Engineered Nanomaterials: Overview of Hazards and Best Management Practices

Mike Ellenbecker, Toxics Use Reduction Institute

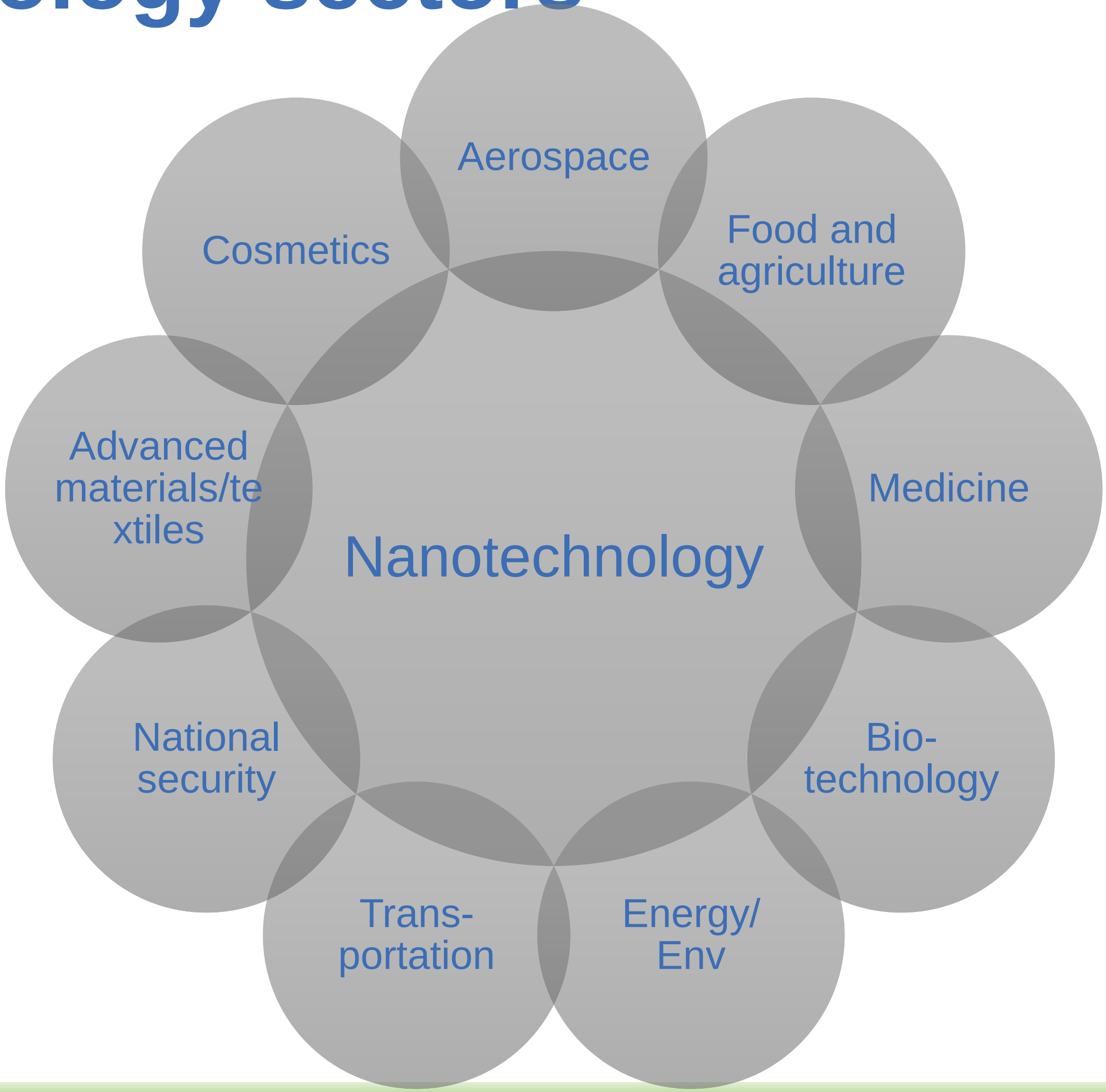
Molly Jacobs, Lowell Center for Sustainable Production

