Safe Handling of Nanomaterials

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Today's Presentation:

- Overview of history and definitions
- Examples of products using nanotechnology
- Discussion of data and data gaps
- Brief overview of exposure monitoring issues
- Guidance on ranking of hazards and control schemes

Today's presentation will not cover safety issues related to:

- Flammability
- Explosivity
- Reactivity

Nanoparticles are found in many places we may not consider...

- Welding fumes
- Diesel exhaust
- Smoke from cooking indoors
- Smoke from candles

What is an "*engineered* nanoparticle"?

- There are multiple characterization schemes
- Most common definition is a particle <100 nm, designed and manufactured by people
- Forms:
  - Aggregated - group of particles that are tightly bonded (e.g. 'sintered', 'fused')
  - Agglomerated - group of particles (typically held together by "Van der Waals" forces) easily broken apart by handling
- Shapes:
  - Spherical
  - Irregular
  - Tubular

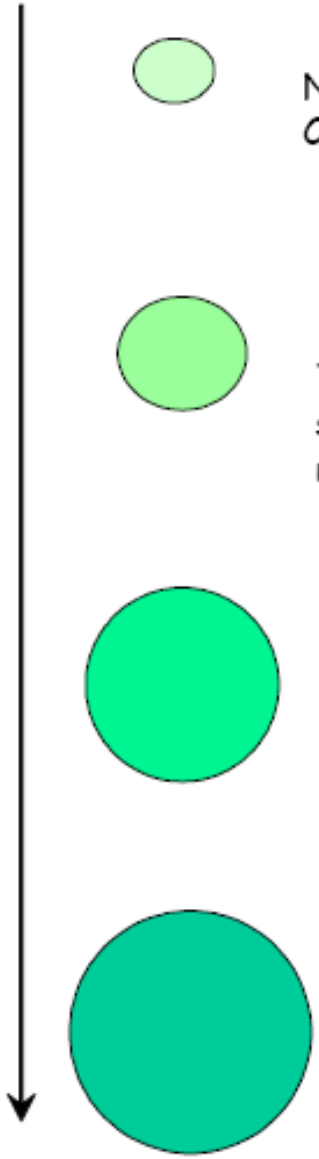
Examples of Engineered Nanoparticles

- Carbon Nanotubes - carbon atoms (single or multi-layer), arranged in a cylindrical tube
  - Needle type of shape similar to some types of asbestos - concerns regarding similar hazard(?)
- "Quantum Dots" - metallic particle assemblies, with unique physical properties:
  - electrical
  - optical
  - magnetic
  - catalytic

Some products currently utilizing nanotechnology

Health	**Electronics**	**Household**	**Misc.**
Air filters Sunscreen Antibacterial treatments Stain Resistors	Computer components and displays	Canola oil Golf clubs Skis Cosmetics Toothpaste	Lubricants Coatings

Increasing Complexity



First Generation ~2001: Passive nanostructures

Nano-structured coatings, nanoparticles, nanostructured metals, polymers, ceramics, Catalysts, composites, displays

Second Generation ~Now: Active nanostructures

Transistors, amplifiers, targeted drugs and chemicals, actuators, adaptive structures, sensors, diagnostic assays, fuel cells, solar cells, high performance nanocomposites, ceramics, metals

