

## Nanotechnology and the Commonwealth: Use and Implications

Thursday, December 7<sup>th</sup> 2017 Toxics Use Reduction Institute



## 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 TURI



Research Program Manager Mary Butow TURI



Research & Reference Specialist



## Nanotechnology 101

### Molly Jacobs

### Senior Research Associate, Lowell Center for Sustainable Production



## What is Nanotechnology

• The study of the Sugar cube 10,000,000 nm (10 mm) Diameter: 10 mm controlling of matter on an atomic and molecular Grain of sand 1,000,000 nm (1 mm) Diameter: 1 mm scale Typical human hair 100,000 nm (0.1 mm, 100 µm) Diameter: 100 µm **Engineered nano objects:** at least one dimension 10,000 nm (0.01 mm, 10 µm) Red blood cells between 1 to 100 Diameter: 5,000 nm 1,000 nm (1 µm) nanometers (nm) roughly 100,000 times Typical virus 100 nm (0.1 µm) Diameter: 100 nm smaller than the diameter Nanoof a human hair 10 nm (0.01 µm) Carbon nanotubes objects Diameters: 2 - 200 nm DNA strand 1 nm (0.001 µm) Diameter: 2 nm

# 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**



## Nanotechnology in the Commonwealth



Dennis

Map d

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





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

## Dr. Michael Ellenbecker Director, Massachusetts Toxics Use Reduction Institute



# 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



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

Fouling release coatings



#### THERMOCYL<sup>™</sup> 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.



TEM Mode: Imaging Microscopist: Candace

HV=100kV Direct Mag: 20000x

## **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, lengthdependent, 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  $\mu$ m) 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-1β, IL6, TNF-α, inflammatory cytokines, KL-6, TGF-β1]

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

## **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 Research Program Manager Toxics Use Reduction Institute



## **Risk Mitigation Matrix**



## Five Principles of Design for Safer Nanotechnology



## 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.





Chiral, wrapping angle 7°

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

**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** Preferred Initial design design range Exposure Toxicity Func. Prop. A Func. Prop. B Wraping Angle **5**.0 7.5 15.0 17.5 22.5 25.0 10.0 12.5 20.0

## **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

### Mary Butow Research & Reference Specialist, Toxics Use Reduction Institute



## Resources

- Nanomaterials
   Fact Sheet
   (www.turi.org/nano)
- TURI Webpage on Engineered Nanomaterials

(<u>https://www.turi.org/Our\_Work/</u> <u>Policy/Policy\_Resources/Engineer</u> ed\_Nanomaterials)

			UMass	Lowell	Site Map	Contact Us
ICS USE REDUCTION INSTITUTE	Toxics Use Reduction Institute Making Massachusetts a Safer Place to Live and Work			Google Custom Search		
MASS LOWELL	ABOUT	OUR WORK	LIBRARY	PUBLIC	CATIONS	NEWS
TURI	» Our Work » Policy » Policy Reso	ources » Engineered Na	nomaterials			
Policy	Engineered Nanomaterials			Publications		
Toxics Use Reduction Act TURA List Policy Resources - REACH - WEEE and RoHS Directives - Engineered Nanomaterials The Toxic Substances Control Act (TSCA)	Engineered nanomaterials are chemical substances or materials that are engineered with particle sizes between 1 to 100 nanometers in at least one dimension. It is well established that engineered nanomaterials derive many functional advantages from their unique physical and chemical properties. These novel properties have spurred tremendous interest in innovations across many industrial, commercial and medical sectors. However, many of the same properties for which nanomaterials are engineered and exploited – such as particle size, surface area and surface reactivity – are also the same as those that influence their inherent hazard and potentially threaten the health of workers, communities and the environment. <b>TURI's activities on nanomaterials</b> TURI's research, grants, education and training programs focus on the safe development and use of engineered nanomaterials among Massachusetts industries			Nanomaterials Fact Sheet Nanoscale Lead-free Solders ("Nano-Solders"): Synthesis, Characterization, and Reflow Properties. 2008. SAFER: Design Principles for Nanotechnology Engineered Nanoparticles: Safer Substitutes for Toxic Materials, or a New Hazard? Precarious Promise: A Case Study of Carbon Nanotubes Exposure Assessment and Safety Consideration for Working Safely with Engineered Nanoparticles		
	The TURI Library's subject guide to nanotechnology health and safely issues provides seminal resources related to the environmental health and safety issues associated with engineered nanomaterials. It includes links to electronic books, organizational websites, reports and journal articles.			The applicability of chemical alternatives assessment for engineered nanomaterials Nanotechnology Guidance: Considerations for Safe Development		
	Additional resources:					
	<ul> <li>Nanotechnology at the National Institute for Occupational Safety and Health (NIOSH). NIOSH is conducting pioneering research and providing guidance on the occupational safety and health implications and applications of engineered nanomaterials.</li> <li>Nanotechnology and the Environment. The Woodrow Wilson International Center for Scholars' Project on Emerging Nanotechnologies contains a number of tools and resources on societal, public health and environment issues associated with nanotechnology.</li> </ul>		cupational Safety ring research and id health materials. odrow Wilson rging f resources on sociated with	Recent Nanomaterials Presentations Toxicology and Health Effects Associated with Engineered Nanoparticles Update on Engineered Nanomaterials		
	Safety of Manufactured Nanomaterials, Organisation for Economic Co-operation and Development (OECD), OECD has			Update on Nanotechnology EHS		

## **More Resources**

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



## **Questions?**

#### • Contact us:

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