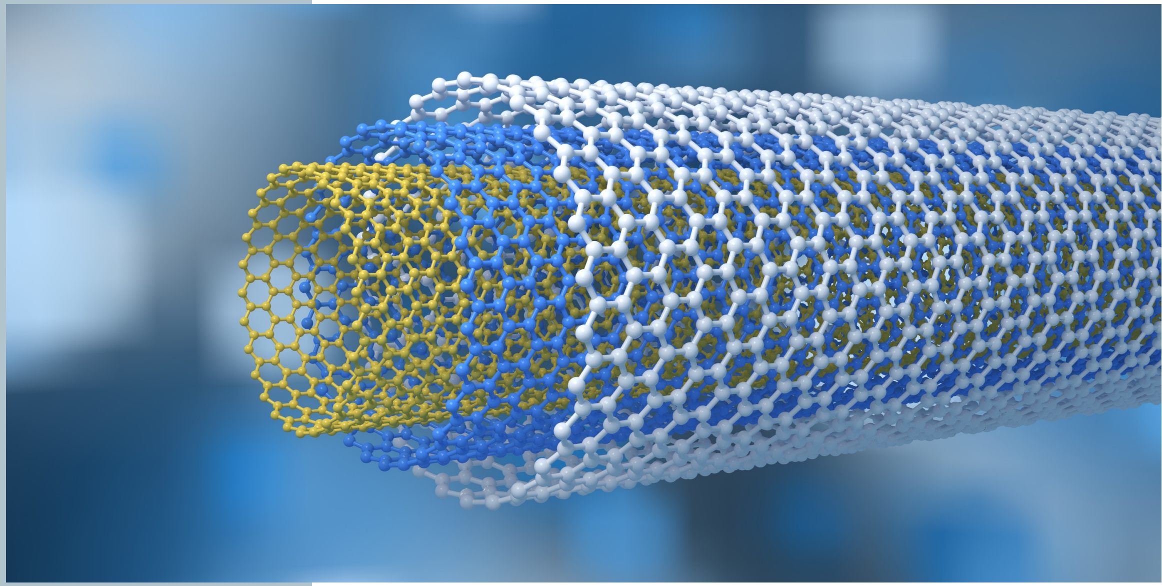
November 8, 2023

Nanomaterials “what are they” and “why we’re concerned for public health



