1.13b) with a broadening/shifting of the hump around 1400 cm\(^{-1}\) due to the iron (Figure 1.13c). Based upon the forgoing, and by comparison with known chelate ligand systems, we propose that the fullerenol acts as a chelate alkoxide-like ligand to the metal centers. Given the nature of the fullerenol it is not expected that an organized structure would be formed. The lack of ordered structure (observed by TEM and AFM) is expected given the variation of possible isomers (and species) in samples of fullerenol. The resulting material is undoubtedly a random cross-linked polymer. Based upon the model proposed by Wilson and co-workers, in which each fullerenol has between 12 and 15 alcohol groups, each fullerenol can potentially bind 3 metal centers in a chelate manner. Wilker and co-workers have shown that in the case of metal cross-linking of DOPA-containing peptides the metal center exists in both ML\(_2\) and ML\(_3\) coordination where L is a chelate ligand, i.e., four and six coordinate. Given the size of C\(_{60}\) there is a question as to the ability of a small metal ion

![Image](image.png)

**Figure 1.11.** XPS spectrum of Fe 2p peak. Fe is present in cross-linked sample and not in fullerenol sample.
Figure 1.12. XPS spectrum of O 1s peak. O 1s peak is shifted, consistent with a change from hydroxide to alkoxide.

such as Fe$^{3+}$ ($r_{ion} = 0.7 \text{ Å}$)$^{32}$ we have undertaken molecular mechanics calculations on the model systems [Fe(C$_{60}$O$_2$)$_2$] and [Fe(C$_{60}$O$_2$)$_3$]. The calculated structures of both model compounds are shown in Figures 1.14 and 1.15 as both stick and space filling representations. From Figures 1.14b and 1.15b it may be seen that both tetrahedral and octahedral coordination are possible.

**Is fullerene cross-linking environmentally significant?** While it is interesting to observe the reaction between metal salts and fullerenols under typical laboratory conditions we are interested in whether the cross-linking/precipitation reaction would be observed under typical environmental effluent and physiological conditions. To make sure that is a realistic solution to environmental clean up of fullerenes we needed to know how much metal is really present in environmental water systems. The National Pollutant Discharge Elimination System (NPDES) guidelines given by the EPA$^{20}$
Figure 1.13. Raman spectra of (a) Fe-fullerenol, (b) fullerol, and (c) Fe(NO₃)₃.
Figure 1.14a. Molecular model of Fe(C$_{60}$O$_{2}$)$_{2}$ shown as (a) ball and stick, and (b) space filling representations.

require, a pH between 6 and 9, and average monthly iron concentration of less than 3.0 mg.L$^{-1}$ (0.05 mM), with a maximum daily concentration of iron of 6 mg.L$^{-1}$ (0.1 mM), and an average monthly total suspended solids concentration of less than 35 mg.L$^{-1}$, and a maximum daily concentration of 70 mg.L$^{-1}$. 
Figure 1.15. Calculated molecular structure of the model compound Fe(C₆₀O₂)₃ shown as (a) ball and stick, and (b) space filling representations.

Following the general procedure described above, a series of reactions were carried out between Fe(NO₃)₃ and fulleroln varying the concentration of reactants and recording the time at which precipitation is first observed. The data can be seen in Table 1.3. As expected from the DLS results, the rate of precipitation is dependent on the concentration of reactants.
Table 1.3. Dependence of time to precipitation on concentration of reactants.

<table>
<thead>
<tr>
<th>[Fe(NO₃)₃] (mM)</th>
<th>[C₆₀(OH)ₙ] (mM)</th>
<th>Time to precipitation (min.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>46</td>
<td>&lt;1</td>
</tr>
<tr>
<td>50</td>
<td>4.6</td>
<td>5</td>
</tr>
<tr>
<td>5</td>
<td>0.46</td>
<td>85</td>
</tr>
<tr>
<td>0.5</td>
<td>0.5</td>
<td>720</td>
</tr>
<tr>
<td>0.1</td>
<td>0.5</td>
<td>4320</td>
</tr>
</tbody>
</table>

In order to provide a comparison with a potential environmental emission of fullerienol or a similar hydroxylated fullerene we can assume the maximum daily concentration of iron of to be 0.1 mM, and an excess of fullerienol. As may be seen from Table 1.3 a 0.1 mM Fe(NO₃)₃ solution reacts with 0.5 mM fullerienol solution such that precipitation occurs after 72 h. However, given the DLS results (*vida supra*) cross-linking and suspended particle formation occurs at significantly shorter reaction times. Even when the [Fe³⁺] is in excess over the fullerienol (i.e., a low level emission) particles over 10 μm are rapidly formed (see Table 1.2). It is clear that under such conditions fullerienol effluent would precipitate at some distance from the source. If the resulting aggregates are stable and non-toxic, then exposure of the aquatic environment may result in the “spontaneous-remediation” of hydroxyfullerenes.

Determining the minimum concentration of iron needed to produce precipitation is also important when considering environmental remediation of fullerienols. Based upon XPS analysis of the Fe-fullerienol formed with excess reagents, a fullerienol:Fe ratio of 3:1 can be initially assumed. In order to quantify the metal uptake a mixture of Fe(NO₃)₃
and fullerenol solutions were allowed to react such that the initial solution concentrations gave a fullerenol:Fe ratio of 3:2. In this manner the reaction can be followed by UV-visible spectroscopy and the amount of unreacted iron determined by the absorption after precipitation was complete. To obtain these data, we started with a known amount of fullerenol (0.5 mL of a 46 mM solution) and added 306 μL of a 50 mM solution of Fe(NO₃)₃. The solution was allowed to react for 2 h., but no precipitation was observed. Successive additions of Fe(NO₃)₃ in 306 μL increments at intervals of at least 1 h were made until cross-linking (precipitation) was evident. Total amount of Fe(NO₃)₃ added was 3.06 mL, making the final solution concentration 43 mM Fe(NO₃)₃. The cross-linked product was centrifuged and the supernatant aspirated and the UV-visible spectrum was measured (Figure 1.16). Using the molar absorptivity of the 293 nm peak in the UV-visible spectrum of aqueous Fe(NO₃)₃ (Figure 1.17). From these data the exact concentration of Fe³⁺ remaining in the supernatant solution is determined to be 0.22 mM Fe³⁺. From this we can determine that 0.15 mmoles were consumed by the reaction with 0.023 mmoles fullerenol.

As noted above the EPA’s National Pollutant Discharge Elimination System (NPDES) guidelines require a pH between 6 and 9. The pH of the as prepared fullerenol solutions and that of 0.1 mM Fe(NO₃)₃ are ca. 6. If M-fullerenol cross-linked polymers are formed in the environment their pH stability is an important consideration. In addition, the pH stability is also of importance given the potential for possible ingestion of M-fullerenol from environmental sources. In order to determine the stability of the M-fullerenol as a function of pH, a sample of Fe-fullerenol was prepared and washed until no color was given to the supernatant (see Experimental). Suspension of Fe-fullerenol in DI water (pH = 6) results in a pH of the supernatant of 6.0 (with no dissolved metal or fullerenol salts observed). The pH was adjusted to higher pH with 1 M NaOH solution and the tube was shaken and centrifuged. At a pH of 8.5 no solid was observed in the tube after centrifugation, indicating that above this the cross-linked product was broken
Figure 1.16. UV-visible spectra of various concentrations of Fe(NO₃)₃ [0.043 mM (red), 0.43 mM (blue), 4.3 mM (brown), and 43 mM (purple)] and the supernatant (green) from an iron-fullerenol cross-linking experiment.

Figure 1.17 Graph of UV-visible data to give a molar absorptivity of Fe(NO₃)₃.

apart. The same process was repeated with the pH adjusted with 1 N HCl. At a pH of 3.0 the supernatant is still colorless, however at a pH of 2.0 the supernatant was slightly colored despite the presence of some retained solids.
The formation of the cross-linked material is irreversible across a wide pH range. For example, no Fe$^{3+}$ is liberated from Fe-fullerenol within the pH range of 3.0 – 8.5. We propose that the relative stability of each M-fullerenol will vary as a function of the formation of the M$^{n+}$ solvate and the metal hydroxide [e.g., Fe(OH)$_4^{2-}$]. Therefore, for environmentally relevant pH levels, the M-fullerenol solid is stable.

Since it has been established that fullerenols form cross-linked polymers with a wide range of metal salts, the question arises as to potential competition between various metal salts for binding to the fullerenol. The relative reactivity of the metals salts may be determined by competitive binding reactions. The reaction of an equimolar (5 mM) solution of two metal salts with fullerenols results in the preferential reaction with one of the salts. UV-visible spectroscopy was utilized to measure the amounts of the salts left in solution after the cross-linking reaction was complete.

As an example of this procedure, an equimolar solution of Fe(NO$_3$)$_3$ and CoCl$_2$ was allowed to react with Fullerenol. After precipitation was observed, the solution was centrifuged and the supernatant decanted. Figure 1.18 shows that the Fe(NO$_3$)$_3$ peak remains at almost the same absorbance, indicating that the concentration of iron in the supernatant is constant. Hence, fullerenol react preferentially with cobalt. Of the other

![Graphs](image)

**Figure 1.18.** UV-visible spectrum of (a) 5 mM Fe(NO$_3$)$_3$, (b) 5 mM CoCl$_2$, and (c) centrifuged supernatant after precipitation of M-fullerenol.
metals investigated only \( \text{Al(NO}_3\text{)}_3 \) was less efficient than \( \text{Fe(NO}_3\text{)}_3 \) in cross-linking with fullerenols, i.e., \( \text{Al}^{3+} \) was dominant in the UV-visible spectrum of the supernatant, rather than \( \text{Fe}^{3+} \) (see Figure 1.19).

As was observed for \( \text{CoCl}_2 \), all the other metal salts were more efficient at binding than \( \text{Fe}^{3+} \). Since we had already calculated the molar absorptivity of \( \text{Fe}^{3+} \), we could determine the amount of \( \text{Fe}^{3+} \) left in each of the supernatant solutions (see Table 1.4). Using this approach a general order of sequestering ability may be determined (\( \text{Zn} > \text{Co} > \text{Cu} > \text{Ag} > \text{Ca} > \text{Fe} > \text{Al} \)). Wilker and co-workers\(^{19} \) have shown that for the cross-linking of marine mussel adhesive proteins (containing 3,4-dihydroxyphenylalanine) the effectiveness of cross-linking is heightened by the use of oxidizing metal ions ([\( \text{MnO}_4\text{]}^- \) and \( \text{Fe}^{3+} \)). However, in the present case while oxidizing species are active, so are non-redox metals, i.e., \( \text{Zn}^{2+} \), \( \text{Al}^{3+} \), and \( \text{Ca}^{2+} \), suggesting that the fullerol acts as a chelate ligand to the metal ions.

**nano-C\(_{60}\) cross-linking.** Stable suspensions of \( \text{C}_{60} \) in water were first reports by Andrievsky, et al. in 1995.\(^5 \) In 2004, cytotoxicity studies were made by Colvin and co-
Table 1.4. Competition for fullerolen binding between Fe$^{3+}$ (5 mM) and various metal salts (5 mM) with fullerolen.

<table>
<thead>
<tr>
<th>Metal source</th>
<th>Absorption @ 293 nm</th>
<th>[Fe$^{3+}$] (mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al(NO$_3$)$_3$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaCl$_2$</td>
<td>0.032</td>
<td>0.0048</td>
</tr>
<tr>
<td>CoCl$_2$</td>
<td>0.158</td>
<td>0.0237</td>
</tr>
<tr>
<td>CuCl$_2$</td>
<td>0.100</td>
<td>0.0150</td>
</tr>
<tr>
<td>KMnO$_4$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>AgNO$_3$</td>
<td>0.056</td>
<td>0.0084</td>
</tr>
<tr>
<td>ZnCl$_2$</td>
<td>0.200</td>
<td>0.0300</td>
</tr>
</tbody>
</table>

Table 1.5. Reaction of metal salts with nano-C$_{60}$ (100 μL).

<table>
<thead>
<tr>
<th>Metal source</th>
<th>[M$^{n+}$] (mM)</th>
<th>Observation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al(NO$_3$)$_3$</td>
<td>5</td>
<td>no precipitation</td>
</tr>
<tr>
<td>CaCl$_2$</td>
<td>5</td>
<td>no precipitation</td>
</tr>
<tr>
<td>KMnO$_4$</td>
<td>5</td>
<td>precipitation</td>
</tr>
<tr>
<td>AgNO$_3$</td>
<td>5</td>
<td>precipitation</td>
</tr>
<tr>
<td>ZnCl$_2$</td>
<td>5</td>
<td>no precipitation</td>
</tr>
</tbody>
</table>
workers,\textsuperscript{8} reporting that nano-C\textsubscript{60} has an LC\textsubscript{50} of 20 ppb. This report, in addition to studies with large mouth bass,\textsuperscript{9} suggests that nano-C\textsubscript{60} is a highly toxic species. They also report that fullerenol is non-toxic with an LC\textsubscript{50} of 40,000 ppb.\textsuperscript{8} One explanation for the water solubility of the C\textsubscript{60} aggregate is that the outside C\textsubscript{60} molecules are partially hydroxylated. If they in fact are, they would be expected to cross-link with metal salts in a manner similar C\textsubscript{60}(OH)\textsubscript{n}. The concentration of the nano-C\textsubscript{60} solution is estimated to be 0.2 - 2 mM in water from its UV-visible spectrum. 100 µL of nano-C\textsubscript{60} was combined with 100 µL of 5 mM of each metal salt, Al(NO\textsubscript{3})\textsubscript{3}, CaCl\textsubscript{2}, CuCl\textsubscript{2}, CoCl\textsubscript{2}, KMnO\textsubscript{4}, AgNO\textsubscript{3}, Fe(NO\textsubscript{3})\textsubscript{3}, and were allowed to react (Table 1.5). Precipitation was observed in the AgNO\textsubscript{3} sample after 24 h and in the KMnO\textsubscript{4} sample after 5 d. From these results in is possible to think that the outside of the nano-C\textsubscript{60} cluster is in fact hydroxylated, although the degree of hydroxylation is lesser than of fullerenol. It is not known why none of the other metal salts produced precipitation upon reaction with nano-C\textsubscript{60}.

**Conclusion**

We have proven fullerenol reacts irreversibly across a wide pH range with a variety of metal salts to form insoluble cross-linked polymers. These metal salts are present at the same concentrations in the environment.

Given the presence in the watershed of many of the metals that are found to cross-link fullerenols, it appears that their release into these environment would result in their conversion from soluble, mobile, compounds into insoluble aggregated particles. Furthermore, the presence of metal salts in vivo raises the question as to the potential fate of hydroxyfullerene species. In order to start to understand the applicability of these cross-linked aggregates to real systems, we have investigated at what rate would an effluent stream containing fullerenol precipitate given the exposure to environmentally acceptable levels of a metal such as iron. Based upon the forgoing, it is clear that the interaction of hydroxyfullerenes with metals is an important issue with regard to waste
treatment, fullerene exposure in the environment, and fullerene-based pharmaceutical agents.

**Experimental Section**

Fullerenes were purchased from Materials and Electrochemical Research Corp. (M.E.R., Tucson, AZ). Metal salts were purchased from Aldrich [Fe(NO₃)₃, ZnCl₂], Mallinkrodt [Al(NO₃)₃], Fisher [KMnO₄, CoCl₂, CaCl₂, B(OH)₃] and J. T. Baker (CuCl). All metal salts were used as received. NaOH and Sephadex G-25 (20-80 μm pore size gel filtration cross-linking polymer) were purchased from Sigma-Aldrich. Ottawa Sand Standard (20-30 mesh) was purchased from Fisher.

Characterization was performed using a FEI XL-30 Schottky field-emission environmental scanning electron microscope (ESEM). The accelerating voltage used was 30 kV. Samples were mounted with carbon tape onto aluminum microscopy specimen mounts (Electron Microscopy Sciences). All insulating samples were sputtered with gold (100 mA, 1 min) before imaging, using a Plasma Sciences CRC 100 sputter coater. SEM images were taken of each of the metal salts by drying a drop of the appropriate solution (0.5 mM) on an SEM sample mount. Images of the M-fullerenol polymers were prepared in a similar manner by drying a drop of the suspended precipitate on to a SEM sample mount. TEM images were obtained using a JEOL 2010 Transmission Electron Microscope at 100 kV utilizing a JEOL FasTEM system. The samples were prepared by reacting 100 μL 0.05 mM Fe(NO₃)₃ with 100 μL 0.0046 mM fullerenol and mixing well. Before any precipitation was evident, 10 μL of this solution was dropped onto a copper coated carbon TEM grid and dried thoroughly before imaging. UV-visible spectra were obtained using a Cary 5000 UV-vis-NIR spectrometer. Liquid samples were obtained using quartz cuvettes. Solid-state UV samples were dried on glass slides. Raman spectroscopy was performed on a Renishaw Raman Microscope. Samples were dried on glass slides. Atomic force microscopy (AFM) was performed on a Digital Instruments
Nanoscope IIIA microscope in tapping mode with 125 μm TESP tips. Samples were mounted with carbon tape by spin coating onto AFM pucks (Ted Pella) using an EC101DT-R790 Photoresist spin coater (Headway Research, Inc.). X-ray photoelectron spectra (XPS) were obtained using a PHI 5700 ESCA system (Physical Electronics) at 15 kV, using an aluminum target and 800 μm aperture. Sample were dried thoroughly and pressed into indium foil.