TURI
TOXICS USE REDUCTION INSTITUTE
UMASS LOWELL

Outline

- Engineered Nanomaterials 101
- TURI engineered nanomaterial fact sheet
  - Hazard properties
  - Safer by design opportunities
  - Best management practices
- Examples of Best Management Practices and Safer Development Principles/Programs and

R&D and Use – Spanning multiple technology sectors



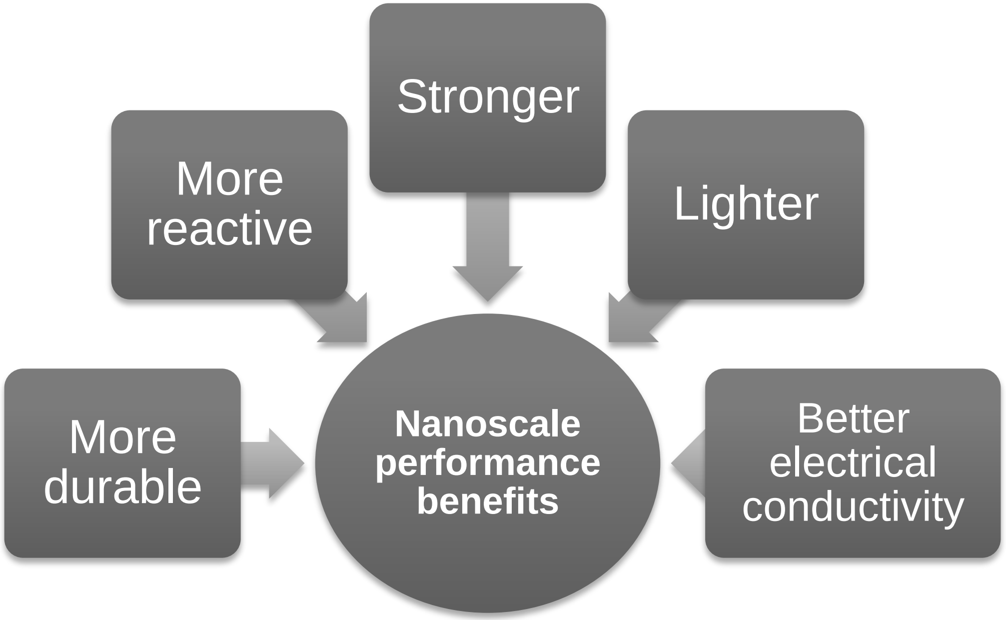
Types of Engineered Nanomaterials