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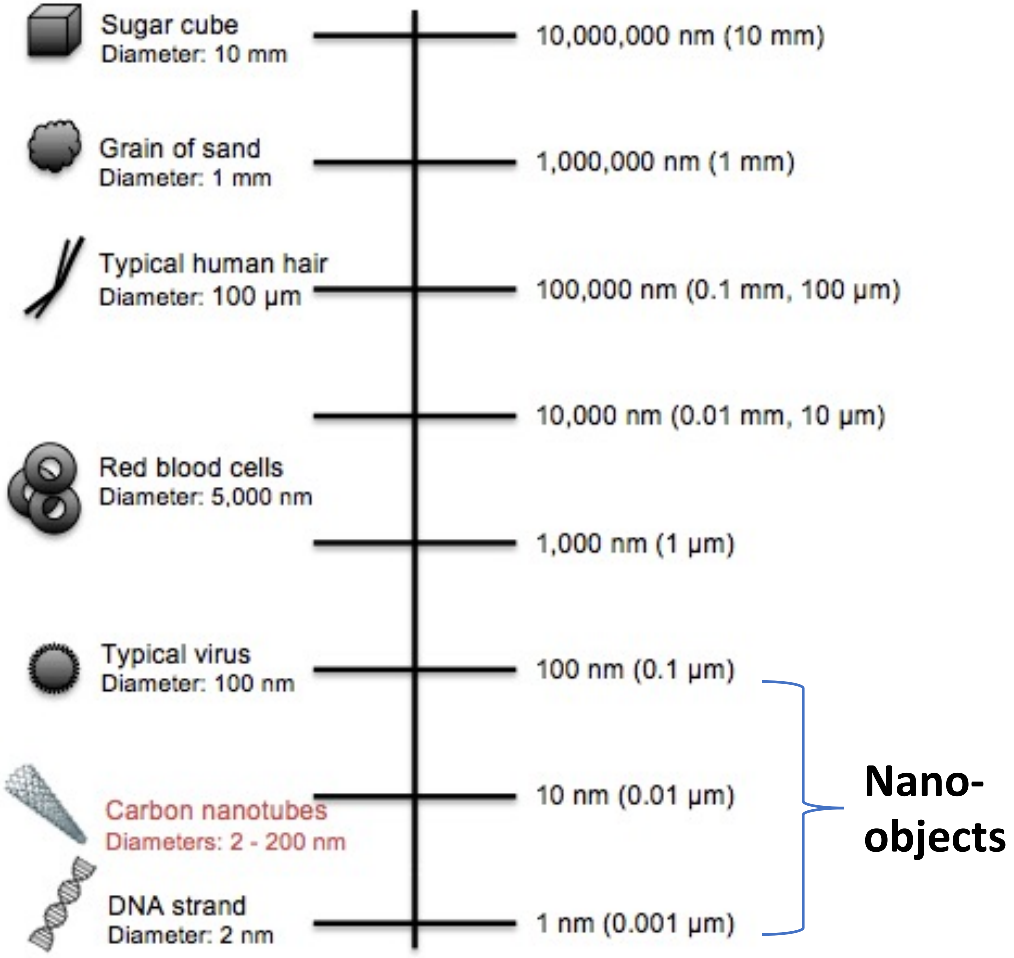
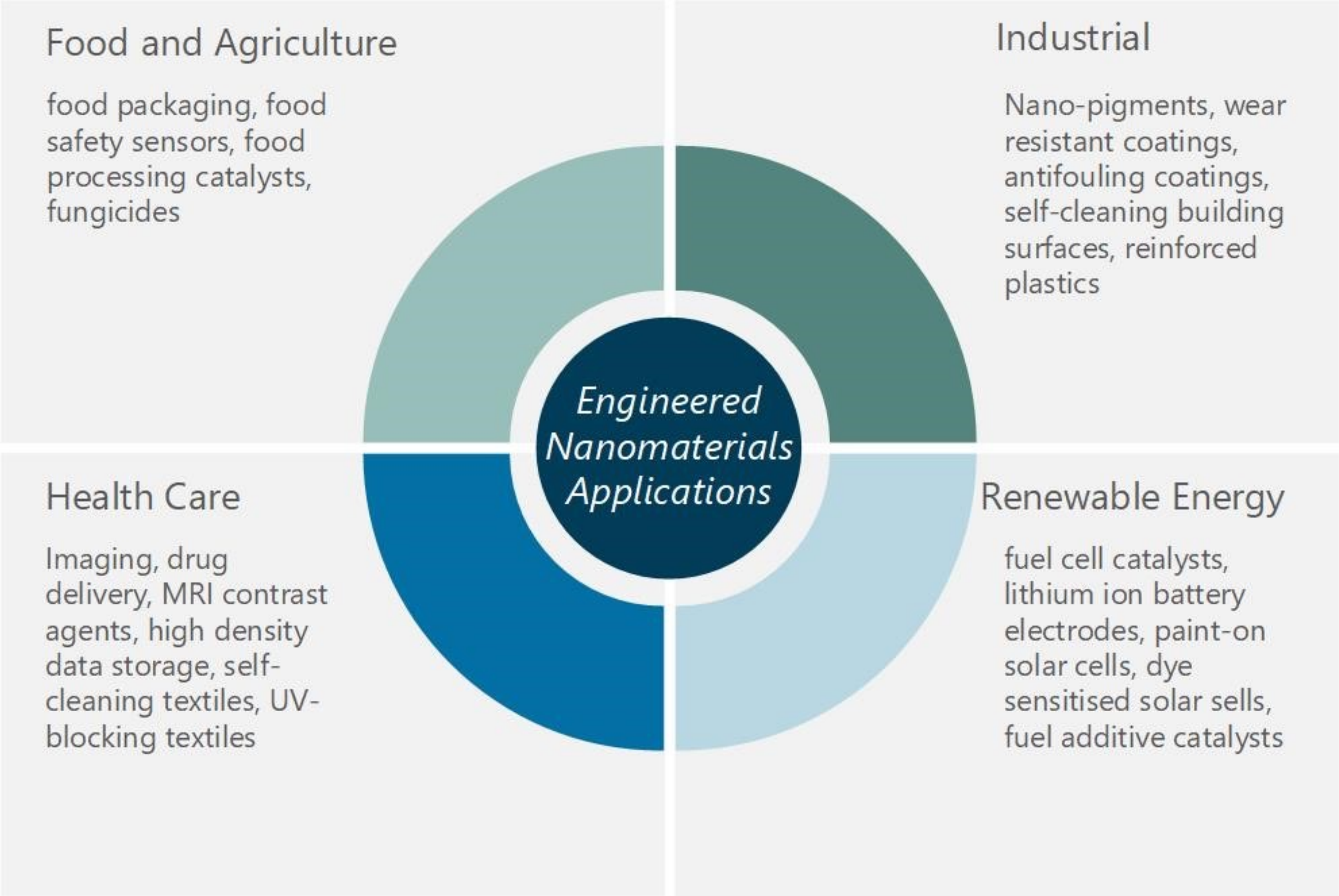
Nanotechnology – What is it?

