Nanomaterials and other Emerging Topics in EH

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Cambridge Public Health Department | CHA Cambridge Health Alliance

Introduction to Nanotechnology EHS

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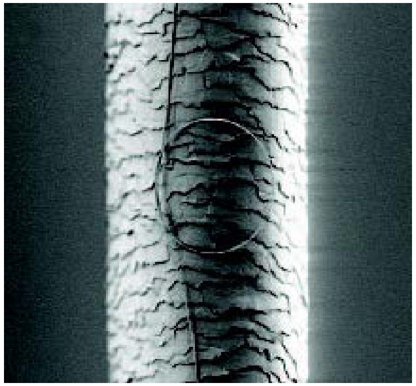
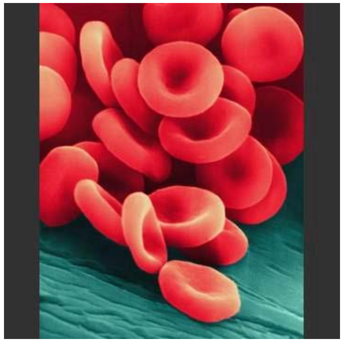
What is Nanotechnology?

- " Nano-" = 10^{-9} unit
- Refers to particles or structures with at least 1 diameter in 1-100 nm Size range
- Compare to:
  - Human Hair = 60 – 120 micrometers
  - DNA = 2 – 12 micrometers
  - Red Blood Cell = 7,000 nm
  - Water molecule = 0.3 nm





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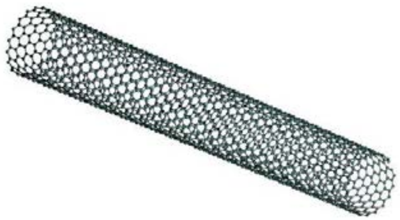
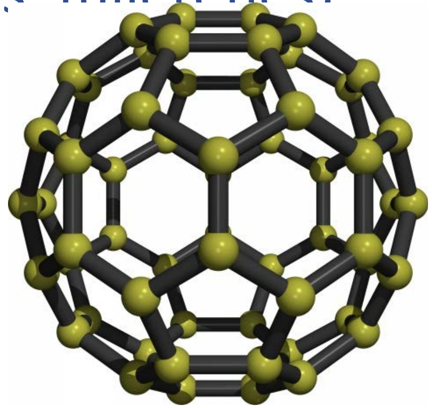
What is a Nanoparticle?

- US Federal Office of Science and Technology Policy: nanotechnology is “R&D…in the length scale of approximately 1 – 100 nanometer range…”
- Some consensus that a nanoparticle is any particle with at least one dimension less than 100 nm

