Transformation of Carbon Nanomaterials in the Environment

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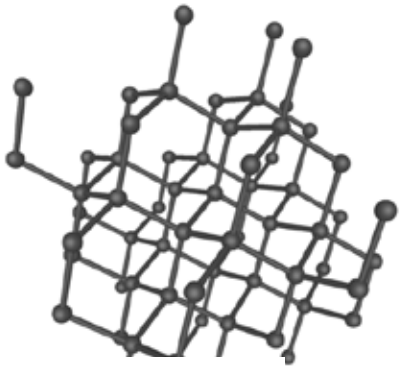
NNI Workshop
on Nanomaterials and
the Environment and
Instrumentation

October 7, 2009

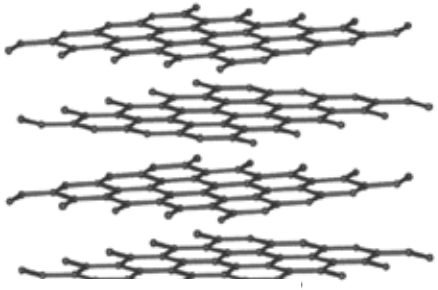
Outline

- Carbon Nanomaterials and their Applications
- Demand and Supply in Carbon Nanotube Market
- Enzymatic Oxidation of Carbon Nanotubes
- Physical and Chemical Modifications of Carbon Nanotubes