Third Generation ~ 2010: 3-D nanosystems and systems of nanosystems

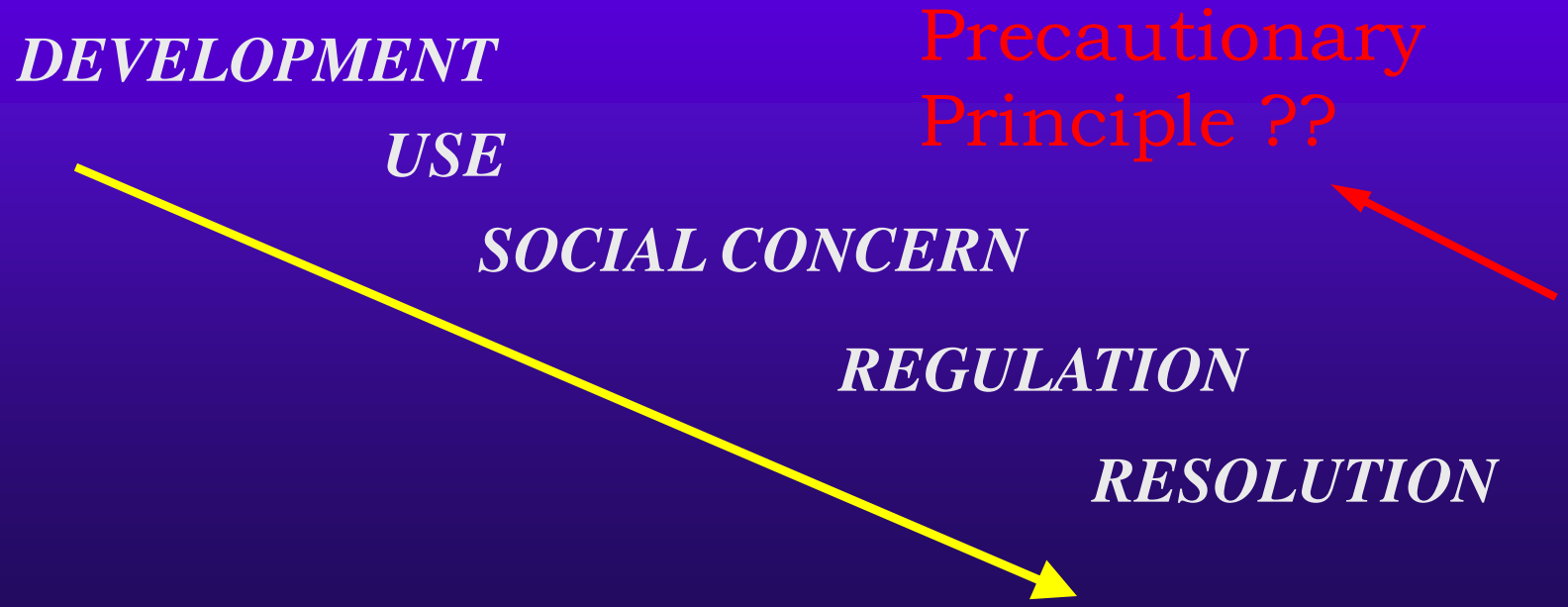
Various assembly techniques, networking at the nanoscale and new architectures, Biomimetic materials, novel therapeutics/targeted drug delivery

Fourth Generation ~2015 Molecular Nanosystems

Molecular devices "by design", atomic design, emerging functions

Public Awareness and Regulatory Trends

- The introduction of new technologies in the past (e.g. nuclear power) goes through a predictable course



Public Awareness and Regulatory Trends

- 2007 - Berkeley, CA - City ordinance enacted requiring researchers and manufacturers to disclose use/manufacture of nanoparticles

Red Herring?

- Germany - “Magic Nano” Sealing Spray
- Sealing spray for glass/ceramic surfaces
- Within 3 days of being on the market, > 150 consumers reported strong cough, shortness of breath, and some with pulmonary edema after use
- Health effects were determined to be related to an additive - no nano-sized particles were even present (referred to thickness of applied film)

Nanoparticle hazards

- Unfortunately, the very same physico-chemical properties that make them attractive for use, also make them unpredictable in their consequences for deleterious effects on humans and the environment….
- *In general - a smaller particle of identical chemical composition is thought to be more hazardous than a larger particle*

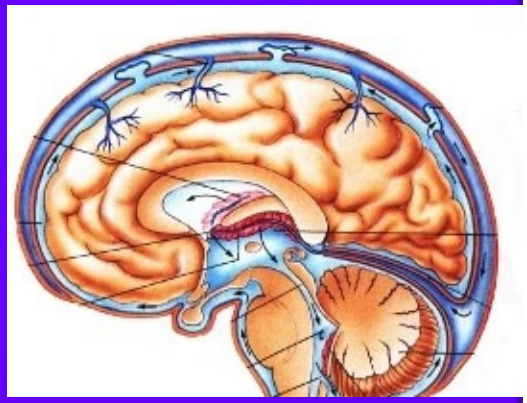
Nanoparticle hazards - background information

- The behavior of nanoparticles in the body is very different from larger particles of the same element/compound - e.g. permeation of the "blood-brain barrier"
- Epidemiological studies suggest exposure to ultrafine particles (generally non-'engineered' nanoparticles) increases cardiopulmonary hazards
- Dermal exposure hazard is also suggested by several studies
- Particle size, surface area, and surface activity may all influence toxicity

Lung Absorption of Particles

- The most important characteristics are aerosol size and water solubility
- particles of 2 to 5 um deposited mainly in tracheobronchiolar regions, cleared by ciliated portions
- particles <1 um penetrate to the alveolar sacs of the lungs, may be absorbed into blood