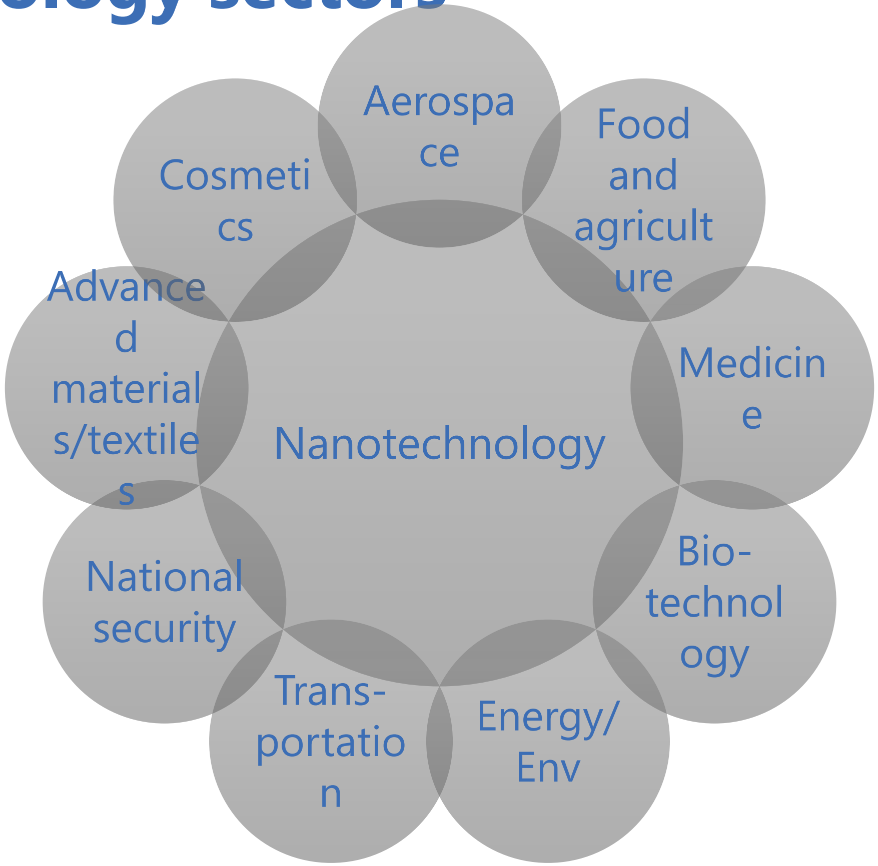
Categories of Nanoparticles

- Naturally-occurring
  (*e.g.,* forest fires, volcanoes)
- Industrial
  (*e.g.,* welding fume, diesel exhaust)
- Engineered
  (*e.g.*, carbon nanotubes, fullerenes)





R&D and Use – Spanning multiple technology sectors



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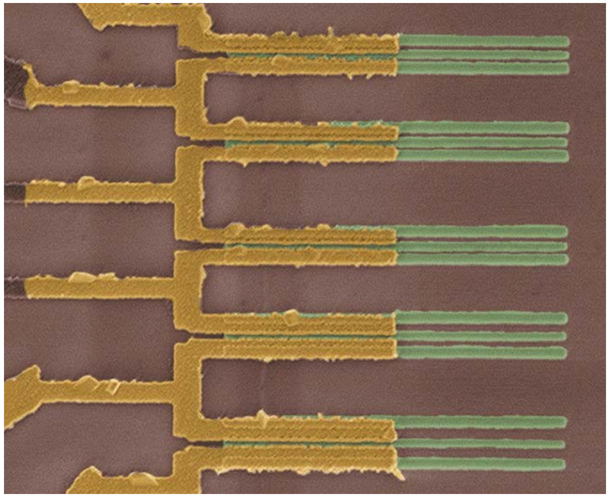
New York Times, 1 Oct 2015

"IBM Scientists Find New Way to Shrink Transistors"

- CNT field effect transistors
- Increase speed and/or reduce power use by a factor of 7



