Introduction to Nanoscience

Study Guide

Chapter 9 - Introduction

We start the chemistry section with Carbon-Based Nanomaterials. In retrospect, we should have started it with the chapter on chemical bonding of nanomaterials. Oh well, perhaps in the next edition if we could be as lucky. Nonetheless, carbon nanotubes in particular, offer a smooth transition from physics into chemistry. The physics of carbon nanotubes for example are extremely well worked out, and beautifully so.

Since we all are familiar with the versatility of carbon in so many kinds of materials, we shall not concern ourselves too much with listing such well-known information. We shall also omit any discussion concerning the bonding in carbon i this study guide as that information was drilled efficiently into our heads in organic chemistry class. We shall focus on fullerenes, nanotubes and diamondoids.

Chapter Objectives:

- Overview the basic differences between graphite and diamond and appreciate how two materials made of the same element can be so different
- Understand the structure of C_{60} and its various geometrical components
- Review the modes of synthesis of fullerenes: arc-dis
- Chemical derivatization of fullerenes produces endohedral and exohedral forms. Learn what those are and how such chemical modification is accomplished
- Understand the reason fullerenes are soft electrophiles
- Learn why C_{60} is able to form into an *fcc* structure
- Review the types of chemical modification that fullerenes undergo
- Carbon nanotubes are able to serve as conductors, semiconductors or insulators depending solely on their structure. It is very important that you understand the reasons for this versatility.
- Distinguish between armchair tubes and zig-zag tubes
- Understand the principle of chirality as it applies to carbon nanotubes
- Learn how to name tubes according to the dual number convention (m,n)

- Familiarization with the terms *chiral vector*, *translation vector*, *chiral angle*, *graphene sheet*, and *translational unit cell*

- Very important: make carbon nanotubes via the transparency method shown in **Figure 9.17**.

Discussion Topic: The differences between diamond and graphite are enormous. Based on structural arguments, please explain the differences.

The fullerene, a relatively new allotrope of carbon, demonstrates further the versatility of the element carbon. The soccer ball structure of C_{60} is nothing short of remarkable. Created under extreme conditions, fullerenes offer one of the most stable and uniform of nanomaterials. Their cage structure allows for interment of various chemical species. Their electrophilic structure promotes simple addition reactions to place active groups on their surface that are available for linking and other reactions.

Discussion Topic: From your past organic chemistry experience, discuss the reactivity of fullerenes and the many kinds of derivatization possible.

Chapter Summary

- Carbon's versatility is well documented

- Fullerenes and carbon nanotubes were introduced. These materials played a great role in defining the *Nano Age* and its potential

- The physics of carbon nanotubes are extremely well-worked out. It is important to become familiar with the structure and how it relates to CNT properties

- Mass spec abundance of fullerenes depends on stability. Even fullerene cage structures tend to be more stable

- C_{60} consists of 90 edges, 32 faces and 60 vertices that correspond to Euler's relation for polyhedral structures: $f + v = e + 2$

- Bonding in fullerenes is not clearly of one type or another but rather an admixture of sp^2 and sp^3

- The fullerene C_{60} is identifiable by diagnostic ^{13}C-NMR and mass spec peaks

- Fullerenes are generally synthesized under high energy circumstances

- Bond strain relief is one of the drivers for fullerene reactivity

- Fullerenes readily undergo electron accepting addition reactions

- *Endohedral* fullerenes are those in which the fullerene is the host and the guest is enclosed within the cage structure

- *Exohedral* fullerenes are those in which the surface is modified with a chemical species

- Two- and three-dimensional arrays can be created with fullerenes by cycloaddition

- C_{60} fullerenes complex into an *fcc* structure

- Vector notation for SWNTs describes their inherent structure: zig-zag, $m = 0$; armchair, $m = n$; and all others are chiral tubes

- SWNTs can be conducting or semiconducting: if $n - m = 3q$, where q is an integer, then the tubes are electrically conducting. By this definition, all armchair tubes are conducting and all others too by the above rule

- The tensile strength of SWNTs can be enormous

- Raman spectra of SWNTs is diagnostic for SWNTs: the E_{2g} tangential mode at ca. 1600 cm^{-1} and the low-energy radial breathing modes at 140 - 400 cm^{-1}

- SWNTs hang around in bundles that are held together by van der Waals forces

- SWNTs usually require purification following synthesis (arc, laser ot CVD) but recent developments have demonstrated high purity samples following synthesis without the need for significant post-synthesis purification

- SWNT growth mechanisms are relatively well-elucidated. The yarmulke mechanism of Smalley is generally considered to be correct

- CNTs, like fullerenes, are modifiable through chemistry. Tubes must be first dispersed (or dispersed due to chemical modification)

- MWNTs grow by tip-growth or base-growth mechanisms. SWNTs generally grow by base growth on supported catalyst

- SWNTs (and MWNTs) can be modified by covalent or non-covalent chemical reactions

- Diamondoid materials form an extremely interesting and useful class of nanomaterials

- One of the most compelling features of diamondoids, aside from their physical properties, is their synthesis can occur at low temperature and pressure
- Diamondoids, like carbon nanotubes, are relatively easy to modify chemically