CENTER FOR GREEN CHEMISTRY & GREEN ENGINEERING AT YALE

SAFE BY DESIGN: EMERGING SUSTAINABLE NANOTECHNOLOGY

Mark Falinski
PhD Candidate, Yale University
Massachusetts TUR Continuing Education Conference
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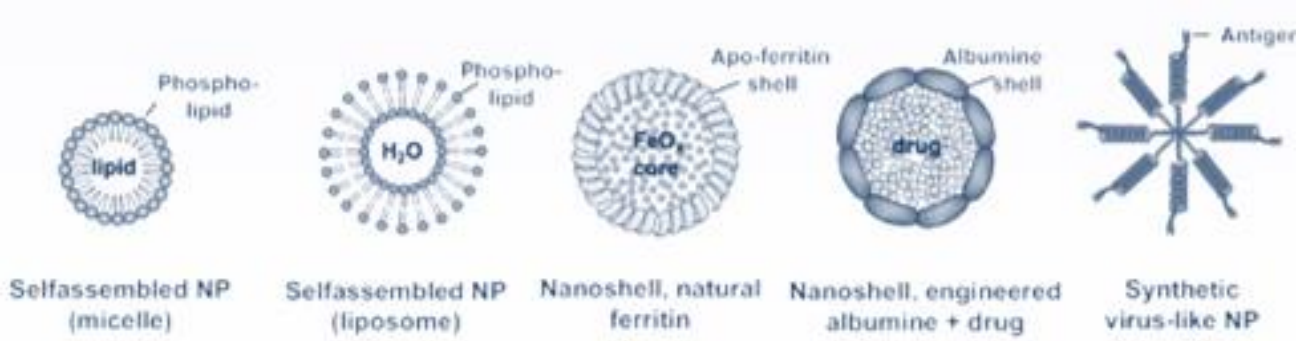
Unique At The Nanoscale (<100 nm)



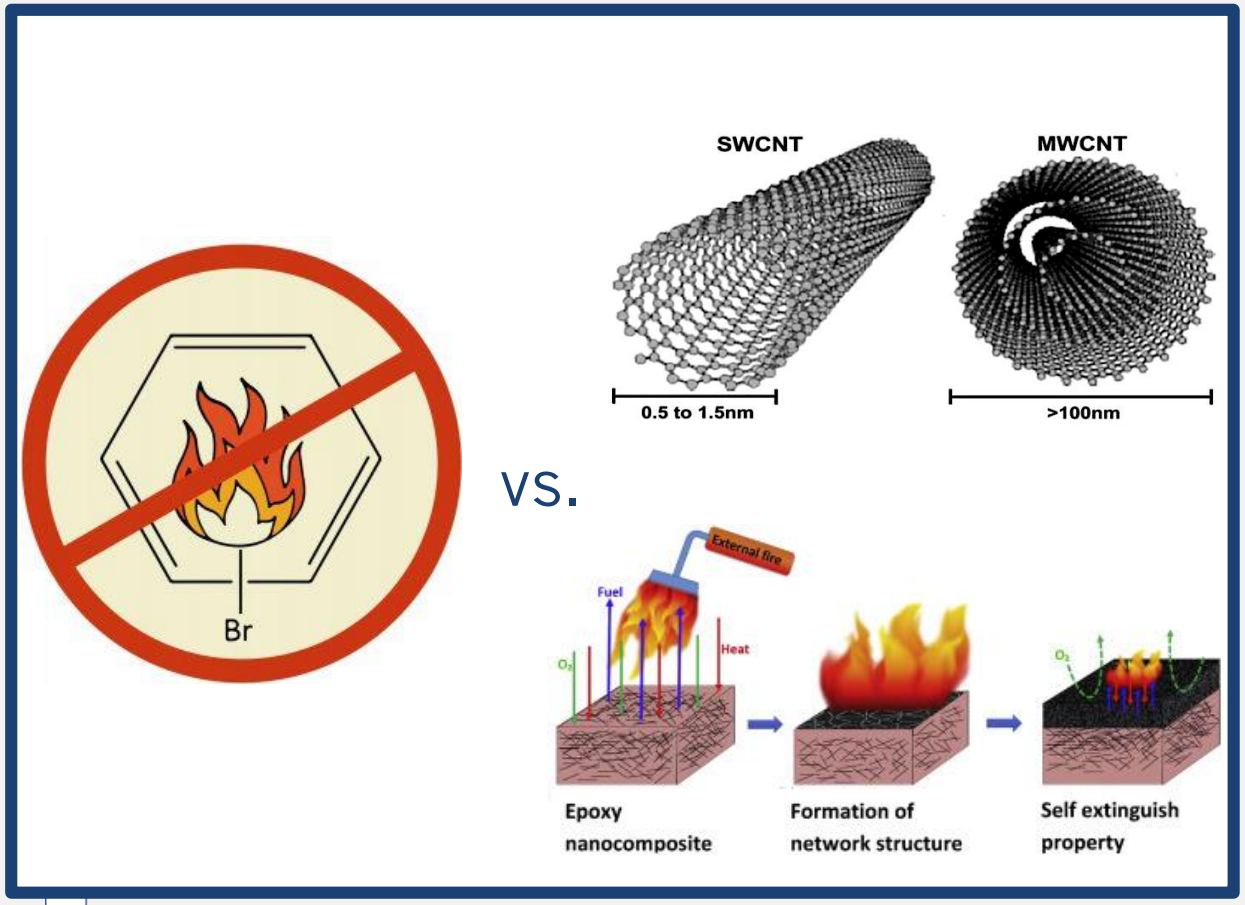
Properties	Applications
High thermal conductivities	Water treatment
Superparamagnetism	Electronics
High surface area	Drug delivery
Enhanced photocatalytic activity	Energy production and storage
Short intraparticle diffusion distance	Textiles
Solar adsorption	Antimicrobial agents
Surface plasmon resonance	Agriculture and food
Enhanced mechanical properties	Paints and coatings
Tunable electrical properties	Optical engineering
	Biomedical applications