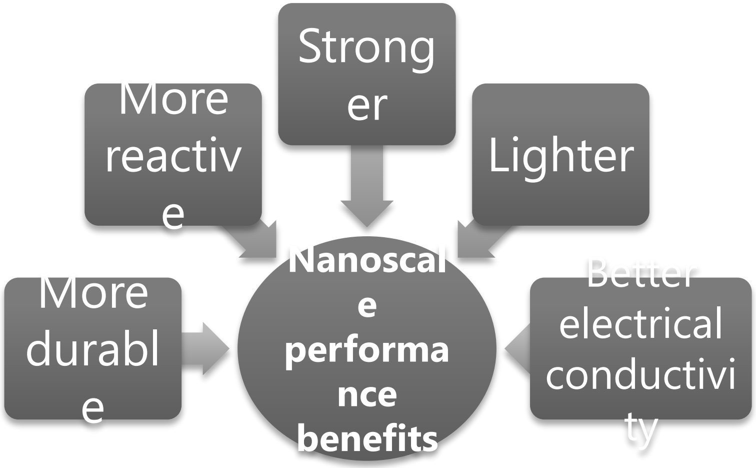
Types of Engineered Nanomaterials

Broad Categories: Engineered Nanomaterials

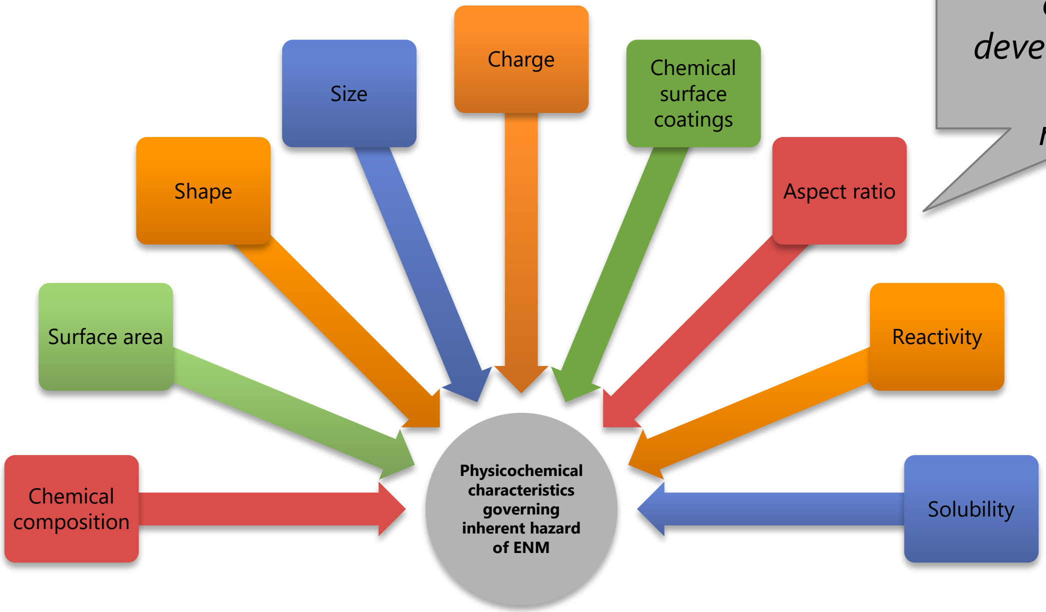
Carbon-based	Metal	Metal Oxides	Dendrimers	Composites	Quantum Dots
fullerenes, carbon nanotubes	Silver, gold, copper	Titanium dioxide, zinc oxide, iron oxide	Hyperbranched polymers, dendrigraft polymers, dendrons	Nano clays, polymer beads	Quantum Dots

Engineered nanomaterials: enhanced performance compared to their bulk counterparts

- At nano-scale:
  - material **properties change** - melting point, fluorescence, electrical conductivity, and chemical reactivity
  - **Surface size is larger** - more material comes into contact with surrounding materials and increases reactivity



Physical-chemical properties: key to performance AND inherent hazard



Can we tune these properties to enhance performance AND reduce their otential hazards to ensure the safe development and use of engineered nanomaterials?

TURI's Engineered NM Fact Sheet (www.turi.org)

- Primer on 4 engineered nanomaterials
  - CNTs, quantum dots, nano titanium dioxide, nanosilver
- Safe use of ENM section

Massachusetts Chemical & Materials Fact Sheet

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Engineered Nanomaterials

(revised December 2017)

This fact sheet is part of a series of chemical and material fact sheets developed by TURI to help Massachusetts companies, community organizations and residents understand the use of hazardous substances and their effects on human health and the environment. This fact sheet also includes information on safer alternatives and safer use options.

Broad categories of nanomaterials

Category	Examples
Metals	Silver, gold, copper
Metal oxides	Titanium dioxide, zinc oxide, iron oxide
Carbon-based	Multi- and single-walled carbon nanotubes, fullerenes
Dendrimers	Hyperbranched polymers, dendrigraft polymers, dendrons
Composites	Nano clays, polymer beads
Crystalline semiconductors	Quantum dots

Engineered Nanomaterials: What are They?

Engineered nanomaterials are a diverse set of very small-scale substances. They are commonly defined as engineered objects that have at least one dimension between 1 to 100 nanometers (nm), or roughly 100,000 times smaller than the diameter of a human hair.[1] While some types of nanomaterials occur naturally or are formed incidentally, this fact sheet focuses on nanomaterials that are intentionally designed, engineered and manufactured for use in commercial materials, devices and structures.

There is tremendous variation among engineered nanomaterials. They can vary not only in chemical composition, but also in size, shape, and surface coatings. They can exist as films or sheets, as fibers, horns, rings, tubes, spheres, or irregularly shaped particles. They can be engineered from nearly any chemical substance or mineral.

The physical, chemical and biological characteristics of nano-scale materials can be substantially different from the characteristics of the same substance of a larger size. Material strength, optical properties, conductivity and reactivity of nanomaterials often far exceed that of their larger bulk counterparts. These novel properties have spurred tremendous interest in nanotechnology across many industrial, commercial and medical sectors.