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

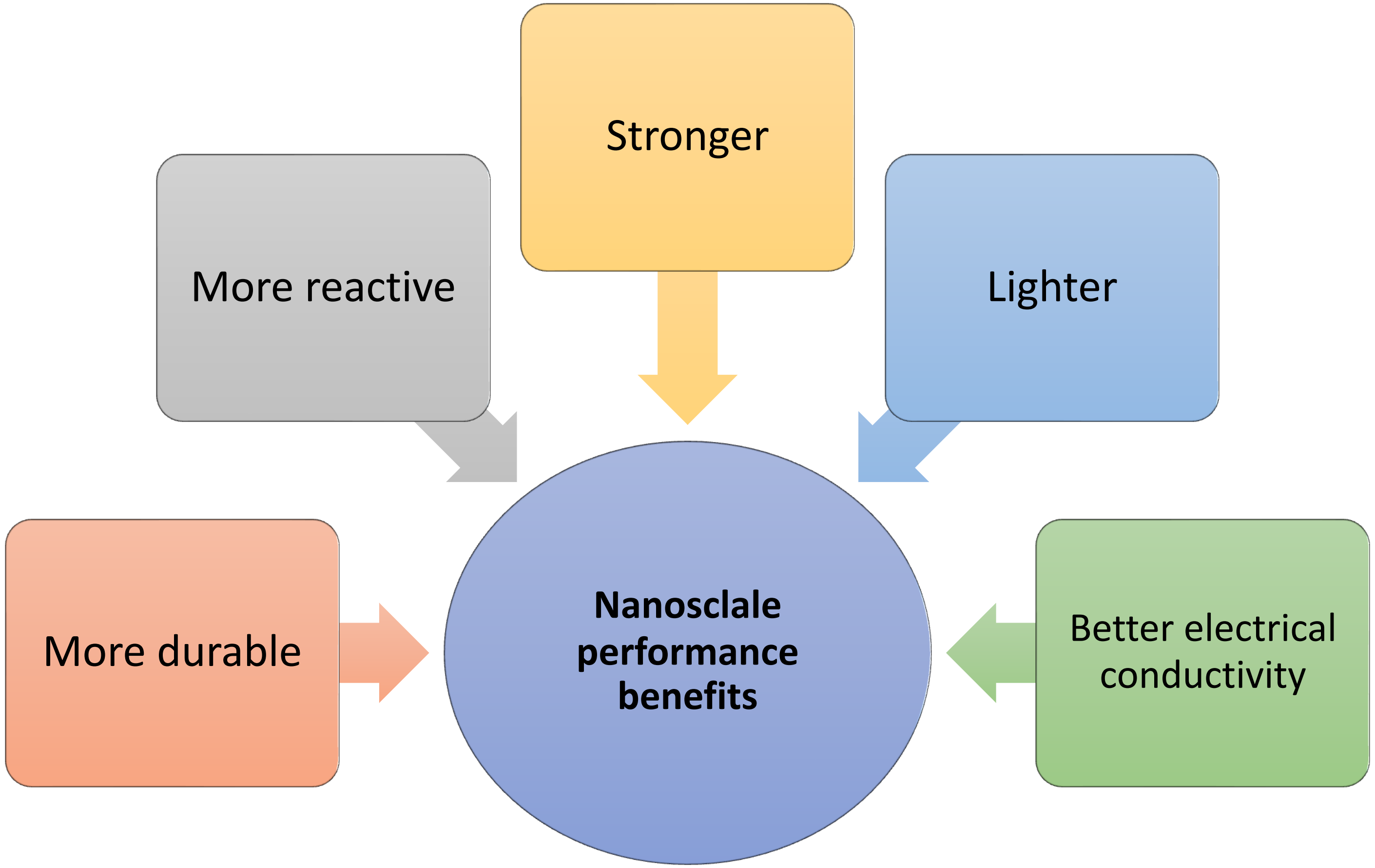


A range of applications – The Promise



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



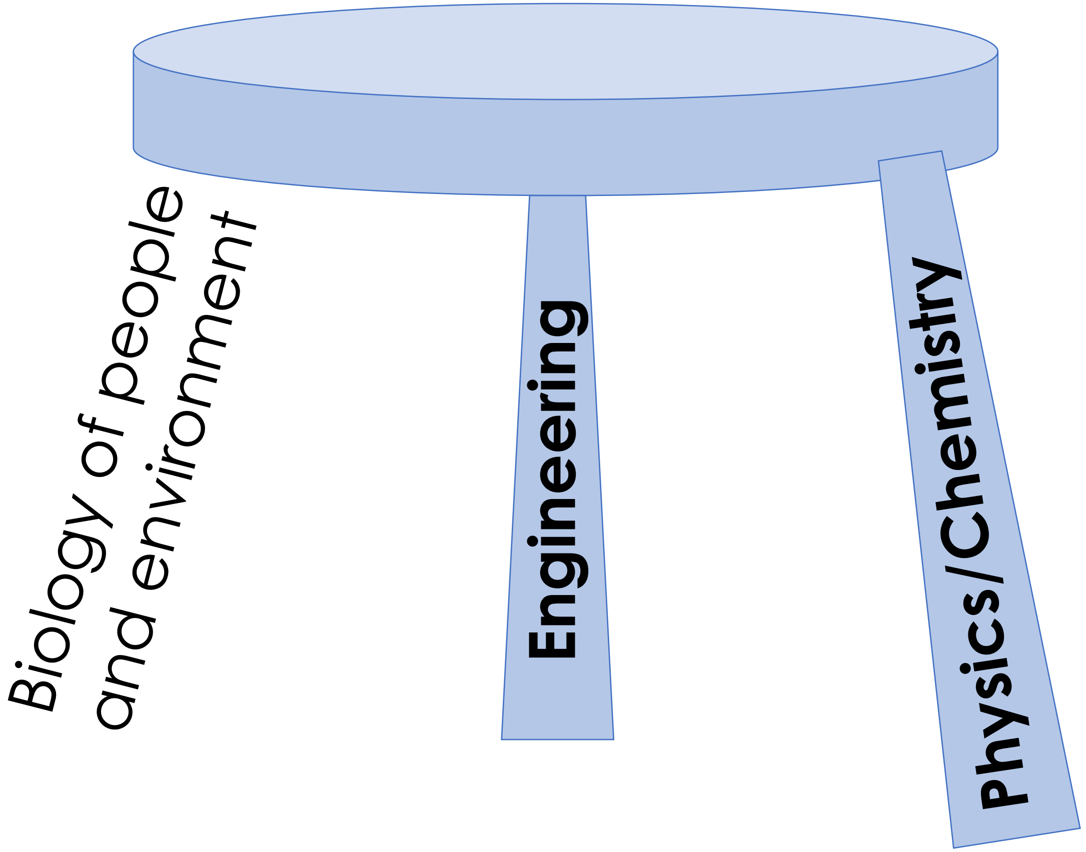
Engineered nanomaterials

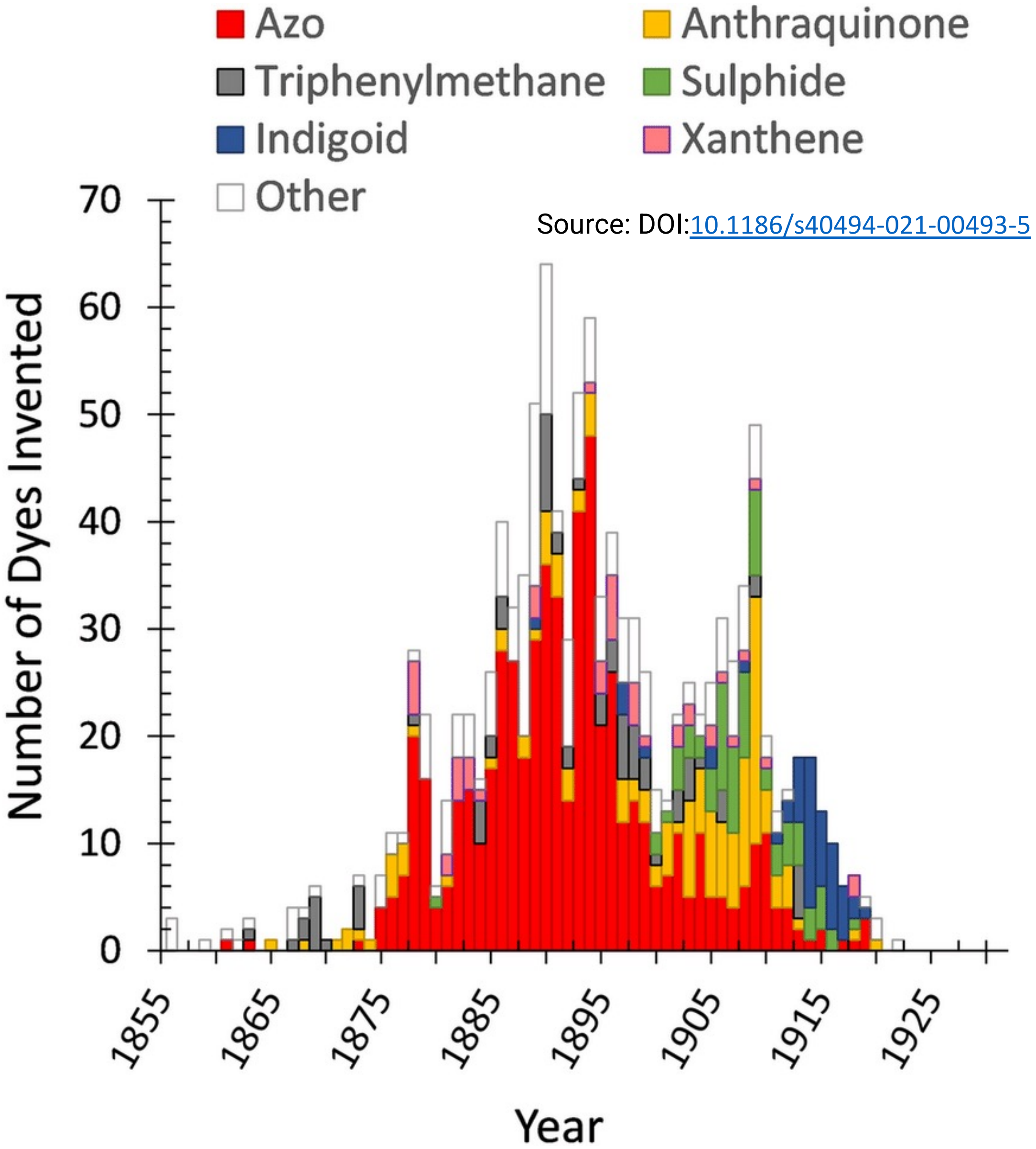
Broad Categories: Engineered Nanomaterials

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

Nanomaterials can be found in nature – but nanotechnology is about ***engineering*** nanomaterials

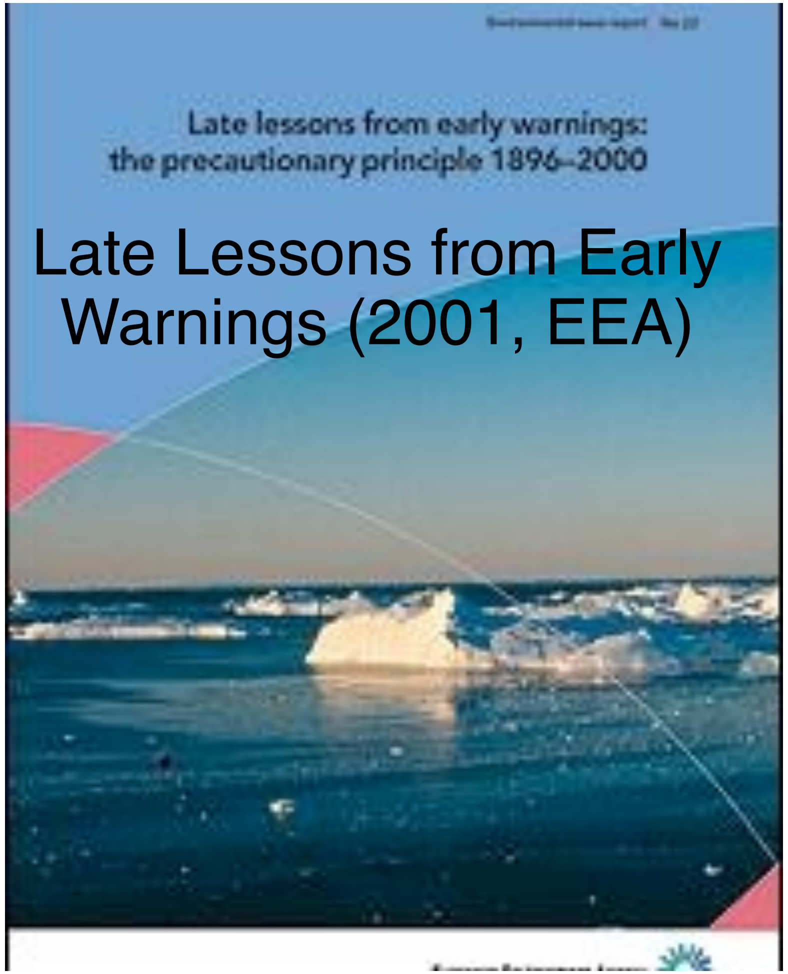
A Familiar Story? A stool without its 3rd leg





Source: DOI:10.1186/s40494-021-00493-5

A Precarious Promise? *An enchantment with performance trumping health and safety?*



Late Lessons from Early Warnings (2001, EEA)

22 Nanotechnology — early lessons from early warnings

Steffen Foss Hansen, Andrew Maynard, Anders Baun, Joel A. Tickner and Diana M. Bowman

Nanotechnology is the latest in a long series of technologies heralded as ushering in a new era of technology-driven prosperity. Current and future applications of nanotechnology are expected to lead to substantial societal and environmental benefits, increasing economic development and employment, generating better materials at lower environmental costs, and offering new ways to diagnose and treat medical conditions. Nevertheless, as new materials based on nanoscale engineering move from the lab to the marketplace, have we learnt the lessons of past 'wonder technologies' or are we destined to repeat past mistakes?