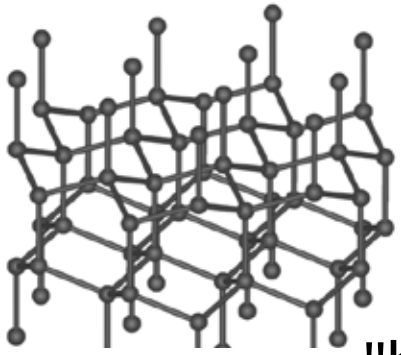
Allotropes of Carbon



Diamond

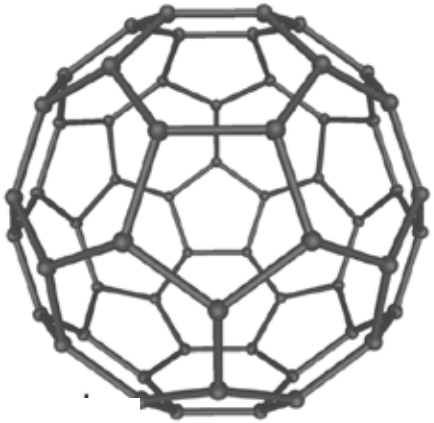


Graphite

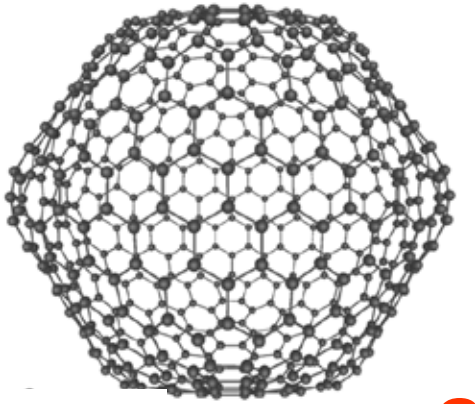


Lonsdaleite

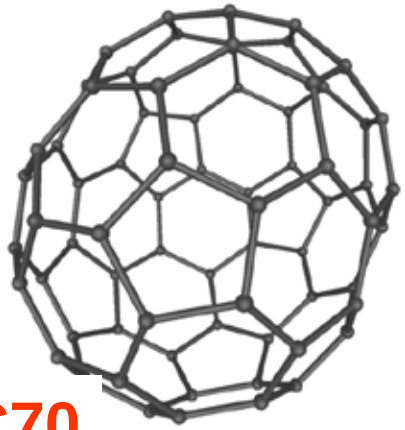
"hexagonal diamond" found in meteorites



C60

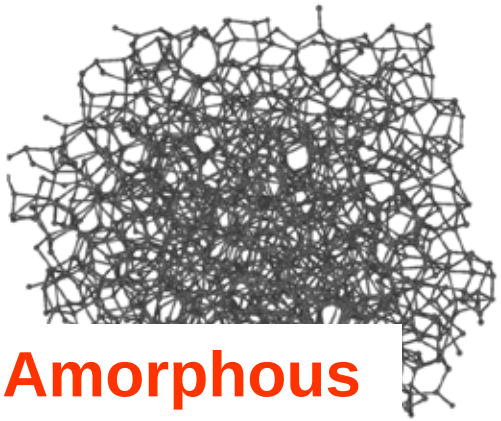


C540

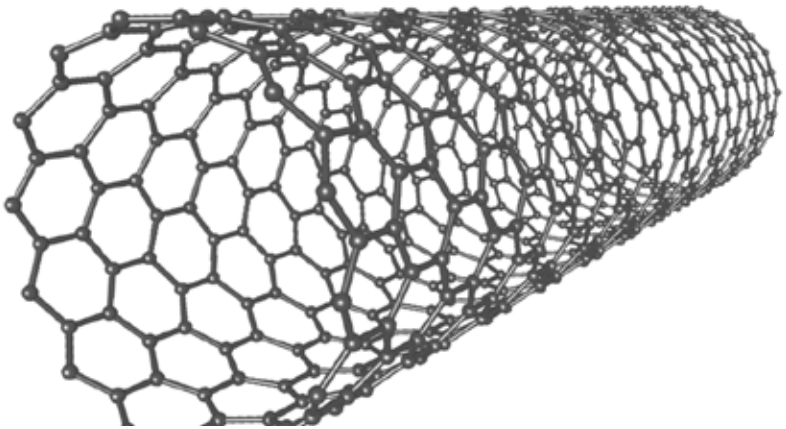


C70

Fullerenes



Amorphous Carbon



Carbon Nanotubes

http://en.wikipedia/org/wiki/Allotropes_of_carbon

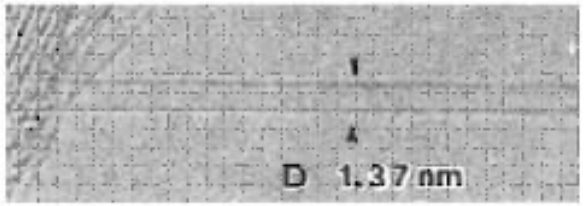
Carbon Nanotubes

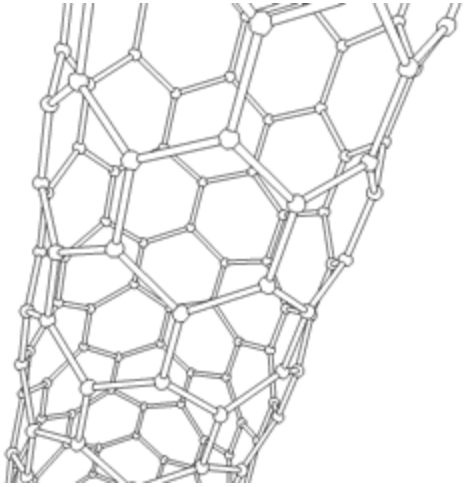
Discovery

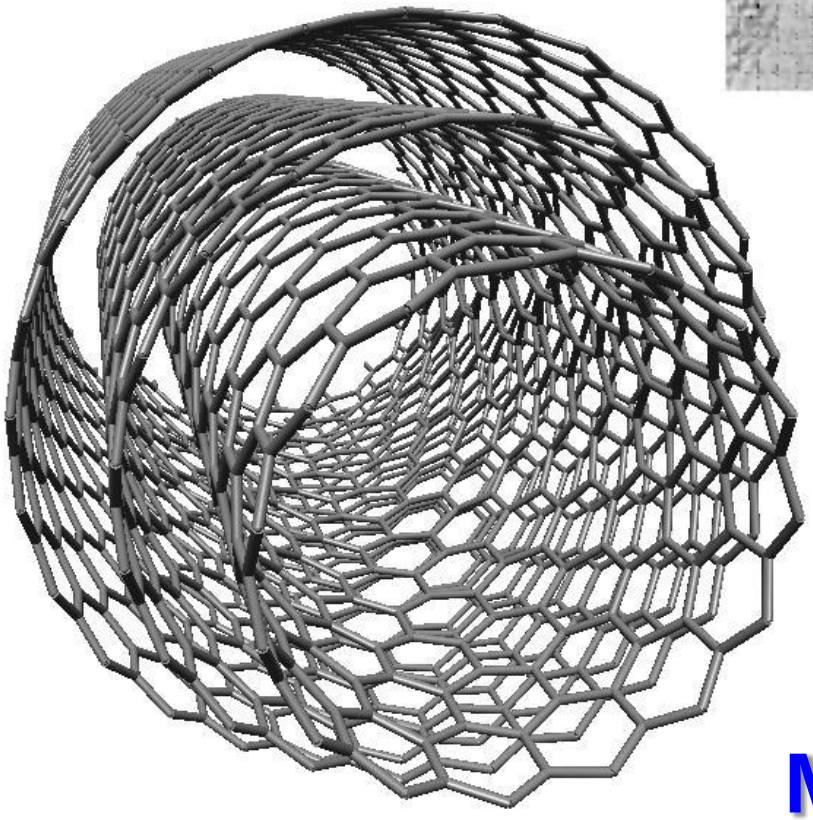
1991 by Sumio Iijima, a senior research fellow at NEC

1993

SWNT

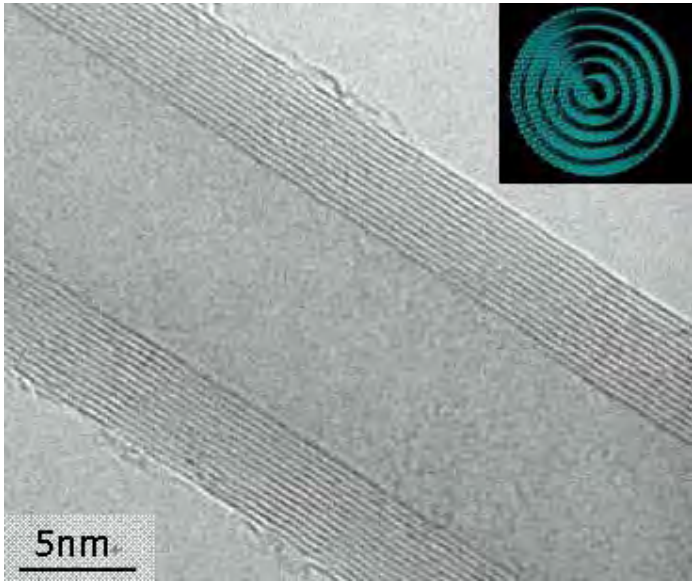






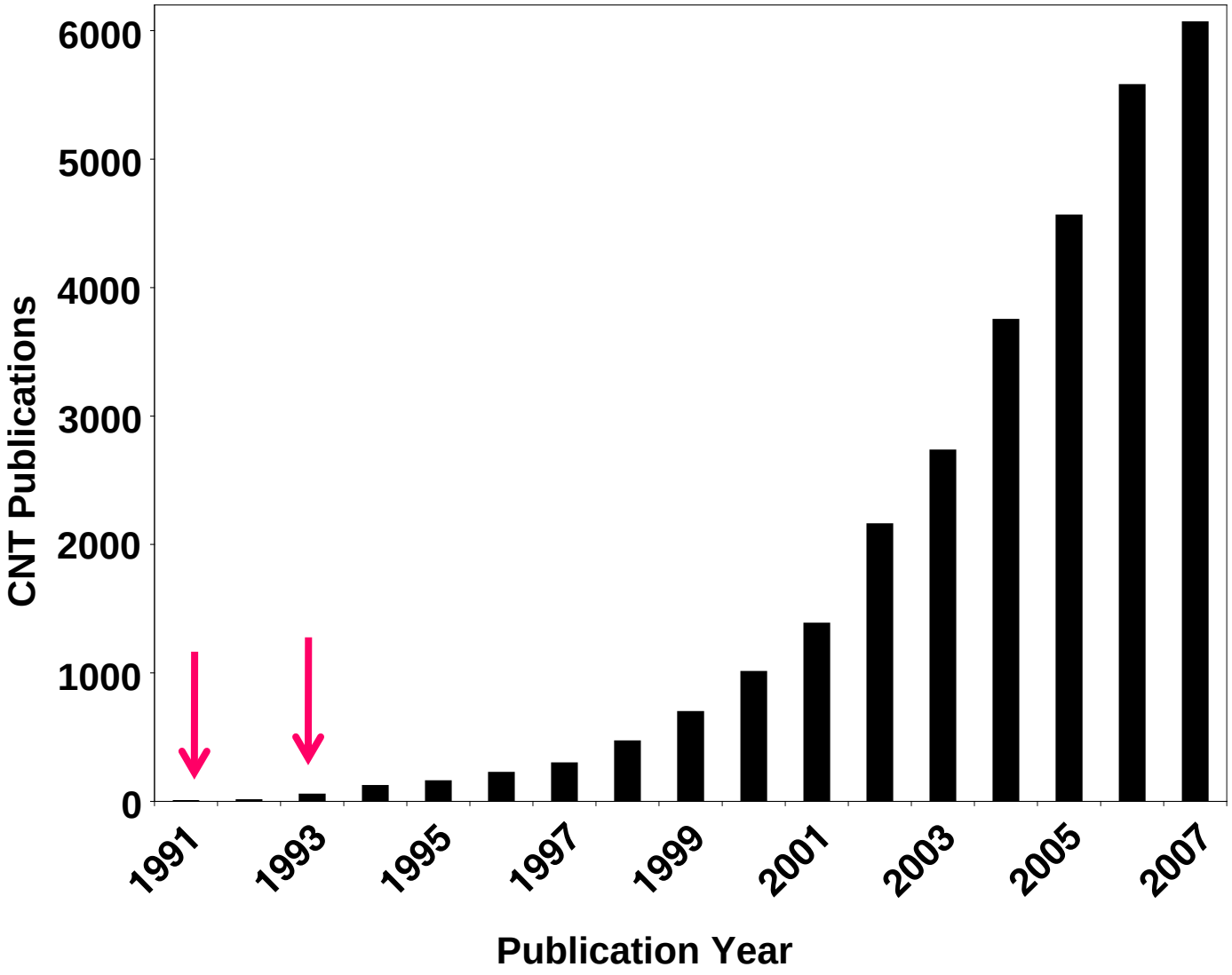
Transmission Electron Microscopy (TEM) images

MWNT



S Iijima “Helical microtubules of graphitic carbon” *Nature* **1991**, *354*, 56

Carbon Nanotube Literature



Number of CNT publications per year between 1991 and 2007
(data obtained from ISI Web of Knowledge)