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

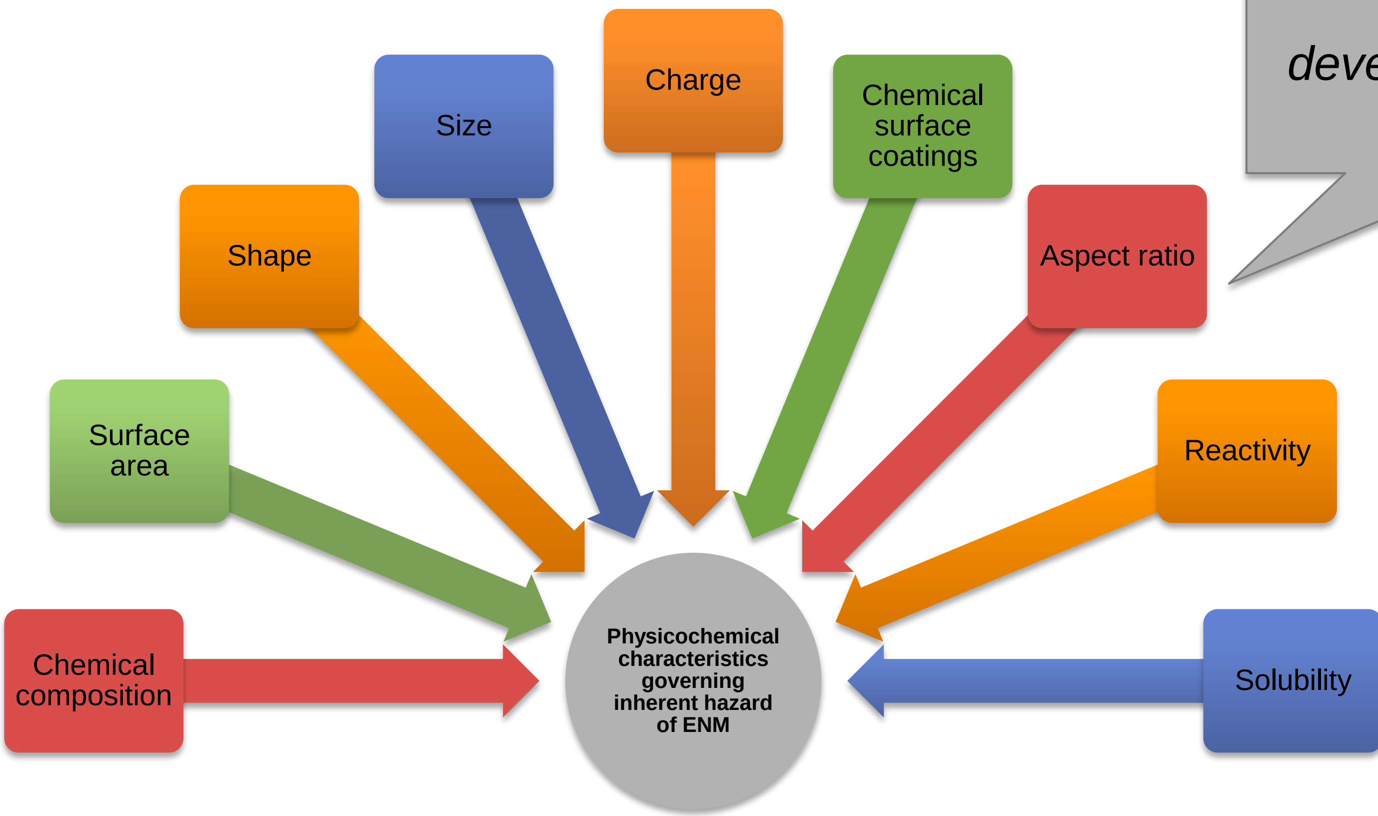
Engineered nanomaterials: enhanced performance compared to their bulk counterparts

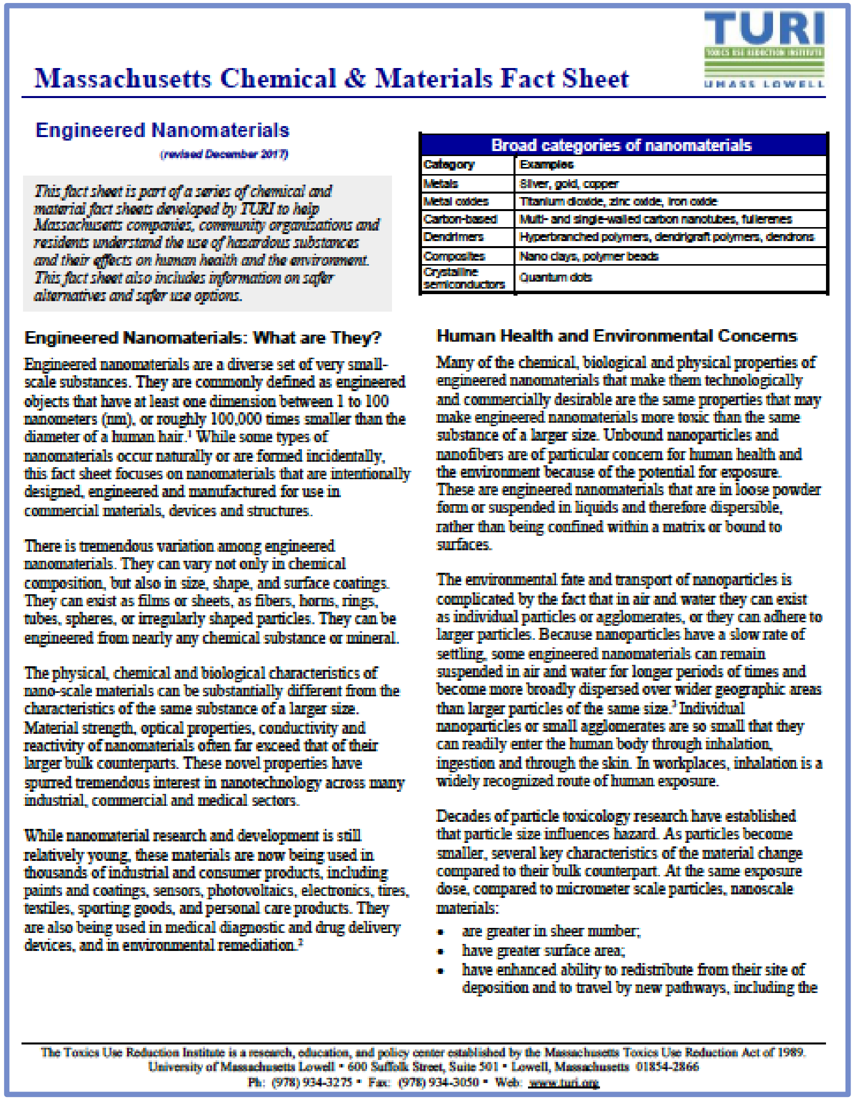
- At nano-scale:
  - material **properties change** - melting point, fluorescence, electrical conductivity, and chemical reactivity
  - **Surface size is larger** - more material comes into contact with surrounding materials and increases reactivity