This chapter first introduces nanotechnology, clarifies the terminology of nanomaterials and describes current uses of these unique materials. Some of the early warning signs of possible adverse impacts of some nanomaterials are summarised, along with regulatory responses of some governments. Inspired by the EEA's first volume of *Late lessons from early warnings*, the chapter looks critically at what lessons can already be learned, notwithstanding nanotechnology's immaturity (1).

Nanotechnology development has occurred in the absence of clear design rules for chemists and materials developers on how to integrate health, safety and environmental concerns into design. The emerging area of 'green nanotechnology' offers promise for the future with its focus on preventive design. To gain traction, however, it is important that research on the sustainability of materials is funded at levels significant enough to identify early warnings, and that regulatory systems provide incentives for safer and sustainable materials.

Political decision-makers have yet to address many of the shortcomings in legislation, research and development, and limitations in risk assessment, management and governance of nanotechnologies and other emerging technologies. As a result, there remains a developmental environment that hinders the adoption of precautionary yet socially and economically responsive strategies in the field of nanotechnology. If left unresolved, this could hamper society's ability to ensure responsible development of nanotechnologies.

Engineered Nanomaterials – Basic Concerns for Human Health and Environment

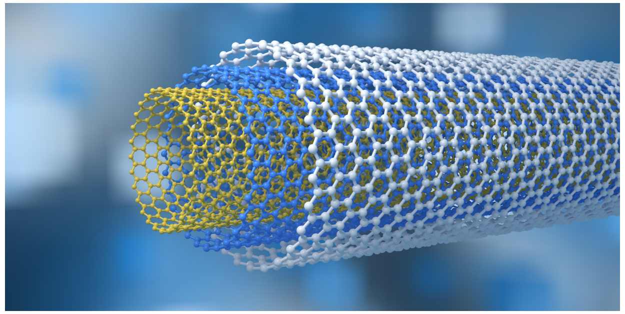
- **Particle size influences toxicity**
  - As particles become smaller, characteristics of the material change
- At the same exposure dose, *compared to micrometer scale particles*, ENMS:
  - are greater in sheer number
  - have roughly 1,000,000 times greater surface area enhancing reactivity
  - have enhanced ability to redistribute from their site of deposition and to travel by new pathways, including the lymphatic and nervous systems, to many tissues and organs
  - have the potential to deliver a higher dose of complex materials attached to their surface
- **Substances that are hazardous in bulk form (e.g., cadmium) can generally be expected to be hazardous at the nanoscale**
  - Substances that are not hazardous in bulk form may, however, be hazardous at the nanoscale because of the above nanoscale properties

What we're learning about potential harms – some examples

- Carbon nanotubes
- Quantum dots
- Nano-titanium dioxide
- Nanosilver

- Note – **these are materials, not chemicals** – tens of thousands of variations, even within the same class of material

Carbon Nanotubes



- 2 broad categories:
  - Single-walled CNTs (SWCNTs)
  - Multi-walled CNTs (MWCNTs)

- **Primary hazard endpoints of concern:**
  - Pulmonary fibrosis; pulmonary inflammation (NIOSH Current Intelligence Bulletin 65, 2013)
    - "Biomarkers of effect" seen in workers exposed
  - Cancer (IARC, Group 2B) [one type of MWCNTs]

Quantum Dots

- Crystalline semiconductors
  - Semiconductor core: CdSe; CdTe; ZnS
  - Semiconductor shell: often ZnS

Televisions	Lasers
Solar cells	Medical imaging
Drug carriers	Biosensors

Primary health hazard endpoints of concern:

- Cd cores are of concern (carcinogenicity); toxicity seems dependent on coatings and release mechanisms of Cd2+ ions
- Organ toxicity (lung, liver, kidney) (Cd-based QDs) (DOI: 10.1002/jat.4180)
- Immune cell activation (DOI: 10.1002/jat.4180)

Nano Titanium Dioxide

Size-dependent effects (i.e., micrometer versus nanoscale matters)

Paints/pigments	Food/drug colorant
Cosmetics	Sunscreens
Photovoltaics	Self-cleaning surfaces

Primary health hazard endpoints of concern:

- Pulmonary inflammation
- Genotoxicity (under certain conditions)
- Carcinogenicity (potential occupational carcinogen, NIOSH)
- organ/liver effects (at high doses)

- No authorization for use in EU spray-based cosmetics/sunscreen products
- On CA Prop 65 list

Nanosilver

- Collodial silver

Textiles

Water treatment

Cosmetics

Food packaging

Food Sensors

Fuel additive catalysts

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 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