Applications of Carbon Nanotubes

Mechanical Reinforcement

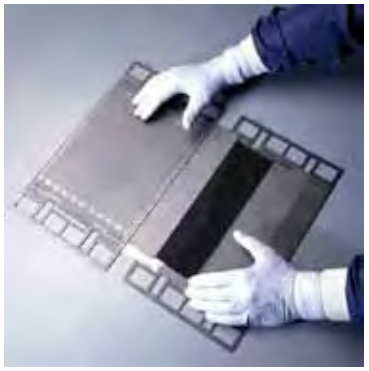
CNT-reinforced tennis racket

'soft' body armor

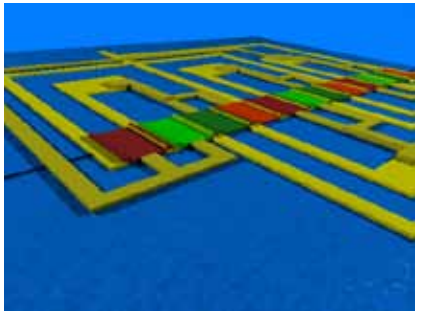
Nissan's X-Trail SUV has CNT-reinforced bumpers

Flat Panel Displays

Fuel Cells & Batteries



Electronic Circuits



Super-strong CNTs may make space elevators feasible

Carbon Nanotube Manufacturers

NANOTUBE -SUPPLIERS .COM

42 nanotube suppliers

Single Walled Nanotube
SWNT - Bundled Thin SWNT - Functionalized SWNT - Short SWNT - Long SWNT

Multi Walled Nanotubes
MWNT - Aligned MWNT - Bundled MWNT - Thin MWNT - Functionalized Short MWNT - Functionalized MWNT - Long MWNT - Short MWNT

Double Walled Nanotubes
DWNT - Bundled Thin DWNT - Functionalized DWNT - Short DWNT

Industrial Grade Nanotubes
Industrial Grade MWNT - Industrial Grade MWNT for super Capacitor - Industrial Grade SWNT

Other types
Triple walled Carbon Nanotubes - Field Emission Grade Carbon Nanotubes

Per Countries
Austria - Belgium - Canada - China - Cyprus - France - Germany - Greece - India - Korea - Russia - Taiwan - United Kingdom - USA

• Bayer MaterialScience has opened a new carbon nanotube (CNT) production facility at Laufenburg on the German-Swiss border, doubling its production capacity to **60 tons** per year.

• Even further in the future, Bayer MaterialScience plans to build an industrial-scale production plant with an annual capacity of **3000 tons**.

• French chemical giant Arkema opened a CNT pilot plant in south-west France in January 2006 with an annual production capacity of **10 tons**.

• Nanocyl in Belgium has a production capacity of **40 tons** a year

August 18, 2009

• CNano Technology Limited (CNano) announced that it has received regulatory approval from the U. S. Environmental Protection Agency (EPA) to sell multi-wall carbon nanotubes (MWNTs) through its subsidiary in the USA.

• MWNTs produced at its **500 tons** per year facility in Beijing, China.

SouthWest NanoTechnologies

- **EPA's Regulation of Carbon Nanotubes under the Toxic Substances Control Act**

Ø Understand the transformation of nanomaterials under different environmental conditions

Ø Measuring impacts of nanoparticles that may be transformed over time in the environment

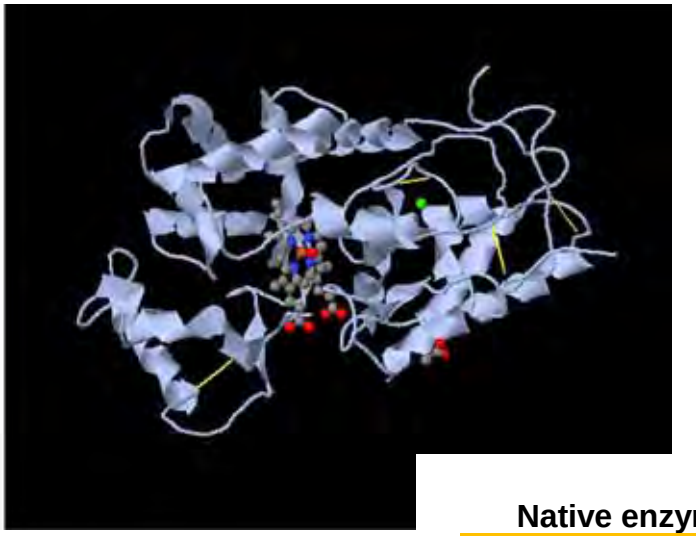
Ø This information would be essential for decision-making regarding handling, disposal, and management of nanoscale materials in commerce, manufacturing and the environment

Are carbon nanomaterials biodegradable in the environment?

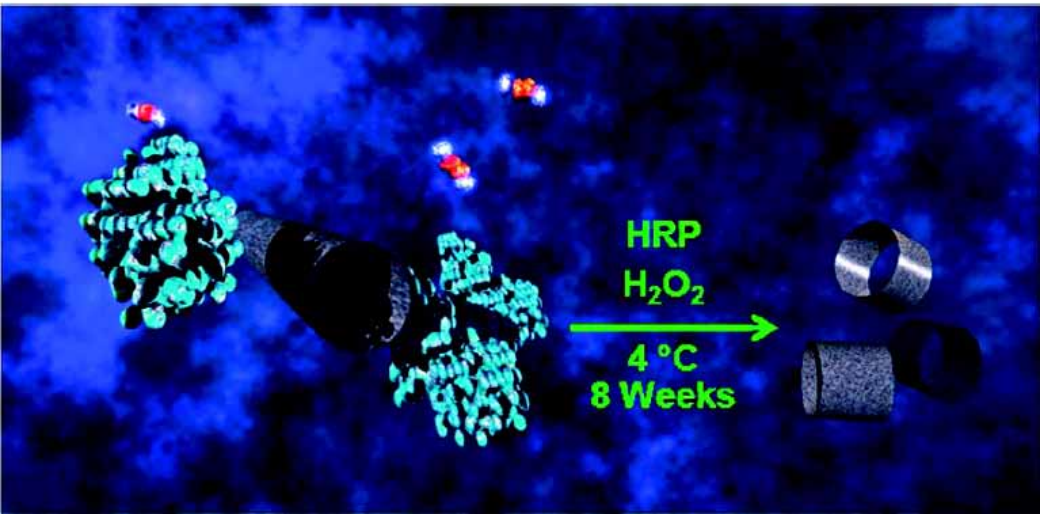
Enzymatic Degradation of CNTs

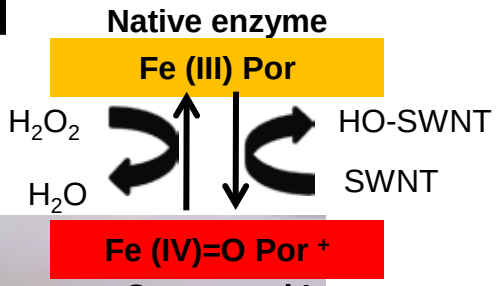
Horseradish Knows!