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
TOXICS USE REDUCTION INSTITUTE
UMASS LOWELL

Massachusetts Chemical & Materials Fact Sheet

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:

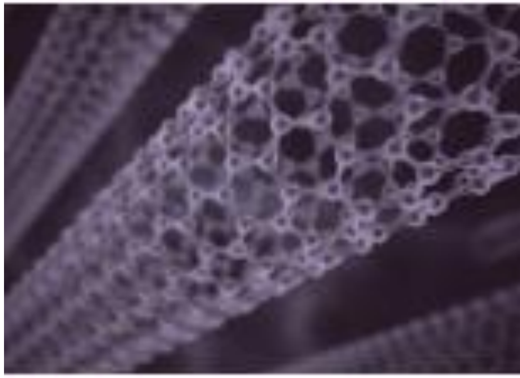
- are greater in sheer number;
- have greater surface area;
- have enhanced ability to redistribute from their site of deposition and to travel by new pathways, including the

The Toxics Use Reduction Institute is a research, education, and policy center established by the Massachusetts Toxics Use Reduction Act of 1989.
University of Massachusetts Lowell • 600 Suffolk Street, Suite 501 • Lowell, Massachusetts 01854-2866
Ph: (978) 934-3275 • Fax: (978) 934-3050 • Web: www.turi.org

TURI's Engineered Nanomaterials Fact sheet

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

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)
  - 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