Best Management Practices – NIOSH Guidances

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

https://www.cdc.gov/niosh/docs/2018-103/default.html

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/

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

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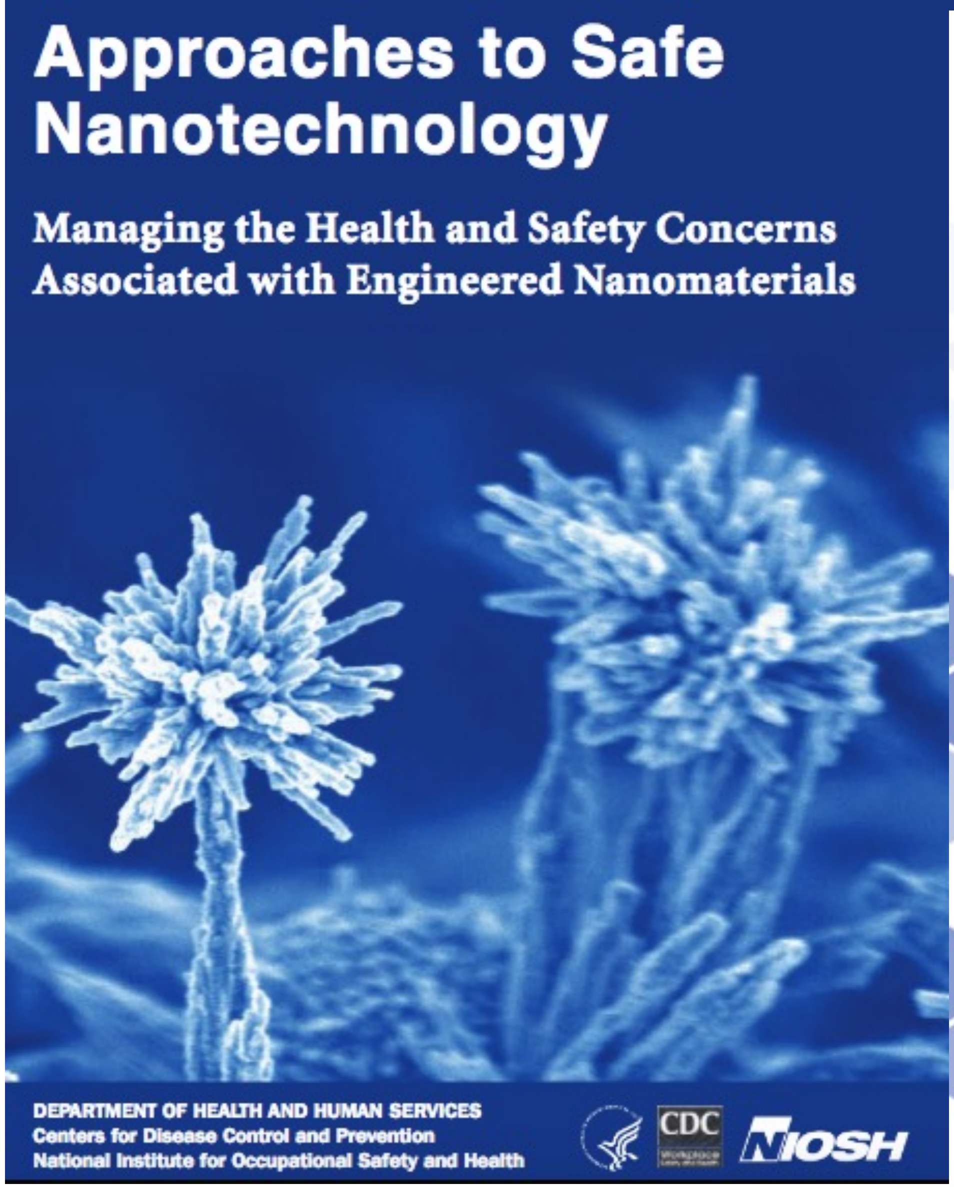
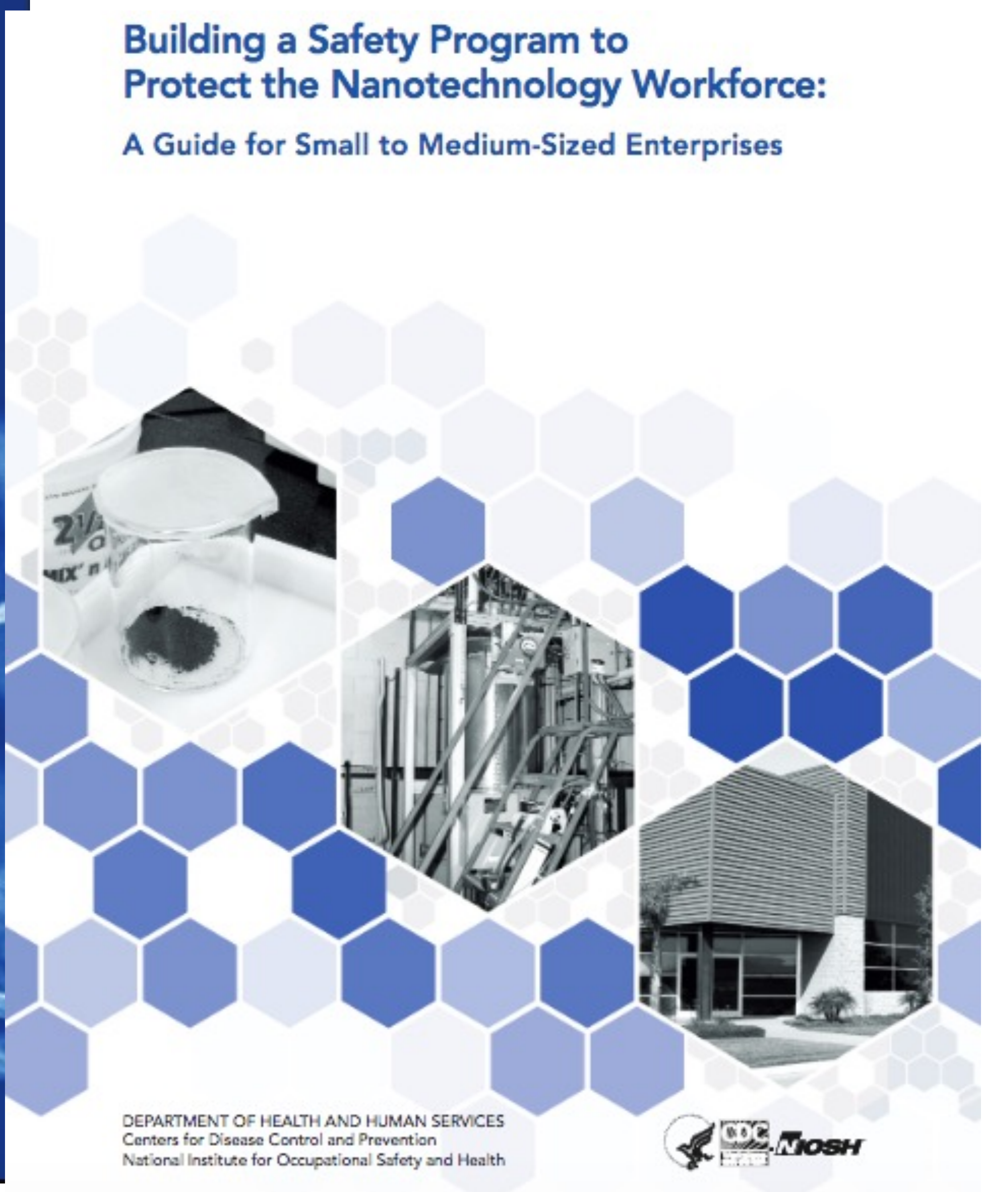
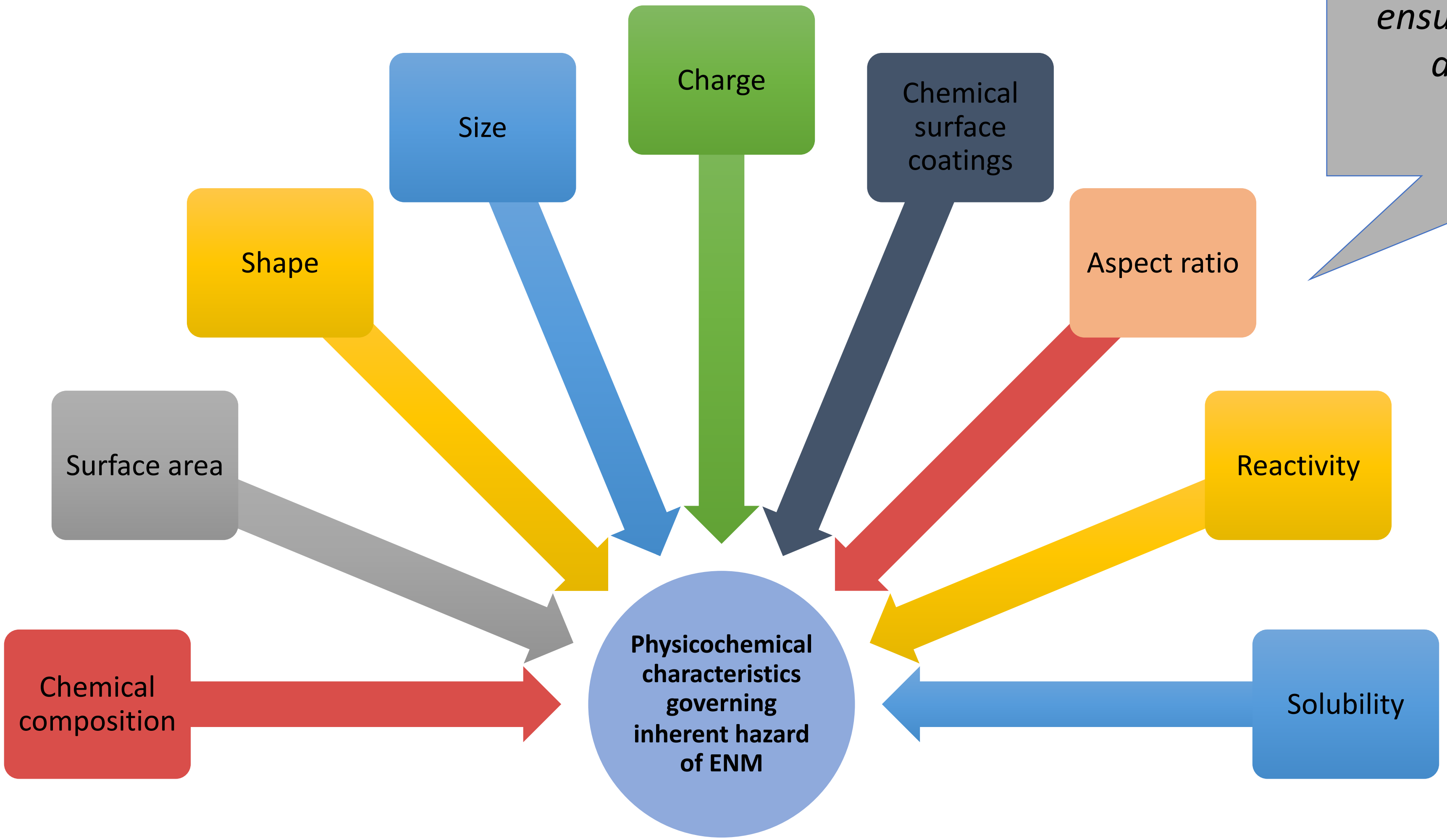