**Synthesis of C$_{60}$(OH)$_n$.** Fullerol was prepared according to a modification of the published method.$^{34}$ C$_{60}$ (350 mg, 0.49 mmol) in toluene (400 mL) was reacted with concentrated NaOH solution (400 mL, 12.5 M) in the presence of tBu$_4$NOH phase transfer catalyst (1 mL 40 % wt/vol) in air. The mixture was stirred 30 minutes, and then allowed to settle for 30 min. The top toluene layer was aspirated. This was then repeated. The reaction mixture was then stirred for 2 d with air flowing over the surface to remove any residual toluene. MeOH was added to a total volume of 1 L with stirring. The solution was filtered through a glass frit filter with fine porosity (4.0 - 5.5 μm). The solid collected in the filter was then dissolved in 100 mL Millipore water and collected in a second filter flask. This was repeated until the solid in the filter was reduced to a thin film. By this method most of the NaOH was removed from the solution. The final collected solution was then rotary evaporated until the volume was reduced to about 5 mL. This dark brown solution was loaded on a Sephadex column. The Sephadex column was prepared in advance by placing 100 g Sephadex G-25 in a beaker with 250 mL Millipore water. The mixture was stirred, then left overnight to cross-link. The column was stoppered first with glass wool and Ottawa Sand Standard, and then Sephadex was poured over it and allowed to settle overnight. Millipore water (pH = 6) was used as an eluent. Fractions (50 mL) were collected and their pH measured. Fractions of pH 6 or 7 and below were combined, and fractions of pH 8 and above were combined. The more basic fractions were put through the column again after the column was flushed with
water to remove the trapped NaOH. This was repeated until all fractions were pH 6 - 7. These fractions were then rotovapped to dryness. A yield of 80 and 110 mg of fullerenol were obtained by this method.

The literature report\textsuperscript{24} of this method suggests that there are significant silica impurities in the fullerenol samples analyzed by XPS. Modifications were therefore made to the procedure to avoid using glassware at high pH by using plastic flasks. Also, the purification on a Sephadex\textsuperscript{TM} column is expensive. This step can be avoided in the following manner. After the MeOH-filtration steps the thin fullerenol film is reduced in volume to 5 mL it is placed in a plastic centrifuge tube. MeOH is added to this solution, the flask is shaken and then centrifuged at 4400 RPM for 15 min using an IEC Centra MP4 centrifuge. The liquid is aspirated and the process repeated until the pH is neutral.

A solution (46 mM) of fullerenol was made by dissolving the fullerenol (50 mg) in Millipore water (1 mL). The solution was pH 8. Additional solutions (4.6 and 0.46 mM) were prepared by subsequent dilutions.

**M-fullerenol.** In a general reaction fullerenol solution (100 \( \mu \)L, 46 mM) was added to a solution of the appropriate metal salt (100 \( \mu \)L, 0.5 M) and the mixture allowed to react at room temperature. A red-brown precipitate was observed after < 1 min. The solid can be isolated by filtration. Reactions were performed with a range of metal salts at this concentration. The experimental variations are shown in Table 2. In addition, a range of concentrations were investigated for

**Environmentally relevant iron concentrations.** A Fe(NO\textsubscript{3})\textsubscript{3} solution (0.1 mM) was allowed to react with a fullerenol solution (100 \( \mu \)L, 0.46 mM). Cross-linking was complete after 72 h. The UV-visible spectrum showed no Fe\textsuperscript{3+} in solution.
Determining minimum concentration of iron needed to produce precipitation. Fullerene solution (0.5 mL, 46 mM) and added Fe(NO₃)₃ (306 µL, 50 mM) and the reaction allowed to proceed for 2 h. Successive additions of Fe(NO₃)₃ in 306 µL increments (at intervals of 1 h.) were made until cross-linking (precipitation) was evident. Total amount of Fe(NO₃)₃ added was 3.06 mL (0.153 mmol). This gave a total volume of 3.56 mL, making it an overall 43 mM Fe(NO₃)₃ solution. The cross-linked product was centrifuged and the supernatant aspirated and a UV spectrum was measured.

Effect of pH on cross-linked product. A large batch of cross-linked Fe-fullerene was prepared by reacting Fe(NO₃)₃ (5 mL, 500 mM) with fullerene (1 mL, 46 mM). Precipitation started right away, but the solution was allowed to react overnight. The suspension was centrifuged at 4400 rpm for 15 minutes, and the supernatant (with the excess Fe³⁺) was filtered and discarded. Millipore water (10 mL) was added to the solid and the flask was shaken well. The suspension was centrifuged and the supernatant removed by filtration. This process was repeated until the supernatant showed no orange color (due to dissolved Fe³⁺). The pH of the as prepared solution was 6. The pH was adjusted with either NaOH (1 M) or HCl (1 N). The tube was shaken and centrifuged to observe any dissolution or decomposition of the Fe-fullerene.

Stability of Fe-fullerene. Fullerenols are not soluble in toluene. 5 mg fullerene added to 800 µL dry toluene. Vial was shaken 1 min. No dissolution was evident. UV showed no C₆₀ or C₆₀(OH)ₙ peaks. Some of the concentrated fullerene-Fe was diluted to 400 µL and added to 400 µL toluene. The vial was shaken for 1 min. The toluene layer remained clear. There was no purple color to indicate C₆₀ was present. UV of the toluene layer showed no C₆₀ or C₆₀(OH)ₙ peaks.
**Competitive cross-linking.** A mixed metal solution was prepared by Fe(NO$_3$)$_3$ (20.2 mg, 5 mmol) with an equimolar amount of an appropriate metal salt (5 mmol) and adding Millipore water (10 mL). The resulting solution was 5 mM with regard to each metal. To this solution was added fullerol (5.5 mg) followed by thorough mixing. After precipitation was observed the solution was centrifuged at 4400 rpm for 15 min. and the supernatant aspirated. UV-visible spectra were obtained of the supernatant from which the iron concentration could be determined. A summary of competitive reactions is given in Table 1.4.

**Metal cross-linking of nano-C$_{60}$.** To solution of an appropriate metal salt (100 µL, 5 mM) was added a solution of nano-C$_{60}$ (100 µL) and the mixture observed for precipitation over a 24 h period. A summary of reactions is given in Table 1.5.

**References**


It should be noted that the mechanism of nano-C60 toxicity effects is yet to be established since proposals that reactive oxygen generation are involved are suspect since fullerenols have been shown to produce both singlet oxygen and superoxide. See, K. D Pickering, and M. R. Wiesner, *Environ. Sci. Technol.*, 2005, ACS ASAP.


The lack of reaction with KCl, HCl, or NaOH suggests that ionic concentration and pH are not associated with the precipitation from aqueous solution.


The lack of reaction with KCl, HCl, or NaOH suggests that ionic concentration and pH are not associated with the precipitation from aqueous solution.


Chapter 2

Synthesis and Purification of FeMoC

Introduction

The vapor growth of SWNTs from catalyst particles occurs by a general vapor-liquid-solid (VLS) growth mechanism.\textsuperscript{1,2} The growth of SWNTs by VLS is believed to occur via two mechanistic steps: nucleation and growth.\textsuperscript{3,4} Nucleation involves both the formation of a catalyst particle and the initial construction of the carbon framework on which the tube is later grown. At growth temperatures (800 – 1000 °C) the catalyst metal atoms aggregate to form a liquid metal nanoparticle. For the growth of SWNTs, it is proposed that the nanoparticle needs to be ca. 50 - 200 metal atoms (1 - 100 nm).\textsuperscript{5} The size of this particle has been proposed to have an effect on the diameter and type (as defined by the SWNT’s $n,m$ value) of tube produced.

A variety of transition metal catalysts and alloys have been studied. The metals most commonly used for SWNT growth are iron, cobalt, nickel, molybdenum, and various bimetallic alloys of these metals.\textsuperscript{6} Iron species, such as iron oxides,\textsuperscript{7} iron nitrates,\textsuperscript{8} Fe(CO)$_5$\textsuperscript{9} and ferrocene,\textsuperscript{10} have been reported as active catalysts. Irrespective of the iron source, the overall goal is to form a nanoparticle less than 100 nm. Many different techniques have been employed including the use of supports, such as MgO or Al$_2$O$_3$, diblock copolymer micelles,\textsuperscript{11} ferritin\textsuperscript{12} and dendrimers.\textsuperscript{13} These supports are usually treated with FeCl$_3$, and then annealed to form Fe$_2$O$_3$ nanoparticles. Arrays of posts and strips, patterned into a thermally evaporated iron surface, have also shown success.\textsuperscript{14} In a recent publication Liu and co-workers have shown the iron-molybdenum nanocluster $[\text{H}_x\text{PMo}_{12}\text{O}_{40}\text{Fe}_{30}(\text{O}_2\text{CMe})_{15}\text{O}_{254}(\text{H}_2\text{O})_{98}](\text{FeMoC})$ to be a suitable catalyst precursor for the growth of SWNTs.\textsuperscript{15}
It is well understood that the electronic properties of SWNTs are dependent on their helicity, which is closely related to their diameter.\textsuperscript{12,16} There is much interest, therefore, in the development of methods that allow for the synthesis of SWNTs with particular helicities. It would be desirable to use pre-formed SWNTs as seeds for the growth of longer SWNTs. In this manner the diameter and chirality of the grown SWNT section would be controlled by the structure of the original SWNT seed. The key conceptual break-through in amplification is, for the first time ever, totally separating the nucleation and the growth of SWNTs. Such a process is likened to the polymerase chain reaction (PCR) used for producing relatively large numbers of copies of DNA molecules from minute quantities of source DNA material. In order to accomplish this goal, it is necessary that a catalyst particle be preferentially docked to the end of an individual SWNT. Heating the catalyst-SWNT conjugate under appropriate conditions would result in the partial consumption of one end of the SWNT while retaining the direct connection, and provide a seed point for subsequent growth upon introduction of a suitable feedstock. This approach would have the additional advantage of not requiring a nucleation step (cap formation\textsuperscript{17}), since only growth onto an existing SWNT would be necessary, and hence potentially lower the reaction temperature and thus the energy consumption: an important parameter for large scale manufacture.

Since the majority of SWNT growth has been shown to occur for iron-based catalysts,\textsuperscript{18} and the use of a well-defined molecular catalyst precursor could simplify characterization, our initial studies have concentrated on the nanocluster $[H_x PMo_{12}O_{40} = H_4 Mo_7 Fe_{30}(O_2 CMe)_{15} O_{254} (H_2 O)_{98}]$ ("FeMoC"), previously proposed to catalyze the growth of SWNTs.\textsuperscript{15} The structure of FeMoC consists of a tetrahedral reduced Keggin $[H_x PMo_{12}O_{40}]^{3-}$ ion inside a spherical icosahedral giant (Keplerate) cage of the $\{(Mo^{VI})Mo^{VI}_5\}_{12}Fe^{III}_{30}$ type (Figure 2.1).
Figure 2.1. Computer representation of FeMoC based upon single crystal data showing the 'cluster-within-a-cage' structure. The central Keggin ion is shown in green, the molybdenum, iron and oxygen atoms of the Keplerate cage are shown in blue, yellow, and red respectively.

In Chapter 3 the methodology for coupling a suitable catalyst precursor (including FeMoC) to a pre-formed SWNT is discussed, however, in this Chapter we have investigated a variety of issues with regard FeMoC itself. The as-published synthesis of FeMoC has a low yield (~4%)\textsuperscript{19} and there appears uncertainty as to the color (described as either dark blue or greenish) as well as its solubility and/or stability in water.\textsuperscript{15,19} Our initial studies confirmed the variability in the color (and the UV-visible spectrum) as well as the analytical purity, prompting a detailed study of the synthesis and the development of appropriate purification procedures. In addition to the purity issue, Liu and co-workers used a pre-catalyst in their growth chamber\textsuperscript{15} and we were interested to determine if pure FeMoC alone would be a catalyst precursor for the growth of SWNTs.
Results and Discussion

The reported synthesis of FeMoC involves the addition of $\text{H}_3\text{P}(\text{Mo}_3\text{O}_{10})_4$ to a pre-made aqueous mixture of FeCl$_2$, Na$_2$MoO$_4$, and MeCO$_2$H. The reaction mixture is acidified and allowed to react for 45 min after which time any insoluble products are removed by filtration. The filtrate is allowed to evaporate to yield crystals of FeMoC.$^{19}$

Following this procedure does indeed yield a dark crystalline material, however, it was found to have inconsistent and irreproducible analysis and spectroscopy suggesting that a mixture of materials co-crystallizes. Furthermore, addition of cold H$_2$O yields a blue solution and a yellow-green insoluble material. UV-visible spectroscopy of the H$_2$O soluble blue fraction (Figure 2.2) does not show any of the characteristic nucleus shell charge transfer between the host and the Keggin guest (550 nm) associated with the FeMoC structure. The ATR spectrum of the blue product (Figure 2.3) does not show the peaks at 1530 cm$^{-1}$ associated with FeMoC or the Keplerate cage.

![Graph](image)

**Figure 2.2.** UV-visible spectrum of the blue water-soluble fraction (in pH 2 water) formed in the synthesis of FeMoC.
The IR spectrum of the blue solid does have the 1058 cm\(^{-1}\) peak corresponding to P, meaning that it is not the Keplerate cage, has Mo=O transition at 966 cm\(^{-1}\), Mo-O-Mo transitions at 949 and 870 cm\(^{-1}\) H\(_2\)O peaks from outer shell at 3300 cm\(^{-1}\). This spectrum lacks FeMoC’s peaks at 2973, 2922 and 1530 cm\(^{-1}\). These facts indicate that it is not the Keplerate nor is it FeMoC.

![ATR of the blue fraction formed in the synthesis of FeMoC.](image)

**Figure 2.3.** ATR of the blue fraction formed in the synthesis of FeMoC.

The yellow-green solid is only slightly soluble in H\(_2\)O but does give the required band at 550 nm in the UV-visible spectrum. However, it is almost obscured by the broad absorption at 335 nm. Investigation of the solubility of the yellow-green solid in a variety of solvents shows that a dark green solution is formed in EtOH with a pale yellow residue remaining. Analysis of each of these fractions indicates that the dark green product formed after washing with cold H\(_2\)O and extraction with EtOH is consistent with the
spectroscopy associated with the single crystal molecular structure previously reported for FeMoC.

Based upon XPS, UV-visible, and ATR spectroscopic analysis, the residual yellow solid remaining in the filter appears to be a partially formed Keplerate cage. It does not have the Keggin ion in the center since it gives no $^{31}$P NMR signal. The yellow solid would not dissolve in common solvents, except acidic water. The UV-visible (Figure 2.4) and ATR (Figure 2.5) spectra of the Keplerate are very similar to the spectrum of the yellow solid from the filter. According to literature, the Keplerate should show and IR peak for MoO$_4$ at 960 cm$^{-1}$, and both spectra have a shoulder at that wavelength. The XPS analysis of the yellow residue from the synthesis (Table 2.1) shows a Fe:Mo:C ratio to be 30:69:25, which is similar to an authentic sample of the Keplerate cage (30:72:24). Furthermore, the lack of solubility in water is consistent with previous reports.$^{19}$

Table 2.1. XPS elemental ratio analysis for the yellow byproducts from FeMoC synthesis.

<table>
<thead>
<tr>
<th>Elemental Ratio</th>
<th>Fe</th>
<th>Mo</th>
<th>O</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yellow residue (Exp.)</td>
<td>30</td>
<td>68.5</td>
<td>222</td>
<td>24.6</td>
</tr>
<tr>
<td>Keplerate (Calcd.)</td>
<td>30</td>
<td>72</td>
<td>382</td>
<td>24</td>
</tr>
</tbody>
</table>

The apparently low solubility of FeMoC, and insolubility of the yellow product, allows for the purification of FeMoC via washing the crude product with cold H$_2$O followed by the Soxhlet extraction of the residue with EtOH. By this route a saturated solution of FeMoC in EtOH is produced that may be evaporated to yield a dark green
Figure 2.4. UV-visible spectra of the yellow solid formed in the synthesis of FeMoC (red) and Keplerate (gray), all in pH 2 water.

Figure 2.5. ATR comparison of Keplerate (blue) and the yellow solid formed in the synthesis of FeMoC (red). Keplerate characteristic peaks at 1620 (H₂O), 1533 vₘₕ(COO), 1409 vₘₕ(COO), 968 v(Mo=O), 854 (m), 778 (s), 623 (m), 438 (m) cm⁻¹.²⁰
solid. The solubility of FeMoC in EtOH as determined (by UV-visible spectroscopy) from the cooled Soxhlet solution after filtration of all solids to be 17.8 mg.mL$^{-1}$ (9.906 x 10$^{-4}$ mol.dm$^{-3}$) at room temperature. The solution was characterized by UV-vis and Raman spectroscopy, see below.

Although spectroscopically identical to the previous reports the TGA and MS of the green product shows the presence of coordinated EtOH$^{19}$ Thus, the green material obtained from Soxhlet extraction has the formula $[\text{H}_x\text{PMo}_{12}\text{O}_{40}\subset\text{H}_4\text{Mo}_{72}\text{Fe}_{30}(\text{O}_2\text{CMe})_{15}\text{O}_{254}(\text{H}_2\text{O})_{98-x}(\text{EtOH})_x]$ where x is calculated to be ca. 30. However, the EtOH content appears to be dependent on the length of the Soxhlet. The mass spectrum of the Soxhlet product shows a broad peak with the maximum isotope distribution at 17969 g.mol$^{-1}$ that corresponds closely to a molecular formula of $\text{H}_3\text{PMo}_{12}\text{O}_{40}\subset\text{H}_4\text{Mo}_{72}\text{Fe}_{30}(\text{O}_2\text{CMe})_{15}\text{O}_{254}(\text{H}_2\text{O})_{68}(\text{EtOH})_{30}$ (Calcd. 17977 g.mol$^{-1}$). Based upon this analysis and a consideration of the coordination environments of the H$_2$O ligands in FeMoC, we propose that EtOH ligands are bound to the Fe$^{3+}$ centers on the outside of the host cage. Since the exact number of EtOH ligands appears to show a slight dependence on the length of the Soxhlet extraction process (i.e., the time and/or concentration of the refluxing EtOH solution) we designate the EtOH complexed product as FeMoC-EtOH.

The AFM of FeMoC-EtOH (Figure 2.6) shows individual nanoparticles with a height of 2 nm. The theoretical diameter of FeMoC (based upon the X-ray crystal structure) is 2.1 nm. Thus, within experimental error the diameter observed is consistent with the retention of the FeMoC structure in FeMoC-EtOH.