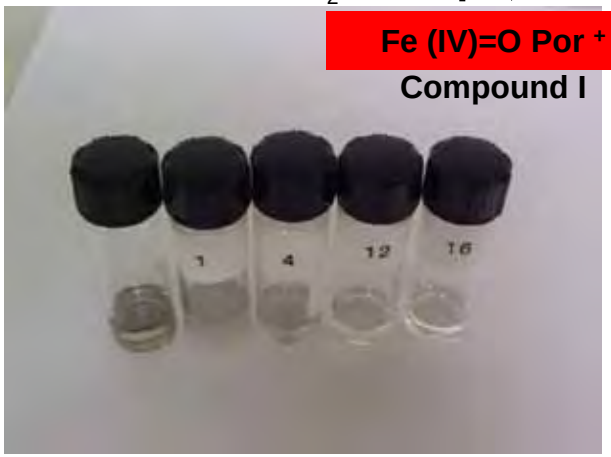
Horseradish Peroxidase (HRP)



Brett Allen



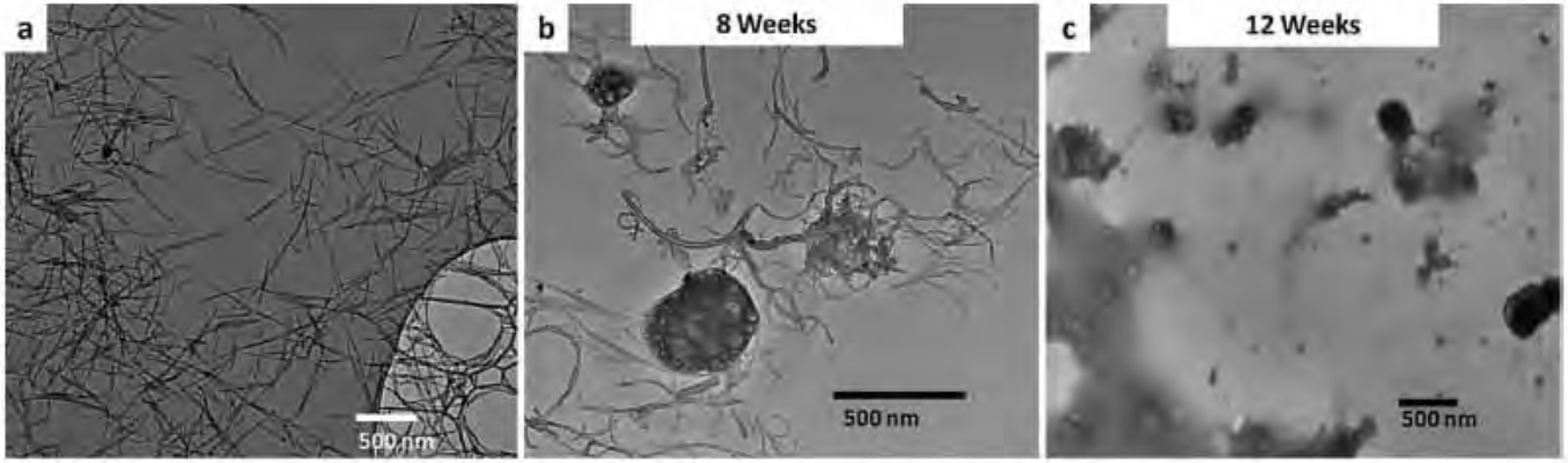




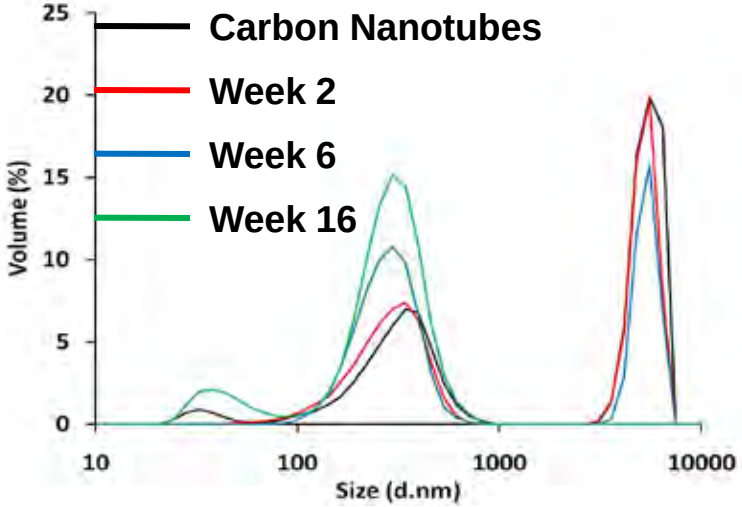
B. L. Allen, et al. *Nano Lett.* **2008**, *8*, 3899

Enzymatic Degradation of CNTs

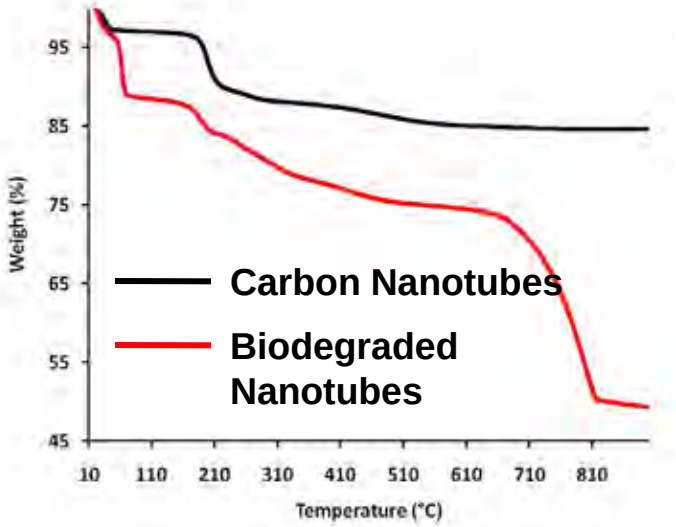
Transmission Electron Microscopy (TEM)



Dynamic Light Scattering (DLS)