While nanomaterial research and development is still relatively young, these materials are now being used in thousands of industrial and consumer products, including paints and coatings, sensors, photovoltaics, electronics, tires, textiles, sporting goods, and personal care products. They are also being used in medical diagnostic and drug delivery devices, and in environmental remediation.[2]

Human Health and Environmental Concerns

Many of the chemical, biological and physical properties of engineered nanomaterials that make them technologically and commercially desirable are the same properties that may make engineered nanomaterials more toxic than the same substance of a larger size. Unbound nanoparticles and nanofibers are of particular concern for human health and the environment because of the potential for exposure. These are engineered nanomaterials that are in loose powder form or suspended in liquids and therefore dispersible, rather than being confined within a matrix or bound to surfaces.

The environmental fate and transport of nanoparticles is complicated by the fact that in air and water they can exist as individual particles or agglomerates, or they can adhere to larger particles. Because nanoparticles have a slow rate of settling, some engineered nanomaterials can remain suspended in air and water for longer periods of times and become more broadly dispersed over wider geographic areas than larger particles of the same size.[3] Individual nanoparticles or small agglomerates are so small that they can readily enter the human body through inhalation, ingestion and through the skin. In workplaces, inhalation is a widely recognized route of human exposure.

Decades of particle toxicology research have established that particle size influences hazard. As particles become smaller, several key characteristics of the material change compared to their bulk counterpart. At the same exposure dose, compared to micrometer scale particles, nanoscale materials:

- are greater in sheer number;
- have greater surface area;
- have enhanced ability to redistribute from their site of deposition and to travel by new pathways, including the

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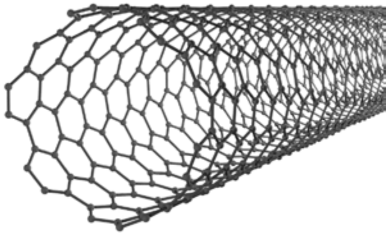
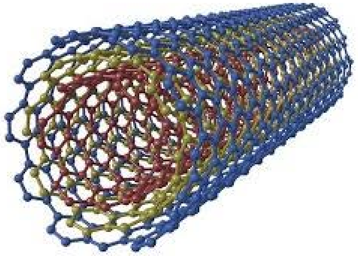
Carbon Nanotubes





- Divided into 2 broad categories:
  - SWCNTs & MWCNTs: Dramatic variation in size, shape, chemical composition, reactivity, etc.
- Emerging as substitutes for chemical toxicants
  - e.g., flame retardants, antifouling paints
- Primary hazard end points of concern:
  - Pulmonary fibrosis ; pulmonary inflammation (NIOSH, many others)
  - Cancer (IARC group 2B) [one type of MWCNTs]

Quantum Dots

- Crystalline semiconductors
  - Semiconductor core: CdSe; CdTe; ZnS
  - Semiconductor shell: most often ZnS
- Primary health hazard endpoints of concern:
  - Cd cores are of concern (carcinogenicity); toxicity seems dependent on coatings and release mechanisms of Cd2+ ions
  - Dose dependent lung injury and inflammation (based on specific functionalized CdSe)

Nano titanium dioxide

- Size-dependent effects (i.e., micrometer versus nanoscale matters)
- Primary health hazard endpoints of concern:
  - Pulmonary inflammation
  - Genotoxicity (under certain conditions)
  - Carcinogenicity (potential occupational carcinogen, NIOSH)
  - organ/liver effects (at high doses)

Nanosilver

- Collodial silver
- Primary health hazard endpoints of concern:
  - Aquatic toxicity – research suggests effects are dependent on the release of silver ions
    - Functionalization/aggregation/sulfidation – all possible mechanisms that reduce impacts

Best Management Practices – NIOSH Guidances

NTRC NANOTECHNOLOGY RESEARCH CENTER

Controlling Health Hazards When Working with Nanomaterials: Questions to Ask Before You Start

