Nanotechnology and the Commonwealth: Use and Implications

Thursday, December 7th 2017

Toxics Use Reduction Institute

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Welcome/Webinar Logistics

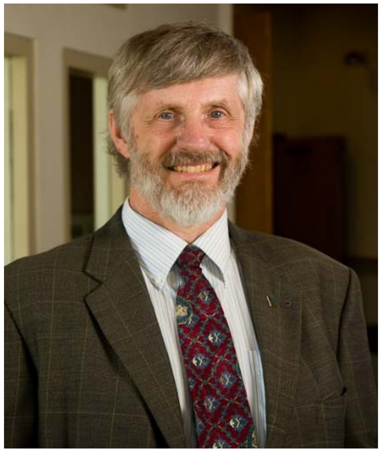
- Due to the number of participants on the Webinar, all lines will be muted
- If you wish to ask a question, please type your question in the Q&A box located in the drop down control panel at the top of the screen
- All questions will be answered at the end of the presentations
- Call is being recorded

Today's Speakers

Molly Jacobs
LCSP

Senior Research Associate

Dr. Mike Ellenbecker
TURI



Director

Dr. Gregory Morose
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Nanotechnology 101

Molly Jacobs

Senior Research Associate, Lowell Center for Sustainable Production

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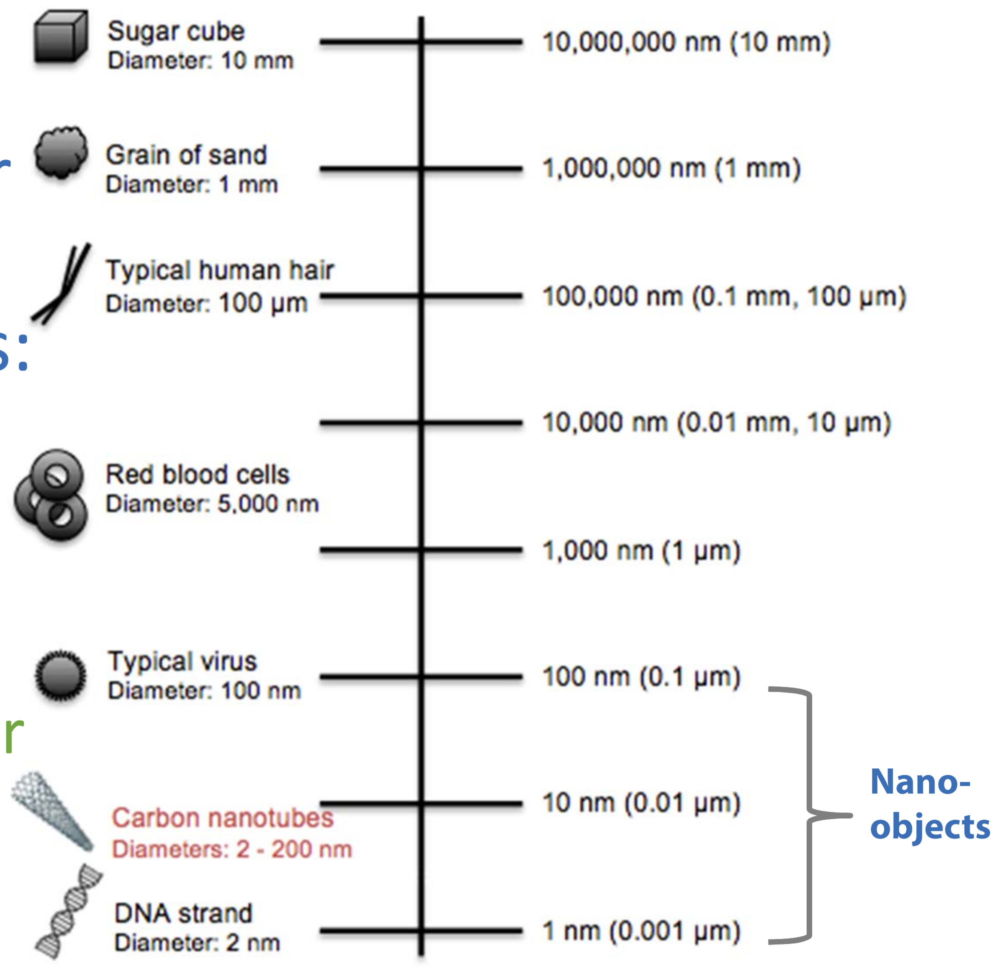
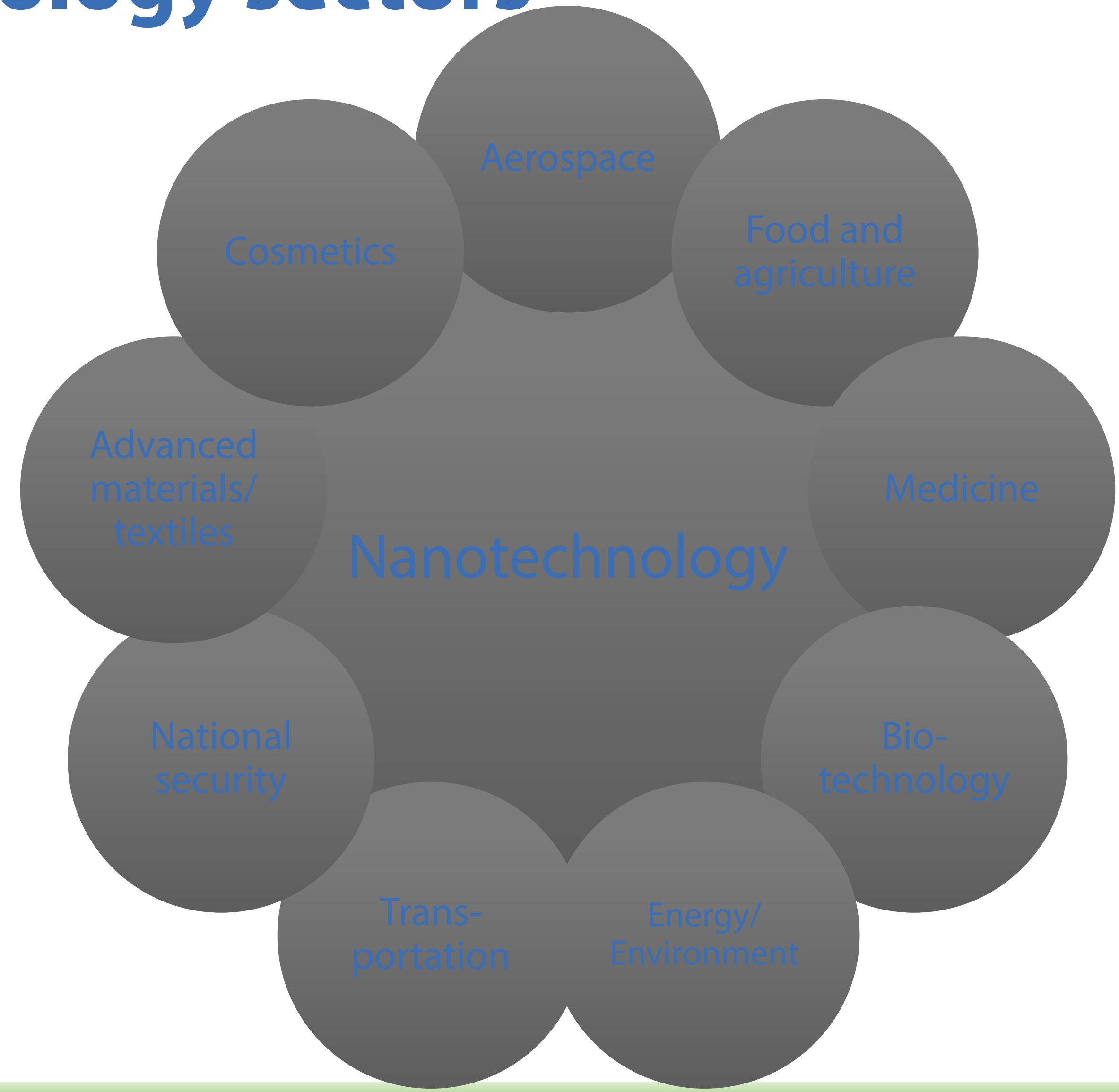
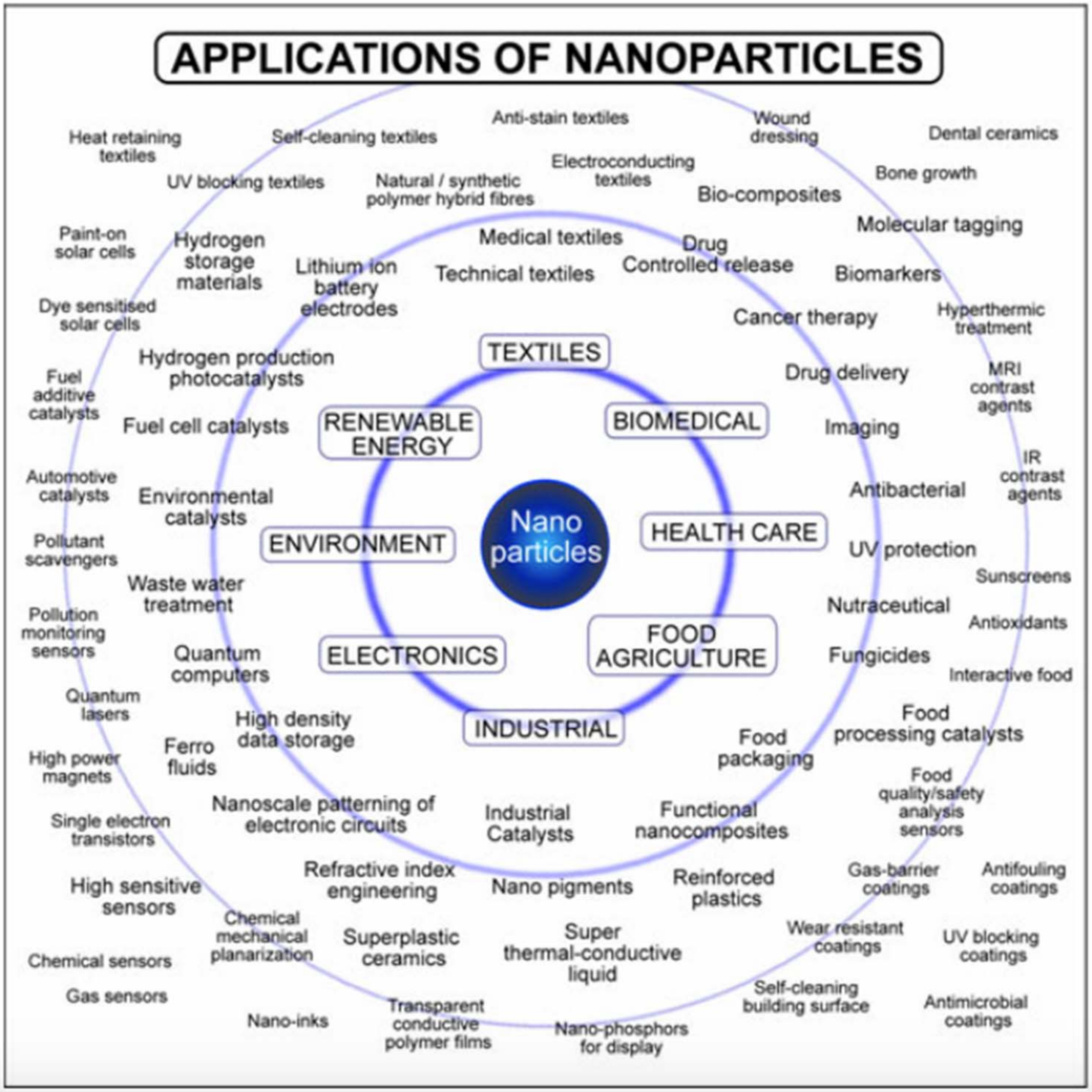
What is Nanotechnology