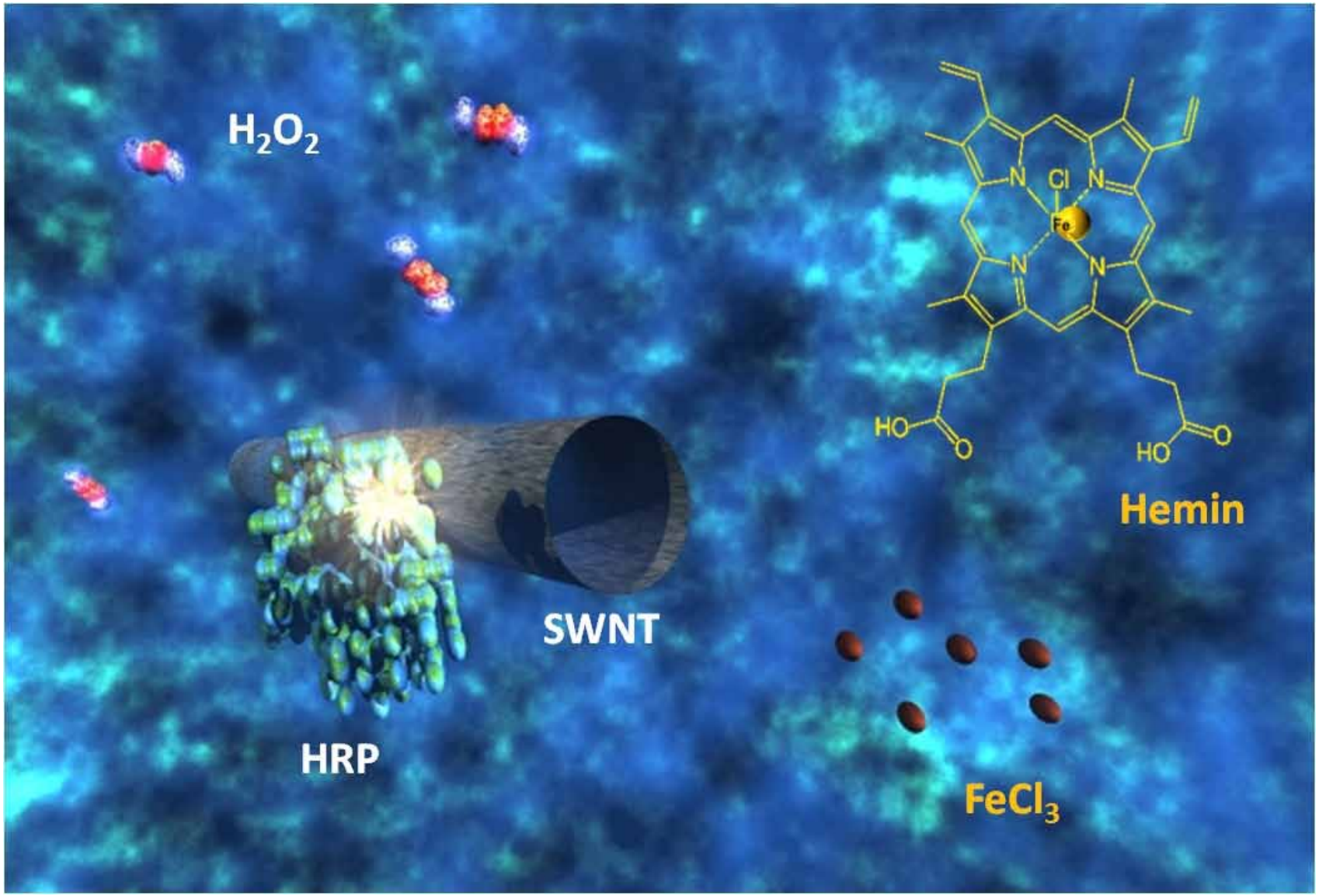
Thermal Gravimetric Analysis (TGA)



Degradation of CNTs as time progresses

B. L. Allen, et al. *Nano Lett.* **2008**, *8*, 3899

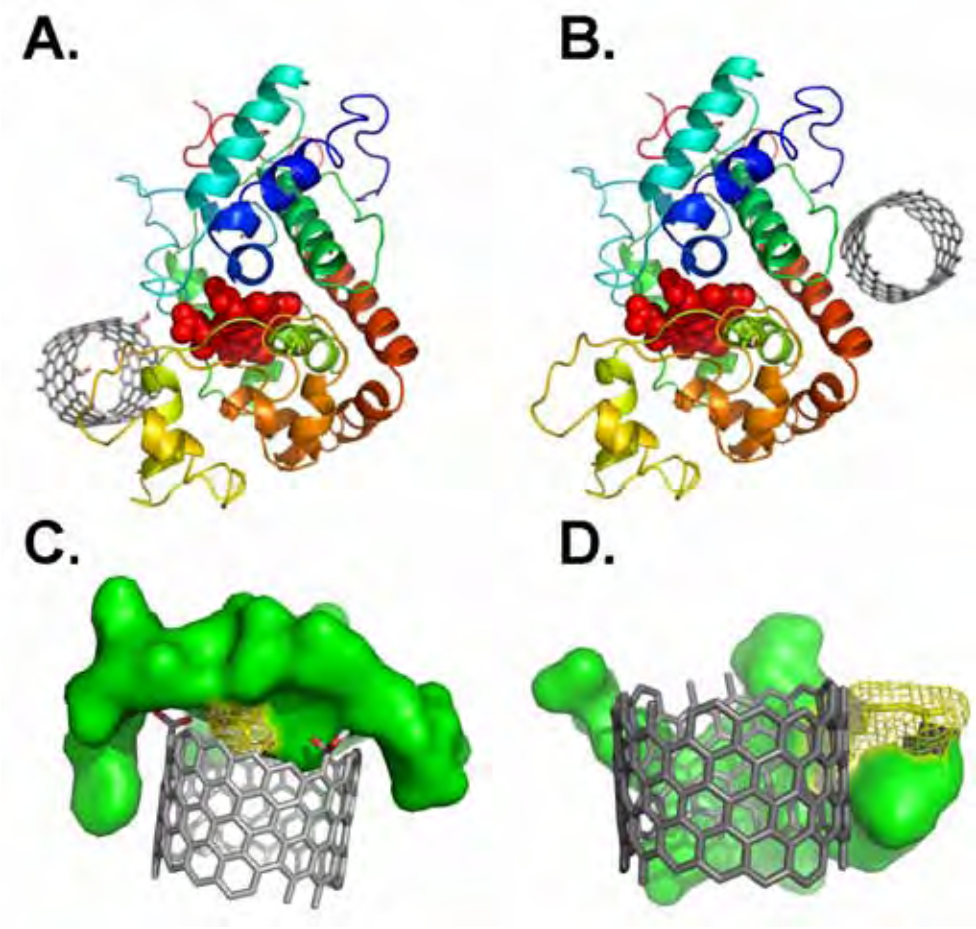
Mechanistic Investigations



Enzymatic oxidation *versus* Fenton-type oxidation

Mechanistic Principles

- Two possible docking sites for SWNTs
  - Proximal to heme (hydrophilic residues)
  - Distal to heme (hydrophobic residues)
- Hydrophilic functionalities required for HRP active site proximity
- Hydrophobic species dock at distal site, no degradation
- Fenton Catalysis by ferrous/ferric iron allows indiscriminate degradation