The UV-visible spectrum of purified FeMoC-EtOH (Figure 2.7) shows bands reported previously to be characteristic of an intervalence [Mo(V) $\rightarrow$ Mo(VI)] charge transfer in the Keggin cluster (885 and 1053 nm) and the nucleus shell charge transfer
**Figure 2.6.** AFM image and associated height analysis of FeMoC-EtOH showing the features to be about 2 nm tall, the theoretical height is 2.1 nm.

between the host and the Keggin guest (545 nm). The ATR spectrum of FeMoC-EtOH (Figure 2.8) shows peaks due H₂O at 1616 cm⁻¹, COO peaks at 1530 and 1411 cm⁻¹. It has the 1061 cm⁻¹ peak corresponding to P-O, confirming that the Keggin ion is present in the species. The spectrum also shows Mo-O-Mo transitions at 949 and ~ 870 cm⁻¹. The 1035 cm⁻¹ peak corresponds to a P-OH shift.

The XPS analysis of FeMoC-EtOH (Table 2.2) shows a Fe:Mo ratio (1:2.7) consistent with the formulation of the encapsulated molybdate ion in the supramolecular cage (calculated = 1:2.8). The calculated concentration of phosphorus is slightly high, however, the low intensity of the P 2p peak (and hence the poor signal to noise) makes quantification difficult. There are signals within the C1s and O1s that correspond to the C-O portion of the acetates (see Figure 2.10) with an O:C ratio of ca. 1.5 (as compared to the theoretical value of 2.0). Furthermore, the carbon content is consistent with the substitution of coordinated water for EtOH ligands.

Müller and co-workers have previously reported that FeMoC is a highly paramagnetic cluster containing 150 unpaired electrons associated with 30 octahedral high-spin d⁵ Fe³⁺ centers.¹⁹ Our ability to prepare purified samples of FeMoC (albeit with EtOH associated with the Fe³⁺ centers) prompted an investigation of the ³¹P NMR
Figure 2.7. UV-visible spectrum of FeMoC-EtOH.

Figure 2.8. ATR of FeMoC-EtOH solid.
Table 2.2. XPS elemental ratio analysis for the products from FeMoC synthesis.

<table>
<thead>
<tr>
<th>Elemental Ratio</th>
<th>Fe</th>
<th>Mo</th>
<th>P</th>
<th>O</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeMoC (Calcd.)</td>
<td>30</td>
<td>84</td>
<td>1</td>
<td>422</td>
<td>30</td>
</tr>
<tr>
<td>FeMoC-EtOH (Exp.)</td>
<td>30</td>
<td>79.5</td>
<td>&lt;3&lt;sup&gt;a&lt;/sup&gt;</td>
<td>316</td>
<td>68.0</td>
</tr>
<tr>
<td>FeMoC(EtOH)&lt;sub&gt;30&lt;/sub&gt; (Calcd.)</td>
<td>30</td>
<td>84</td>
<td>1</td>
<td>422</td>
<td>60</td>
</tr>
</tbody>
</table>

<sup>a</sup> Exact atomic ratio difficult to determine due to low signal to noise.

spectrum of FeMoC-EtOH since the shift and relaxation of the $^{31}$P nucleus should be uniquely influenced by the 30 paramagnetic centers positioned in a spherical manner at a distance of ca. 2 Å. The solid state $^{31}$P NMR spectrum for FeMoC-EtOH is shown in Fig. 2.10.

**Optimization of FeMoC yield.** Müller reports a yield of 17.4% based on Fe.<sup>19</sup>

However, a consideration of the stoichiometry of the reaction as reported in the literature (Table 2.3.) shows that while both FeCl<sub>2</sub> and Na<sub>2</sub>MoO<sub>4</sub> are limiting reagents it is the latter on which the yield should be calculated. The MeCO<sub>2</sub>H is in large excess while H<sub>3</sub>[P(Mo<sub>3</sub>O<sub>10</sub>)(<sub>4</sub))] is in slight excess. The reactant ratios described in Muller’s synthesis produces 83 mg of pure FeMoC. This corresponds to only a 4.03% yield based on Na<sub>2</sub>MoO<sub>4</sub>. *Hardly the high yield reported!* Since Müller’s yield was low, this prompted us to try and improve the yield.

Performing the reaction under stoichiometric conditions results in only a small increase in the isolated yield. Despite the Na<sub>2</sub>MoO<sub>4</sub> being a limiting reagent, increasing its concentration resulted in the reduction in the yield of FeMoC. A similar effect was observed by the reduction of MeCO<sub>2</sub>H (Table 2.3). Conversely, an increase in the FeCl<sub>2</sub>
Figure 2.9. X-ray photoelectron spectra of (a) C 1s and (b) O 1s for FeMoC-EtOH.

content resulted in a dramatic increase in FeMoC yield to ca. 12%. Further increases resulted in higher yields. The oxidation state of the iron reagent is clearly important since substituting Fe(II) for Fe(III) resulted in no FeMoC being formed, despite the presence of Fe(III) in FeMoC's Keplerate cage. A batch of FeMoC was prepared by changing the
Figure 2.10. $^{31}$P NMR spectrum of FeMoC-EtOH.

Table 2.3. Product yield as a function of reagent ratio.$^a$

<table>
<thead>
<tr>
<th>Exp.</th>
<th>Na$_2$MoO$_4$</th>
<th>FeCl$_2$</th>
<th>MeCO$_2$H</th>
<th>H$_3$[P(Mo$<em>3$O$</em>{10}$)$_4$]</th>
<th>Yield (%)$^b$</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8.27(mmol)</td>
<td>5.03(mmol)</td>
<td>174(mmol)</td>
<td>1.37(mmol)</td>
<td>4.0</td>
<td>Literature</td>
</tr>
<tr>
<td>2</td>
<td>72</td>
<td>30</td>
<td>15</td>
<td>1</td>
<td>4.7</td>
<td>Stoichiometric</td>
</tr>
<tr>
<td>3</td>
<td>8.27</td>
<td>5.03</td>
<td>87</td>
<td>1.37</td>
<td>3.4</td>
<td>[MeCO$_2$H]/2</td>
</tr>
<tr>
<td>4</td>
<td>16</td>
<td>5.03</td>
<td>174</td>
<td>1.37</td>
<td>1.7</td>
<td>2[Na$_2$MoO$_4$]</td>
</tr>
<tr>
<td>5</td>
<td>8.27</td>
<td>5.03 (FeCl$_3$)</td>
<td>174</td>
<td>1.37</td>
<td>0</td>
<td>Fe$^{3+}$ v. Fe$^{2+}$</td>
</tr>
<tr>
<td>6</td>
<td>8.27</td>
<td>10</td>
<td>174</td>
<td>1.37</td>
<td>12.4</td>
<td>2[FeCl$_2$]</td>
</tr>
<tr>
<td>7</td>
<td>8.27</td>
<td>20</td>
<td>174</td>
<td>1.37</td>
<td>25.3</td>
<td>4[FeCl$_2$]</td>
</tr>
</tbody>
</table>

$^a$ All reactions normalized to pH = 2 and stirred for 45 minutes prior to filtration.

$^b$ Based upon Na$_2$MoO$_4$ as the limiting reagent.
order of the reaction steps by putting the Keggin ion \( \text{H}_3\text{P(Mo}_3\text{O}_{10})_4 \) in first. The UV spectrum was unchanged, and no improvement in yield was achieved.

As discussed above, the literature synthesis of FeMoC suggested the pH should be adjusted to 2 prior to evaporation of the solution. To determine if the pH of the solution affects FeMoC formation, one large batch of FeMoC was prepared as described above (all amounts reactants and solvents were doubled) up to the point of acetic acid addition. This batch was divided into four equal parts and the pH adjusted to 1.14, 2.11, 2.75 and 3.01. These results can be seen in Figure 2.11 and show that the yield is highly dependent on the pH of the reaction mixture. Based on this data, it can be concluded that pH plays an important role in FeMoC formation. Above pH 2.75, FeMoC is not formed. As the pH of the solution is lowered, the yield of FeMoC produced is increased and formation happens more quickly. The pH of the reaction also appears to have some effect on the yield, with lower the pH the yield is increased and precipitation is initiated more quickly. The \( \text{pK}_a \) values for phosphomolybdic acid are \( 1.61 \pm 0.10 \), \( 2.28 \pm 0.08 \), \( 2.41 \pm 0.12 \). This tells us that the highest yield was produced when the phosphomolybdic acid was fully protonated.

**Solution stability of FeMoC.** Investigating the solubility/reactivity of FeMoC with other common solvents showed that stable solutions were formed with EtOH, MeOH and H\(_2\)O (see below). Suspensions (without apparent reaction) were observed for MeCN, acetone, Et\(_2\)O, IPA, CH\(_2\)Cl\(_2\), CHCl\(_3\), pentane, hexane, benzene and toluene. In toluene a colloidal suspension appears to be stable for 24 hours, however, precipitation occurs after that time. Suspensions in THF and DMF changed color to yellow and orange, respectively, indicating chemical reaction (possibly ligand substitution), but no solubility was observed. The formation of a yellow (iron containing) product was also observed for the long-term storage of FeMoC in MeOH solution. The solubility of FeMoC in MeOH (2 mg.mL\(^{-1}\)) is poor compared to that in EtOH (12 mg.mL\(^{-1}\) at room temperature), and
Figure 2.11. Plot of FeMoC-EtOH yield as a function of reaction pH.

Over the 30 day period some of the FeMoC precipitated out of solution, but the solubility is still adequate for our needs. In contrast, FeMoC is indefinitely stable in EtOH solution, and no change is observed in the UV-visible spectrum of an EtOH solution after 4 weeks.

Liu and co-workers have reported that FeMoC was soluble in water;\textsuperscript{15} however, in their original report Müller \textit{et al.} suggested it was insoluble.\textsuperscript{20} Given this confusion and the supposed blue color of the former FeMoC, we have investigated the stability of purified FeMoC-EtOH in water. FeMoC stability in water of different pHs was investigated. FeMoC was dissolved in water (0.5 mg.mL\textsuperscript{-1}) and the pH was adjusted to appropriate values with HCl. At pH 1 FeMoC is only partially soluble, and after 24 h no peaks indicative of FeMoC are observed. Along with the decomposition of FeMoC there is a concomitant decrease in the pH of the solutions in the UV-visible spectrum. As may be seen from Figure 2.12, the stability of FeMoC increases with increased pH. At pH 2 FeMoC is essentially decomposed after 2 days; however, at pH 3 - 5 FeMoC bands in the UV-visible spectra were discernable through 7 days. After 9 days from the solution pHs had changed from 4 to 3.6 and from 5 to 4.2.
Figure 2.13. Plot of concentration versus time for FeMoC in aqueous solution at pH 2 (■), 3 (□), 4 (●) and 5 (○).

The desire to react FeMoC with functionalized SWNTs in a water solution, but the low stability of FeMoC in water, prompted the investigation of its stability in MeOH/H$_2$O mixtures.$^{19}$ As may be seen from Figure 2.14, FeMoC is completely stable in MeOH solution over 9 days at room temperature. During that corresponding time decomposition of over 80% occurs, however, use of a 1:1 MeOH/H$_2$O solution results in the retention of 90% after 9 days.

**Thermal decomposition of FeMoC-EtOH.** Liu and co-workers reported$^{15}$ that as a catalyst precursor for the growth of SWNTs, FeMoC was heated to 700 °C in air (to decompose the organic ligands) and then reduced in H$_2$ at 900 °C prior to introduction of the growth gas. In our growth studies we have found that the efficacy of FeMoC as a catalyst precursor is dependant on the protocol for conversion to a metal catalyst. In order to understand these results we have investigated the thermal decomposition of purified FeMoC-EtOH by TGA, TGA-MS, and XPS.
Figure 2.14. Plot of concentration versus time of FeMoC in MeOH (○), MeOH/H₂O 1:1 (●), and H₂O at pH 4.5 (■) at room temperature.²⁰

The TGA of samples of FeMoC-EtOH heated to 1000 °C are shown in Figure 2.15; the Fe:Mo ratio of the products formed upon heating to 400, 700 and 900 °C are given in Table 2.4. TGA-MS shows that, irrespective of the atmosphere, the mass loss that occurs prior to 200 °C is due loss of coordinated EtOH and H₂O, while the mass loss at ca. 400 °C is consistent with the decomposition of the organic substituents and loss of additional H₂O (presumably the water of coordination that is inside the FeMoC cage).

Under H₂ atmosphere there is a further mass loss at ca. 600 °C that is consistent with the reduction of the metal oxide (formed upon pyrolysis) to metal (mass loss: calcld. 67%; exp. 72%). This is confirmed by XPS analysis (Table 2.4) that shows only a small change in the Fe:Mo ratio. As expected there is no reduction reaction in either air or argon at 600 °C, though both show mass loss at higher temperatures (Figure 2.15). Based upon XPS analysis the continuing mass loss starting at 800 °C in air is consistent with the sublimation of molybdenum oxides. Under argon the Fe:Mo ratio appears to change but
towards a slight loss of iron (see Table 2.4). However, the mass loss starts at a lower temperature but is incomplete. We propose that under an oxidizing environment (such as air) all the molybdenum is converted to volatile oxides, while under argon the oxide material formed upon pyrolysis contains a mixture of molybdenum oxides (or a mixed iron-molybdenum oxide) of which only a fraction are volatile below 1000 °C. Based upon the forgoing, we propose that the choice of thermal treatment prior to reduction with H₂ and introduction of the SWNT growth gas (e.g., CH₄, C₂H₄, etc.) will control the Fe:Mo ratio, and possible activity, of the catalyst.

An additional consideration is whether Fe and Mo segregation occurs in hydrogen when heated slowly. The reduction of Fe₂O₃ to Fe⁰ and the reduction of MoO₃ to Mo⁰ occur around 400 °C and 600 °C, respectively. Thus, during the decomposition of FeMoC under H₂ iron metal will form in the presence of molybdenum oxide. Subsequent reduction of molybdenum oxide will result in a mixture of Fe and Mo. According to the binary phase diagram the MoFe alloy is stable up to 1235 °C once formed. However, if segregation occurs first, several phase transitions have to be overcome to form the alloy.

**Table 2.4.** Fe:Mo ratio as determined by XPS for FeMoC-EtOH thermal decomposition products under air, argon, and hydrogen atmospheres.a

<table>
<thead>
<tr>
<th>Carrier gas</th>
<th>400</th>
<th>700</th>
<th>900</th>
</tr>
</thead>
<tbody>
<tr>
<td>air</td>
<td>1:2.61</td>
<td>1:2.72</td>
<td>1:0.47</td>
</tr>
<tr>
<td>Ar</td>
<td>1:2.58</td>
<td>1:2.61</td>
<td>1:2.94</td>
</tr>
<tr>
<td>H₂</td>
<td>1:2.53</td>
<td>1:2.36</td>
<td>1:2.32</td>
</tr>
</tbody>
</table>

a Measured Fe:Mo ratio prior to thermolysis = 1:2.65.
Figure 2.15. TGA of FeMoC-EtOH under different atmospheres.

Conclusion

A purification method has been developed for FeMoC that has about 30 of its coordinated H₂O ligands substituted with EtOH. This product has been fully characterized by UV, IR, XPS, TGA, MS, SEM, and AFM. Its stability and solubility has been investigated. FeMoC-EtOH has been shown to be soluble in ethanol and methanol. It is stable in these solvents for at least 4 weeks. FeMoC-EtOH is significantly less stable in water. FeMoC is stable through 7 days at pH 3 - 5, but decomposes after 2 days at pH 2 and below. pH also has an influence on the formation of FeMoC in the reaction solution. Above pH 2.75 FeMoC is not formed and the yield is increased slightly as the pH is lowered. The yield of FeMoC has also been improved over literature preparation (from 4 to 25 %) by increasing the amount of FeCl₂.4H₂O added to the reaction. The most important observation is that FeMoC-EtOH has been shown to be a SWNT catalyst precursor.

Experimental

General procedures and analysis were carried out as described in Chapter 1. Acetic acid, MeCO₂Na.3H₂O and NaCl were purchased from Fisher Chemical (Fair
Lawn, NJ). FeCl$_2$.4H$_2$O, FeCl$_3$.6H$_2$O, (NH$_4$)(MeCO$_2$) and H$_3$[PMo$_{12}$O$_{40}$], were purchased from Sigma-Aldrich (St. Louis, MO). Na$_2$MoO$_4$ was purchased from Strem Chemical (Newburyport, MA). N$_2$H$_4$.H$_2$SO$_4$ and (NH$_4$)$_6$Mo$_7$O$_{24}.4$H$_2$O were purchased from Alfa Aesar (Ward Hill, MA). All reagents were used as received.

TGA-MS data was collected on a TGA Q-500 Thermogravimetric analyzer- Mass Spectrometer. Platinum pans (TA instruments, Schaumburg, IL), H$_2$ and Ar gases were used. $^{31}$P NMR data was collected on a Bruker Advance 200 MHz Spectrometer.

**FeMoC-EtOH.** FeCl$_2$.4H$_2$O (1.0 g, 5.03 mmol) is dissolved in Millipore water (75 mL) resulting in a clear slightly yellow solution. To this solution Na$_2$MoO$_4$.2H$_2$O (2.0 g, 8.27 mmol) was added, turning the solution a cloudy rust-red. Glacial acetic acid (10 mL, 59 mmol) was added turning the solution from cloudy to clear red. This is followed by H$_3$[P(Mo$_3$O$_{10}$)$_4$] (2.5 g, 1.37 mmol), producing a dark blue solution. The solution’s pH was adjusted to 2 with HCl and then stirred at room temperature for 45 minutes. The solution was then filtered through a fine glass frit. The filtrate was kept in an open beaker for at least 5 days to allow crystallization. The crystals were then vacuum filtered, washed with H$_2$O and dried. The solid was transferred to a filter thimble and placed inside a Soxhlet extractor. EtOH was refluxed in the extractor overnight and a dark green solution was collected. Yield: 0.083 g, 4.03 %.

