

Zhen Chen, Alexander Lamb, Chang Liu, Lan Luo
 Advisor: Professor Nancy A. Burnham (Department of Physics, WPI)
 Co-advisor: Dr. Jo Anne Shatkin (CLF Ventures, Inc.)
 An Interactive Qualifying Project (2010)

Nanosilver

Toxicity

- Mostly acute toxicity studies
- Overall poor consistency
- In vivo: Mammal cells: Minimum $LC_{50} = 0.53 \text{ mg/l}$ (28 h)
- In vitro: Rat: No observed effect ($515 \mu\text{g}/\text{m}^3$ in air)
 Oysters & fish: Minimum $LC_{50} = 34.6 \mu\text{g}/\text{l}$ (96 h)
- Comparative: Nano \approx Ionic
 Coated > Uncoated
 Large vs. Small?
- Mechanism: Oxidative stress
 "Trojan Horse"?

Environmental

- Reduced or no toxicity in simulated environment
- Toxicity increased by detergent and antibiotics
- 3-14% into water from consumer products

Risk Assessment

Production	Release	Remaining	Surface Water	Accumulation Time	Concentration
800 t/a	$\times 14\%$	$\times 100\%$	37200 km ³	20 a	$= 6.0 \times 10^{-5} \text{ mg/L}$
4.7 t/a	$\times 3.2\%$	$\times 5\%$	189900 km ³	1 a	$= 4.0 \times 10^{-11} \text{ mg/L}$

$$C_{\text{allowed}} = EC_{50, \text{min}} / 1000 = 3.46 \times 10^{-5} \text{ mg/L}$$

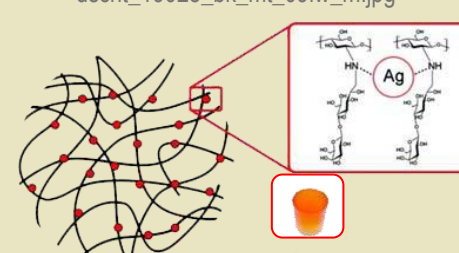
$$C_{\text{pred, high}} = 6.0 \times 10^{-5} \text{ mg/L} \quad \text{!}$$

$$C_{\text{pred, low}} = 4.0 \times 10^{-11} \text{ mg/L} \quad \text{✓}$$

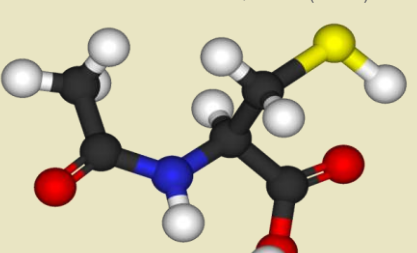
Risk Mitigation



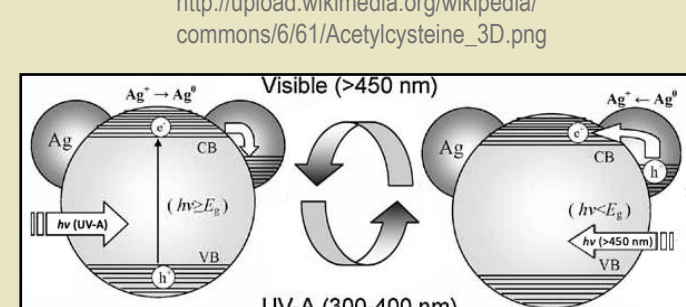
Microscopic image: Environ. Sci. Technol. 42, 4133 (2008)
 Stock image: http://andyjordan.com/images/large/large_dscnt_19025_bk_ni_09nw_m.jpg



Biomacromolecules 10, 1429 (2009)