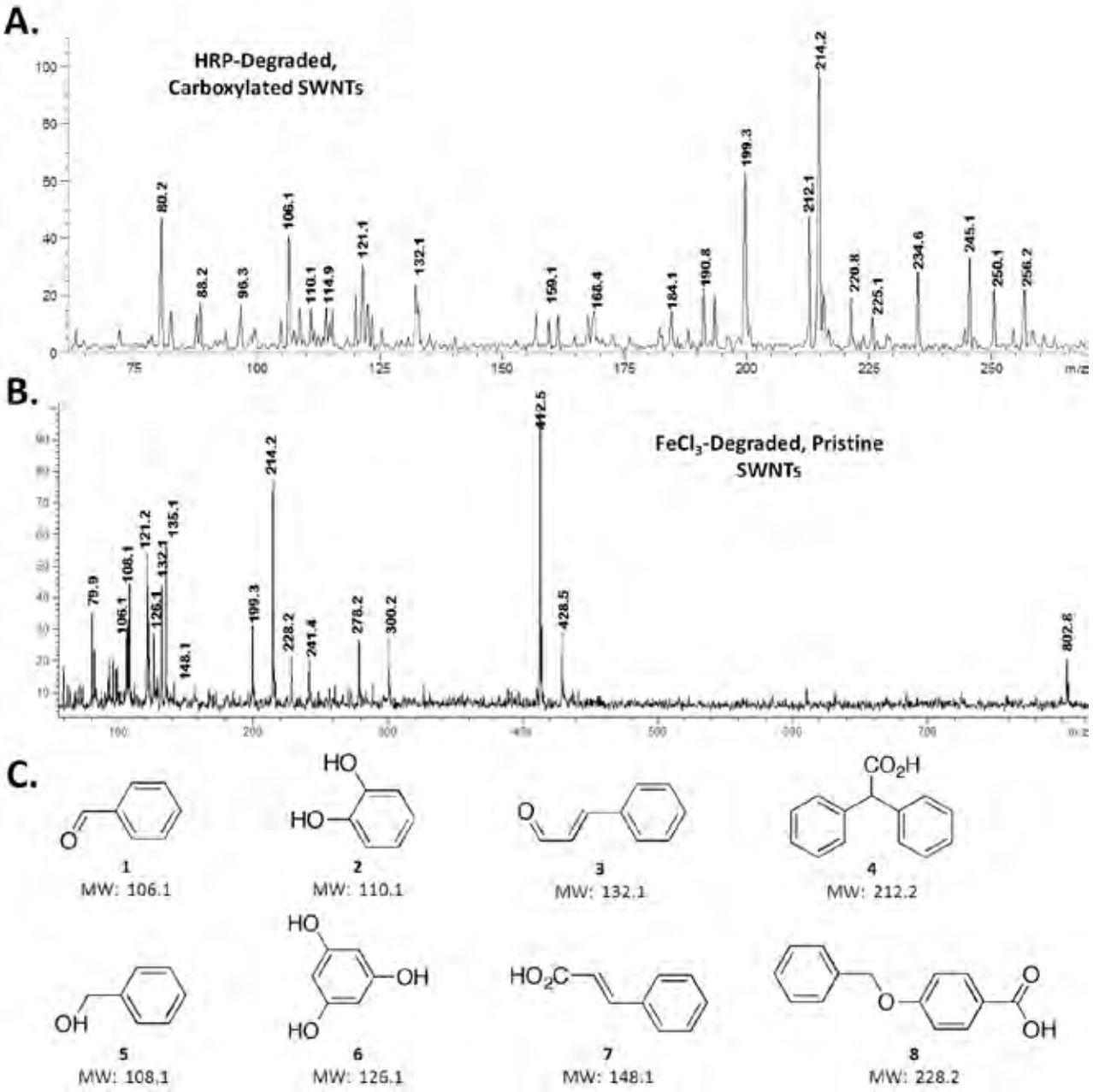
Effect of CNT functionalization on the enzymatic degradation

B. L. Allen, et al. *submitted*

Products Characterization

Intermediate products (LC-MS)

The end product is CO_2 (GC-MS)



B. L. Allen, et al. *submitted*

Decomposition of C60 Fullerol

• Overview of the potential environmental fates of fullerols

• Extracellular hydroquinone-driven Fenton chemistry produced by white rot fungi (producing lignolytic enzymes)

K.M. Schreiner *et al. Environ. Sci. Technol.* **2009**, *43*, 3162.

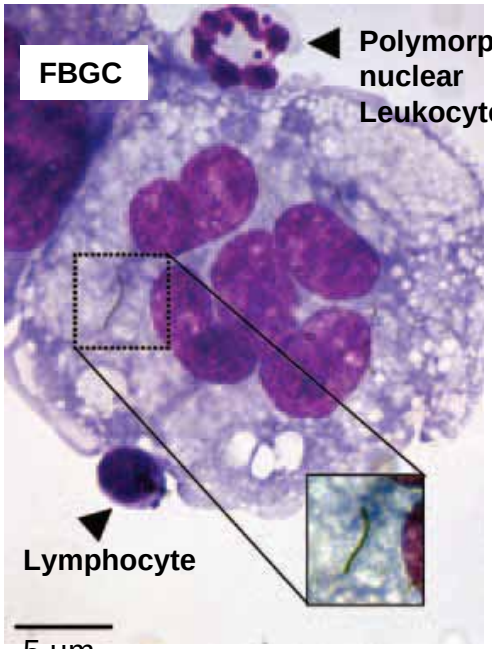
Toxicity of Carbon Nanotubes

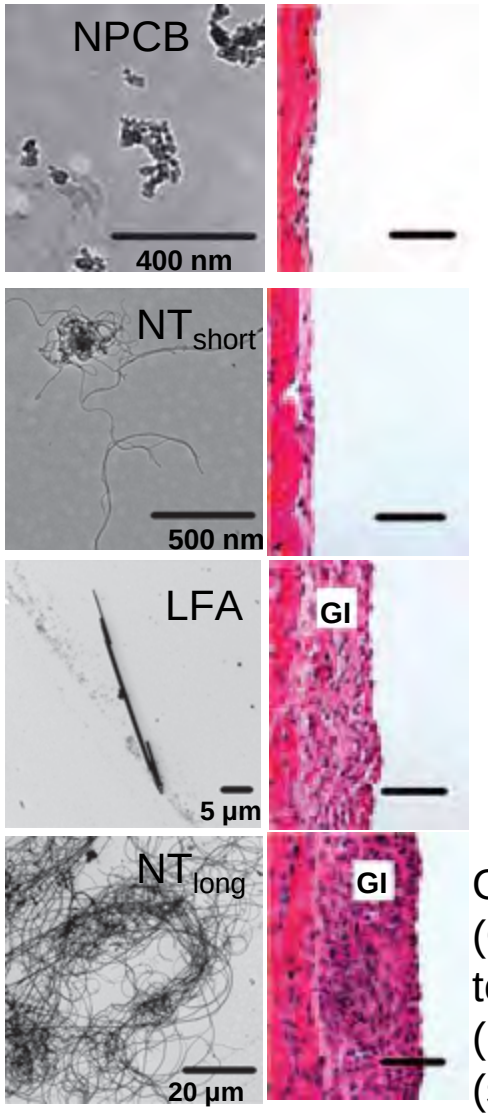
Nanotubes may cause:

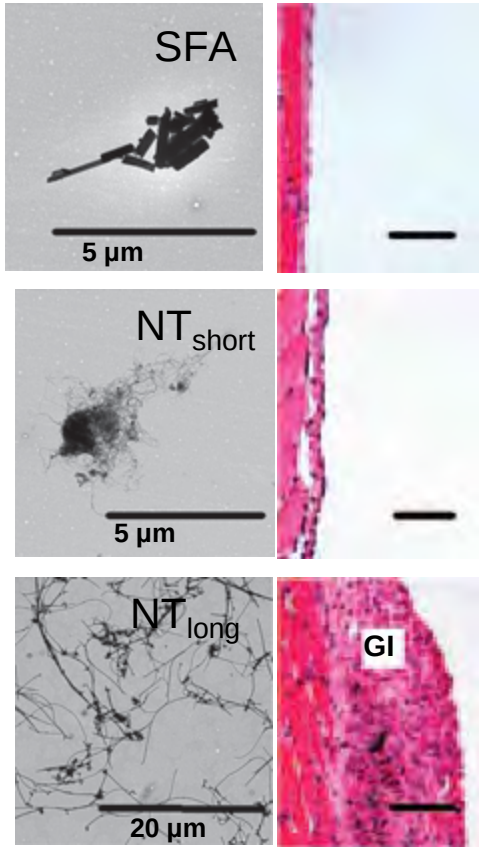
- Inflammatory response in cell cultures and the lungs of animal models
- Mesothelioma (lung cancer)

Nanotube Uptake

- Frustrated phagocytosis in macrophages
- Formation of foreign body giant cells (FBGCs)