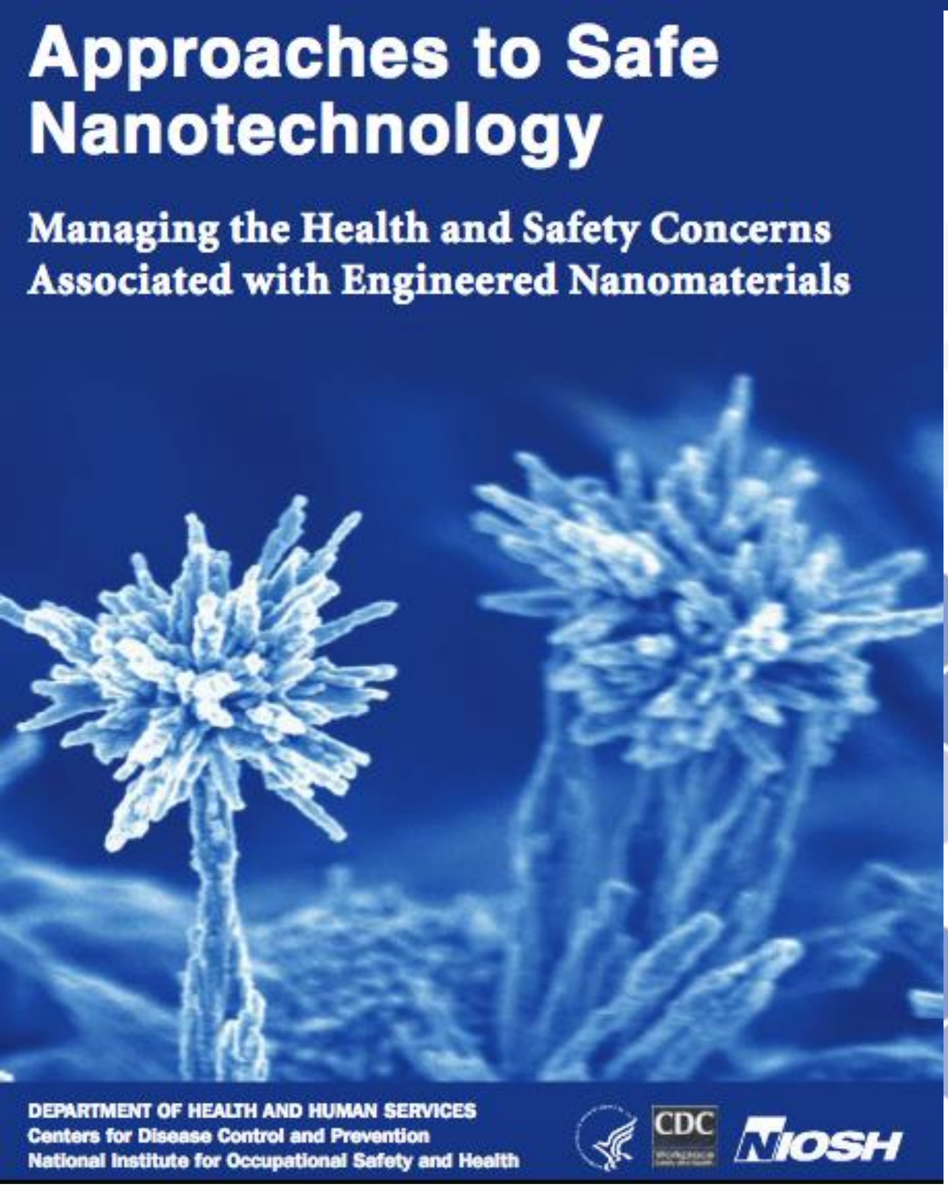
If the measures above do not effectively control the hazard, what personal protective equipment can be used? Have you considered personal protective equipment for the non-nanomaterial base material or liquid?