http://upload.wikimedia.org/wikipedia/commons/6/61/Acetylcysteine_3D.png

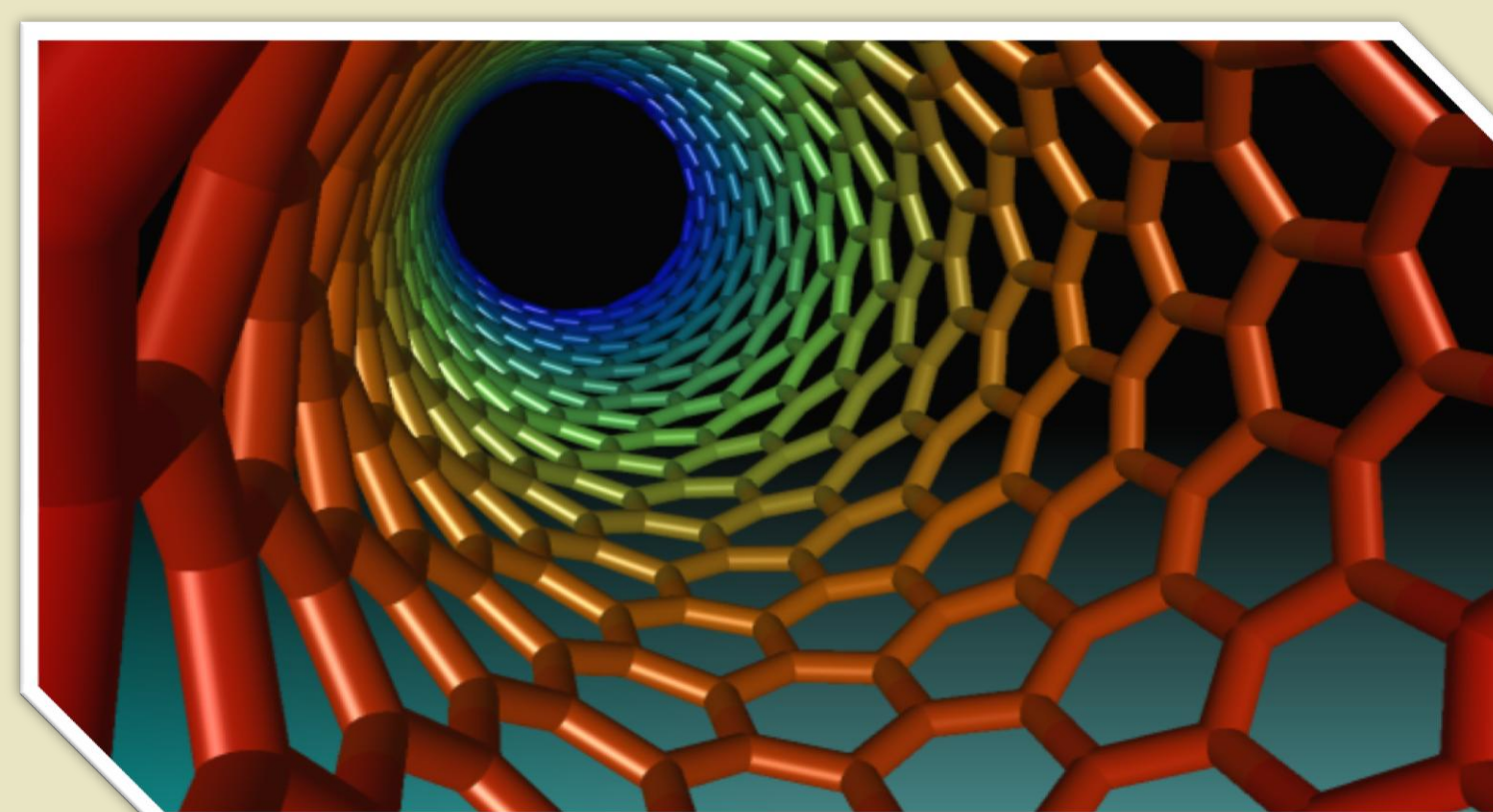


Small 5, 341 (2009)

- Silver-retaining socks
 Larger particles incorporated into fabric matrix; non-oxidizing detergent
- Silver-trapping gels
 Polysaccharide or carbopol gels:
 Antibacterial but non-toxic
- Nanosilver-binding ligands
 Sulfur-containing ligands:
 Sulfide ion or N-acetyl-L-cysteine
- Photo-switchable nanosilver
 Nanosilver on TiO₂ template
 Antibacterial activity can be switched on and off by light irradiation

Introduction

Engineered nanoparticles have shown great promise in medicine, electronics, physics, and environmental science. In particular, nanosilver has been gaining popularity in consumer products as an antibacterial agent. Carbon nanotubes, an excellent material for electronic devices, are also expected to be widely produced and used in the near future.



Carbon nanotube model
http://geoffhutchison.net/gallery/main.php?g2_view=core.DownloadItem&g2_itemId=363&g2_serialNumber=2

However, the possibility of environmental risks from these nanoparticles has raised concern, which has motivated regulations and guidelines for their manufacturing and usage. To date, these efforts are still at a preliminary stage, largely because the level of environmental risk from nanoparticles has not been well characterized.