- The study of the controlling of matter on an atomic and molecular scale
- Engineered nano objects: at least one dimension between 1 to 100 nanometers (nm)
  - roughly 100,000 times smaller than the diameter of a human hair



R&D and Use – Spanning multiple technology sectors





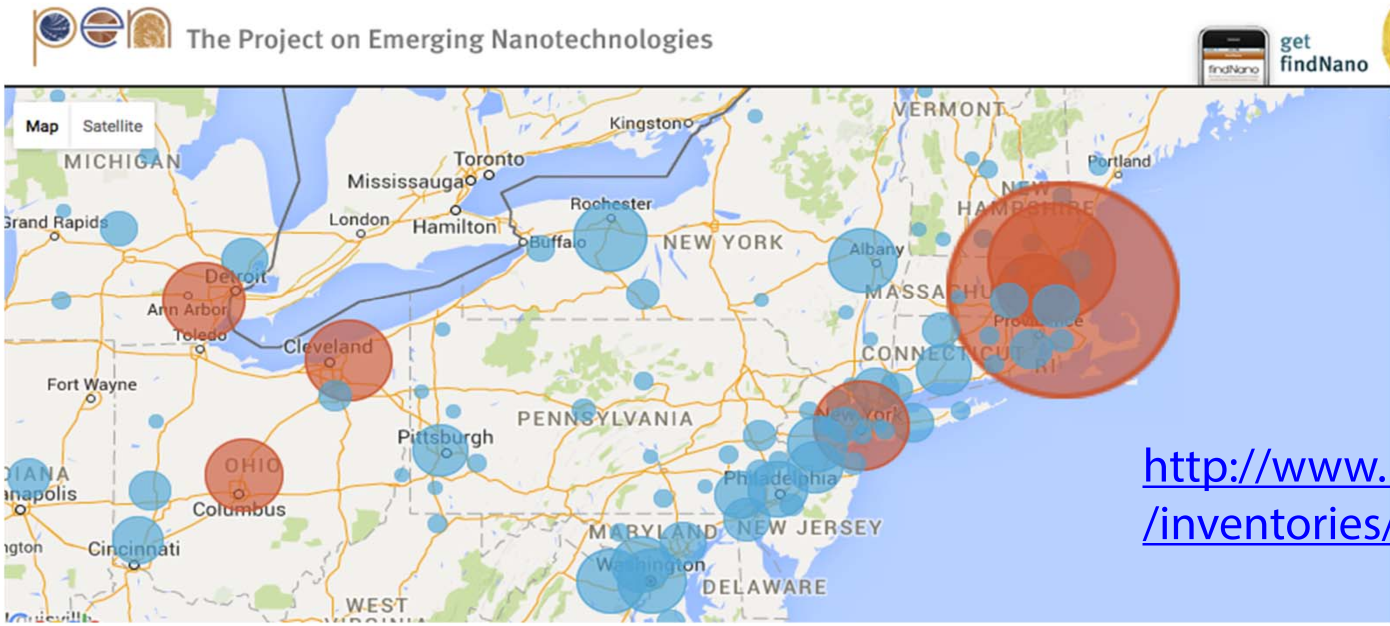
Source: Takuya Tsuzuk. *International Journal of Nanotechnology (IJNT)*, **Vol. 6, No. 5/6,** 2009 *as cited by Nanowerk*

Types of Engineered Nanomaterials

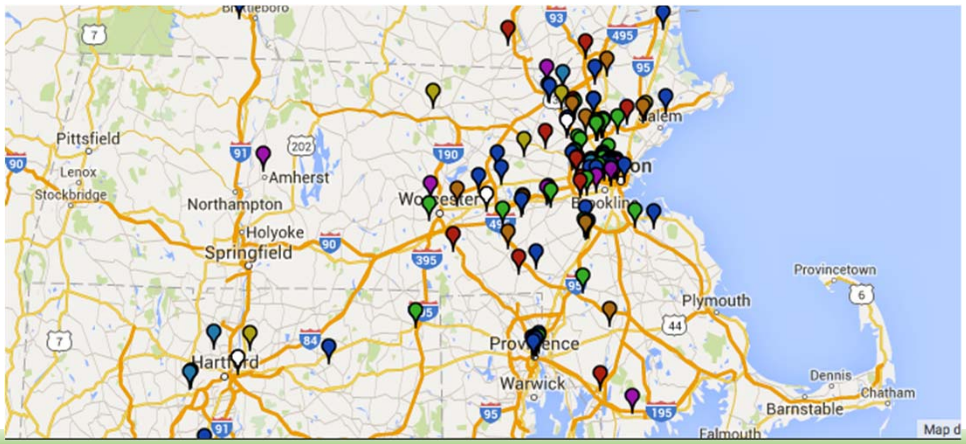
Broad Categories: Engineered Nanomaterials

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

Nanotechnology in the Commonwealth



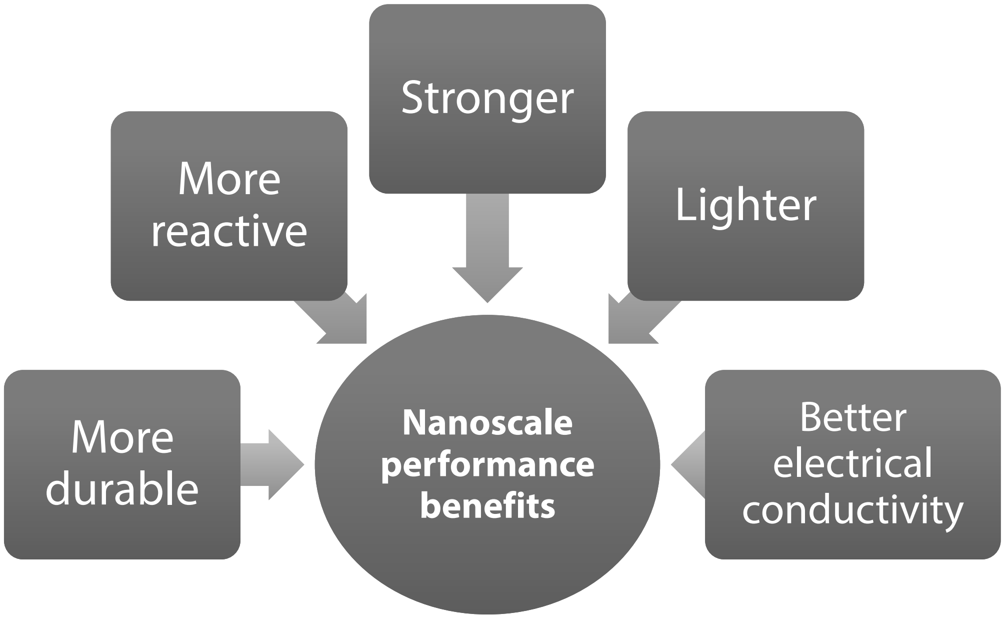
http://www.nanotechproject.org/inventories/map/