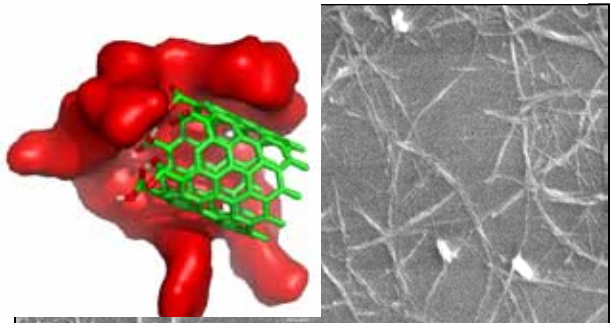


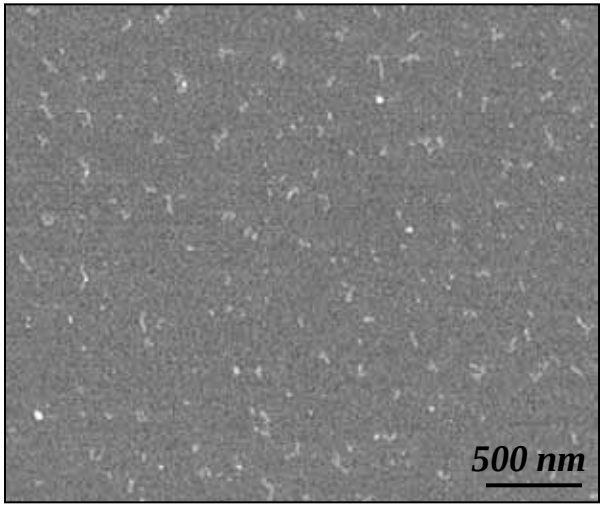
Granulamatous inflammation (GI) from long MWNTs similar to long fiber amosite (LFA) (brown asbestos) (scale bare 50 µm)

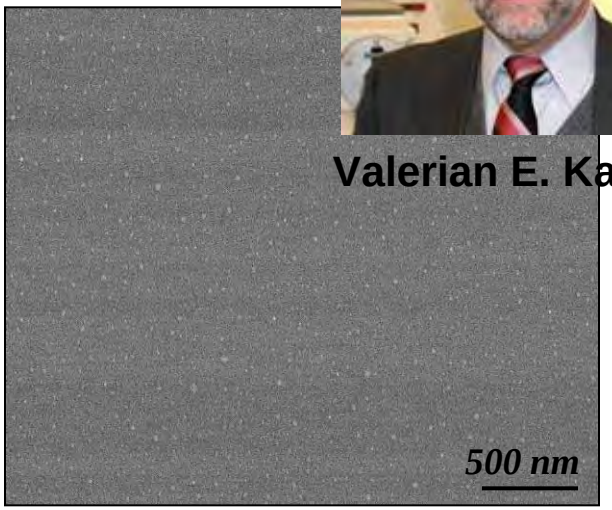
C.A. Poland *et al.* *Nature Nanotech.* **2008**, *3*, 423.

Biodegradation by Neutrophils

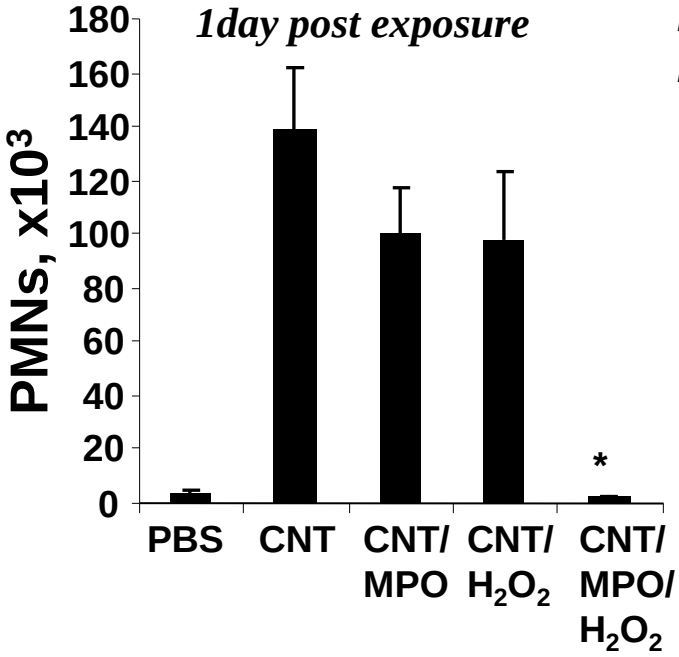
***Myeloperoxidase* (MPO)**



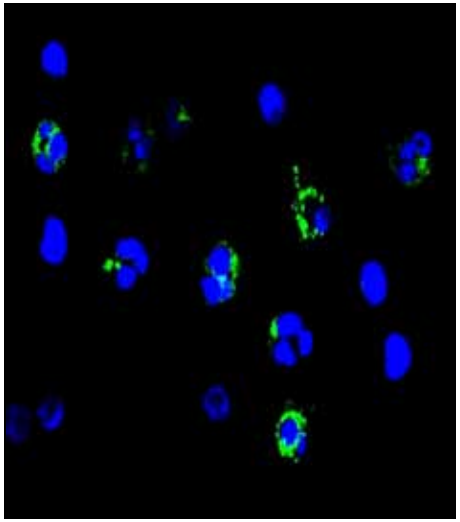


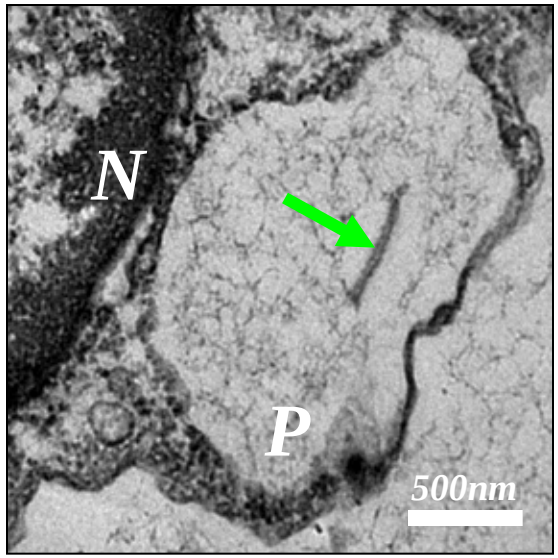


Valerian E. Kagan



Myeloperoxidase (MPO) is a peroxidase enzyme present in neutrophils (PMNs)