**Keplerate synthesis.** Using a modification of the literature method$^{21}$ N$_2$H$_4$.H$_2$SO$_4$ (0.8 g, 6.1 mmol) was added to a solution of H$_2$O (250 mL), (NH$_4$)(MeCO$_2$) (12.5 g, 162.2 mmol) and (NH$_4$)$_6$Mo$_7$O$_{24}.4$H$_2$O (5.6 g, 4.5 mmol). The solution was stirred for 10 minutes, then 50% MeCO$_2$H (83 mL, 725.1 mmol) was added. The solution was stored in and open flask at 20 ºC for 4 days that resulted in red/brown crystals. The crystals were filtered and washed with 90% EtOH, and Et$_2$O, then dried in air. Yield was 3.3 g, 52 %. This product (1.4 g, 0.05 mmol) was added to a solution of
H₂O (75 mL), FeCl₃·6H₂O (1.1 g, 4.1 mmol), and MeCO₂Na·3H₂O (1.1 g, 8.1 mmol) and stirred 24 hours. HCl (1 mL, 1N) and NaCl (2.0 g, 34.2 mmol) were added and the solution was heated to 90 °C and stirred. Filtering while hot produced a golden filtrate which was then allowed to cool to 20 °C. Yellow crystals where obtained after 2 days. The crystals where filtered and washed 2 times with a small amount of iced water and dried in air. Yield was 0.22 g, 14 %.

**FeMoC in EtOH solubility.** A saturated solution of FeMoC in EtOH was produced by Soxhlet extraction. The precipitated FeMoC was filtered from the solution. 0.5 mL of the remaining solution was diluted to 500 mL in EtOH. The UV-visible spectrum of this solution was taken and the 550 nm peak absorbance value was obtained. Using this value, the concentration of the original solution could be determined using the absorption coefficient, λ. The concentration was 17.8 mg·mL⁻¹ purified FeMoC in EtOH. A similar method was used to determine the solubility in MeOH (2 mg·mL⁻¹ at room temperature).

**Stability of FeMoC in H₂O.** FeMoC-EtOH (5 mg) was dissolved in H₂O (10 mL) and the pH adjusted to the required value (1 - 5). The initial UV-visible spectrum was taken and subsequent spectra were taken every 24 hours.

**Synthesis of FeMoC under stoichiometric conditions.** FeCl₂·4H₂O (7.95 g, 40 mmol) was dissolved in Millipore H₂O (75 mL). Na₂MoO₄·2H₂O (23.7 g, 98 mmol) was added, followed by glacial MeCO₂H (3.4 mL, 20 mmol). H₃[PMo₁₂O₄₀] (2.5 g, 1.37 mmol) was added and the pH was adjusted to 2.0 with 1 N HCl. The solution was stirred 45 minutes and filtered through a fine glass frit filter. The filtrate was allowed to crystallize for 5 days and then it was filtered and the solid collected and dried. The solid
was placed in a Soxhlet extractor and purified FeMoC was collected in EtOH. The EtOH solution was evaporated to dryness. Yield: 1.134 g, 4.73%.

**Synthesis of FeMoC with excess of FeCl₂.** FeCl₂·4H₂O (2.0 g, 10.06 mmol) was dissolved in Millipore H₂O (75 mL). Na₂MoO₄·2H₂O (2.0 g, 8.27 mmol) was added, followed by glacial MeCO₂H (10 mL, 59 mmol). H₃[PMo₁₂O₄₀] (2.5 g, 1.37 mmol) was added and the pH was adjusted to 2.0 with 1 N HCl. The solution was stirred 45 minutes and filtered through a fine glass frit filter. The filtrate was allowed to crystallize for 5 days and then it was filtered and the solid collected and dried. The solid was placed in a Soxhlet extractor and purified FeMoC was collected in EtOH. The EtOH solution was evaporated to dryness. Yield: 256 mg, 12.43%. The reaction was repeated using 4.0 g of FeCl₂·4H₂O. Yield: 522 mg, 25.34%.

**Synthesis of FeMoC with excess of Na₂MoO₄.** FeCl₂·4H₂O (1.0 g, 5.03 mmol) was dissolved in Millipore H₂O (75 mL). Na₂MoO₄·2H₂O (4.0 g, 16.54 mmol) was added, followed by glacial MeCO₂H (10 mL, 59 mmol). H₃[PMo₁₂O₄₀] (2.5 g, 1.37 mmol) was added and the pH was adjusted to 2.0 with 1 N HCl. The solution was stirred 45 minutes and filtered through a fine glass frit filter. The filtrate was allowed to crystallize for 5 days and then it was filtered and the solid collected and dried. The solid was placed in a Soxhlet extractor and purified FeMoC was collected in EtOH. The EtOH solution was evaporated to dryness. Yield: 52 mg, 1.68%.

**Synthesis of FeMoC with half equivalent of MeCO₂H.** FeCl₂·4H₂O (1.0 g, 5.03 mmol) was dissolved in Millipore H₂O (75 mL). Na₂MoO₄·2H₂O (2.0 g, 8.27 mmol) was added, followed by glacial MeCO₂H (5 mL, 29.5 mmol). H₃[PMo₁₂O₄₀] (2.5 g, 1.37 mmol) was added and the pH was adjusted to 2.0 with 1 N HCl. The solution was stirred 45 minutes and filtered through a fine glass frit filter. The filtrate was allowed to
crystallize for 5 days and then it was filtered and the solid collected and dried. The solid was placed in a Soxhlet extractor and purified FeMoC was collected in EtOH. The EtOH solution was evaporated to dryness. Yield: 69 mg, 3.35%.

**Synthesis of FeMoC using Fe³⁺ instead of Fe²⁺.** FeCl₃.6H₂O (1.0 g, 3.7 mmol) was dissolved in Millipore H₂O (75 mL). Na₂MoO₄.2H₂O (2.0 g, 8.27 mmol) was added, followed by glacial MeCO₂H (10 mL, 59 mmol). H₃[PMo₁₂O₄₀] (2.5 g, 1.37 mmol) was added and the pH was adjusted to 2.0 with 1 N HCl. The solution was stirred 45 minutes and filtered through a fine glass frit filter. The filtrate was allowed to crystallize for 5 days and then it was filtered and the solid collected and dried. The solid was placed in a Soxhlet extractor and purified FeMoC was collected in EtOH. The EtOH solution was evaporated to dryness. Yield: 36 mg of a yellow solid.

**Synthesis of FeMoC at various pH.** FeCl₂.4H₂O (2.0 g, 10.06 mmol) was dissolved in Millipore H₂O (150 mL). Na₂MoO₄.2H₂O (4.0 g, 16.54 mmol) was added. The solution was divided into four batches (see below). To the first batch was added half the normal amount of glacial MeCO₂H (2.5 mL, 14.75 mmol). The solution pH was 3.05. H₃[PMo₁₂O₄₀] (0.625 g, 0.3425 mmol) was added and the solutions allowed to stir for 45 minutes, filtered, and left to crystallize. The pH was taken after 2 days and found to be 3.01. After 10 days, crystals were observed. After 12 days the solution filtered and Soxhlet extracted with EtOH. Yield: 435 mg of a yellow solid. The products from each of the remaining batches were isolated in an analogous manner, but with different addition and reaction pHs. To the second batch was added the normal amount of glacial MeCO₂H (5 mL), producing a pH of 2.75. After 10 days, crystals were observed. After 13 days the solution filtered and Soxhlet extracted with EtOH. Yield: 14 mg, 1.36% FeMoC. To the third batch was added glacial MeCO₂H (5 mL) and the solution pH was adjusted with HCl (1 N) to a pH of 1.94. After 6 days, crystals were observed. After 7 days the solution
filtered and Soxhlet extracted with EtOH. Yield: 16 mg, 1.55% of FeMoC. To the fourth batch was added glacial MeCO₂H (5 mL) and the solution pH was adjusted with HCl (1 N) to a pH of 1.01. After 6 days the solution filtered and Soxhlet extracted with EtOH. Yield: 78 mg, 7.57% of FeMoC.

References


2. We note that the process by which a molecular carbon precursor decomposes on and within a catalyst particle to form a SWNT has been incorrectly referred to as chemical vapor deposition (CVD). The CVD process involves the deposition of an element or compound on a surface by the vapor and surface decomposition of chemical precursor.


Chapter 3

Attachment of Transition Metal Catalysts to SWNTs

Introduction

Since their discovery in 1991 by Iijima, single-walled carbon nanotubes (SWNT) have attracted attention due to their unique physical and chemical properties. SWNTs can be either metallic or semi-conducting, depending on their diameter and chirality (n,m values), which is determined by the metal catalyst used in their synthesis.

The availability of gram quantities of carbon nanotubes of one type or the other is necessary to the implementation of proposed applications, such as nanotubes high performance composites and molecular electronics. The current methods of SWNT synthesis, including electric-arch discharge, HiPco, CVD, and laser-arch ovens, employ metal catalysts of various sizes and shapes that produce a mixture of nanotubes with a range of sizes, shapes, and properties. Attempts to separate gram quantities of one type of nanotube from another have thus far been unsuccessful. However, small amounts of a specific type have been isolated with some success. If this small amount could be amplified, then it would be of major advantage to carbon nanotube research.

As discussed in Chapter 2, there are a variety of catalysts that have been employed in SWNT production. In this chapter the methodology for coupling a suitable catalyst precursor to a pre-formed SWNT is discussed. Two types of SWNTs were employed to this end, dodecylated SWNTs (dd-SWNTs) and isophthalic acid SWNTs (IPA-SWNTs). Some of the catalysts include $[\text{H}_x\text{PMo}_{12}\text{O}_{40}\text{C}_4\text{Mo}_{72}\text{Fe}_{30}(\text{O}_2\text{CMe})_{15}\text{O}_{254}(\text{H}_2\text{O})_{68}(\text{EtOH})_{30}]$ (FeMoC-EtOH), $[\text{Fe}_3\text{O}(\text{CH}_3\text{CO}_2)_{6}(\text{R})_3]$ (iron trimers), and Fe(NO$_3$)$_3$. Attaching a catalyst to SWNTs, be it on the end of the tube or along the sidewalls, produces what will be referred to as SWNT-cat.
Results and Discussion

**SWNT-cat from dd-SWNTs.** Dodecylated SWNT (dd-SWNT, I), solution in CHCl$_3$ was obtained from the Billups lab (Rice University, Houston, TX) where they were prepared via a published procedure.$^{10}$ The tubes have open ends with carboxyl functional groups on them. These groups are fortunate side-products of the SWNT purification process.$^{11}$ The dd-SWNTs have heights of 1.2 – 3 nm indicating individual SWNTs or bundles of a few SWNTs (Figure 3.1). They have lengths in the range of 300 – 1000 nm. Our collaborators found that these carboxylic acid groups could be used to attach FeMoC-EtOH to the ends of the SWNTs. However, the yield was less than desired. FeMoC-EtOH is more attracted to a functional group such as pyridine than a carboxyl group. By reacting these carboxyl groups with a coupling agent, 1,3-dicyclohexyl carbodiimide (DCC), in the presence of 4-hydroxypyridine, pyridine groups are bound to the end of the dd-SWNTs (Scheme 3.1). Pyridine ended dd-SWNTs (py-dd-SWNT) spin-coated from chloroform are singles (height of 1.0 nm) or small bundles (1.9 – 2.1 nm). AFM images of py-dd-SWNTs also show many round features unattached to
Figure 3.1. AFM image of dd-SWNTs on mica.

Scheme 3.1. DCC coupling of 4-hydroxypyridine to carboxyl groups on dd-SWNT ends.

the SWNTs (Figure 3.2), that were present to a lesser degree in the dd-SWNT images (Figure 3.1).

When py-dd-SWNTs are incubated with FeMoC, the FeMoC attaches to the ends of the SWNTs (SWNT-cat). AFM images show py-dd-SWNTs that are 0.7 – 1.0 nm in height, while the catalyst particles on the ends of the tubes that are 2.1 – 2.4 nm in height (Figure 3.3). FeMoC has been reported to be 2.1 nm in diameter. In this image ca. 50% of the py-dd-SWNTs had catalyst particles attached to the ends of the tubes.
Figure 3.2. AFM image of py-dd-SWNTs on mica.

Figure 3.3. AFM images of FeMoC-EtOH attachment to py-dd-SWNTs on mica.

Another group member had shown that by exchanging some of the outside EtOH or H₂O ligands of FeMoC, the solubility of FeMoC could be altered. We thought that it was possible that functionalizing SWNT-cats made with FeMoC could change the solubility of the SWNT-cat (II and III). The first functional group that was added to the SWNT-cat solution was 1-hexadecane thiol. Bundles make up half of the tubes seen in
Figure 3.4. AFM image of SWNT-cat functionalization with 1-hexadecane thiol on mica.

AFM images (Figure 3.4). Some singles (height of 1.04 nm) have large catalyst particles on the ends. The catalyst height is greater than FeMoC alone, 5.8 - 6.4 nm and ~ 2 nm respectively. 1-hexadecane thiol has a length of less than 0.5 nm, so it cannot be due just to hexadecane thiol alone. It is possible that two FeMoC molecules functionalized with thiol are at the ends of the tubes. The solubility was not observed to be increased (i.e., more SWNTs seen in same size AFM image), so this possibility was not further investigated.

SWNT-cat functionalization with tetraethylene glycol was also attempted, but no SWNTs were ever observed in AFM images. Since fewer SWNTs were observed in both
**Figure 3.5.** AFM image of 1:4 py-dd-SWNTs:FeCl$_2$ in CHCl$_3$ on mica.

glycol and thiol samples, solubility is considered to be worse, not better, than before. It was determined that simply functionalizing the catalyst on the end was not enough to change the solubility of the whole SWNT-cat.

Other sources of iron were investigated as possible catalyst precursors. A large excess of FeCl$_2$ was evident in a 1:4 py-dd-SWNTs: FeCl$_2$ in water solution (Figure 3.5). A few SWNTs, most likely small bundles, of 1.8 – 1.9 nm in height were observed with particles on the ends. The iron particles were 3.7 – 4.2 nm in height.

There are about the same number of individual SWNTs (~ 0.9 nm in height) in the AFM images of the FeCl$_3$ sample (Figure 3.6). Also, the catalyst particles on the ends of the tubes are slightly bigger (2.7 – 5.2 nm). The same amount of catalyst may be aggregated into fewer larger particles than in the FeCl$_2$ sample. Only a few short tubes could be found in images from a 1:4 py-dd-SWNTs:Fe(NO$_3$)$_3$ solution (Figure 3.7). The SWNTs were 0.8 – 1.0 nm in height, consistent with individual SWNTs. Catalyst particles found at the end of the tubes were 1.5 – 1.8 nm in height. No excess catalyst was observed.
Figure 3.6. AFM image of 1:4 py-dd-SWNTs:FeCl₃ on mica.

Figure 3.7. AFM image of 1:4 py-dd-SWNTs:Fe(NO₃)₃ on mica.

Individual SWNTs (~ 0.9 nm height) were observed when the iron trimers were attached to py-dd-SWNTs (Figure 3.8). The particles on the ends of the SWNTs were 1.3 nm in height. Larger bundles of tubes were 11.5 nm in height.

We wanted to prove that the Fe was attaching to the ends of the SWNTs. To this end, we attempted to attach Fe₃(CO)₁₂ to py-dd-SWNTs. It was hoped that we could
Figure 3.8. AFM image of py-dd-SWNTs:[Fe$_3$O(O$_3$CCH$_3$)$_6$(H$_2$O)$_3$] on mica.

observe the attachment by IR. However, no SWNTs could be found by AFM in the attempt to attach Fe$_3$(CO)$_{12}$ to py-dd-SWNTs. Fe$_3$(CO)$_{12}$ spherical particles were measured to have heights between 3.0 nm and 4.6 nm. The IR spectrum of this sample does not show CO peaks around 2100 cm$^{-1}$,\textsuperscript{13} but it does have some small dd-SWNT peaks at 2921 and $\sim$2850 cm$^{-1}$. The IR spectrum of dd-SWNTs shows peaks corresponding to C-H at 2919 and 2845 cm$^{-1}$ and C=C at 1529 cm$^{-1}$,\textsuperscript{14}

$$3 \text{ Fe}_2(\text{CO})_9 \xrightarrow{hv} \text{ Fe}_3(\text{CO})_{12} + 3 \text{ Fe(} \text{CO})_5$$ \hspace{1cm} (3.1)

In literature nickel has also been shown to be an effective catalyst for SWNT growth.\textsuperscript{15} 4.4 – 6.7 nm Ni(CO)$_4$ particles were observed in AFM images, but no SWNTs. However, the IR spectrum of this sample shows no strong characteristic peaks of dd-SWNTs or Ni(CO)$_4$.\textsuperscript{16,17} There is a small broad peak around 2920 cm$^{-1}$ that could be a dd-SWNT peak.
**SWNT-cat from IPA-SWNTs.** The dd-SWNTs are only soluble in CHCl₃. We were interested in investigating SWNT-cats in other solvents, such as water and ethanol. By functionalizing the side-walls of SWNTs with isophthalic acid (IPA-SWNTs, IV) solubility in both water and ethanol is possible. They are shown to be individuals or small bundles of ~2 tubes by AFM (Figure 3.9). Heights of the features are 1.1 – 1.5 nm. The SWNTs are 300 - 1500 nm in length.

![Chemical Structure](image)

**IV**

**Figure 3.9.** AFM image of IPA-SWNTs from water on mica.

Since FeMoC attaches to dd-SWNTs by reacting with the carboxylic acid groups on the ends of the tubes, we wanted to utilize the carboxyl groups in the isophthalic acid
Figure 3.10. AFM image of 1:40 IPA-SWNTs:FeMoC solution, incubated for 4 h. at 50 °C on mica.

Figure 3.11. AFM image of 1:40 IPA-SWNTs:Fe-trimer solution, incubated for 4 h. at 50 °C on mica.

to decorate the side-walls of the IPA-SWNTs with iron catalysts. With more iron in the tube’s vicinity, perhaps the chances of creating an active catalyst would be better. AFM images of a 1:40 IPA-SWNTs:FeMoC solution showed excess catalyst and a few SWNTs with diameters of 2.78 - 4.75 nm (Figure 3.10). The diameter range of the IPA-SWNTs reacted with FeMoC is increased compared to IPA-SWNTs alone. The IPA-SWNTs
Figure 3.12. AFM image of 1:40 IPA-SWNTs: Fe(NO$_3$)$_3$ on mica.