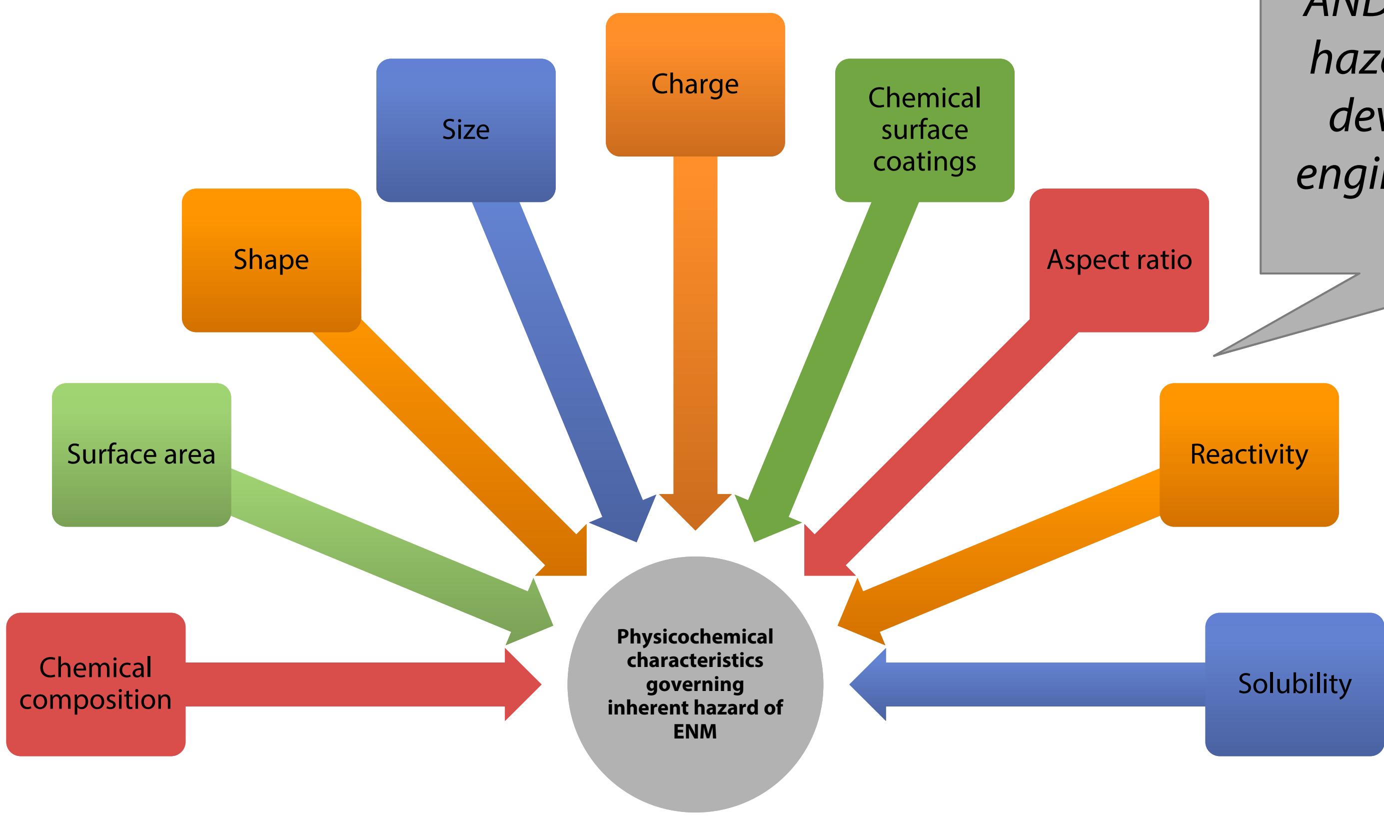
MA is among the top 5 in the country for commercial and R&D activity on nanomaterials/nanotechnology

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 potential hazards to ensure the safe development and use of engineered nanomaterials?

A deep dive on environmental safety and health aspects of one engineered nanomaterial: Carbon Nanotubes

Dr. Michael Ellenbecker

Director, Massachusetts Toxics Use Reduction Institute

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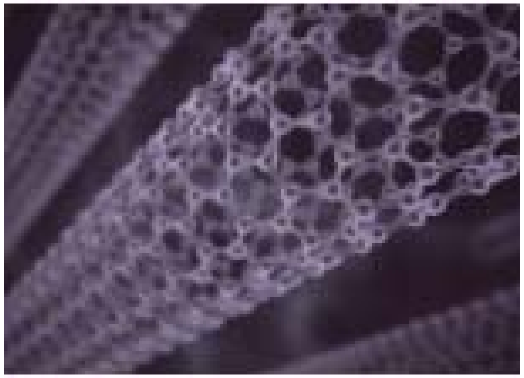
Engineered Carbon Nanotubes – What are They?

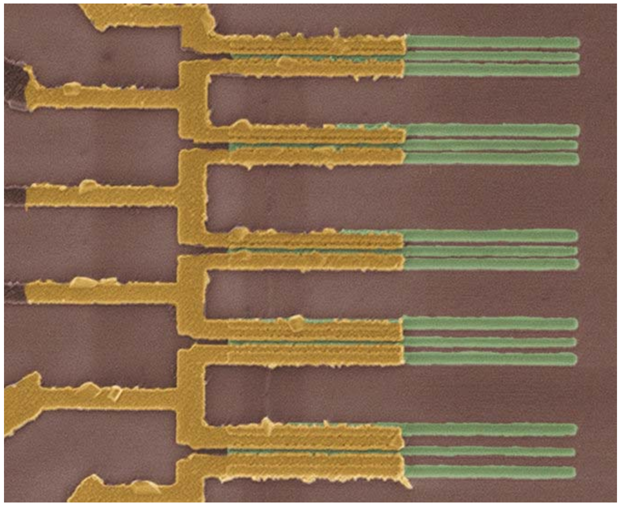


- Discovered in 1991
- Divided into 2 broad categories:
  - Single-walled CNTs (SWCNTs)
  - Multi-walled CNTs (MWCNTs)
- Important: CNTs are not a single material. ~50,000 SWCNTs and likely even more potential combinations of MWCNTs
  - Vary based on size, shape, chemical composition, reactivity, etc.

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



Emerging as substitutes for chemical toxicants

BIOCYL™ X1

Fouling release coatings

Anti-fouling marine paints [substitutes for tributyltin, copper boat paints, etc]

THERMOCYL™ X1

Flame retardant coatings for non-metallic substrates

Flame retardants for electronics, wire/cable, textiles, foams [substitutes for halogenated flame retardants]

CNT Toxicity

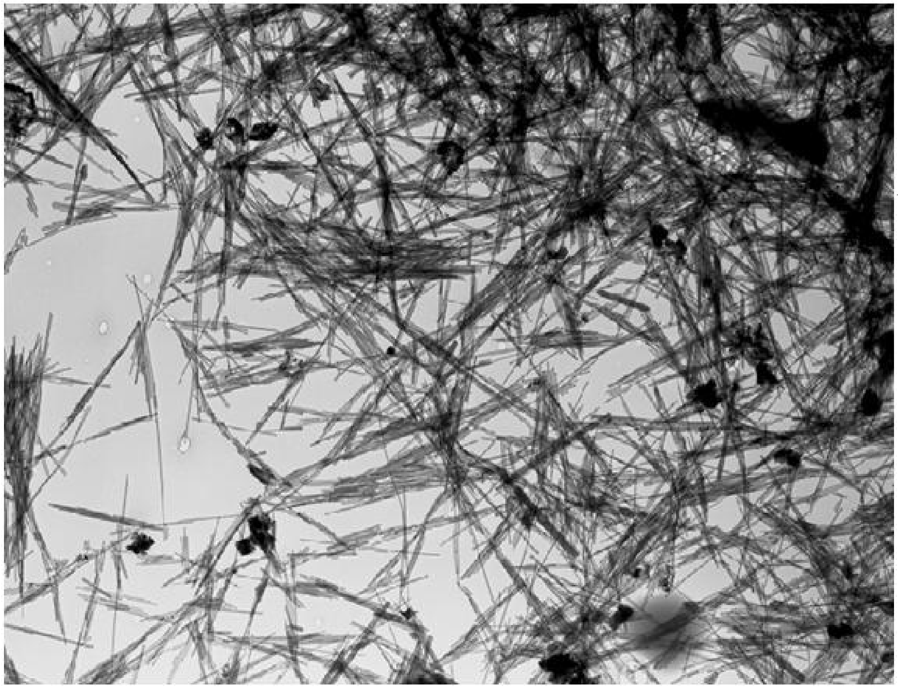
- Many studies published in the last 10 years
- Primary end points of concern:
  - Pulmonary fibrosis
  - Inflammation
    - Lung tissue
- Cancer
  - Lung tumor promoter
  - Mesothelioma

Current Intelligence Bulletin 65, Occupational Exposure to Carbon Nanotubes and Nanofibers.
Available at: http://www.cdc.gov/niosh/docs/2013-145/pdfs/2013-145.pdf.