Here are some questions you should ask yourself before starting work with nanomaterials.	Here are some options you can use to reduce exposures to nanomaterials in the workplace. These options correspond with the questions on the left.		
(1) FORM Have you done a job hazard analysis? What is the physical form of the nanomaterial? How much are you using? Can you reduce exposure to the nanomaterial by changing its form (for example, putting powder into a solution) or reducing the amount you are using?	**DRY POWDER** (typically highest potential for exposure)	**SUSPENDED IN LIQUID**	**PHYSICALLY BOUND/ ENCAPSULATED** (typically lowest potential for exposure)
(2) WORK ACTIVITY How are you using the nanomaterial? Could the work activity cause exposure? Is the likelihood of exposure low or high? Can you change the way you do the activity to reduce the exposure?	**Applies to Dry Powder Nanomaterials** • Higher potential for exposure: Dumping bags of powder, bagging or sieving of products • Lower potential for exposure: Scooping/weighing of product, transporting containers with light surface contamination or closed barrels/bottles/bags	**Applies to Nanomaterial Suspended in Liquids** • Higher potential for exposure: Spraying, open top sonication, producing a mist • Lower potential for exposure: Cleaning up a spill, pipetting small amounts, brushing	**Applies to Physically Bound/Encapsulated Nanomaterial** • Higher potential for exposure: Cutting, grinding, sanding, drilling, abrasive blasting, thermal release • Lower potential for exposure: Manual cutting and sanding, painting with a roller or brush
(3) ENGINEERING CONTROLS Based on the form and the work activity, what engineering controls will be effective? What are the key design and operational requirements for the control? How does the non-nanomaterial base material or liquid affect exposure?	**Applies to Dry Powder Nanomaterials** • Chemical fume hood • Glove box • Nanomaterial handling enclosure • Ventilated bagging or dumping stations • High-efficiency particulate air (HEPA)-filtered local exhaust ventilation	**Applies to Nanomaterial Suspended in Liquids** • Chemical fume hood • Glove box • Nanomaterial handling enclosure • Local exhaust ventilation • Ventilated spray booth	**Applies to Physically Bound/Encapsulated Nanomaterial** • Chemical fume hood • Glove box • Local exhaust ventilation • Downdraft table • Wet cutting/machining • Ventilated tool shroud • Blasting cabinet
(4) ADMINISTRATIVE CONTROLS Have you considered the role of administrative controls? Have you set up a plan for waste management? Have you considered what to do in case of a spill or how you will maintain equipment?	**Applies to All Nanomaterial Forms** • Establish a chemical hygiene plan • Perform routine housekeeping • Train workers • Use signs and labels • Restrict access to areas where nanomaterials are used	• Handle and dispose of all waste materials (including cleaning materials/gloves) in compliance with all applicable federal, state, and local regulations • Use sealed/closed bags or containers, and secondary containment • Label containers, such as "contains nanoscale titanium dioxide"	• Wet wipe or use a HEPA-filtered vacuum • Do not dry sweep or use compressed air • Incorporate nanomaterial safety into existing programs such as hazard communication
(5) PERSONAL PROTECTIVE EQUIPMENT If the measures above do not effectively control the hazard, what personal protective equipment can be used? Have you considered personal protective equipment for the non-nanomaterial base material or liquid?	**Applies to All Nanomaterial Forms** • Nitrile or chemical resistant gloves • Lab coat or coveralls • Safety glasses, goggles, or face shield	• Respiratory protection when indicated and engineering controls cannot control exposures, and in accordance with federal regulations (29 CFR 1910.134) • NIOSH guidance on respirators can be found at www.cdc.gov/niosh/topics/respirators/	• Use personal protective equipment during spill cleanups and equipment maintenance

CDC NIOSH Centers for Disease Control and Prevention National Institute for Occupational Safety and Health

Are you interested in learning more about how you can safely work with nanomaterials or want to stay up-to-date on nanotechnology safety? See the NIOSH NTRC website for more information and links to guidance documents: www.cdc.gov/niosh/topics/nanotech/