Figure 3.13. AFM image of 1:40 IPA-SWNT:Fe(acac)$_3$ on mica.

reacted with FeMoC have heights which correspond to a single tube (0.8 – 1.4 nm) and FeMoC (2.1 nm).

AFM images of a 1:40 IPA-SWNTs:Fe-trimer solution also showed excess catalyst and SWNTs with diameters of 0.74 - 5.00 nm (Figure 3.11). The diameter range of the IPA-SWNTs reacted with Fe-trimers is consistent with uncoated individual SWNTs (0.74 nm), and heavily coated SWNTs or coated bundles (5.00 nm).
Figure 3.14. AFM image of 1:10 IPA-SWNTs:α-D-glucose on mica.

Figure 3.15. AFM image of 1:10 IPA-SWNTs:L-lysine on mica.

Many SWNTs were found in the IPA-SWNT-Fe(NO₃)₃ sample (Figure 3.12). This is due to the fact that the IPA-SWNTs have a greater solubility in EtOH (300 mg.L⁻¹) than do the dd-SWNTs in CHCl₃ (30 mg.L⁻¹). The single SWNTs in this sample were 0.9 nm in height and the catalyst particles are 2.0 nm in height. The SWNTs are also in bundles of up to 9.8 nm in height. A 1:40 IPA-SWNT: Fe(acac)₃ solution was made.
Only a few SWNTs were evident in this sample (1.4 nm) (Figure 3.13). There was an excess of Fe(acac)$_3$, some of the aggregates were 2.8 nm in height.

In hopes of changing the solubility of the IPA-SWNTs, α-D-glucose was added to a IPA-SWNT in water solution (Figure 3.14). The SWNTs were singles (0.7 – 1.4 nm) and bundles (1.9 – 4.0 nm). In addition to glucose, SWNT coupling with L-lysine was also attempted (Figure 3.15). AFM images showed excess lysine and aggregated SWNTs. The aggregates are made up of bundles that are 2.5 – 2.7 nm in height. Functionalization of the IPA-SWNT-cats seemed not to improve solubility, but rather promote aggregation.

**Conclusion**

Catalysts have been attached to SWNTs, making viable SWNT-cat for SWNT amplification. SWNTs, either dd- or IPA-SWNTs, have been attached to a variety of catalysts, such as FeMoC-EtOH, Fe(NO$_3$)$_3$, FeCl$_2$, FeCl$_3$, and Fe(acac)$_3$. Our collaborators have been working on reductively docking the catalysts to the SWNTs, and then growth on surfaces and in the gas phase. To date, reductive docking and etching has

![Scheme 3.3](image)

**Scheme 3.3.** Reductive docking and growth from SWNT-cat. X is either the carboxyl or pyridine end groups.
been observed for SWNT-cats made with FeMoC, Fe-trimers, and Fe(NO₃)₃. Growth from these reductively docked seeds has been slower to achieve. Growth has been observed so far only for IPA-SWNTs-Fe(NO₃)₃. This work is on-going.

**Experimental**

dd-SWNTs in CHCl₃ (30 mg.L⁻¹) were obtained from the W. E. Billups' Laboratory (Rice University, Houston, TX). IPA-SWNTs in ethanol (300 mg.L⁻¹) were received from J. M. Tour's laboratory (Rice University, Houston, TX). Fe(NO₃)₃, FeCl₂·4H₂O, FeCl₃·6H₂O, Fe(acac)₃, L-lysine, α-D-glucose, and tetraethylene glycol were purchased from Aldrich (St. Louis, MO). Ni(CO)₄ and Fe₂(CO)₉ were purchased from Strem Chemical (Newburyport, MA). 1-hexadecanethiol was obtained from Fluka (Buchs, Switzerland). Diethyl ether was purchased from Fisher Chemical (Fair Lawn, NJ). All chemicals were used as received.

**py-dd-SWNT solution.** 4-hydroxypyridine (0.1 mg, 0.001 mmol) and DCC (0.2 mg, 0.001 mmol) were added to dd-SWNTs in CHCl₃ (10 mL, 30 mg.L⁻¹). The solution was stirred at room temperature overnight.

**FeMoC-EtOH attachment to py-dd-SWNTs.** 5 E-4 M FeMoC-EtOH was prepared by dissolving 90 mg in absolute EtOH (10 mL). 114 µL of the 5 E-4 M FeMoC-EtOH was added to 10 mL of the above py-dd-SWNT solution. The solution was incubated for 4 h. at 30 °C.

**SWNT-cat functionalization with thiol.** py-dd-SWNTs in CHCl₃ (5 mL, 30 mg.L⁻¹) were added to a FeMoC-EtOH solution (200 µL, 50 mM). This solution was
incubated for 4 h. at 50 °C. This solution was added drop-wise to 1-hexadecane thiol (20 µL, 6.5 mM in EtOH) under nitrogen. The solution was then heated to 80 °C for 1 h.

**SWNT-cat functionalization with glycol.** py-dd-SWNTs in CHCl3 (5 mL, 30 mg.L\(^{-1}\)) were added to a FeMoC-EtOH solution (200 µL, 50 mM). This solution was incubated for 4 h. at 50 °C. This solution was added drop-wise to tetraethylene glycol (20 µL, 12 mM in EtOH) under nitrogen. The solution was then heated to 80 °C for 1 h.

1:4 py-dd-SWNTs:FeCl\(_2\). FeCl\(_2\).4H\(_2\)O (9.9 mg, 0.05 mmol) was dissolved in CHCl3 (10 mL) to give a 5 E-3 M FeCl\(_2\) solution. 1 mL of the 5 E-3 M FeCl\(_2\) solution was diluted with CHCl3 (10 mL) to give a 5 E-4 M FeCl\(_2\) solution. 104 µL of the 5 E-4 M FeCl\(_2\) solution was added to py-dd-SWNTs in CHCl3 solution (500 µL, 200 mg.L\(^{-1}\)). The mixture was incubated for 4 h. at 50 °C. The solution was analyzed by AFM.

1:4 py-dd-SWNTs:FeCl\(_3\). FeCl\(_3\).6H\(_2\)O (13.5 mg, 0.05 mmol) was dissolved in CHCl3 (10 mL) to give a 5 E-3 M FeCl\(_3\) solution. 1 mL of the 5 E-3 M FeCl\(_3\) solution was diluted with CHCl3 (10 mL) to give a 5 E-4 M FeCl\(_3\) solution. 104 µL of the 5 E-4 M FeCl\(_3\) solution was added to py-dd-SWNTs in CHCl3 solution (500 µL, 200 mg.L\(^{-1}\)). The mixture was incubated for 4 h. at 50 °C. The solution was analyzed by AFM.

Ni(CO)\(_4\) attempted attachment to py-dd-SWNTs. py-dd-SWNTs in CHCl3 solution (30 mL, 30 mg.L\(^{-1}\)) was placed in a centrifuge tube and placed in an ice-acetone bath. Ni(CO)\(_4\) was added by transferring the gas from the cylinder, which was placed in a warm water bath, via tubing and a glass pipette. The Ni(CO)\(_4\) was allowed to bubble through the SWNT solution for 5 minutes until white solid Ni(CO)\(_4\) was observed in the bottom of the centrifuge tube. The solution was left overnight in the ice-acetone bath to warm to room temperature slowly. A needle was put through the centrifuge vial cap to
allow excess Ni(CO)₄ to evaporate. After being allowed to warm to room temperature overnight, the SWNTs were either floating on top of the cloudy greenish CHCl₃ solution or stuck to the side-walls of the vial. The vial was centrifuged at 4400 RPM for 15 minutes, and then the CHCl₃ was decanted. The SWNT solid was then resuspended in CHCl₃ (5 mL) and analyzed by AFM and IR.

**Fe₃(CO)₁₂ attempted attachment to py-dd-SWNTs.** In glove box, Fe₂(CO)₉ (5 mg, 0.014 mmol) was weighed into a schlenk flask. py-dd-SWNT in CHCl₃ solution (20 mL, 30 mg.L⁻¹) was dried under vacuum, and then suspended in diethyl ether (20 mL). This suspension was added to the Fe₂(CO)₉ and the reddish-brown solution was stirred while exposed to light 24 h. The solution was centrifuged at 4400 RPM for 15 minutes and the orange ether layer [orange due to excess Fe₂(CO)₉] was aspirated. Clean diethyl ether (20 mL) was added and the centrifuge vial was shaken. The vial was centrifuged and the orange ether layer aspirated. This was repeated until the ether layer was clear (total of 5 times). The ether layer was aspirated leaving a brown-black solid. The solid was then suspended in CHCl₃ (5 mL) and analyzed by AFM and IR.

**1:40 IPA-SWNTs:Fe(NO₃)₃.** IPA-SWNT (1.33 mL, 225 mg.L⁻¹) was diluted to with Millipore water (10 mL) to give a 30 mg.L⁻¹ solution. A 5 E-3 M Fe(NO₃)₃ solution was made by dissolving Fe(NO₃)₃ (2 mg, 0.005 mmol) in Millipore water (1 mL). Fe(NO₃)₃ (26 µL, 5 E-3 M) was added to give a 1:40 Fe:SWNT solution. The solution was incubated for 4 h. at 50 °C.

**1:40 IPA-SWNTs:Fe(acac)₃.** A 5 E-3 M Fe(acac)₃ solution was prepared by dissolving Fe(acac)₃ (18 mg, 0.05 mmol) in Millipore water (10 mL). Fe(acac)₃ solution (1 mL, 5 E-3 M) was diluted with Millipore water (10 mL) to give a 5 E-4 M Fe(acac)₃
solution. Fe(acac)$_3$ solution (20 µL, 5 E-4 M) was added to IPA-SWNT solution in water (1 mL, 225 mg.L$^{-1}$). The mixture was incubated for 4 h. at 50 °C.

1:10 IPA-SWNTs:α-D-glucose. A 2 E-2 M glucose solution was prepared by dissolving glucose (36 mg, 0.2 mmol) in Millipore water (10 mL). α-D-glucose solution (100 µL, 2 E-2 M) was diluted with Millipore water (10 mL) to give a 2 E-4 M solution. α-D-glucose solution (100 µL 2 E-4 M) was diluted with Millipore water (10 mL) to give a 2 E-6 M solution. α-D-glucose solution (50 µL, 2 E-6 M) was added to IPA-SWNTs in water solution (1 mL, 225 mg.L$^{-1}$). The solution was incubated for 4 h. at 50 °C, and then analyzed by AFM.

1:10 IPA-SWNTs:L-lysine. A 2 E-2 M L-lysine solution was prepared by dissolving glucose (29 mg, 0.2 mmol) in Millipore water (10 mL). L-lysine solution (100 µL 2 E-2 M) was diluted with Millipore water (10 mL) to give a 2 E-4 M solution. L-lysine solution (100 µL, 2 E-4 M) was diluted with Millipore water (10 mL) to give a 2 E-6 M solution. L-lysine solution (50 µL, 2 E-6 M) was added to IPA-SWNTs in water (1 mL 225 mg.L$^{-1}$). The solution was incubated for 4 h. at 50 °C, and then analyzed by AFM.

References

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Chapter 4

Epoxidation/Cage Opening of C$_{60}$

Introduction

Fullerene research thus far has focused on modification to the outside of the carbon cage to change specific chemical properties, such as solubility or reactivity, to suit a particular target application. Although fullerenes have been shown to undergo facile reduction$^{1,2}$ and to readily react with nucleophiles,$^{3,4}$ oxidation has presented a problem.$^5$ In this chapter, it is our goal to use transition metal catalysis previously known to epoxidize aromatic species to epoxidize fullerenes. The aromatic nature of fullerenes has been well established.$^{10,6}$ The epoxide group is an excellent starting point for further derivatisation, which would facilitate the realization of fullerene applications. More specifically, a fullerene with at least 8 epoxide groups on it could be converted to 16 hydroxide groups, allowing for water solubility. The previous method of polyhydroxylating C$_{60}$ is time consuming, requiring a minimum of 4 days to complete (see Chapter 1).

Fullerenes have previously been epoxidized by several methods, such as ozonation,$^7$ photooxidation,$^8$ electrochemical oxidation,$^9$ or the use of oxidizing agents.$^{10}$ However, these methods have never been able to produce more than 6 epoxide species on a fullerene.

When choosing a catalyst for adding epoxide functional groups to a fullerene, it is essential to pick one that does not bind to C$_{60}$ and one that has been previously proven an efficient epoxidation catalyst for other species. The catalyst that we chose to investigate was Mo(O)$_2$(acac)$_2$. This species is well known as a catalyst for olefin epoxidation in the presence of hydroperoxide.$^{11}$
Scheme 4.1. Catalyst cycle for the Mo(O)\(_2\)(acac)\(_2\) catalyzed epoxidation of olefins.

Since C\(_{60}\) has olefinic characteristics, but does not always behave as one, it was not certain that this catalyst would be effective for C\(_{60}\). Through a systematic investigation of all reaction variables, we have shown that this catalyst does produce as many as 13 epoxide groups per fullerene.

Results and Discussion

Based upon literature precedent an olefin:peroxide:catalyst ratio of 1:1:0.002 was suggested.\(^\text{12}\) However, when this solution was prepared and stirred overnight at room temperature, no epoxidation of C\(_{60}\) was observed by MS. The procedure was repeated increasing the amount of catalyst and peroxide resulting in a ratio of 1:1.33:0.04. This solution did not show any epoxide formation either. I then tried stirring the solution at 60 °C for 24 h. This produced a fullerene monoepoxide, i.e., C\(_{60}\)O. The catalyst and
peroxide concentrations were increased again to a ratio of 1:4:0.4 in an attempt to push the reaction to go further. The solution was divided in half and overnight one part was stirred at room temperature and the other was stirred at 60 °C. The solutions were initially purple, but the heated sample changed to red during the night. The unheated sample turned red after 48 more hours of stirring. Epoxides were produced in both samples. The MS of the heated samples showed $C_{60}(O)_n$, $n = 1 - 5$, while the room temperature reaction showed $n = 1 - 4$. It was evident that the concentrations of peroxide and catalyst were appropriate to achieve some epoxidation and that heating the solutions speed the reaction.

The epoxide product was characterized by MS, UV-visible spectrum, IR, and $^{13}$C NMR (Figures 4.1 – 4.4). We have previously shown that there exists a good correlation between the relative MS peak height (Figure 4.1) and the molar fraction of each $C_{60}(O)_n$ species. Thus, the relative yield of each epoxide (i.e., $n = 1, 2, 3,$ etc) can be determined. The additional peaks in the IR spectrum of the $C_{60}(O)_n$ samples are consistent with the presence of an epoxide (Figure 4.2) as is the bands present in the UV-visible spectrum (Figure 4.3). The IR spectrum of C$_{60}$($O$)$_n$ shows, compared to that of C$_{60}$ alone, additional peaks at 1362, 1260 and 1196 cm$^{-1}$ in the spectrum of the epoxide correspond to the in/out of plane C-O stretching, while the peak at 842 cm$^{-1}$ is characteristic of the C-O-C stretch. The solution $^{13}$C NMR spectrum of C$_{60}$ shows a single resonance at 142.9 ppm. The C$_{60}$($O$)$_n$ $^{13}$C NMR shows a small fullerene peak at 143 ppm, and multiple peaks from 129.1 - 128.3 ppm. The multiple peaks indicate that some of the fullerene’s symmetry has been broken, in our case by the formation of epoxide. Since there are 30 possible sites for an epoxide group to attach, many isomers are possible for $n \geq 2$ making a more detailed analysis difficult.

To investigate the dependence of epoxide formation on reaction time, a solution was prepared using an olefin:peroxide:catalyst ratio of 1:4:0.4. Samples were removed from the reaction mixture at $t = 0, 2, 4, 8, 10, 12, 24, 48$, and 72 hours and analyzed by
Figure 4.1. Representative mass spectrum of $\text{C}_6\text{O}_n$ formed from the catalytic epoxidation of $\text{C}_6\text{O}$ at 60 °C using an olefin:peroxide:catalyst ratio of 1:4:0.4.

Figure 4.2. IR spectra of $\text{C}_6\text{O}$ (blue) and $\text{C}_6\text{O}_n$ (red) formed from the catalytic epoxidation of $\text{C}_6\text{O}$ at 60 °C using an olefin:peroxide:catalyst ratio of 1:4:0.4.

MS. There was a clear dependence of epoxide formation on time of reflux up to 4 hours, after which no additional epoxides are formed (as shown in Table 4.1 and Figure 4.5).
Figure 4.3. UV-visible spectra of C_{60} and C_{60}(O)_{h} formed from the catalytic epoxidation of C_{60} at 60 °C using an olefin:peroxide:catalyst ratio of 1:4:0.4.

Figure 4.5. $^{13}$C NMR of heated sample with an olefin:peroxide:catalyst ratio of 1:4:0.4 in toluene-d_{8}. 
During the first 4 hours of reaction (Figure 4.5) there is the expected increase in the oxidation level of the fullerene, however, it should be noted that the relative yield of C\textsubscript{60}O was greater after 72 hours than at 4 hours! Since the epoxidation of C\textsubscript{60} with MeReO\textsubscript{3}/H\textsubscript{2}O\textsubscript{2} has shown that continued oxidation of C\textsubscript{60} results in the formation of higher oxides (n = 9). Thus in the present case it would appear that the higher oxides C\textsubscript{60}(O)\textsubscript{n} with n > 2 are reacting further.

**Table 4.1.** Data collected from mass spectra of samples taken at different reaction time at 110 °C.

<table>
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<th>MoO\textsubscript{2}(acac\textsubscript{2}) (mg)</th>
<th>\textsuperscript{4}BuOOH (mL)</th>
<th>Time (h.)</th>
<th>Max n C\textsubscript{60}(O)\textsubscript{n}</th>
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</table>
Figure 4.5. Graph of data showing epoxide formation dependence on time of reflux, taking relative abundance into account. Relative abundance was calculated by measuring the heights of all of the peaks and calculating each peak’s height as a percentage of the total.