Cancer & MWCNTs

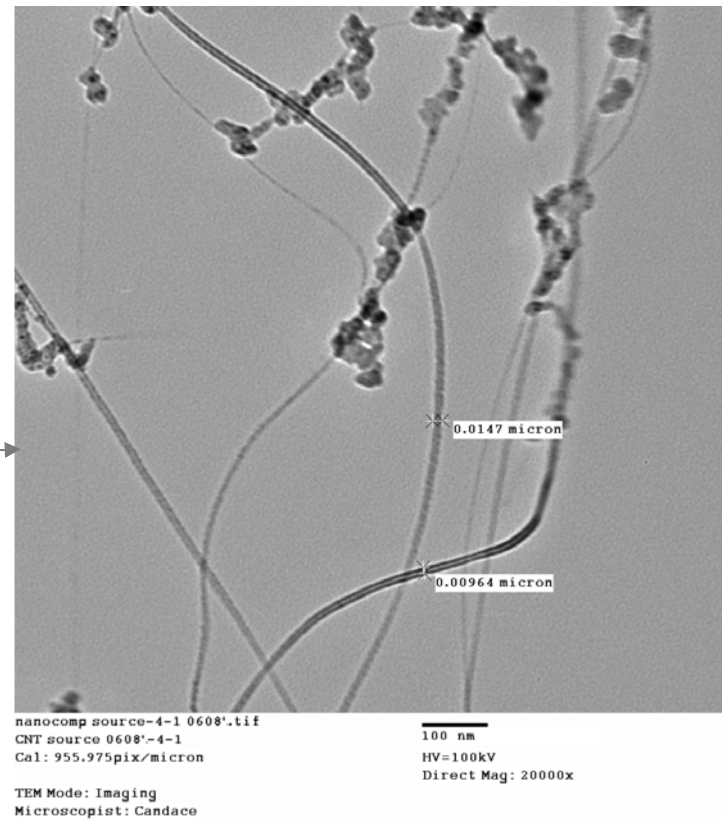
- Tumor promotion [high aspect ratio MWCNTs]:
  - mouse inhalation study, first exposed to methylcholanthrene (MCA) via intraperitoneal injection.
  - Strong promotion of lung tumors [pulmonary adenomas and adenocarcinomas]
  - Strong promotion of malignant serosal tumors consistent with sarcomatous mesothelioma

Sargent LM, et al. *Part Fibre Toxicol*. 2014 Jan 9;**11**:3. doi: 10.1186/1743-8977-11-3.



Asbestos

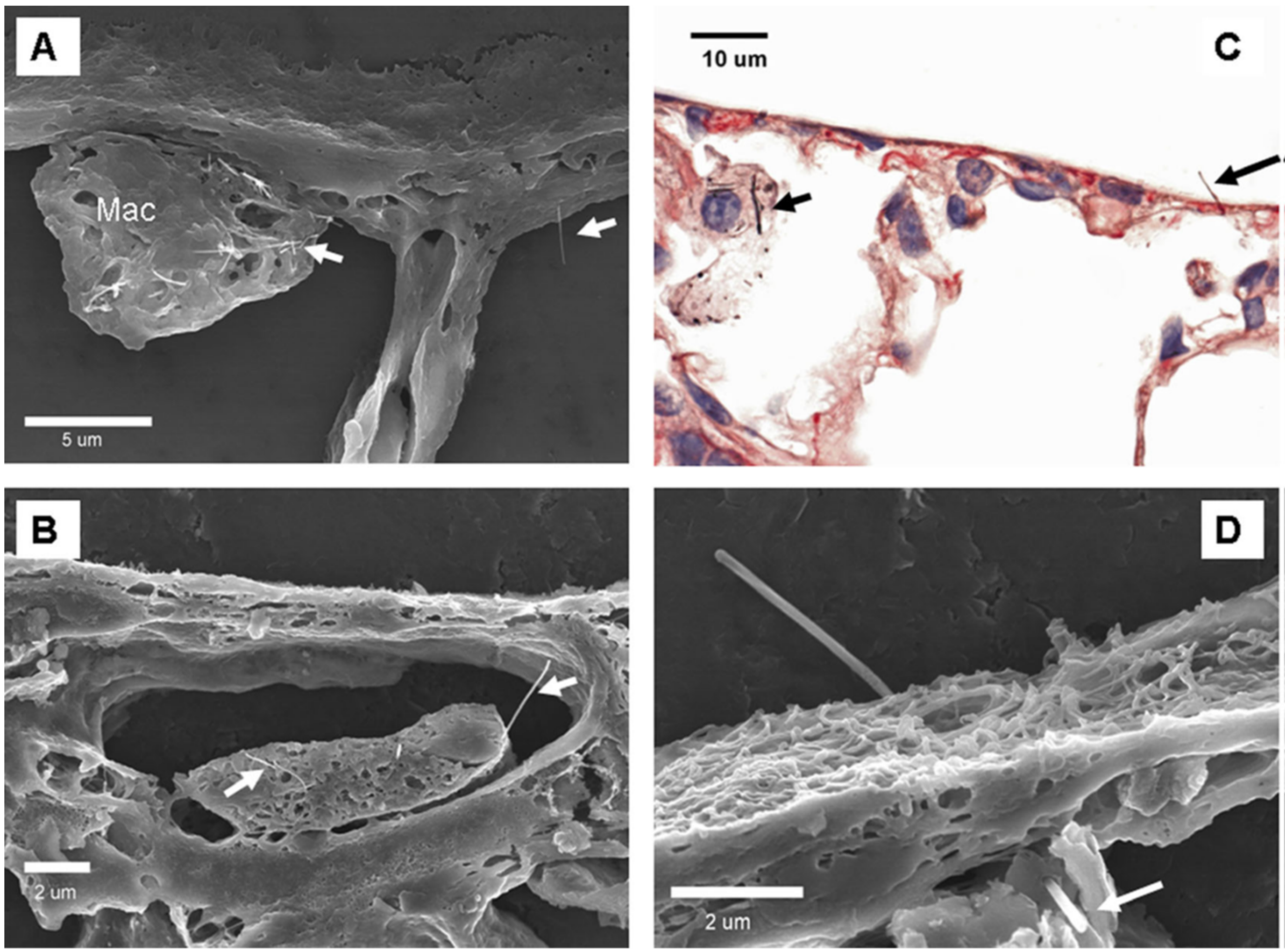
CNTs



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.



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, Possible Human Carcinogen

Grosse Y et al. *Lancet Oncol*. 2014;**15(13):** 1427-28.

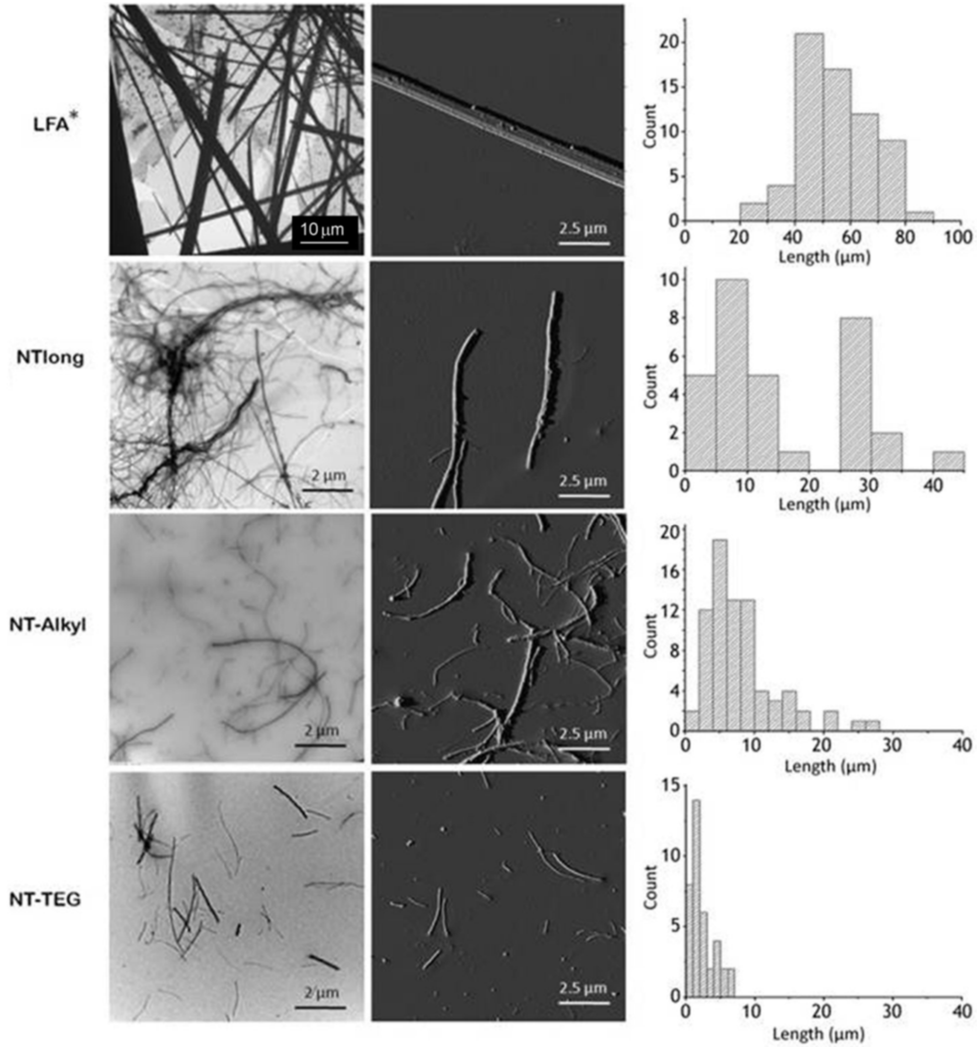
Fiber Morphology Important

- In animal studies thus far:
  - SWCNTs do not cause mesothelioma
  - Thin (d < 15 nm) MWCNTs – ditto
  - Thick (d > 150 nm) MWCNTs – ditto
- But – all commercially available MWCNTs :

  15 nm < d < 150 nm
- Short (L < 1-5 μm) MWCNTs – ditto

Can we make them all short?