General guidance, including for small businesses: essential elements of a risk management program

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?



More fundamental protection:

Can we design out the hazard?

Safer and More Sustainable Nanotechnology

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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.

Where is regulation?

US EPA

- Toxics Substances Control Act – regulated by molecular composition (e.g., CAS #) not size
  - ”Existing” – subject to a reporting rule (2017)
    - nano-silica; nano-gold; nano-titanium oxide
  - ”New”
    - Requires pre-manufacturing notices (PMNs) and review of safety through EPA’s new chemicals review program
- Federal Insecticide, Fungicide and Rodenticide Act (FIFRA)
  - Anti-bacterial materials, e.g., nanosilver

Other US authorities:

- OSHA
- FDA
- CSPC

No restrictions on ENMs to date

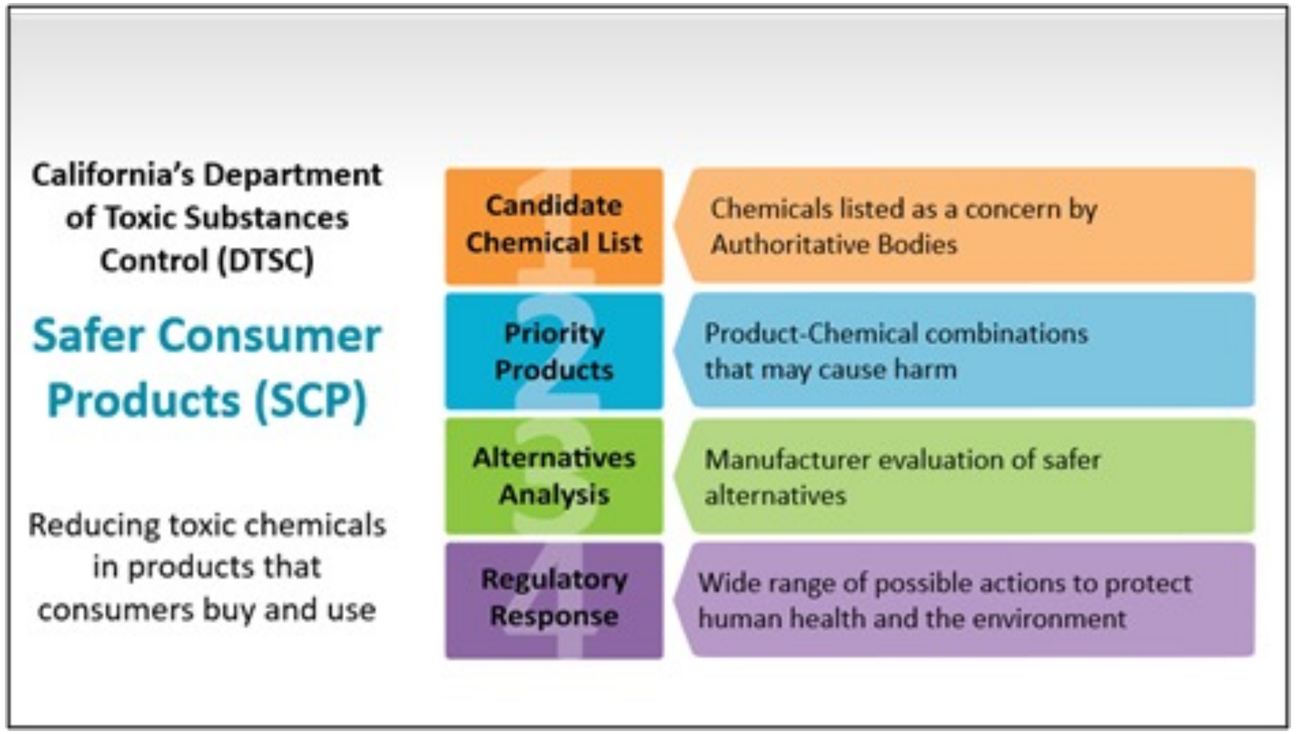
It’s a different story in the EU

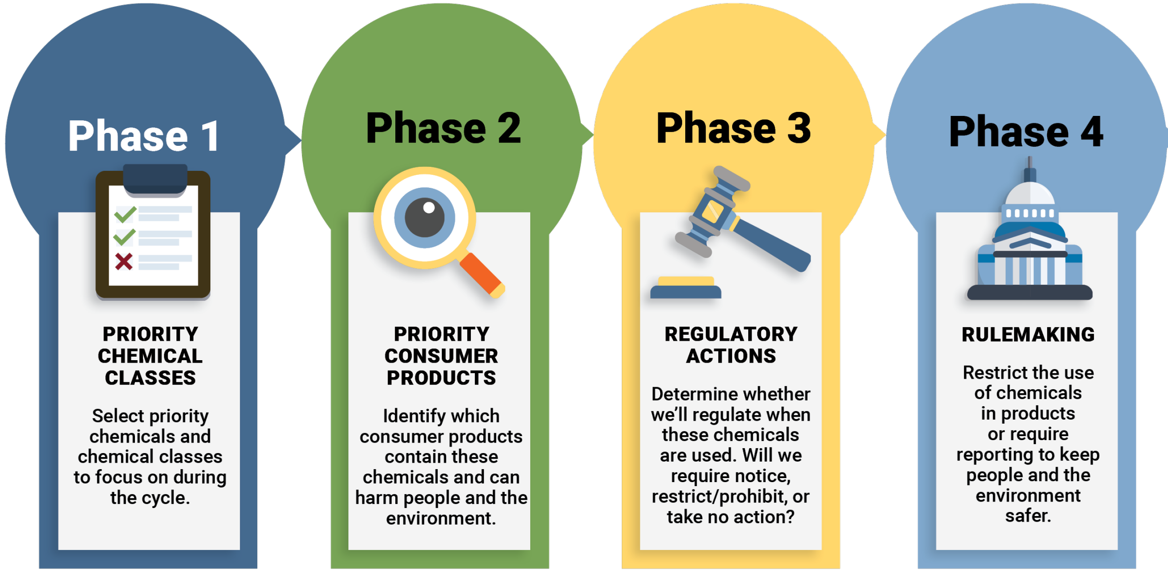
A New Driver for Use of ENMs – Alternatives to Chemicals of Concern

Now emerging (in development or commercially available) as replacements for functions currently being served by chemicals of concern. Examples include:

- Multi-walled carbon nanotubes (MWCNTs) as replacements for halogenated flame retardants
- Nanowhiskers as a replacement for per- and polyfluroralkyl substances (PFAS) in stain resistant textiles and carpets
- Organosilicates as replacements for PFAS surfactants in aqueous film forming foams
- Polymer nanocomposites as replacements for phthalate plasticizers
- Range of nanomaterials as replacements for copper-based anti-fouling agents

State programs focus on phasing out toxic chemicals not set up to deal with ENMs





SAFER PRODUCTS FOR WASHINGTON

We can have our cake and eat it too
BUT we need

- Support for EH&S research
- Anticipatory governance/policy structures
- Actions for protection despite uncertainty

Thank you!

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Reflections by others?