By varying catalyst concentration it was observed that the number of epoxides/fullerene increases with increasing concentration (Table 4.1 and Figure 4.6). In a similar manner increased \(^{1}BuOOH\) concentration increases the average number of epoxides per \(C_{60}\) (Table 4.1 and Figure 4.7). In each case the percentage yield of C60O appears to increase with increased reagent concentration. Since the MeReO\(_3\)/H\(_2\)O\(_2\) catalyst system shows the expected trend of higher \(n\) values with higher reagent concentration, we propose that the present system must result in the conversion of \(C_{60}(O)_{n}\) where \(n > 1\) to another product.

To explore the dependence of epoxide formations on temperature, a series of reactions were conducted with stirring at different temperatures. It was found that the
Figure 4.6. Graph of data concerning the dependence of relative abundance of epoxides on catalyst concentration.

Figure 4.7. Graph of data concerning the dependence of relative abundance of epoxides on peroxide concentration.
number of epoxides/fullerene increases with increasing temperature up to 60 °C, after which the number of epoxides possible lessens (Table 4.2 and Figure 4.8), again suggesting the conversion of $C_{60}(O)\text{n}$ ($n \gg 1$) to other products. Thus, there are two reactions occurring. The first involves the epoxidation of $C_{60}$. The second reaction involves the subsequent reactions of $C_{60}(O)\text{n}$. As can be seen from the above data, the maximum number of epoxides groups produced from these experiments was $n = 13$. While stirring at 60 °C produced the greatest number of epoxides per fullerene, refluxing temperature produces a higher concentration of epoxides in the sample.

**Table 4.2.** Data collected from mass spectra of samples taken at different temperatures after 24 h.

<table>
<thead>
<tr>
<th>MoO$_2$(acac)$_2$ (mg)</th>
<th>tBuOOH (mL)</th>
<th>Temp (°C)</th>
<th>Max n $C_{60}(O)n$</th>
<th>Solution color</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>3</td>
<td>0</td>
<td>5</td>
<td>purple</td>
</tr>
<tr>
<td>20</td>
<td>3</td>
<td>35</td>
<td>10</td>
<td>reddish purple</td>
</tr>
<tr>
<td>20</td>
<td>3</td>
<td>60</td>
<td>13</td>
<td>red</td>
</tr>
<tr>
<td>20</td>
<td>3</td>
<td>110</td>
<td>7</td>
<td>red</td>
</tr>
</tbody>
</table>

Separation of the fullerene epoxides from unreacted fullerenes and the catalyst was desired. Several attempts were made using DMF, acetone, and/or centrifuging, none of which worked well. HPLC was attempted when the previous methods failed. The HPLC trace of the reaction mixture (Figure 4.11) shows that while there is still some $C_{60}$...
Figure 4.8. Graph of data concerning the dependence of relative abundance of epoxides on temperature.

left in the sample (as shown by the small peak around 9.2 min), most of the $C_{60}$ has been converted to something else (corresponding to the earlier peaks around 3 - 5 min.). This additional product is significantly more polar than $C_{60}$ and $C_{60}(O)_n$. The UV-visible detector indicates that the peak at 5.5 min correspond to a fullerene epoxide. However, the large peaks very early in the spectrum cannot all be conclusively attributed to epoxides. The UV spectra are not consistent with either fullerene or the epoxide, although since fullerenes with such a high number of epoxide groups have never been made before their UV-visible characters are not fully known. Since the mass spectrum of this sample shows only small amounts of the higher epoxides are produced, it is unlikely that the large peaks early in the spectrum are those.

The HPLC and MS results prompted us to go back and reexamine our data. Previously overlooked were the peaks in the MS indicating species with masses less than $C_{60}$. Upon reexamination, it was noted that these peaks came at regular intervals of
Figure 4.9. HPLC trace of a reaction mixture from the MoO$_2$(acac)$_2$ catalyzed epoxidation of C$_{60}$ sample.

Figure 4.10. UV-visible spectrum taken at (a) 9.2 min, (b) 5.5 min, and (c) 4.1 min.
24 mass units (e.g., Figure 4.11). The explanation determined through analyzing this data was that the catalyst was opening the fullerene cage. The loss of 24 mass units corresponds to the loss of 6 carbons atoms and the addition of 3 oxygen atoms (Calcd. = 696.6; Obsd. = 696.1). The fullerene cage was loosing a six-membered ring and gaining three epoxides groups. The major products identified were C\textsubscript{54}O\textsubscript{3}, C\textsubscript{48}O\textsubscript{6}, and C\textsubscript{42}O\textsubscript{9}. The calculated structure for C\textsubscript{54}O\textsubscript{3} is shown in Figure 4.12.

![Figure 4.11.](image1) Mass spectrum of epoxidized sample showing open-cage fullerene peaks.

![Figure 4.12.](image2) Calculated structure of C\textsubscript{54}O\textsubscript{3} formed by the oxidative removal of one C\textsubscript{6} ring and the generation of three furan groups. Oxygen atoms shown in red.
This new observation explains the inconsistent results that were obtained in the epoxidation runs at high temperatures, long reaction times, and high reagent concentrations. For instance, it was odd that for the highest concentration of catalyst, showed no epoxide peaks. If the formation of the cage opened fullerenes is included in the summary of product yield as a function of catalyst concentration (Figure 4.13) then the reason for the low yield of C_{60}(O)_{n} is apparent. Now it can be concluded that the catalyst was working too well, i.e., it was eating away the fullerenes and fullerene epoxides that were initially produced leaving mostly the open-cage fullerenes. The most holes, 4 six-membered rings missing, in the open-cage fullerenes were observed for the highest concentration (100 mg) catalyst sample. Other samples with fullerenes having at least one six-membered ring missing were samples with more than 20 mg catalyst, reflux times longer than 2 h, greater than 3 mL peroxyde and at all temperatures.

![Graph of C_{60}(O)_{n} and open-cage fullerene relative abundance as a function of catalyst concentration.](image)

**Figure 4.12.** Graph of C_{60}(O)_{n} and open-cage fullerene relative abundance as a function of catalyst concentration.
Open-cage fullerenes have been reported before, but never with such simple functionalities surrounding the open hole. Previously reported open-cage fullerenes have had bulky groups around the opening, such as phenyls,\textsuperscript{15} pyridines,\textsuperscript{16} and acetylsl.\textsuperscript{17} With only epoxides or hydroxides surrounding the openings on our cages, the ease of introducing small molecules or ions into the center of the cage would be greater. Open-cage fullerenes are of interest because of possible applications towards endohedral fullerenes. Current methods of producing endohedral fullerenes include introduction of desired material during fullerene formation,\textsuperscript{18} application of high pressures and temperatures,\textsuperscript{19} and ion implantation.\textsuperscript{20,21,22} These methods have encapsulated such molecules and ions such as La,\textsuperscript{23} and alkali metals,\textsuperscript{24} and noble gases.\textsuperscript{25}

We propose that an added advantage to our open-cage fullerenes lies in the nature of the hole itself. Not only do the epoxides surrounding the hole allow for unhindered entrance of the small molecule/ion, but the coordination environment of the hole (3 furan oxygens) also has a crown ether-like structure. After encapsulation of the small molecule/ion, the endohedral fullerene could be exposed to an alkali metal that would complex with the fullerene, closing the hole and trapping the small molecule/ion inside (Figure 4.13).

![Diagram](image)

**Figure 4.13.** Proposed creation of the rational design for an endohedral fullerene.
The cage-opening method could possibly be applied to single-walled carbon nanotubes as a way to open the ends of the tubes, while leaving the sidewalls pristine. Current methods of SWNT end openings include concentrated acid treatment that also leaves side-wall defects. If this method does eat holes into the side-walls of nanotubes, then it could be used a new method of cutting the nanotubes into smaller pieces. Applications for cut nanotubes are described in Chapter 3. There is research continuing in the Barron research group to investigate these possibilities.

**Conclusion**

Fullerenes have been epoxidized via transition metal catalysis. More epoxides have been produced by this method than was previously possible. Through experiment optimization, the greatest number of epoxides per fullerene (n = 13) were produced by stirring the fullerene solution for 24 h at 60 °C with 3 mL tBuOOH and 20 mg Mo(O)\textsubscript{2}(acac)\textsubscript{2} catalyst. This catalyst also opens the fullerene cage. The cage is opened by removal of one six-membered carbon ring and addition of three epoxide groups. The greatest number of segments removed (n = 4) resulted from refluxing for 24 h. with 3 mL tBuOOH and 100 mg catalyst.

**Experimental**

C\textsubscript{60} (99.5%) was obtained from MER corp. (Tucson, AZ). Mo(O)\textsubscript{2}(acac)\textsubscript{2} (99%) was bought from Alfa Aesar (Ward Hill, MA) and anhydrous tBuOOH (5.5 M in decane) was bought from Fluka (Buchs, Switzerland). Toluene-d\textsubscript{8} (99.5%) was purchased from Cambridge Isotope Laboratories, Inc. (Andover, MA). 1 N HCl, glacial acetic acid, sulfuric acid and 1 N NaOH were purchased from Fisher Scientific (Fair Lawn, NJ). All were used as received. High Performance Liquid Chromatography was preformed on a Waters Alliance 2690 HPLC. The column used was a Cosmosil 37980-01 (4.6 mm inner diameter x 250 mm in length) with toluene eluent. The flow rate was 1 mL/min, and a
UV detector was used. The samples analyzed were used as produced from the reaction without work-up. MALDI MS was performed on a BiflexIII Matrix Assisted Laser Desorption Ionization Mass Spectrometer (Bruker Daltonics). The solutions were in toluene with a sulfur matrix.

1:1:0.002 Fullerene:BuOOH:Mo(O)₂(acac)₂. 100 mg (0.14 mmol) fullerene was dissolved in dry degassed toluene (50 mL). This solution was syringed into a flask containing 1 mg (0.003 mmol) Mo(O)₂(acac)₂ under N₂(g). 0.75 mL (0.14 mmol) BuOOH was added and the solution was stirred at room temperature overnight. Alternative reaction conditions are listed in Tables 4.1 and 4.2.

References


Doug paper


Chapter 5

Sodium Crown Ether Solubilized SWNTs

Introduction

As discussed in Chapter 2, single-walled carbon nanotubes (SWNTs) have a myriad of potential applications. In addition to the issue of producing a large quantity of a specific kind of tube, the poor solubility of SWNTs is another obstacle that must be overcome to implement these applications and exploit the unique characteristics of nanotubes.

Several methods have previously been employed to solubilize SWNTs. Ausman, et al. reported in 2000 that it was possible to disperse SWNT bundles in organic solvents, such as toluene via sonication. However, these suspensions were only stable for a few days at most. Covalent methods of functionalization have produced the very promising results so far allowing suspensions/solutions to be stable for months. The first report of extensive functionalization of a SWNT was by Margrave and co-workers in 1998. Functionalization with fluorine created a starting point for further modification of the SWNT sidewalls, which would allow solubility in solvents of almost any kind. As an alternative to fluorination, which required high temperature and pressures, carboxylation of SWNTs was achieved in 2002 by Zhao, et al. via simple acid oxidation. This functionality provided water solubilization in addition to another starting point for further functionalization. Several groups took advantage of this to functionalize tubes with such species as PEG and long chain aliphatic amines to give suspensions of tube bundles in H₂O, THF and 1,2-dichlorobenzene. The basic strategy of these methods is the functionalization of the ends of the SWNT or sidewall defects. A large amount of bundled SWNTs is evident for many of these methods.
As an alternative to defect exploitation, Billups and co-workers introduced free radical chemistry as a route to nanotube functionalization. By decomposing benzoyl peroxide in the presence of an alkyl halide, the SWNT sidewalls are decorated with alkyl functionalities. The discovery of SWNT solubility in oleum (H₂SO₄, 20% free SO₃) led to further functionalization using diazonium chemistry. Up to 90% of the functionalized SWNTs are observed as individuals and the rest exist in small bundles. Solubility up to 240 mg.L⁻¹ in water was achieved as well as good solubility in DMF and EtOH. With sonication, other superacids such as 100% H₂SO₄, trifluoromethanesulphonic (triflic) acid, and chlorosulphonic acid produced solutions with concentrations of SWNTs up to 45 mg.L⁻¹. These solutions were optically homogeneous and it was proposed that the solubilized tubes existed as protonated polycarbocations balanced by conjugate base anions.

All of the above covalent functionalization methods have one problem in common: extensive covalent functionalization modifies SWNT properties by disrupting the continuous \( \pi \)-system of SWNTs. Noncovalent methods of solubilization are therefore preferable since the electronic nature of the SWNT is not perturbed. The most popular method of noncovalent SWNT solubilization is the use of surfactants. In 2003, the application of a range of surfactants, such as SDS, Triton X-405, and Pluronic of several molecular weights, enabled solutions with solubilities of 0.5 mg.mL⁻¹ in water to be achieved. Unfortunately, this process is time consuming and the final yield is very low. The use of sodium dodecylbenzene sulphonate and long sonication times to get a 20 mg.mL⁻¹ suspension of SWNTs (>63% as individuals) that was stable for over 3 months. Polymer wrapping has also been used to solubilize SWNT. Polymers such as poly(methaohylenevinylene), tetraformylporphyrins and diaminopyrenes, and organic dyes have been used to produce soluble suspensions that are stable up to two years. Encasing SWNTs within cross-linked, amphiphilic copolymer micelles enable enhanced solubility in polymer matrices, polar and non-polar solvents and was suggested
to be especially good for nanocomposites. Non-wrapping, short, rigid conjugated polymers allow access to a majority of the SWNT surface.\textsuperscript{17} Although surfactants and polymers have provided much improved solubility of tubes and they do not destroy the structure of the SWNT, there are inherent problems in the methods. The surfactants and polymers block direct access to the SWNT sidewall. The surfactants are difficult to remove and often frustrate the clarity of AFM images. Also, these methods use sonication and/or high shear mixing to initiate dispersal that often results in cutting the tubes and therefore loss of high aspect ratio.\textsuperscript{18}

In 2004, researchers at Rice University used a Birch Reduction to solubilize individual tube in liquid ammonia.\textsuperscript{19} Although this is not an ideal solvent, as it is a gas at room temperature, the method allows direct access to the SWNT surface for further modification through addition of alkyl halides that yield solubility in CHCl\textsubscript{3}, THF, and DMF. Alkali metals may also be used to reduce the SWNTs, creating polyelectrolyte salts that are soluble in polar solvents such as DMSO, NMF, DMF, and NMP.\textsuperscript{20} These solutions are stable for over one year under inert atmosphere and show Raman spectra typical of charged SWNTs.

We wanted to investigate the possibility of using a sodium crown ether complex to create SWNT salts. The complex would impart some air stability to the solution which the naked alkali solutions previously reported lack. In addition, the crown ether complex should increase the number of solvents in which the salt would be soluble. Dibenzo-18-crown-6 is a well-studied molecule and is known to form stable complexes with alkali metals, like Na\textsuperscript{+}.\textsuperscript{21,22} Although the potassium complex forms more readily, the sodium complex is more stable.\textsuperscript{23} Also, once formed, the sodium complex is soluble in toluene, EtOH, H\textsubscript{2}O, MeOH, CH\textsubscript{2}Cl\textsubscript{2}, hexane, and DMF. This means that we could utilize the salt forming ability of sodium in common solvents. The salt-forming method we propose offers direct access to SWNT surface (i.e., no covalently or non-covalently bound
moieties on the SWNT surface), wider range of solubilites, and air stability upon completion of the reaction.

**Results**

Dibenzo-18-crown-6 was added to a suspension of SWNTs in toluene over a sodium-mercury amalgam. A cloudy grey SWNT solution appeared to be produced indicative of a dispersion of SWNTs in the solution.

AFM analysis of the solution in toluene showed what looked like straight bundles of tubes of 2.5 - 6.7 nm height with lengths of singles ~576 nm (Figure 6.1a). The straightness of the bundles was unexpected and is atypical of previously observed SWNT samples solubilized by different methods. The procedure was repeated for purified SWNTs. The AFM images of this sample differed from that of the sample prepared from raw SWNTs in that the features appeared thicker and looked less like SWNTs (Figure 6.1b) with features of 18.5 – 48.3 nm in height. The difference in the two AFM images prompted us to take an image of dibenzo-18-crown-6 alone in toluene (Figure 6.1c). As may be seen from a comparison with Figures 1a and 1b, the images with and without raw SWNTs looked the same, suggesting the straight features observed in the solubilized SWNTs in toluene were primarily dibenzo-18-crown-6.

Since the images obtained thus far were mostly, if not entirely, dibenzo-18-crown-6, a sample with 5 times the previously used quantity of purified SWNTs was made. No difference was evident in AFM images. A sample of purified SWNTs with an excess of Na was produced in the hope that the excess Na would bring more SWNTs into solution. However, no appreciable differences in the AFM images were observed. Half the normal amount of dibenzo-18-crown-6 was used to make another solution, however, no change was observed in the products by AFM. Clearly the excess dibenzo-18-crown-6 was precluding imaging of the SWNTs that appeared present based upon the color of the solution. It was then thought that perhaps the excess dibenzo-18-crown-6 could be
Figure 5.1. AFM images on mica of the products from the reaction of Na/Hg amalgam, dibenzo-18-crown-6, and (a) raw or (b) purified SWNTs in toluene. The AFM of dibenzo-18-crown-6 from toluene solution is shown for comparison (c).

removed by centrifuging the sample. Indeed, the AFM analysis of the clear gray supernatant after centrifugation showed many single tubes (or small bundles) with
heights in the range of 1.1 - 1.6 nm, and lengths up to 400 nm (Figure 6.2). Thus, it appears that the reduction of SWNTs with Na/Hg amalgam in toluene does occur. Furthermore, the presence of the dibenzo-18-crown-6 results in the resulting complex to be soluble in toluene. We propose that the SWNTs are solubilized, albeit at a low level, by the formation of an ionic complex between the [Na(dibenzo-18-crown-6)]⁺ complex and the reduced SWNTs (Scheme 5.1).