Functionalization can affect Length



Ali-Boucetta, *et al.*, *Angew. Chem. Int. Ed*. 2013, **52**, 2274 –2278, DOI: 10.1002/anie.201207664

Human Studies

- Few human studies to date
  - Case reports of CNTs found in the lungs of 911 first responders
  - Recent case-control study revealed MWCNT manufacturing workers (levels 3x above the NIOSH REL) found biomarkers of effect similar to conclusions from tox studies
    - increase in serum & sputum inflammatory & fibrotic biomarkers [IL-1**β**, IL6, TNF-**α**, inflammatory cytokines, KL-6, TGF-**β**1]

Wu, M. et al. *Environ. Health Perspect*. 2010; **118**: 499–504.
Fatkhutdinova LM et al. *Toxicol and App Pharmacol*. 2016; **299**: 125–131.

Emerging Ecotoxicity Concerns

- Daphnids *(Daphnia magna)*
  - Interferes with food uptake & movement at low concentrations [MWCNTs & SWCNTs]; More toxic with longer exposures; Impaired growth and reproduction at very low levels
- Juvenile rainbow trout *(Oncorhynchus mykiss)*
  - Systemic toxicity at very low levels (consistent with GHS classification of "extremely toxic to aquatic life")
- Powerful anti-microbial agent
  - Implications for sewage treatment plants

*variation in findings given differing physicochemical characteristics

Source: Petersen, et al. *Env Sci Technol* 2011; **45(23):**9837-9856.

CNTS in Products

- If CNTs are bound in a matrix (e.g., incorporated into an epoxy matrix), are they still of concern?
- In normal use, probably not, but cutting, sanding, etc., can release CNT fibers
- A recent study found no difference in pulmonary effects between CNT and non-CNT epoxies, but increased liver function damage with the CNT epoxy

Source: Saber, et al., *Particle and Fiber Toxicology* 2016; **13**:37.

Principles for Safer Nano

Dr. Gregory Morose
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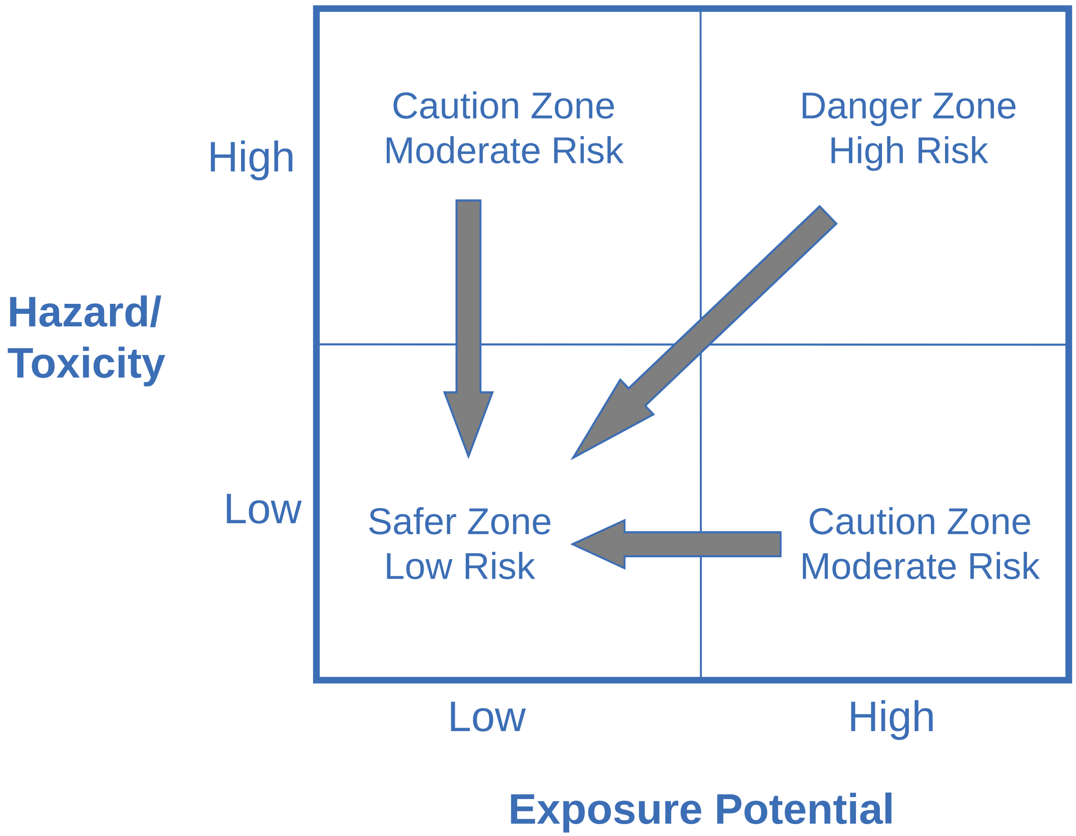
Risk Mitigation Matrix



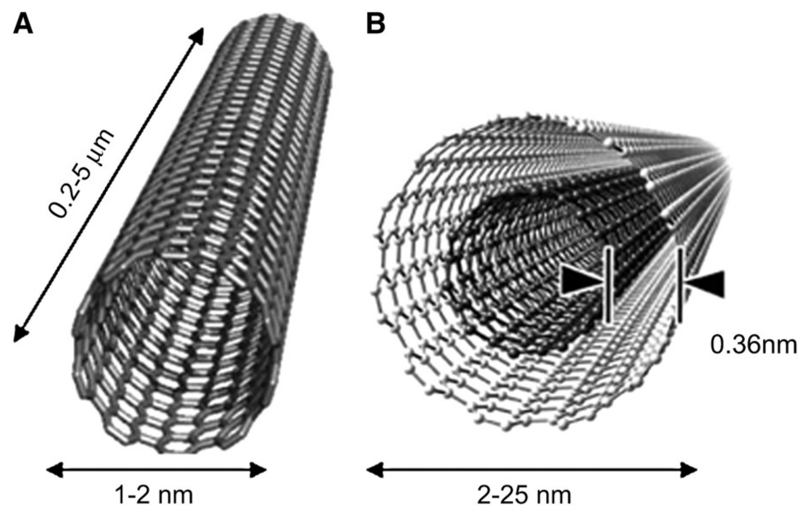
Five Principles of Design for Safer Nanotechnology

S	**Size, surface, and structure**	**#1**
A	**Alternative materials**	**#2**
F	**Functionalization**	**#3**
E	**Encapsulation**	**#4**
R	**Reduce the quantity**	**#5**

Principle 1: Size, Surface, Structure

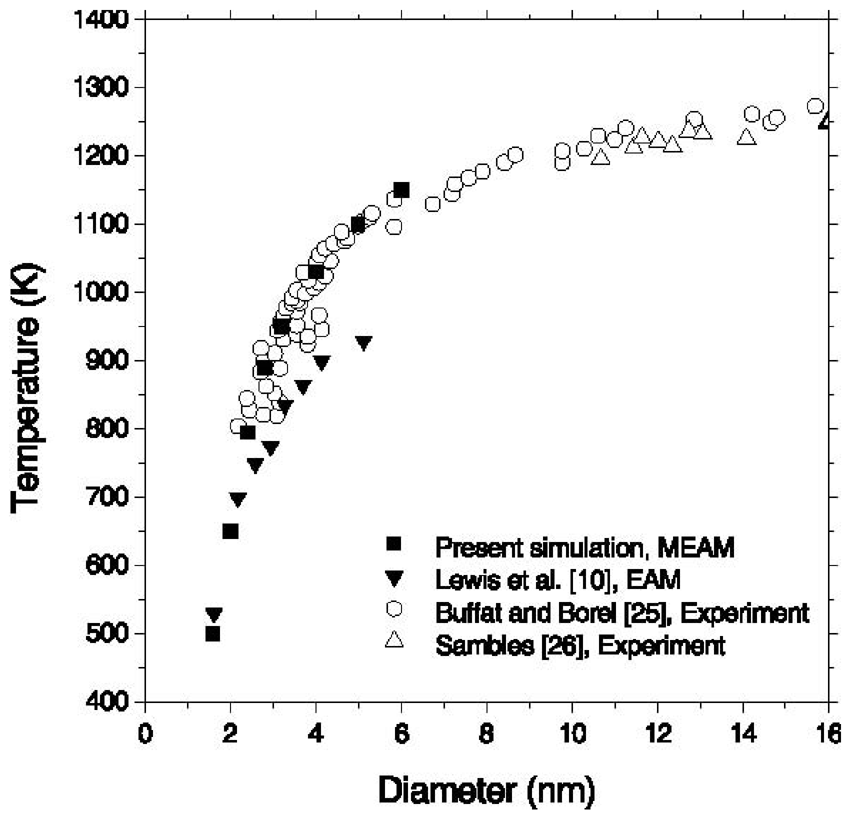
Three major characteristics of nanoparticles (size, surface, and structure).