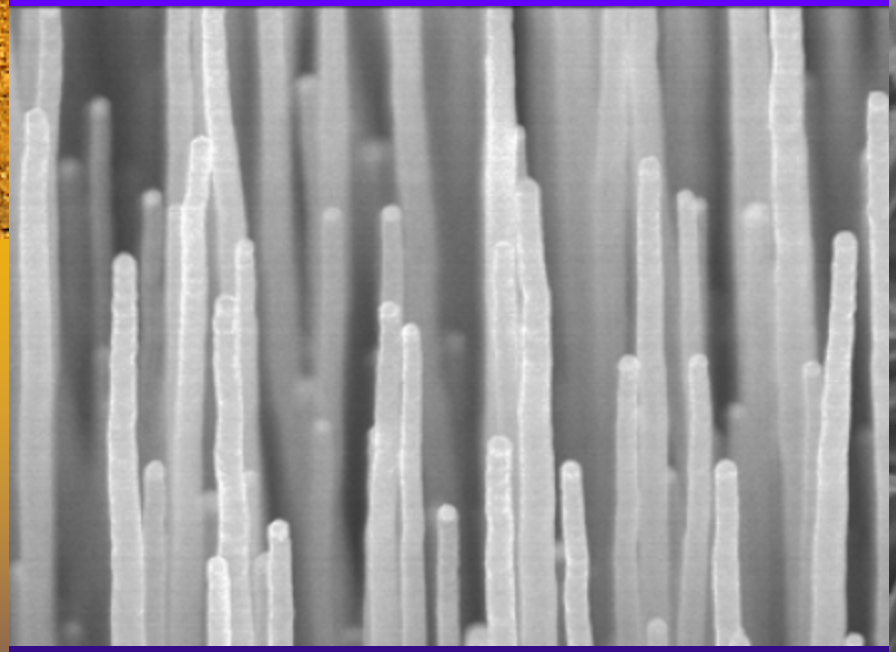
The Blood-brain barrier



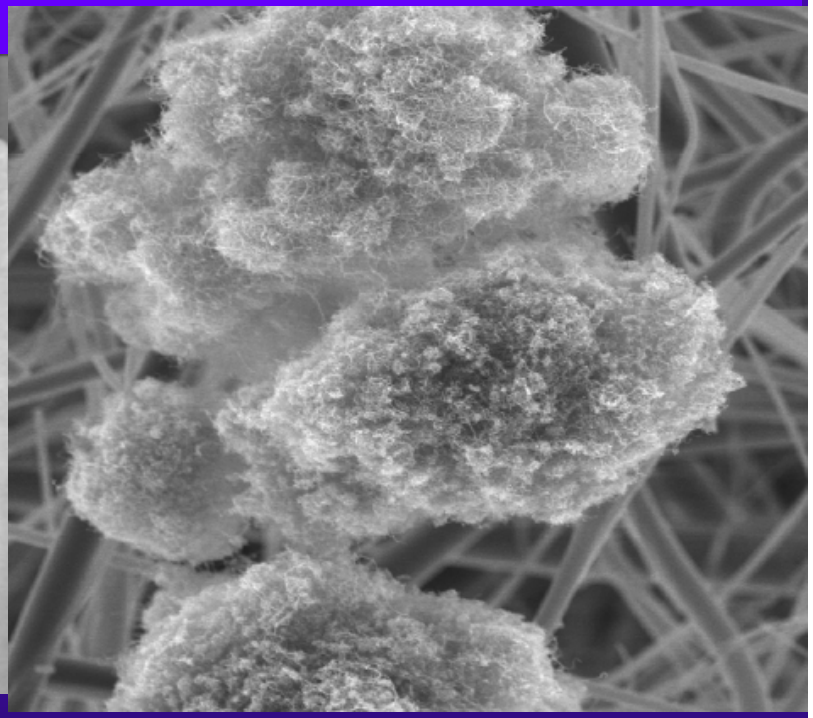
- Unique physiological feature in the human body - is less permeable than are most other areas of the body
- Lipid/fat solubility plays an important role
- A few chemicals can enter the brain by carrier-mediated processes - e.g. methylmercury
- Many nanoparticles are thought to pass through the blood-brain barrier readily

Nanoparticle hazards - background information

- A primary difficulty in conducting toxicity studies is generating a reliably sized and measurable particle stream for inhalation studies
- Self-mitigating behavior of some nanoparticles: aggregation → chain-formation → sedimentation
- 3 groups of particles (by size):
  - Small (< 80 nm) - agglomerate quickly, settle
  - Large (>2000 nm) - coarse, settle quickly
  - Intermediate (80 - 2000 nm) - 'accumulate', but can stay suspended in air for days to weeks