![AFM image](image)

**Figure 5.2.** AFM image of the products from the reaction of Na/Hg amalgam, dibenzo-18-crown-6, and purified SWNTs in toluene after removing excess dibenzo-18-crown-6 by centrifugation on mica.

The Raman spectrum of the [Na(dibenzo-18-crown-6)]ₙ[SWNT] complex looks almost exactly like the toluene spectrum, with the exception of the characteristic SWNT peak at 1593 cm⁻¹. The toluene spectrum has a slight hump at 1588 cm⁻¹, but the sharpness of the peak at 1593 cm⁻¹ in the complex spectrum indicates that there are SWNTs present in the sample solution, albeit in low concentration.

The ATR-IR spectrum of raw SWNTs (Figure 5.4a) has few characteristic peaks and therefore contributes little to the spectrum of the [Na(dibenzo-18-crown-6)]ₙ[SWNT]
Scheme 5.1. Representation of the reaction between Na/Hg amalgam, dibenzo-18-crown-6, and purified SWNTs in toluene and the formation of a [Na(dibenzo-18-crown-6)]ₙ[SWNT] complex.

complex (Figure 5.4b). The [Na(dibenzo-18-crown-6)]ₙ[SWNT] complex is almost identical to what the manufacturer reports for dibenzo-18-crown-6. The only differences are that in the spectrum of the complex there is a hump around 3300 cm⁻¹ and a small peak around 1750 cm⁻¹.

MALDI-MS data (Figure 5.5) was not expected to show any SWNT peaks, as their masses are too great and widely varied for this kind of analysis. However, the MS does show the Na(dibenzo-18-crown-6) molecule. Its molecular weight is calculated to be 383.390 and is found to be 383.136.

The TGA of the [Na(dibenzo-18-crown-6)]ₙ[SWNT] complex in air shows the loss of organics, such as residual toluene, below 200 °C. Dibenzo-18-crown-6 has a melting point of 163 °C and will decompose starting around 250 °C. SWNTs will decompose in air around 400 °C.

As an alternative to centrifuging the sample, extraction into EtOH was attempted. Since dibenzo-18-crown-6 is soluble in toluene, but less soluble in ethanol²³ centrifuging the sample was not necessary, and the extraction of the sample into EtOH left the excess dibenzo-18-crown-6 in the toluene. After extraction into EtOH, the SWNTs appeared as
Figure 5.3. Raman spectra of toluene (red) and \([\text{Na(dibenzo-18-crown-6)}]_n[\text{SWNT}]\) complex in toluene (black).

small, curled bundles (Figure 5.7) with heights of 0.6 – 4.4 nm and lengths of 341 – 1074 nm.

Given these results, extraction into other solvents was also attempted. The range of solvents investigated is shown in Table 5.1. The resulting solutions were investigated by UV-visible spectroscopy from which the solubility of the \([\text{Na(dibenzo-18-crown-6)}]_n[\text{SWNT}]\) complex was obtained. The SWNT concentrations are estimates based on the absorption coefficient of the 763 nm band for suspensions in water of SWNTs solubilized in 1% SDS (0.043 mg.L\(^{-1}\)). This estimate was considered appropriate to use for our calculations since it is for unfunctionalized SWNTs and isn’t affected by the SDS concentrations at that wavelength. In toluene solution the van Hooves peaks are slight (Figure 5.8a), but observed, and concentration was determined to be 2.2 mg.L\(^{-1}\). The van Hooves are also observed in the ethanol solution (Figure 5.8b) and the concentration of SWNTs was found to be 2.4 mg.L\(^{-1}\).
Figure 5.4. ATR-IR spectra of (a) raw SWNTs and (b) $[\text{Na}($dibenz-18-crown-6$)]_n[\text{SWNT}]$ complex.
Figure 5.5. Maldi-MS of $[\text{Na(dibeno-18-crown-6)}]_n[\text{SWNT}]$ complex.

For toluene, CHCl$_3$ and EtOH, a clear light gray solution was obtained. In contrast, the solution in MeOH was cloudy and in H$_2$O, the SWNTs were mostly aggregated between the aqueous and toluene layers. The van Hooves peaks were most evident in the CH$_2$Cl$_2$, which also had the highest SWNT concentration.

**Conclusion**

Single-walled carbon nanotubes have been solubilized via a new method and characterized by AFM, Raman, IR, and UV-visible spectroscopy. Creation of a SWNT salt with the Na$^+$ counter ion complexed with dibenzo-18-crown-6 allows for modest solubility in a variety of solvents, especially CH$_2$Cl$_2$ and DMF, without sidewall functionalization. In toluene the SWNT solution is contaminated by excess dibenzo-18-crown-6, but this can be reduced by centrifugation.
Figure 5.6. TGA of (a) [Na(dibenzo-18-crown-6)]_n[SWNT] complex and (b) dibenzo-18-crown-6.
Figure 5.7. AFM image of the products from the reaction of Na/Hg amalgam, dibenzo-18-crown-6, and purified SWNTs in toluene after extraction into EtOH.

Figure 5.8. UV-visible spectrum of the [Na(dibenzo-18-crown-6)]_n[SWNT] complex in (a) toluene and (b) EtOH.
Table 5.1. The concentration of Na/dibenzo-18-crown-6 solubilized purified SWNTs in various solvents.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Absorption at 763 nm</th>
<th>[SWNT] (mg.L⁻¹)</th>
<th>Dielectric constants at 20 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₂Cl₂</td>
<td>0.604</td>
<td>14.05</td>
<td>9.08</td>
</tr>
<tr>
<td>DMF</td>
<td>0.491</td>
<td>11.42</td>
<td>37.06</td>
</tr>
<tr>
<td>hexane</td>
<td>0.200</td>
<td>4.65</td>
<td>1.89</td>
</tr>
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<td>toluene</td>
<td>0.163</td>
<td>3.79</td>
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</tr>
<tr>
<td>EtOH</td>
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<tr>
<td>CHCl₃</td>
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<tr>
<td>H₂O</td>
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<td>0.10</td>
<td>80.10</td>
</tr>
</tbody>
</table>

Experimental

Experimental and materials as described in Chapters 1 – 4. For the initial experiment, raw HiPCO SWNTs from batch 113.1 were used without purification. For subsequent reactions, purified batch 143.2 was used received.²⁴ Dibenzo-18-crown-6, Hg, and Na were purchased from Aldrich Chemical and used as received. Reagent grade solvents were purchased from Fisher Chemical and used as received, except for toluene which was distilled over sodium prior to use.

Reaction of SWNTs with Na/Hg amalgam in the presence of dibenzo-18-crown-6. A Na/Hg amalgam was prepared under nitrogen by adding cleaned pieces of
Na\(_{(s)}\) (200 mg, 8.7 mmol) to Hg (20 mL, 1.35 mol). Dry degassed toluene (50 mL) was syringed into the Schlenk flask. Purified SWNTs (10 mg) were added, followed by dibenzo-18-crown-6 (300 mg, 0.83 mmol). The mixture was stirred for 4 days. After stirring, the cloudy grey toluene layer was separated from the amalgam and characterized by AFM. The reaction was repeated with (a) purified SWNTs (50 mg), or (b) excess Na (130 mg, 5.65 mmol), or (c) less dibenzo-18-crown-6 (150 mg, 0.42 mmol). All other quantities being kept the same for each run.

\([\text{Na(dibenzo-18-crown-6)}]_n[\text{SWNT}]\). A Na/Hg amalgam was prepared under nitrogen in a Schlenk flask by adding cleaned pieces of Na\(_{(s)}\) (200 mg, 8.7 mmol) to Hg (20 mL, 1.35 mol). Dry degassed toluene (50 mL) was syringed into the Schlenk flask. Raw SWNTs (10 mg) were added, followed by dibenzo-18-crown-6 (300 mg, 0.83 mmol). The mixture was stirred for 4 days. After which, the cloudy grey toluene layer was separated from the amalgam by transferring to a clean Schlenk flask. A portion of this solution (3 mL) was extracted into EtOH (5 mL). The solutions were characterized by UV and AFM. Extraction into a range of solvents was also performed, see Table 5.1.

References


Chapter 6

Effect of Carbon Nanomaterials on Calcium Carbonate Crystallization

Introduction

Calcium carbonate (CaCO₃) comprises many common materials such as marble, limestone, and chalk. It is used as a coating for or additive to medicines, foods, papers, plastics, and printing ink. Biomineralization of calcium carbonate occurs in many organisms such as eggshells, coral reef, and shellfish.¹,² It plays an important role in the immobilization of CO₂ in the global environment.³,⁴

Calcium carbonate has three major polymorphic structures: calcite, aragonite, and vaterite. Calcite is the most stable at room temperature and atmospheric pressures. Calcite is rhombic in shape and is the least soluble of the three polymorphs. Aragonite is rod-like in structure, less stable and more soluble than calcite. Aragonite formation is preferred at elevated temperatures, higher pH or in the presence of large cations.⁵,⁶ Vaterite is the least stable, most soluble, is spherical in shape, and is a precursor to the other polymorphs.⁷

Although the mechanism of calcium carbonate crystallization is not completely understood, nucleation theory proposes that fine globular particles form when Ca²⁺ and CO₃²⁻ ions meet in solution. Nucleation produces a mixture of vaterite, which then turns to calcite with aging.⁸ When soluble additives are present, the additive can either serve as a nucleation site, or attach to a crystal face soon after formation and affect subsequent crystal growth orientation, size, morphology, and crystallization rate.⁹ Additives that effect calcium carbonate crystallization that have been investigated in the past include large cations,¹⁰ simple alcohols,¹¹ peptides,¹² ammonia,¹³ and polymers.¹⁴

Crystallization of calcium carbonate is interesting because despite the extensive work done in this field there is still much to be known about this everyday material.
Calcium carbonate-organic hybrid materials, such as seashells, are of interest due to their high mechanical strength (up to 3000 times that of the mineral itself) and unusual optical properties. Synthetic attempts to reproduce this effect using organic matrixes have thus far resulted in inferior products. Especially interesting is the concept of fullerene based organic-inorganic nanocomposites for applications such as nonlinear optics and photoelectrochemistry. In the past they have been prepared using porous inorganic oxides or aerogels. 

Previously in the Barron group it was demonstrated that polyhydroxylated fullerenes (fullerenols) had the ability to nucleate growth of silica by liquid phase deposition (LPD). Based upon this result we were intrigued by the idea of both the production of duce a fullerenol or single walled carbon nanotube (SWNT) based \( \text{CaCO}_3 \) nanocomposite and the effect of fullerenols on the nucleation of \( \text{CaCO}_3 \). In this chapter the effect of various fullerenes and SWNTs on the crystallization of calcium carbonate is reported.

**Results and Discussion**

Calcium carbonate was precipitated from a saturated solution at 30 °C in 24 h (see Experimental). The ESEM image (Figure 6.1a) and powder XRD spectrum (Figure 6.2a) of the precipitate was consistent with the formation of calcite. The crystals were 1.3 – 5.0 μm in size. Elevating the temperature to 50 °C produced rhombic crystals of approximately the same size (0.75 – 4 μm). The crystals were slightly deformed, as can be seen by the rounded edges (Figure 6.1b). The XRD data for this sample was consistent with calcite, although the peaks are broader than in the 30 °C sample (Figure 6.2b) indicating that the crystallinity is reduced for precipitation at higher temperatures.

**Nucleation of CaCO\(_3\) with \( C_{60}(\text{OH})_n \).** Calcium carbonate precipitation in the presence of fullerenols showed spherical clusters of ~127 μm diameter, 5-pointed flower shaped clusters of ~100 μm in and triangular crystals ~ 10 μm/side (Figure 6.3 and 6.4). XRD analysis indicates that there is a mixture of calcite (JCPDS # 5-586) and
Figure 6.1. ESEM images of CaCO$_3$ precipitation at (a) 30 °C and (b) 50 °C.

vaterite (JCPDS # 33-286) phases in the sample (Figure 6.5). Based upon the relative intensity of the peaks the calcite phase is the major phase. Instead of filtration to remove the precipitate from solution, the water was evaporated in one of the CaCO$_3$/fullerenol samples. Spherical clusters of ~57 μm diameters, 5-pointed flower shaped clusters ~50 μm in diameter, and triangular crystals ~ 2 μm per side were observed (Figure 6.6). By evaporating the water instead of filtering, the features are smaller but less distinct (best
Figure 6.2. Powder XRD spectrum of CaCO₃ precipitation at (a) 30 °C and (b) 50 °C.
observed in triangular features). Clearly, the presence of the fullerenols has a major effect on the morphology of the CaCO₃ crystals and a minor effect on the crystal phase. The proposed mechanism for C₆₀(OH)ₙ nucleation involves the reaction of the fullerenol hydroxides with the H₂SiF₆ causing precipitation of SiO₂ onto the fullerene cage (Eq. 6.1). The fullerenol hydroxide group acts in a similar manner to the addition of water as an initiator for silica growth by LPD (Eq. 6.2).

\[
\text{H}_2\text{SiF}_6 + 2\text{OH}^- \xrightarrow{\text{eq.}} \text{SiO}_2 + 2\text{F}^- + 4\text{HF}
\]

\[
\text{H}_2\text{SiF}_6 + 2\text{H}_2\text{O} \xrightarrow{\text{eq.}} \text{SiO}_2 \downarrow + 6\text{HF}
\]

(Figure 6.3. ESEM image of CaCO₃ precipitated in the presence of fullerenes.

Since pH is known to have an effect on the crystallization of CaCO₃ a similar reactive seeding may be occurring. To ascertain if a change of pH (due to the fullerene-hydroxide) is the cause of the morphology change (rather than the actual fullerenol) the pH was monitored during the crystallization of CaCO₃ at 30 °C (Figure 6.7) and the pH of the various CaCO₃ solutions with additives were determined (Table 6.1). While fullerenols in
Figure 6.4. ESEM images of the various morphologies formed for the growth of CaCO₃ in the presence of fullerenols.
Figure 6.5. Powder XRD data for CaCO$_3$ (black) and CaCO$_3$ precipitated in the presence of fullerenols (red). Both samples were formed at 30°C.

H$_2$O have a pH of 8.3, the solution pH of the combination of fullerenol and CaCO$_3$ (7.7) is within the range observed during precipitation of CaCO$_3$, see Table 6.1. In order to further ensure that the morphological changes observed by the addition of C$_{60}$(OH)$_n$ was not due to changes in pH with the addition of fullerenols the precipitation was accomplished in the presence of NaOH. Calcium carbonate precipitation with NaOH produced inter-grown rhombic crystals ~4 μm and rod-like crystals ~400 nm wide and 2 μm long (Figure 6.8). Although this is a change from what was observed in the ESEM images of CaCO$_3$ by itself, it is also different from what is observed with CaCO$_3$ is precipitated in the presence of fullerenols. Elevated pH levels favor aragonite formation (which has rod-like morphology). The XRD spectrum showed a mixture of calcite and aragonite (JCPDS # 45-1471) (Figure 6.9). Calcium carbonate precipitation with excess NaOH showed similar results. Thus, the morphology changes observed with the addition
Figure 6.6. ESEM images of CaCO₃ formed in the presence of fullerenols after evaporation of the solution.
Figure 6.7. Graph of change in pH during crystallization of CaCO₃ at 30 °C.

Table 6.1. pH of solutions used for precipitation of CaCO₃.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Concentration</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Millipore water</td>
<td>n/a</td>
<td>6.3</td>
</tr>
<tr>
<td>C₆₀(OH)ₙ</td>
<td>0.018</td>
<td>8.3</td>
</tr>
<tr>
<td>C₆₀</td>
<td>0.028</td>
<td>6.1</td>
</tr>
<tr>
<td>CaCO₃</td>
<td>saturated (0 h)</td>
<td>5.4</td>
</tr>
<tr>
<td>CaCO₃</td>
<td>saturated (24 h)</td>
<td>7.8</td>
</tr>
<tr>
<td>CaCO₃ + C₆₀(OH)ₙ</td>
<td>sat. soln./0.018 mmol</td>
<td>7.7</td>
</tr>
<tr>
<td>CaCO₃ + C₆₀</td>
<td>sat. soln./0.028 mmol</td>
<td>7.6</td>
</tr>
</tbody>
</table>
Figure 6.8. ESEM image of CaCO$_3$ precipitated in the presence of NaOH (1.25 mM) at a pH of 8.

Figure 6.9. Powder XRD spectrum of CaCO$_3$ precipitation with NaOH.

of C$_{60}$(OH)$_n$ are not due to changes in the pH of the solution, but the reactivity of the fullereneol.
In previous work, fullerenols have been shown to seed the growth of silica spheres, while insoluble C$_{60}$ has produced only amorphous silica identical in morphology of LPD silica in the absence of any additive.\textsuperscript{23} Similar results were observed for calcium carbonate. Fullerenols nucleated the growth of calcite and vaterite crystals of new morphologies, as seen by ESEM and powder XRD, while fullerenes did not seem to have any effect. Since fullerenes are not soluble in water, the difference between precipitation

\begin{center}
\textbf{Figure 6.10.} ESEM image of CaCO$_3$ precipitation with (a) SDS and (b) SDS-C$_{60}$.
\end{center}
with fullerenes and with fullerensols is not surprising. In order to determine if it is the solubility of the C$_{60}$(OH)$_n$ that facilitates the morphological changes, a method of solubilizing C$_{60}$ was desired. Sodium dodecylsulfate (SDS) has been used solubilize C$_{60}$ in water solutions. To see if the addition of surfactant would have any effect on increasing the solubility of C$_{60}$, SDS was added to the to CaCO$_3$ solution along with C$_{60}$. ESEM images of CaCO$_3$ precipitation with surfactant alone and CaCO$_3$ precipitation with surfactant and fullerenes are shown in Figure 6.10. The amorphous precipitate is undoubtedly due to the SDS and has no relation to fullerenes.