If changed, can affect fundamental nanoparticle properties such as color, conductivity, melting temperature, reactivity etc. as well as alter the hazard and exposure potential of the nanoparticle.



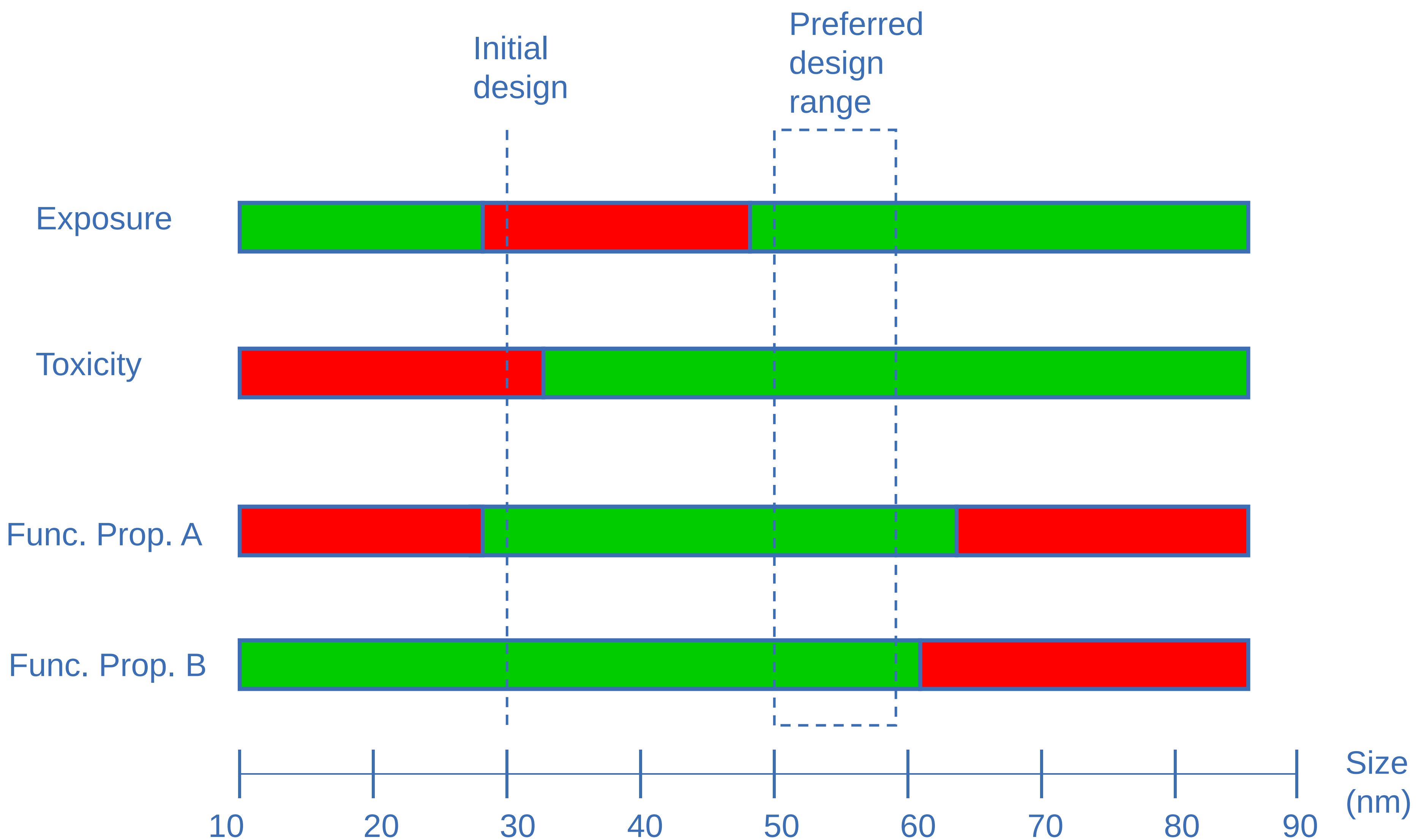
Size: Effect on Properties

The size of a nanoparticle includes the dimensions for diameter, length, width, etc. which affects the fundamental properties of the nanoparticle.



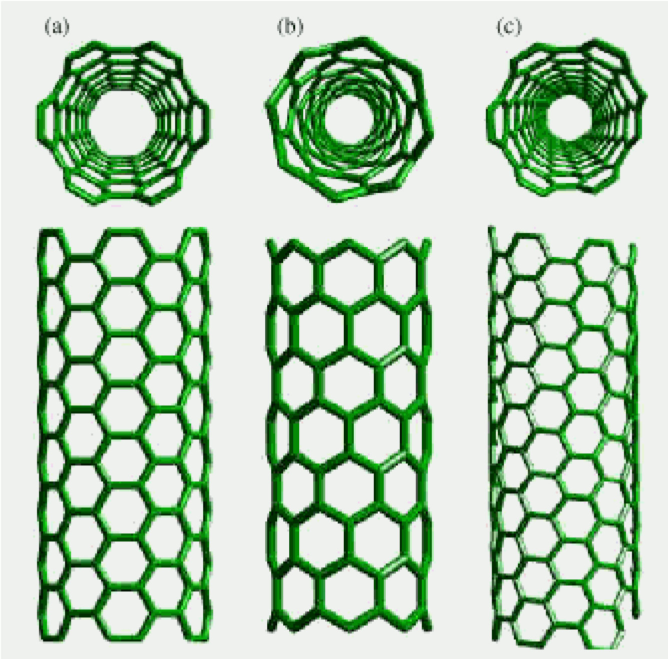
Source: Shim Jae-Hyeok, Lee Byeong-Joo Cho, Young Whan. Thermal stability of unsupported gold nanoparticle: a molecular dynamics study. *Surface Science* 2002;**512**:262–8.

Size Dependent Properties

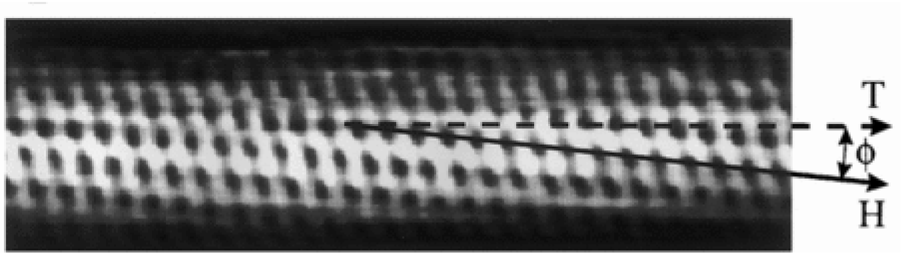


Structure: Effects on Properties

Minor variations of carbon nanotube wrapping angle or diameter affect functional properties.