Guidelines for Nanosilver

- Research and application of risk mitigation strategies
- Research priorities: In vivo studies on environmentally relevant species
 Comparative toxicity and mechanism
 Human dermal exposure
 Environmental transport and fate models
 Environmental monitoring tools
- Production data: Forceful stewardship program by government
- Consumer awareness: Companies should label products as "Contains nanosilver"

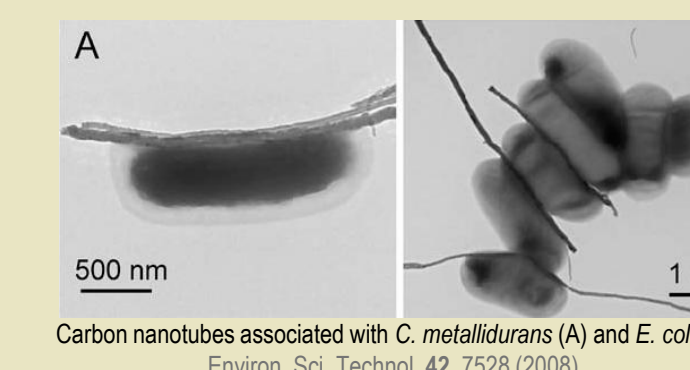
Guidelines for Carbon Nanotubes

- Mitigation: Antioxidant surfactant, tocopheryl polyethylene glycol succinate (TPGS), prevents oxidative damage to cell membranes
 Safe surfactant for "green" processing of carbon nanomaterials
- Research priorities: More studies on long term environmental fate and transport
 Comparative toxicity and mechanism
 More in vivo studies on environmentally relevant species
 Better standardization of models and characterization
- More green manufacturing methods
- Data collection from government

Carbon Nanotubes

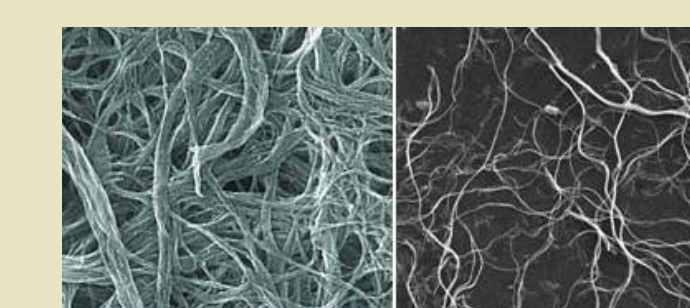
Toxicity

- Roughly 200 studies are available on nanotube toxicity.
- The majority of the reviewed papers report that nanotubes are toxic.
- Mostly acute toxicity studies on lung cells and macrophage cells, and respiratory toxicity studies on rats and mice.
- Toxicity Mechanisms of Carbon Nanotubes
 - Interaction between nanotubes and bacteria, damage to cell membrane.
 - Depletion of micronutrient contents in cell culture
 - Free radical generation by scavenging activity.
 - Effect of physical and chemical properties (surface area, shape, length, solubility, functionalization, etc.)
 - Effect of metal catalysts.
- Magnitude
 - Lowest median lethal concentration:
 1.04 mg/l in algae; 22 $\mu\text{g}/\text{ml}$ in macrophage (in vitro)



Carbon nanotubes associated with *C. metallidurans* (A) and *E. coli* (B)
 Environ. Sci. Technol. 42, 7528 (2008)

- Comparative
 - Toxicity similar to asbestos?
 - What role do catalysts and purification methods play?



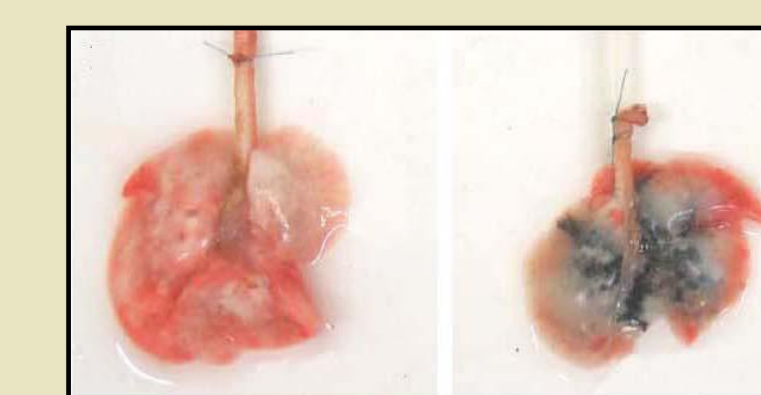
Carbon nanotubes (left) and chrysotile 'A' standard asbestos (right) both exhibit large length to diameter ratios.
<http://www.physorg.com/news/141048611.html> (left)
<http://usgsprobe.cr.usgs.gov/pict2.html> (right)

Environmental

- Showed decreased toxicity after 2.5-7 years of exposure to natural organic matter.
- Settle more quickly in water without natural organic matter.

Risk Assessment

- Most nanotubes that are ingested are purged and not retained by the body.
- The respiratory risk that is posed is not well understood due to a lack of studies on long term biopersistence.



Rat lungs exposed to 5 mg of MWCNT (left) and ground MWCNT (right)
 Toxicology and Applied Pharmacology 207, 221 (2005)