**Precipitation of CaCO$_3$ in the presence of functionalized SWNTs.** In a similar manner to the seeding of silica or CdS by fullerensols, SWNTs have been coated by these materials. Since neither purified SWNTs nor fluorinated SWNTs (F-SWNTs) are soluble in water, CaCO$_3$ precipitation in the presence of these materials appears to be the same as for C$_{60}$ or in the absence of an additive. Precipitation with surfacted F-SWNTs produced CaCO$_3$ morphologies similar to that of SDS-surfacted C$_{60}$.

Since the hydroxyl groups on fullerenes provided water solubility and possibly the nucleation sites for CaCO$_3$ precipitation, hydroxylated SWNTs seemed an obvious material for investigation. Hydroxylated SWNTs were obtained from the Wilson Lab (Rice University) and were made by Fenton’s reaction.

The addition of solid HO-SWNTs to the saturated CaCO$_3$ solution resulted in no change in the morphology or crystal phase of the precipitated CaCO$_3$. This appears to be because the HO-SWNTs do not readily dissolve even though the solution pH was adjusted to 9, where these SWNTs are most soluble in water. This problem may be avoided by first dissolving the HO-SWNTs in pH 9 water, then adding this solution to the saturated CaCO$_3$ solution, see Experimental. ESEM images of precipitation from a CaCO$_3$ saturated solution when hydroxylated SWNT solution was added to it did show evidence of coated SWNTs embedded in the deformed calcite crystals (Figure 6.11). The CaCO$_3$-SWNT composites are 60 – 115 nm thick. Given that HO-SWNTs have been
reported to usually be isolated as individuals SWNTs, approximately 0.8 – 1.6 nm in height, the CaCO₃ coating may be estimated to be 30 - 57 nm thick (radius around bundle).

Figure 6.11. ESEM images of CaCO₃ precipitated in the presence of HO-SWNTs.

Calcium carbonate precipitation in the presence of isophthalic acid functionalized-SWNT (IPA-SWNT) solution is shown in the ESEM images in Figure 6.12. Isophthalic acid functionalized SWNTs were obtained from the Tour Lab (Rice
University). They are made in a superacid solvent via a radical initiated aryldiazonium functionalization reaction.\textsuperscript{28} Isophthalic acid functionalized SWNTs are more soluble in water than the hydroxylated SWNTs (300 mg.L\textsuperscript{-1} and 20 mg.L\textsuperscript{-1}, respectively) and can be used at neutral pH. Like the HO-SWNT mediated CaCO\textsubscript{3} precipitation, coated SWNTs are evident embedded in the deformed CaCO\textsubscript{3} crystals. The coated SWNTs are

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{image.png}
\caption{ESEM images of CaCO\textsubscript{3} precipitation with isophthalic acid SWNTs.}
\end{figure}
25 – 50 nm thick. Since isophthalic acid functionalized SWNTs have been reported to usually be isolated in bundles of 2 - 3 SWNTs, approximately 1.6 – 4.5 nm in height, a coating thickness of 12 - 23 nm is estimated.

Powder XRD analysis of both of the water-soluble SWNT samples did not show spectra corresponding to any of the three polymorphic phases. The XRD indicates that the samples are essentially amorphous (Figure 6.13). Thus, the surface functionalized SWNTs affect both the morphology and the crystallinity of CaCO₃.

![Graph](image)

**Figure 6.14.** Powder XRD spectrum of CaCO₃ precipitation with hydroxylated SWNTs.

**Nucleation of BaCO₃ with C₆₀(OH)ₙ.** In order to ascertain whether fullerenols would have an effect on the precipitation of other inorganic materials, barium carbonate was substituted for calcium carbonate. Barium carbonate’s most stable polymorph, witherite, has a hexagonal rod-like structure as can be seen in Figure 6.14. When C₆₀(OH)ₙ is added to a saturated BaCO₃ solution, the rod-like structure persists, but the
Figure 6.14. ESEM images of BaCO$_3$ precipitation at 30 °C.

crystals seem to be fused together (Figure 6.15). The XRD diffraction patterns (Figure 6.16) are the same for both and consistent with witherite (JCPDS # 05-0378).

Conclusions

The addition of water-soluble species such as fullerenols and hydroxylated and isophthalic acid functionalized SWNT solutions change the morphology and crystal phase of CaCO$_3$ precipitates. It is interesting to note that fullerenols produce star-shaped
calcite crystals that may be related to the 5-fold symmetry of the fullerene cage. The effect on crystal growth of the $C_{60}(OH)_n$ is not a simple function of the pH of the solution, although it may be due to reactivity of the hydroxyl groups. Precipitation with water-soluble hydroxylated and isophthalic acid functionalized SWNTs produces CaCO$_3$ coated SWNTs with the CaCO$_3$ being amorphous rather than crystalline. Carbon materials that are not water-soluble, such as $C_{60}$, purified SWNTs, and F-SWNTs have no impact on CaCO$_3$ crystallization.
Figure 6.16. Powder XRD spectra of BaCO$_3$ (red) and BaCO$_3$ precipitation with fullerensols (black).

Experimental

Fullerenes were obtained from MER corp. (Tucson, AZ). Fullerensols synthesized according to a published procedure.$^{30}$ For modifications to the procedure and chemicals used in the synthesis refer to Chapter 1. Purified SWNTs were obtained from CNI (Houston, TX).$^{31}$ Fluorinated SWNTs were obtained from John L. Margrave’s laboratory (Rice University).$^{32}$ Cut (ca. 30 nm in length) HO-SWNTs were used as received from Lon Wilson’s laboratory (Rice University).$^{33}$ Isophthalic acid functionalized SWNT solution was used as received from James Tour’s laboratory (Rice University).$^{34}$ CaCO$_3$ precipitated powder was purchased from Mallinckrodt (St. Louis, MO). Buffers of pH 4.01, 7.00, and 10.01, Ba(OH)$_2$, NaOH and 1 N NaOH solution were purchased from Fisher Chemical (Fair Lawn, NJ).

Powder X-ray diffraction data was obtained using a Siemens Powder Diffraktometer. An emission current of 20 mA and an accelerating voltage of 30 kV were used. The angles analyzed were between 20 and 80°. The step size was 0.1° and each step
was counted for 10 seconds. The sample was mounted to the sample holder with double-sided tape. The pH measurements were taken on an 230 A 230 A Orion pH meter calibrated using buffer solutions of pH 4.01, 7.00, and 10.01.

**Calcium carbonate precipitation.** A solution of CaCO$_3$ (2 g.L$^{-1}$) was prepared by dissolving CaCO$_3$ (200 mg, 2.0 mmol) in Millipore water (100 mL). This was stirred for 1 h in a 30 °C water bath with CO$_2$ bubbling through the solution. The excess CaCO$_3$ solid was removed by filtration. Stirring was resumed at 30 °C for 3 h with further bubbling of CO$_2$. Precipitation occurred when the solution was allowed to rest at 30 °C for 48 h. The resulting white precipitate was collected via filtration and characterized by scanning electron microscopy and XRD. Similar conditions were used for precipitation at 50 °C.

**Calcium Carbonate precipitation with fullerene(s).** A solution of CaCO$_3$ (2.0 g.L$^{-1}$) was prepared by dissolving CaCO$_3$ (200 mg, 2.0 mmol) in Millipore water (100 mL). This was stirred for 1 h in a 30 °C water bath with CO$_2$ bubbling through the solution. The excess CaCO$_3$ solid was removed by filtration. C$_{60}$(OH)$_n$ (20 mg, 0.018 mmol) was added to give a 0.18 mM solution, and the pH was measured. Stirring was resumed at 30 °C for 3 h with further bubbling of CO$_2$. Precipitation occurred when the solution was allowed to rest at 30 °C overnight. The resulting brown precipitate was collected via filtration and by solvent evaporation, and then characterized by SEM and powder XRD.

**Calcium carbonate precipitation with C$_{60}$.** A solution of CaCO$_3$ (2.0 g.L$^{-1}$) was prepared by dissolving CaCO$_3$ (200 mg, 2.0 mmol) in Millipore water (100 mL). This was stirred for 1 h in a 30 °C water bath with CO$_2$ bubbling through the solution. The excess CaCO$_3$ solid was removed by filtration. C$_{60}$ (20 mg, 0.028 mmol) was added
and the pH of the solution was taken. Stirring was resumed at 30 °C for 3 h with further bubbling of CO₂. Precipitation occurred when the solution was allowed to rest at 30 °C for 48 h. The resulting grey precipitate was collected via filtration and characterized by SEM and XRD.

**Calcium carbonate precipitation with surfactant.** A solution of CaCO₃ (2.0 g.L⁻¹) was prepared by dissolving CaCO₃ (200 mg, 2.0 mmol) in Millipore water (100 mL). This was stirred for 1 h in a 30 °C water bath with CO₂ bubbling through the solution. The excess CaCO₃ solid was removed by filtration. SDS (10 mL, 1% solution) in water solution was added to give an overall 0.1% SDS concentration. Stirring was resumed at 30 °C for 3 h with further bubbling of CO₂. Precipitation occurred when the solution was allowed to rest at 30 °C for 24 h. The resulting white precipitate had a pearly luster. It was collected via filtration and by solvent evaporation, and then characterized by SEM and powder XRD.

**Calcium carbonate precipitation with C₆₀ and surfactant.** A solution of CaCO₃ (2.0 g.L⁻¹) was prepared by dissolving CaCO₃ (200 mg, 2.0 mmol) in Millipore water (100 mL). This was stirred for 1 h in a 30 °C water bath with CO₂ bubbling through the solution. The excess CaCO₃ solid was removed by filtration. C₆₀ (15 mg 0.021 mmol) and SDS (10 mL, 1% solution) in H₂O solution were added to give an overall SDS concentration of 0.1%. Stirring was resumed at 30 °C for 3 h with further bubbling of CO₂(g). Precipitation occurred when the solution was allowed to rest at 30 °C for 24 h. The resulting brown precipitate had a pearly luster. It was collected via filtration and by solvent evaporation, and then characterized by SEM and XRD.
Calcium Carbonate precipitation with NaOH. A solution of CaCO₃ (2.0 g.L⁻¹) was prepared by dissolving CaCO₃ (200 mg, 2.0 mmol) in Millipore water (100 mL). This was stirred for 1 h in a 30 °C water bath with CO₂ bubbling through the solution. The excess CaCO₃ solid was removed by filtration. NaOH (5.0 mg, 0.14 mmol) was added and stirring was resumed at 30 °C for 3 h with further bubbling of CO₂. Precipitation occurred when the solution was allowed to rest at 30 °C overnight. The resulting white precipitate was collected via filtration and by solvent evaporation, and then characterized by SEM and XRD.

Calcium carbonate precipitation with SWNTs. A solution of CaCO₃ (2.0 g.L⁻¹) was prepared by dissolving CaCO₃ (200 mg, 2.0 mmol) in Millipore water (100 mL). This was stirred for 1 h in a 30 °C water bath with CO₂ bubbling through the solution. The excess CaCO₃ solid was removed by filtration. SWNTs (20 mg) were added, and stirring was resumed at 30 °C for 3 h with further bubbling of CO₂. Precipitation occurred when the solution was allowed to rest at 30 °C for at least 24 h. The resulting precipitate was collected via filtration and characterized by SEM and XRD.

Calcium carbonate precipitation with F-SWNTs. A solution of CaCO₃ (2.0 g.L⁻¹) was prepared by dissolving CaCO₃ (200 mg, 2.0 mmol) in Millipore water (100 mL). This was stirred for 1 h in a 30 °C water bath with CO₂ bubbling through the solution. The excess CaCO₃ solid was removed by filtration. F-SWNTs (30 mg) were added, and stirring was resumed at 30 °C for 3 h with further bubbling of CO₂. Precipitation occurred when the solution was allowed to rest at 30 °C for at least 24 h. The resulting grey precipitate was collected via filtration and characterized by SEM and XRD.
Calcium carbonate precipitation with surfactant and F-SWNTs. A solution of CaCO₃ (2.0 g.L⁻¹) was prepared by dissolving CaCO₃ (200 mg, 2.0 mmol) in Millipore water (100 mL). This was stirred for 1 h in a 30 °C water bath with CO₂ bubbling through the solution. The excess CaCO₃ solid was removed by filtration. F-SWNTs (30 mg) and SDS (10 mL, 1% solution) in water solution was added to give an overall SDS concentration of 0.1%. Stirring was resumed at 30 °C for 3 h with further bubbling of CO₂. Precipitation occurred when the solution was allowed to rest at 30 °C for at least 24 h. The resulting grey precipitate was collected via filtration and characterized by SEM and XRD.

Calcium carbonate precipitation with hydroxylated SWNT solution. A solution of CaCO₃ (2.0 g.L⁻¹) was prepared by dissolving CaCO₃ (200 mg, 2.0 mmol) in Millipore water (100 mL). This was stirred for 1 h in a 30 °C water bath with CO₂ bubbling through the solution. The excess CaCO₃ solid was removed by filtration. To this was added a HO-SWNT solution (1 mL, 10 mg in 7 mL) in pH 9 water. The solution became very slightly cloudy. Stirring was resumed at 30 °C for 3 h with further bubbling of CO₂. Precipitation occurred when the solution was allowed to rest at 30 °C for 24 h. The resulting precipitate was collected via filtration and characterized by SEM and XRD.

Calcium carbonate precipitation with isophthalic acid functionalized SWNT solution. A solution of CaCO₃ (2.0 g.L⁻¹) was prepared by dissolving CaCO₃ (200 mg, 2.0 mmol) in Millipore water (100 mL). This was stirred for 1 h in a 30 °C water bath with CO₂ bubbling through the solution. The excess CaCO₃ solid was removed by filtration. To this was added a solution of isophthalic acid SWNTs (0.5 mL, 200 mg.L⁻¹). Stirring was resumed at 30 °C for 3 h with further bubbling of CO₂. Precipitation occurred when the solution was allowed to rest at 30 °C for 48 h. The resulting precipitate was collected via filtration and characterized by SEM and XRD.
Barium carbonate precipitation. A solution of Ba(OH)$_2$ (2 g.L$^{-1}$) was prepared by dissolving Ba(OH)$_2$ (200 mg, 1.2 mmol) in Millipore water (100 mL). This was stirred for 1 h in a 30 °C water bath with CO$_2$ bubbling through the solution. The excess BaCO$_3$ solid was removed by filtration. Stirring was resumed at 30 °C for 3 h with further bubbling of CO$_2$(g). Precipitation occurred when the solution was allowed to rest at 30 °C for 48 h. The resulting white precipitate was collected via filtration and characterized by SEM and XRD.

Barium carbonate precipitation with fullerols. A solution of Ba(OH)$_2$ (2 g.L$^{-1}$) was prepared by dissolving Ba(OH)$_2$ (200 mg, 1.2 mmol) in Millipore water (100 mL). This was stirred for 1 h in a 30 °C water bath with CO$_2$ bubbling through the solution. The excess BaCO$_3$ solid was removed by filtration. C$_{60}$(OH)$_n$ (20 mg, 0.018 mmol) was added, and stirring was resumed at 30 °C for 3 h with further bubbling of CO$_2$. Precipitation occurred when the solution was allowed to rest at 30 °C overnight. The resulting brown precipitate (no reddish color as in pure fullerol solution) was collected via filtration and by solvent evaporation, and then characterized by SEM and XRD.

References


J. L. Hudson and J. M. Tour, personal communication.


Conclusion

In this thesis we have advanced the inorganic chemistry of fullerenes and SWNTs. Investigations into the reactions of hydroxyfullerenes have proven fullerrenol reacts irreversibly across a wide pH range with a variety of metal salts to form insoluble cross-linked polymers. These metal salts are present at the same concentrations in the environment, indicating the interaction of hydroxyfullerenes with metals is an important issue with regard to waste treatment, fullerene exposure in the environment, and fullerene-based pharmaceutical agents.

A purification method has been developed for FeMoC and its stability and solubility has been investigated. FeMoC-EtOH has been shown to be soluble in ethanol and methanol. It is stable in these solvents for at least 4 weeks. The yield of FeMoC has also been improved over literature and has been shown to be a SWNT catalyst precursor. Catalysts have been attached to SWNTs, making a viable SWNT-cat for SWNT amplification.

Fullerenes have been epoxidized via transition metal catalysis. More epoxides have been produced by this method than was previously possible. Through experiment optimization, 13 epoxides per fullerene were produced. This catalyst also opens the fullerene cage. The cage is opened by removal of one six-membered carbon ring and addition of three epoxide groups. Four of these segments removed have been removed from the fullerene cage. Some the possibilities arising from these results include new routes to hydroxyfullerenes and endohedral fullerenes.

Single-walled carbon nanotubes have been solubilized via a new method. Creation of a SWNT salt with the Na⁺ counter ion complexed with dibenzo-18-crown-6 allows for modest solubility in a variety of solvents without sidewall functionalization. The addition of water-soluble species such as fullerenols and hydroxylated and isophthalic acid functionalized SWNT solutions change the morphology and crystal
phase of CaCO$_3$ precipitates. Fullerenols produce star-shaped calcite crystals and precipitation with water-soluble hydroxylated and isophthalic acid functionalized SWNTs produces SWNTs coated with amorphous CaCO$_3$. Carbon materials that are not water-soluble, such as C$_{60}$, purified SWNTs, and F-SWNTs have no impact on CaCO$_3$ crystallization.
Appendix

Publications


R. Anderson, E. Whitsitt, D. Ogrin, M. Stewart, C. L. Edwards, R. E. Smalley, J. M. Tour, and A. R. Barron, A study on the formation, purity and ligand substitution chemistry of the nanocluster [{$_{x}$PMo$_{12}$O$_{40}$}H$_{4}$Mo$_{72}$Fe$_{30}$(O$_{2}$CMe)$_{15}$O$_{254}$(H$_{2}$O)$_{98}$], in preparation.

Presentations


R. E. Anderson and A. R. Barron, Effect of Additives in Calcium Carbonate Crystallization, Abstracts of Papers, 58th Southwest Regional Meeting of the ACS, Austin, TX, November 3 – 6, 2002.