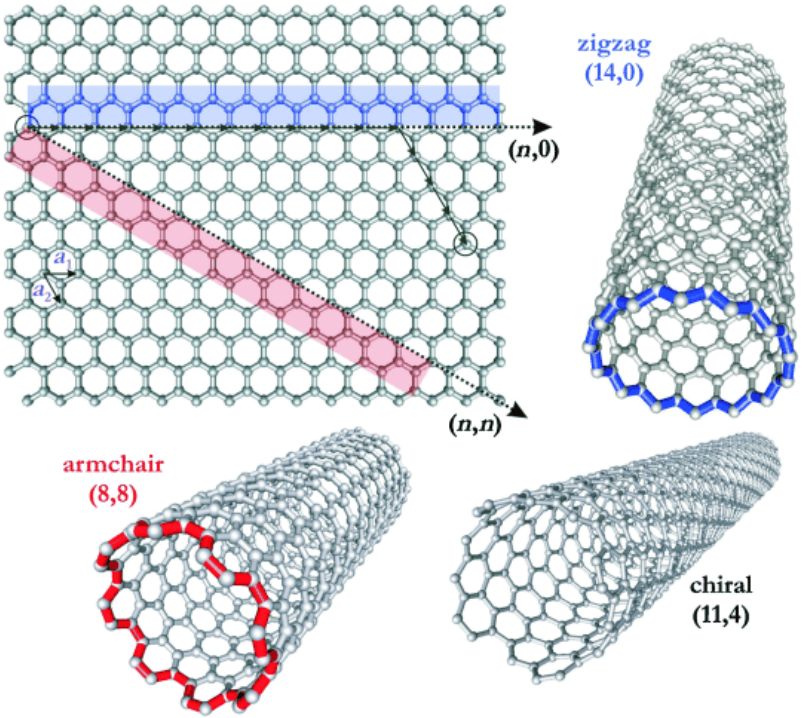
N=Nucleus
P=Phagosome

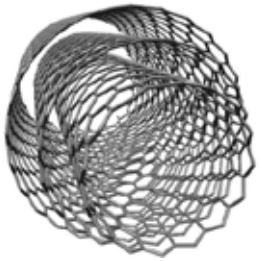
V. E. Kagan et al. *submitted*

Dehaloperoxidase from Marine worm (Amphitrite ornata)

Multitude of Carbon Nanotubes

- Diameter
- Chirality

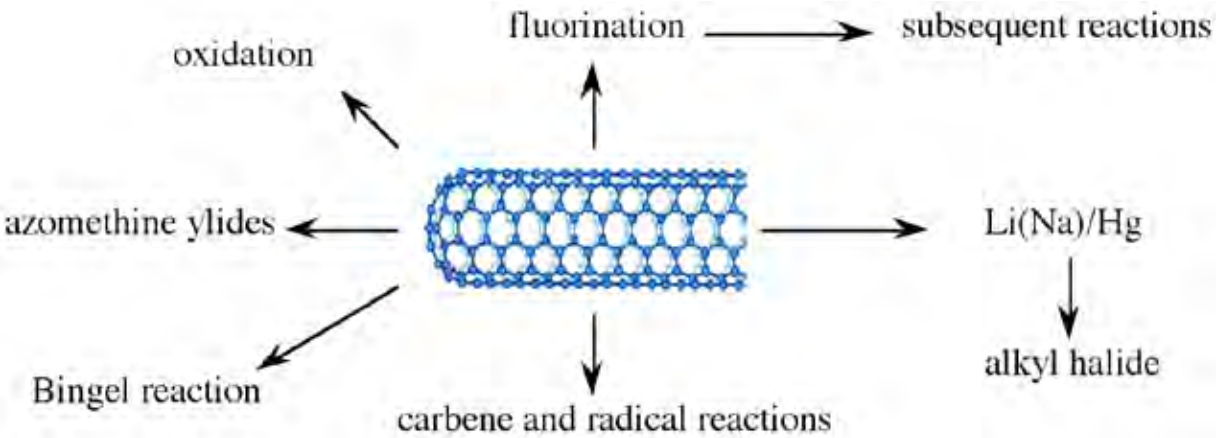




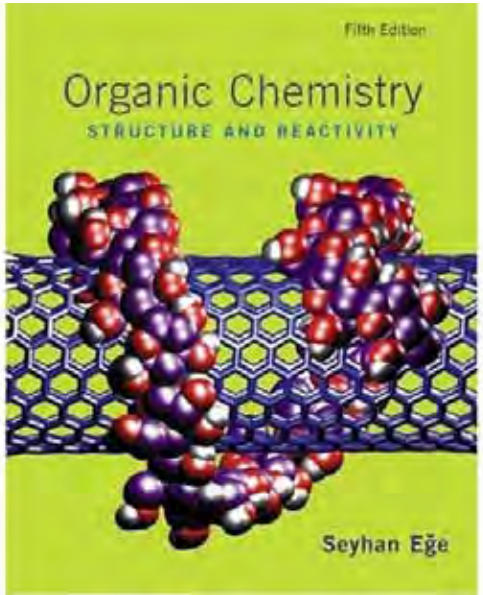
- Number of walls
- Bundles

Chemical Functionalization

- covalent

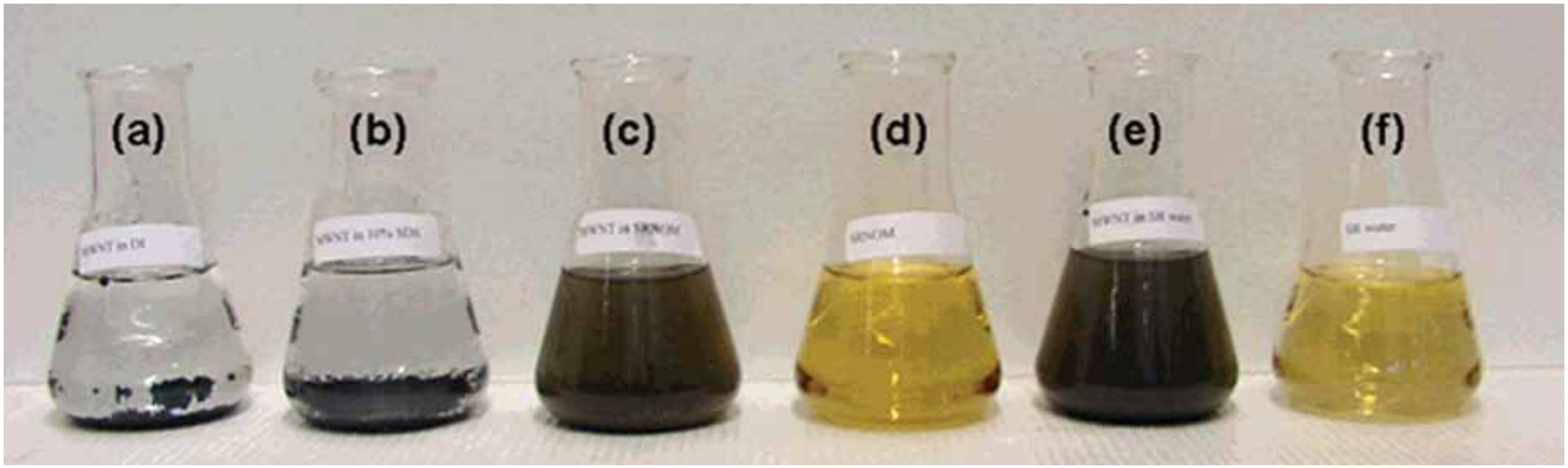


- noncovalent



How transformation in the environment would affect the oxidation?

Suwannee River Natural Organic Matter (NOM) Stabilizes Carbon Nanotubes in the Aqueous Phase



Jae-Hong Kim *et al. Environ. Sci. Technol.* **2007**, *41*, 179-184

Conclusions

Unique properties of carbon nanotubes –
· high aspect ratio · strength/elasticity
· conductivity · optical
– enable many great applications

For their applications, unique properties of carbon nanomaterials should be matched with controllable biodegradation

Can we synthesize biodegradable carbon nanotubes by design
or perhaps activate this property at the end of the nanotube product cycle?

Acknowledgements

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Valerian Kagan, EOH
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CMU:
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Bruce Krogh, ECE
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Thank you