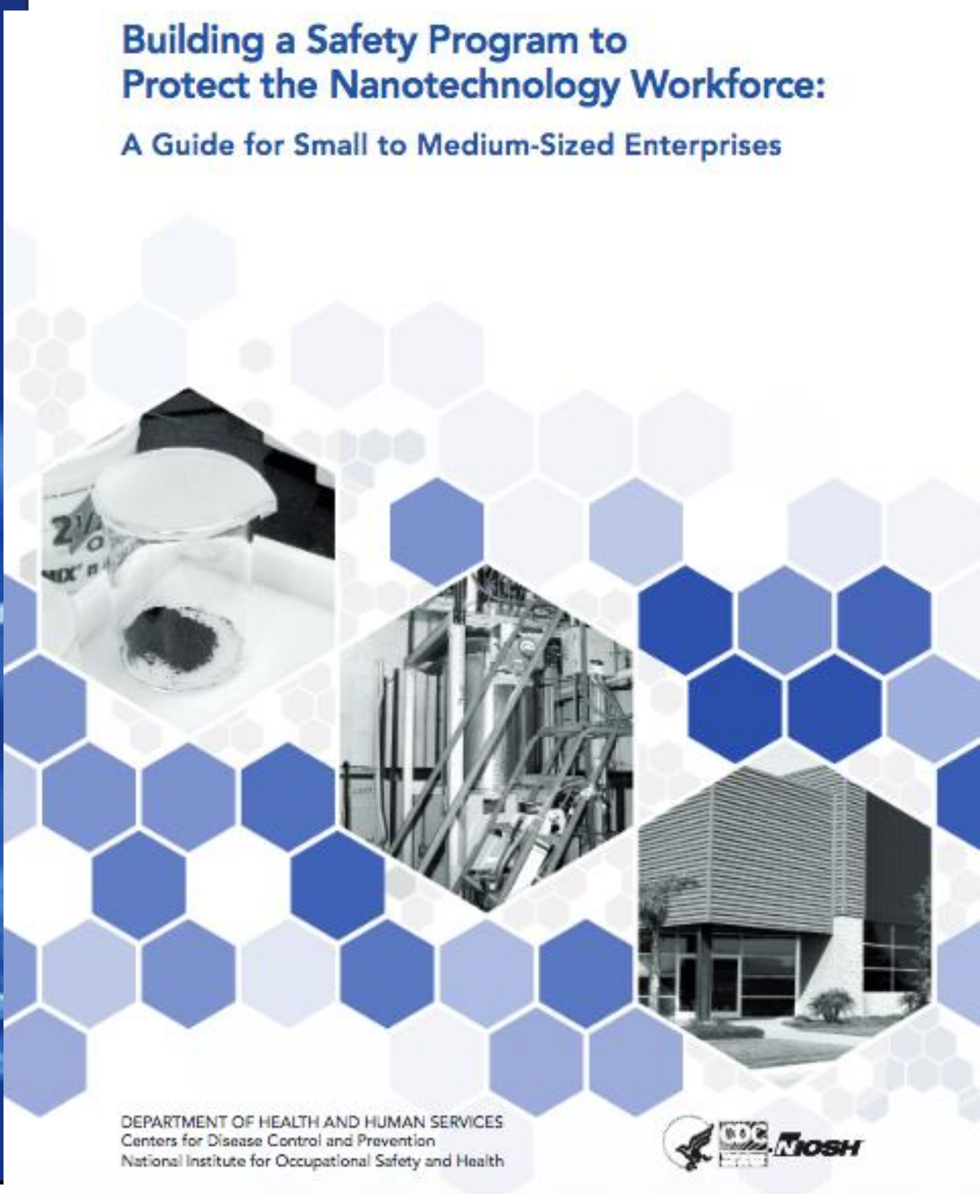
Applies to All Nanomaterial Forms
- Nitrile or chemical resistant gloves
- Lab coat or coveralls
- Safety glasses, goggles, or face shield
- Respiratory protection when indicated and engineering controls cannot control exposures, and in accordance with federal regulations (29 CFR 1910.134)
- NIOSH guidance on respirators can be found at www.cdc.gov/niosh/topics/respirators/
- Use personal protective equipment during spill cleanups and equipment maintenance

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/

DHHS (NIOSH) Publication No. 2018-103 | February 2018
https://www.doi.org/10.26616/NIOSHPUB2018103





General guidance, including guidance for small businesses that include essential elements of a risk management program

Best Management Practice – Environmental Management

- Good Question???
- Efforts (US and internationally) have focused on workplace controls to date
- Environmental management best practices dependent on industrial hierarchy of controls

2017

EMERGE Workshop

Emerging Technologies & Advanced Manufacturing
Emergency Preparedness & Response
Emergent National Security Implications

Virginia Tech Research Center – Arlington
900 N Glebe Rd
Arlington, VA 22203

April 4–5, 2017

Chair:
Matthew Hull
mahull@vt.edu
Office: 540.231.5812

Workshop Objectives

- **Establish a community of practice** that brings together technology developers, emergency management and national security experts
- Exchange information pertinent to the **identification and management of risks associated with accelerating technology development, convergence and advanced manufacturing**
- **Identify critical knowledge gaps** that may hinder risk assessment, emergency preparedness/response and national security from unprecedented changes in technology development and manufacturing

Principles of Design for SAFER Nanotechnology

Morose, G. *J Cleaner Prod.* 2010;18:285-289.

Size, Surface & Structure: Diminish or eliminate the hazard by changing the size, surface or structure of the nanoparticle while preserving the functionality of the nanomaterial for the specific application

Alternative Materials: Identify either a nano or bulk safer alternative that can be used to replace a hazardous nanoparticles

Functionalization: Add additional molecules (or atom) to the nanomaterial to diminish or eliminate the hazard while preserving the desired properties for a specific application

Encapsulation: Enclose a nanoparticle within another less hazardous material

Reduce the quantity: Where the above principles can not be used, and use is necessary, investigate opportunities to use smaller quantities