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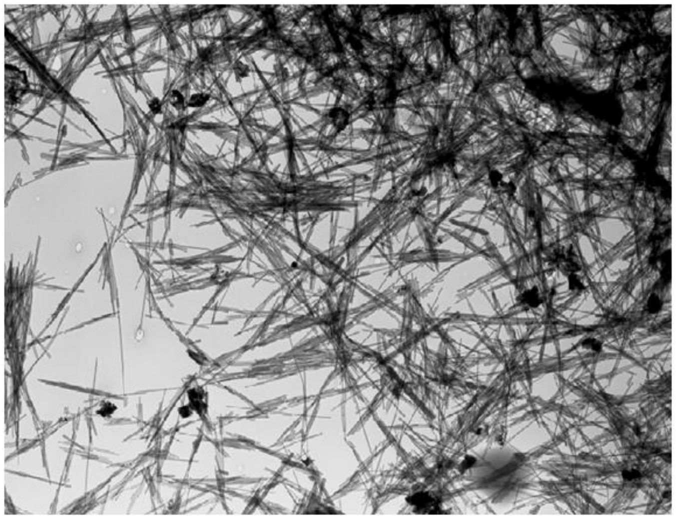
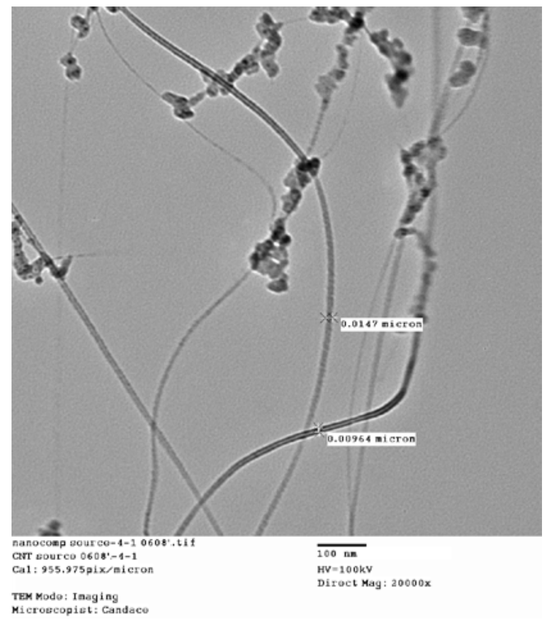
Focus on Carbon Nanotubes





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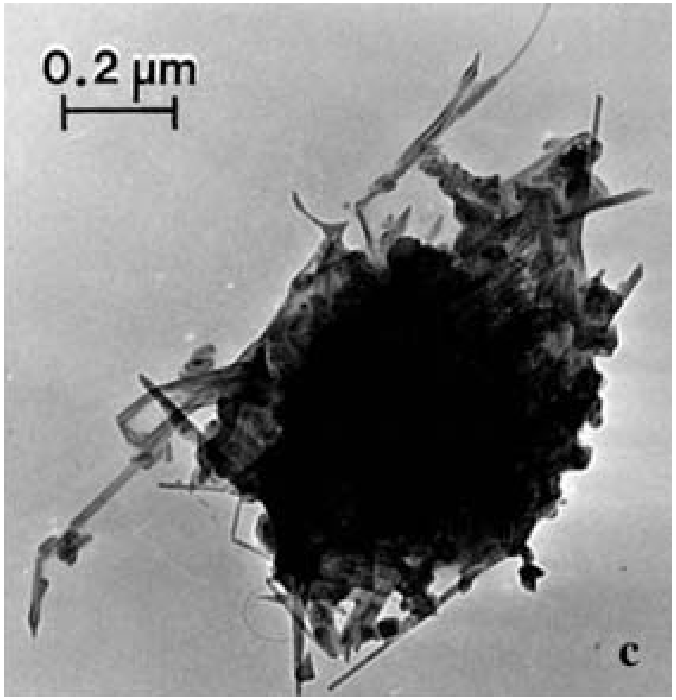
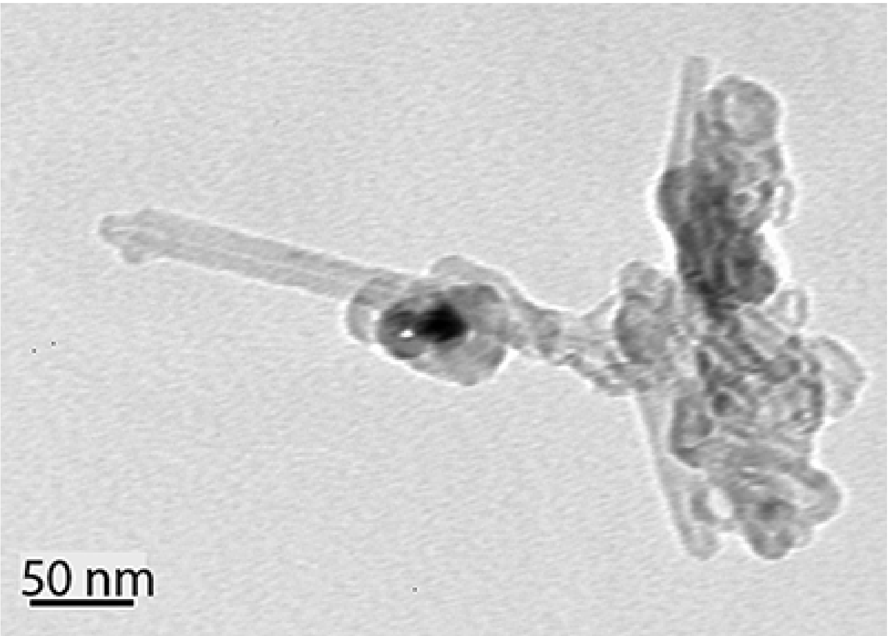
10,000 Year-Old Greenland Ice Core