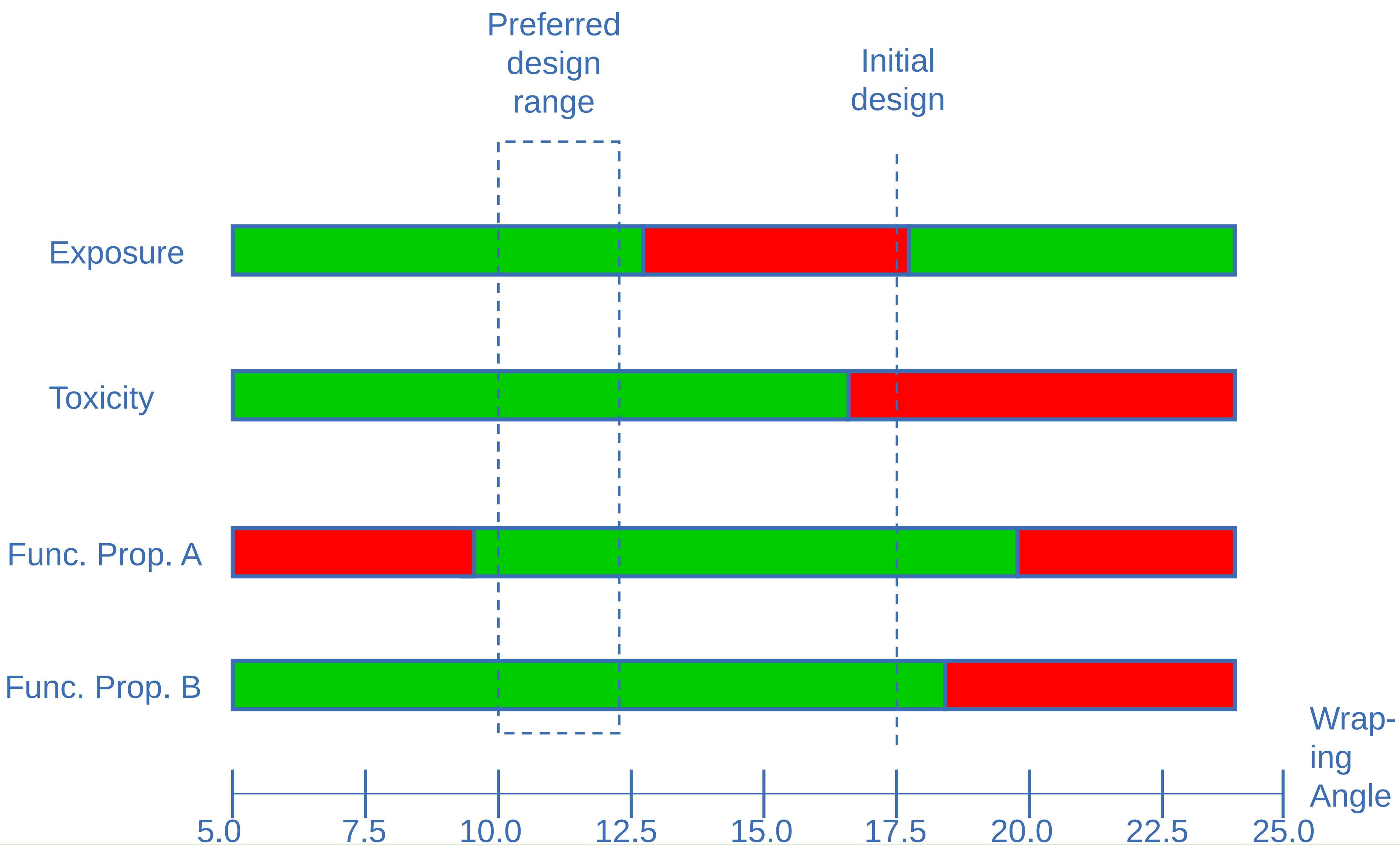
a) armchair, (b) zigzag, (c) chiral



Chiral, wrapping angle 7º

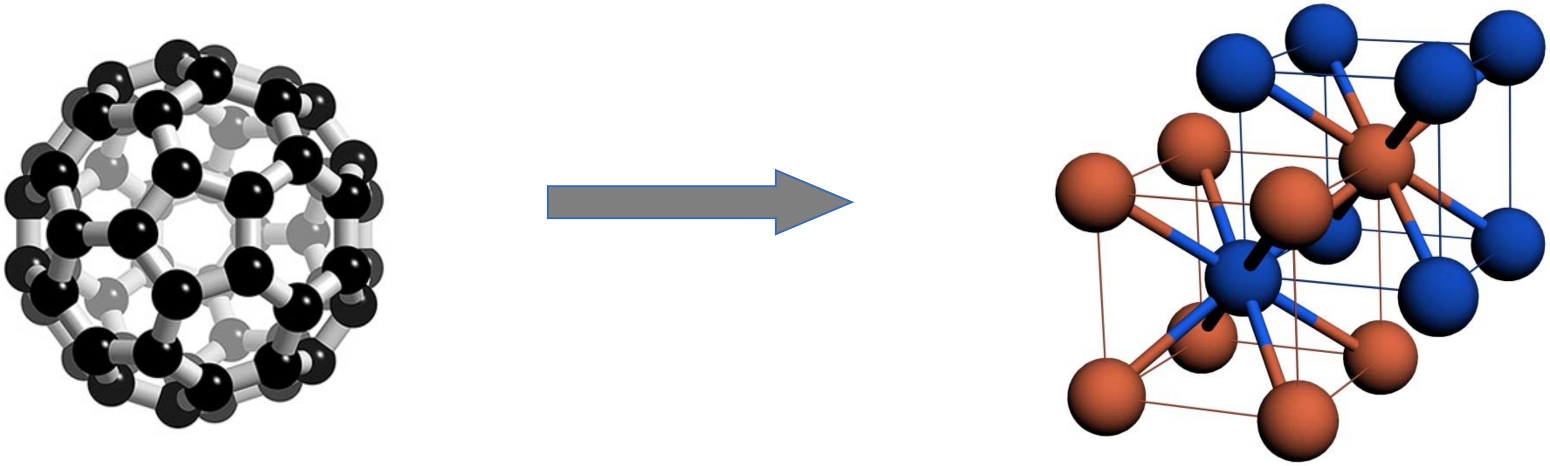
Source: Wildoer Jeroen WG, Venema, Liesbeth C, Rinzler Andrew G, Smalley Richard E, Dekker Cees. Electronic structure of atomically resolved carbon nanotubes. *Nature* 1998;January; **391**:59–62.

Structure Dependent Properties



Principle 2: Alternative Materials

This approach involves identifying an alternative material (nano or bulk), that can be used to replace the hazardous nanoparticle.

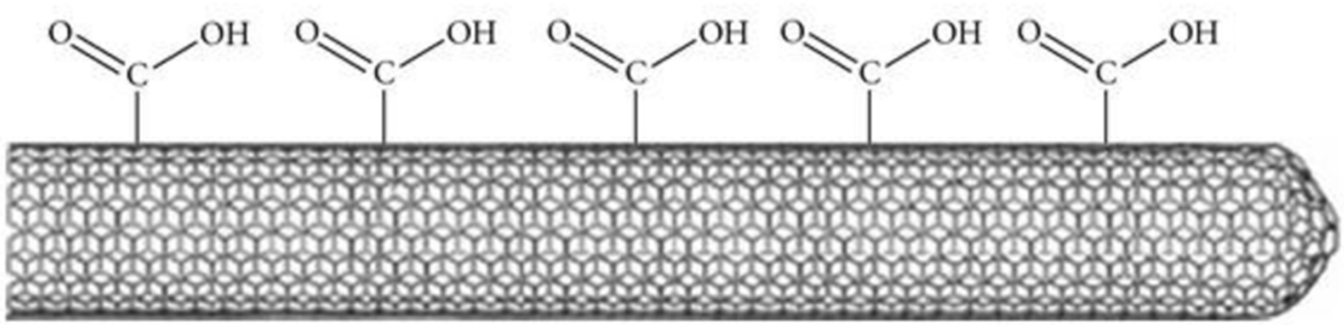


Principle 3: Functionalization

Functionalization is the intentional bonding of atoms or molecules to nanoparticles to change the properties of the nanoparticles.

Functionalize the nanoparticle in a manner such that the desired product properties are preserved, but the hazard and/or exposure potential of the nanoparticle is reduced or eliminated.

For example, functionalization to promote excretion of nanomaterials.



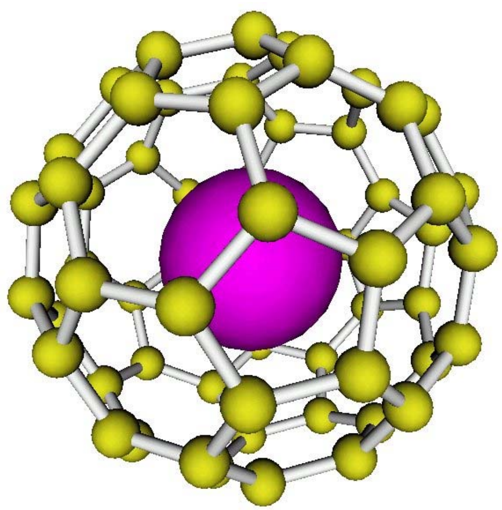
Source: Lara Lacerda, Anuradha Soundararajan, Singh Ravi, Pastorin Giorgia, Al-Jamal Khuloud T, John Turton. Dynamic imaging of functionalized multi-walled carbon nanotube systemic circulation and urinary excretion. *Advanced Materials* 2008;**20**:225–30.

Principle 4: Encapsulation

Encapsulation is a method used to completely enclose a nanoparticle within another material.

The intent of this principle is to enclose a potentially hazardous nanoparticle within a material that is less hazardous.

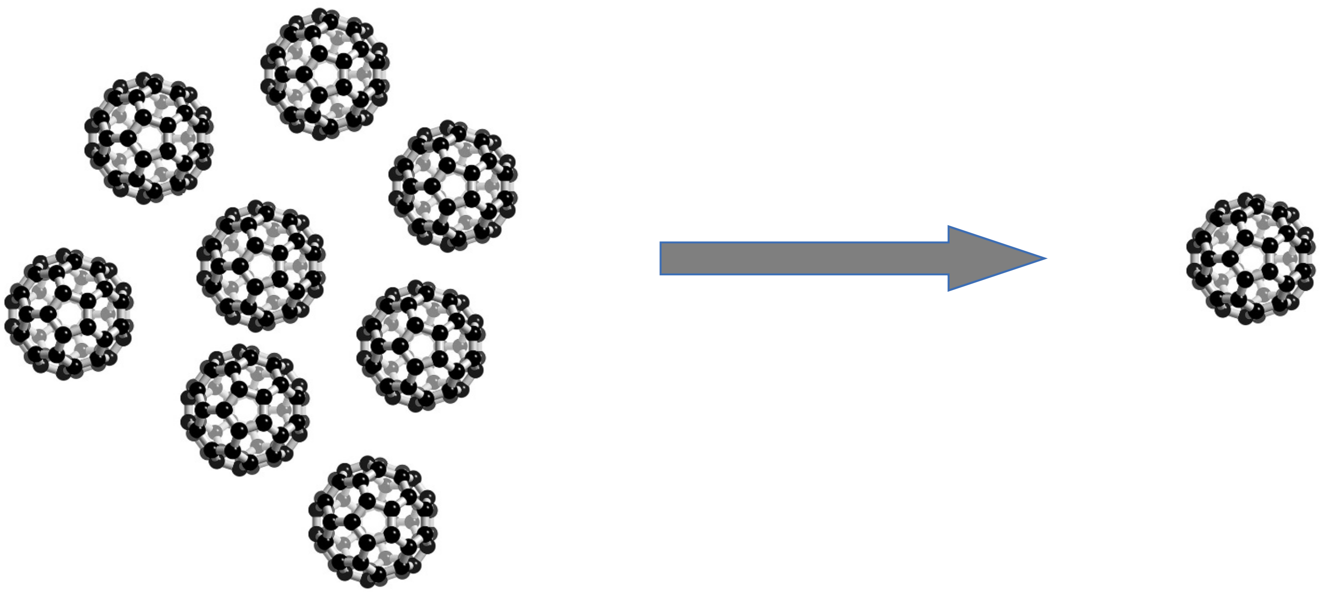
For example, functionalize nanomaterials (dyes) used in two-photon photodynamic therapy.