“Raw” Carbon Nanotubes



Agglomerated Nanotube

Environmental Fate of Nanoparticles

- Bioavailability - can the material be taken into a 'target organ' to cause ill effects
- Bioaccumulation - how likely is it to be stored in the body for extended time periods
- Biotransformation - can the material be changed to a more toxic compound
- None of these issues are well understood yet

Nanoparticle Exposure Assessment

- Air sampling methods have had very limited validation
- There is significant uncertainty regarding evaluation and control of potential exposures

Nanoparticle Exposure Assessment

- Comprehensive exposure assessment has to consider many factors:
  - particle size
  - particle surface area
  - particle shape
  - surface chemistry
  - mass concentration
  - degree of agglomeration

Occupational Exposures

Synthesis Process	Particle Formation	Exposure Source or Worker Activity	Primary Exposure Route
Gas Phase	in air	Direct leakage from reactor, especially if the reactor is operated at positive pressure.	Inhalation
		Product recovery from bag filters in reactors.	Inhalation / Dermal
		Processing and packaging of dry powder.	Inhalation / Dermal
		Equipment cleaning/maintenance (including reactor evacuation and spent filters).	Dermal (and Inhalation during reactor evacuation)
Vapor Deposition	on substrate	Product recovery from reactor/dry contamination of workplace.	Inhalation
		Processing and packaging of dry powder.	Inhalation / Dermal
		Equipment cleaning/maintenance (including reactor evacuation).	Dermal (and Inhalation during reactor evacuation)
Colloidal/ Attrition	liquid suspension	If liquid suspension is processed into a powder, potential exposure during spray drying to create a powder, and the processing and packaging of the dry powder.	Inhalation / Dermal
		Equipment cleaning/maintenance.	Dermal

Hazard Controls

- **Control banding** is the best available risk management framework at this time, given:
- Lack of toxicity data
- Lack of standards exposure monitoring methods
- Lack of occupational exposure standards

Classification scheme for selecting lab-scale controls*

"Dustiness"	Quantity Handled	Haz. Class A	Haz. Class B	Haz. Class C	Haz. Class D
Solids or Sealed Containers	Any	LB1	LB1	LB1	LB1
Suspensions with Minimal Potential for Droplet Dispersion	Any	LB1	LB1	LB1	LB1
Granular/ Agglomerated Powders or Dispersible Suspensions	< 100 mg	LB1	LB1	LB1	LB1
	100 mg – 1 kg	LB1	LB1	LB1	LB1-2
Powders	< 100 mg	LB1	LB1	LB2	LB2
	100 mg – 1 kg	LB1	LB1	LB2	LB2
Highly Dispersible Powders	< 100 mg	LB1	LB1-2	LB2	LB3
	100 mg – 1 kg	LB1	LB2	LB2	LB3

**** credit to AIHA Distance Learning Program***

Lab Hazard Controls

LB 1	LB 2	LB 3
• Open bench operations. • Keep sample containers sealed. • Clean surfaces around analytical equipment • frequently. • Collect waste in sealed containers with spill basins.	• Use fume hoods or local exhaust to collect vapors and gases from lab analyses. • Use local exhaust if powders are released.	• Consider placing analytical equipment inside ventilated enclosures.

NOTE RE ENGINEERING CONTROLS (!) - Containment must be 'complete' (no leaks), or nanoparticles may escape and become suspended in room air

Respirators as PPE

- NIOSH Certifies particle filtering respirators by 'challenging' them with either:
  - sodium chloride aerosols (75 nm particle size)
  - or dioctyl phthalate (185 nm particle size)
- Leakage around the face-seal is likely to pose a greater exposure risk than penetration through the filtration matrix (but on the same order as a gas or vapor)

General Hazard Reduction Strategies

- Designate handling areas - post, limit access
- If material is a dry powder, or pelletized - determine if it can be handled as a liquid or slurry
- Minimize aerosolization potential - slow stirring speeds, airtight transfer points, pouring
- Purchase dry material in pre-weighed portions
- Use local exhaust where possible to ventilate transfer points, bulk material handling
- Use wet wiping methods and HEPA vacuums only to clean up any spills

- *Note: a number of the graphics used in this presentation were excerpted from the U.S. EPA "Nanotechnology White Paper", February, 2007*