https://medium.com/@mutlay/carbon-nanotubes-are-not-invented-and-this-is-bad-for-our-health-8e35307a8349

CNT Collected from a Deere Engine

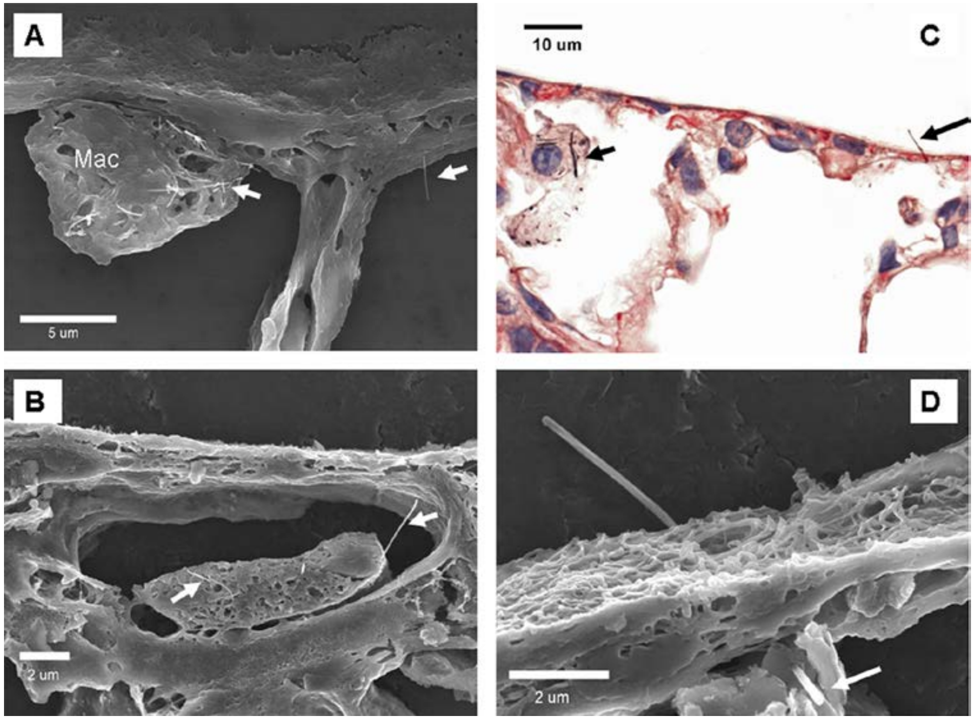


Heejung S. Jung, Art Miller, Kihong Park & David B. Kittelson (2013) Carbon nanotubes among diesel exhaust particles: real samples or contaminants?, Journal of the Air & Waste Management Association, 63:10, 1199-1204, DOI: [10.1080/10962247.2013.812048](10.1080/10962247.2013.812048)

CNTs cause Mesothelioma?

- Carbon nanotubes introduced into the abdominal cavity of mice show asbestos-like pathogenicity in a pilot study, Poland, et al., Nature Nano., 2008.
- Induction of mesothelioma in p53+/- mouse by intraperitoneal application of multi-wall carbon nanotube, Takagi, et al., J. Toxicol. Sci, 2008.

Mercer, et al., Distribution and persistence of pleural penetrations by multi-walled carbon nanotubes, *Part. Fibre Tox.*, 2010.



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CNTs cause Mesothelioma?, Cont.