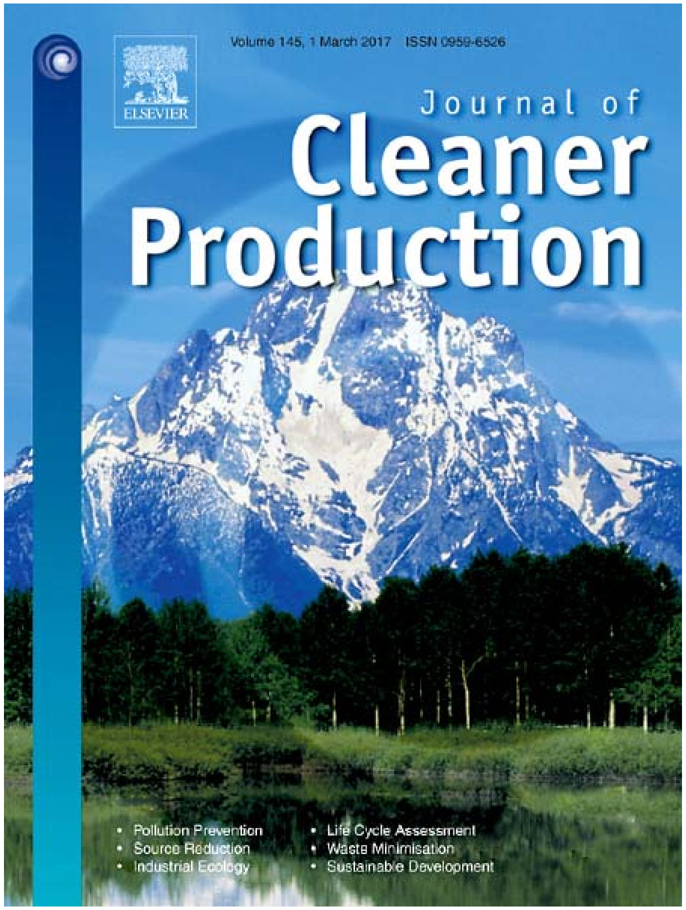
Source: Gao De, Agayan Rodney R, Xu Hao, Philbert Martin A, Kopelman Raoul. Nanoparticles for two-photon photodynamic therapy in living cells. *Nano Letters,* November, 2006;**6(11);** 2383–2386.

Principle 5: Reduce the Quantity

There may be situations where applying the above design principles cannot reduce or eliminate the nanoparticle hazard while maintaining the desired product functionality.



SAFER Article



Morose, Gregory, “The 5 Principles of Design for Safer Nanotechnology”, *Journal of Cleaner Production*, **Volume 18**, February 2010, pp. 285 – 289.

TURI and Engineered Nanomaterials: Programs and Resources

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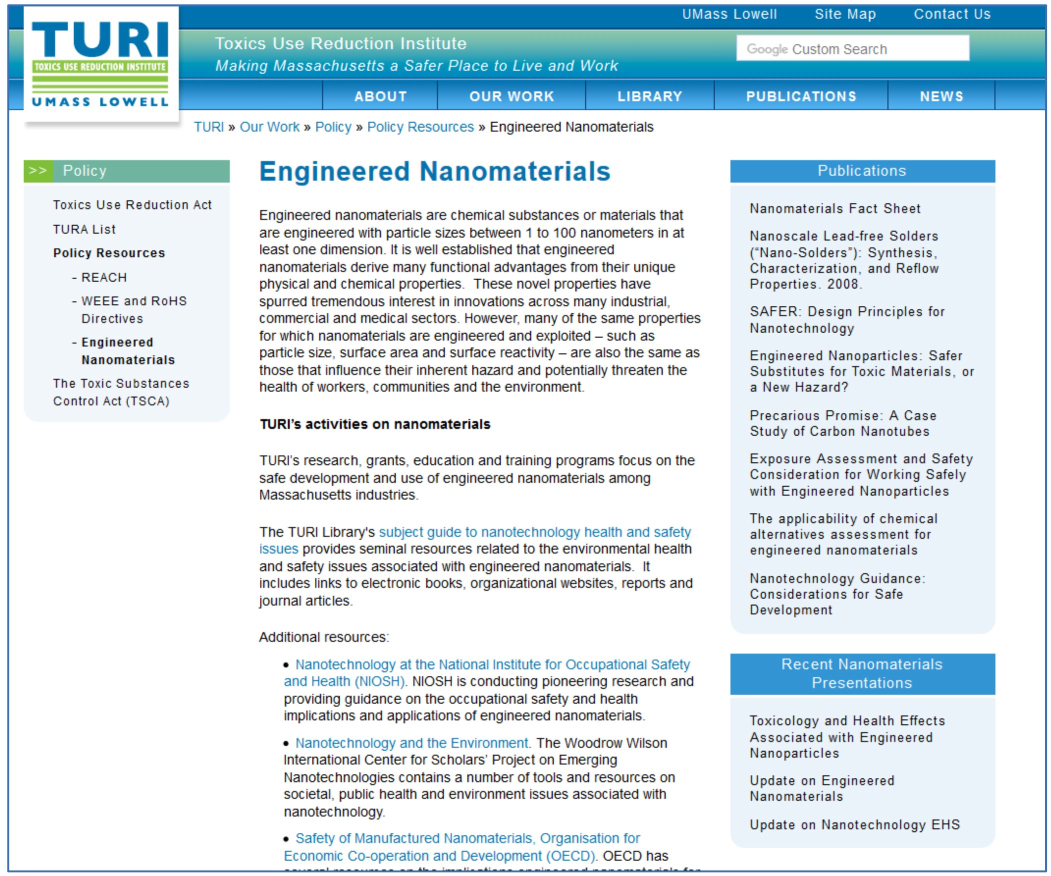
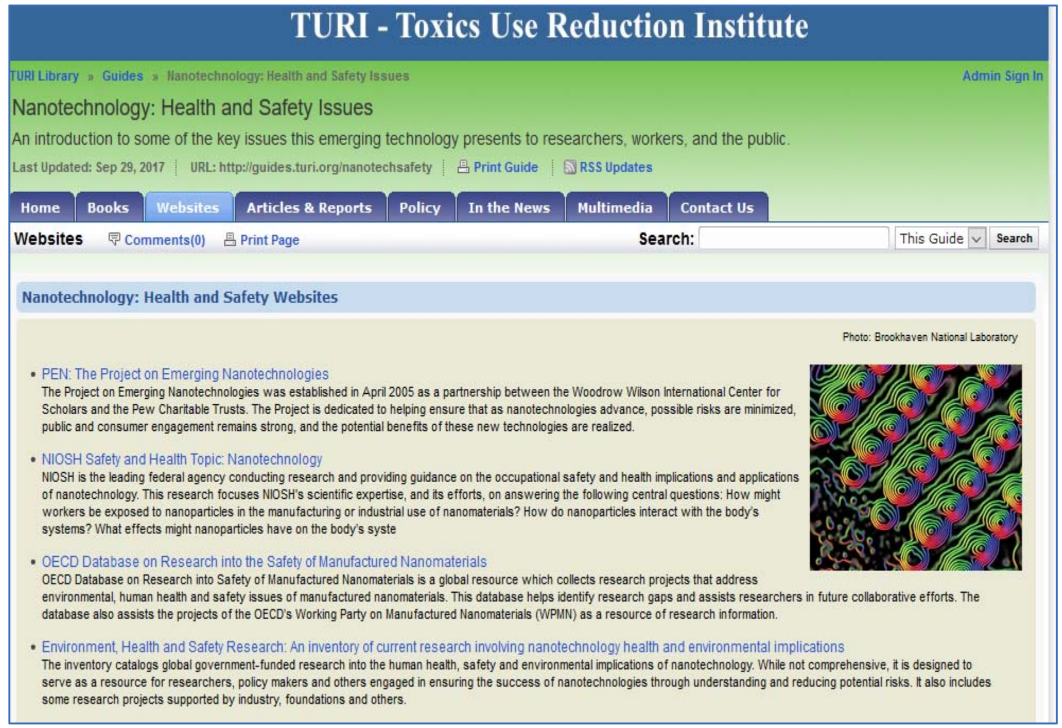
Resources

- Nanomaterials Fact Sheet (www.turi.org/nano)
- TURI Webpage on Engineered Nanomaterials (https://www.turi.org/Our_Work/Policy/Policy_Resources/Engineered_Nanomaterials)



More Resources

- TURI Library
  - Books
  - Reports
  - Databases
- Nanomaterials EH&S Library Guide



Questions?

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