Poland: “Here we show that exposing the mesothelial lining of the body cavity of mice, as a surrogate for the mesothelial lining of the chest cavity, to long multiwalled carbon nanotubes results in asbestos-like, length-dependent, pathogenic behaviour… Our results suggest the need for further research and great caution before introducing such products into the market if long-term harm is to be avoided.”

Dec 2014 – IARC designates “certain MWCNTs” as 2B, Suspect Human Carcinogen

Honoring a Precautionary Approach

Put simply, we must adopt a precautionary approach to engineered nanomaterials. This is critically important for carbon nanotubes.

We cannot wait for national regulations before taking action.

Public health officials must become involved.

Why Should Local Health Departments Be Aware?

- Nanomaterial sector companies are <u>not</u> being regulated for the special materials used, processed or manufactured (state or federal)
- Emerging research points to special biological risks to go along with the special properties of some compounds
- Very little work on health effects, particularly L/T
- Occupational exposures and concerns from neighbors

Concerns Beyond OccHealth and Community Health Risks

- Some Engineered Nanomaterials (ENMs) can pose <u>explosive hazards</u>
- Special hazard awareness training is not required for local First Responders
- Many towns are not aware that ENMs are present
- Since many assume State or Federal oversight, there is often false assurance at the local level
- Of course that's if its being considered at all….

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Local Scenarios: Fire Department Readiness

The Fire Department responds to a fire and in reviewing the emergency response plan sees that there are nanomaterials in use. They ask if the firefighters should use respiratory protection and if the neighborhood should be evacuated. Concerns remain about the explosivity of airborne nanomaterials.

Local Scenarios: Planning, Zoning, Permitting

The Planning Board is reviewing a proposal for a nanofacilty that is setting up operations in the town and asks you for an opinion on what questions they should ask the proponents, concerning safe operations.

Local Scenarios: Neighborhood Concerns

A neighborhood group is concerned about whether a nanofacility near them is emitting particles. They seek assurance that appropriate controls are in place.

Local Scenarios: Workplace Safety

A nano facility is operating in town, providing jobs to local residents. A group of workers has requested that the facility receive an inspection from the health department to determine if workers are receiving adequate protection.

A Sensible Strategy for BOHs and Fire Departments

- Approaching an R&D lab, manufacturer, or end-user to request voluntary cooperation with local first response agencies is common and usually seen as appropriate
- Using a planning framework is less of a concern for a sector that is often "shy" or concerned about IP theft
- Without State/Federal rules or conclusive health risk data the preventive approach is a Best Practice and is consistent with the public health mission

Cambridge Public Health Department

Handling Emerging EH Concerns

- PFAS, EMF exposures (5G installs), EDCs (PCBs, dioxins, plasticizers, pesticides), LED lights/circadian health, biotech/biosafety may be brought to BOHs for response
- Public forums, policy statements, stakeholder advisory groups, or simple referral to State/Federal and non-profit content experts
- Some communities may have ability to hire consultants, lit reviews, policy papers. Most do not have this luxury.
- **MA BEH, MA DEP ORS, EPA, CDC, ATSDR**, reputable NGOs
- Use our amazing networks: **BOHs, MHOA, MEHA, MAHB**

Working with Emerging Tech

1976 - Concerns about Recombinant DNA were brought to local elected officials. Moratorium enacted.

1977- Public Debate, Special Session of City Council,

Cambridge began oversight of biotech research (CERB)

1981 – Standard regulations (like Food Code)

1981- present – Biotech chooses Cambridge, consolidates

1990s – present – Mass Biotech Council (MassBio) begins to grade communities on their “readiness” for the sector and emphasize local oversight as positive factor.

Today – Clear rules bring predictability, public assurance

Next Steps: Local Options

- Cambridge Nanomaterials Advisory Committee (2006-2007)
- Nanomaterials Health and Safety Survey co-sponsored by Fire Department
- Option to enact local reporting requirements to protect workers, neighbors and first responders
- **Work with statewide efforts to require oversight/registry of nanomaterials**

Cambridge Public Health Department

Other Recent Issues of Concern

- PFAS
- Artificial turf v. organic lawns
- Alternatives to methylene chloride for paint stripping
- Water instead of perc for dry cleaning
- EMF and 5G installations
- LED lights and circadian health

Information on many of these topics, and more, can be found on the TURI website: www.turi.org.