Gubala et al, Pure App Chem, 2018

What are we trying to "nano-replace"?

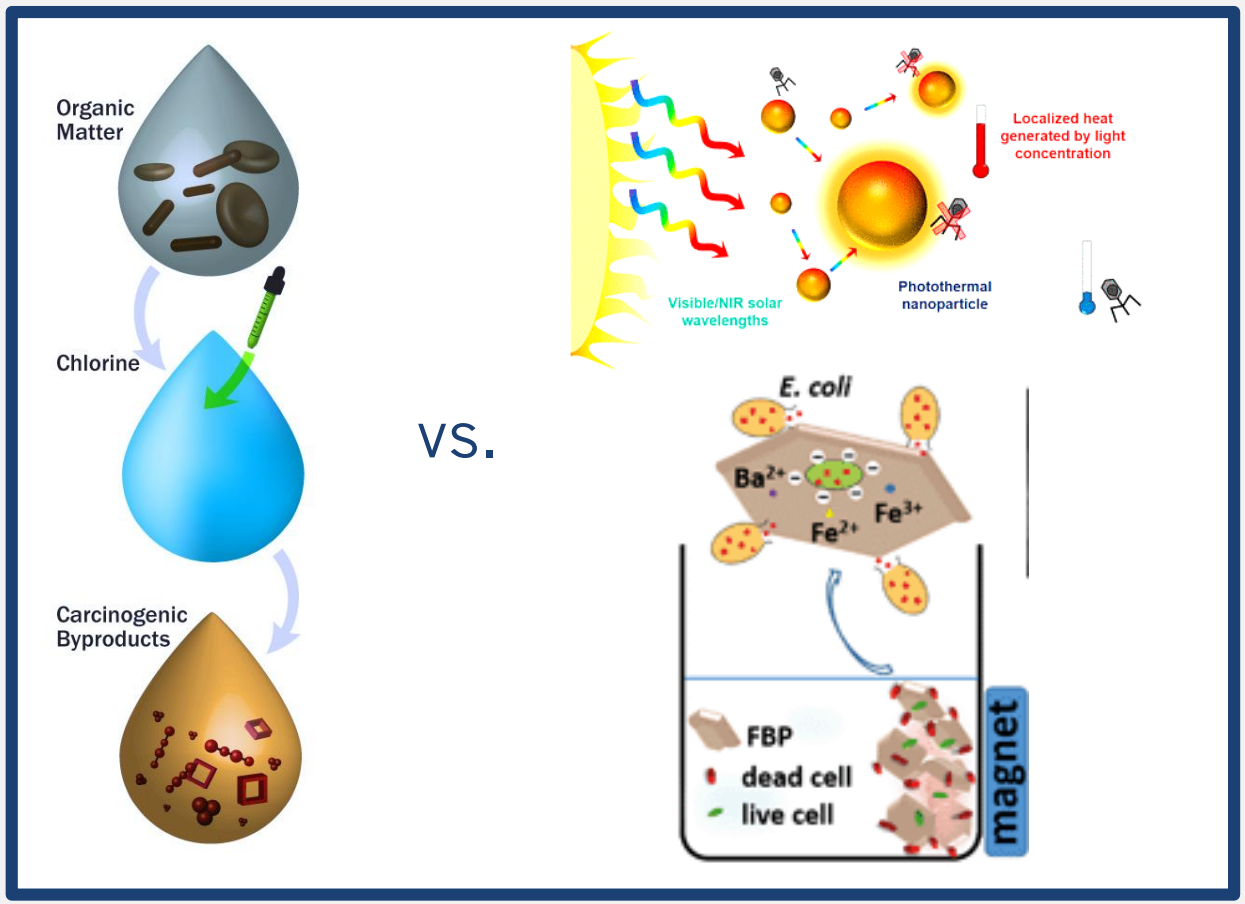
Example:

Brominated Flame Retardants



Example:

Chlorinated Disinfection Byproducts



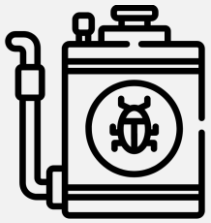
Shabestari et el, Carbon, 2017

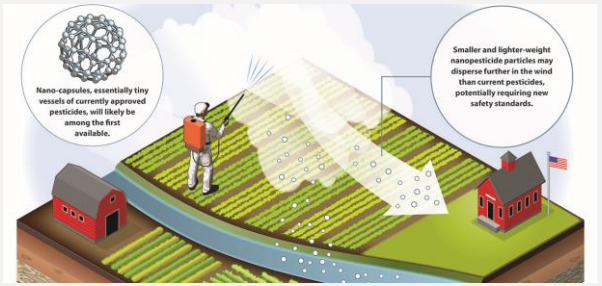
Song et el, ES:Nano, 2018

Loeb et el, ES&T, 2018

Other potential or in-use nano-replacements

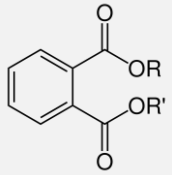
Chemical Pesticides

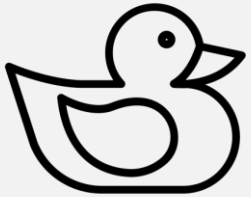


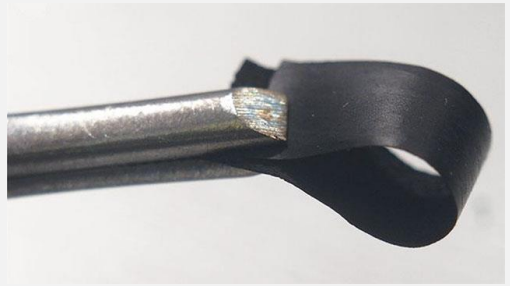


Nano-metal/metal oxide nanopesticides

Phthalate Plasticizers

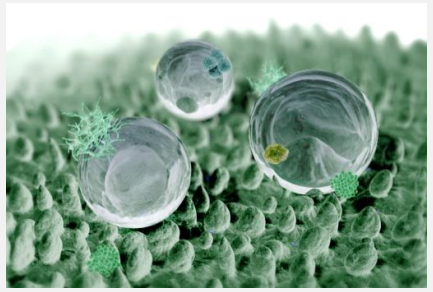






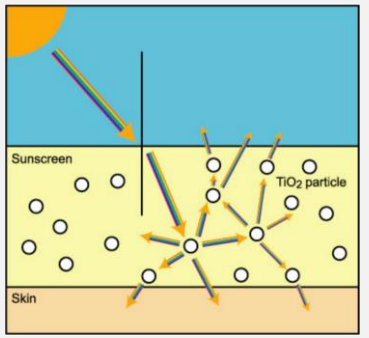
Carbon nanotube plastic composites

PFAS (in clothing)



Nano-enabled clothing fibers

Chemical Sunscreens

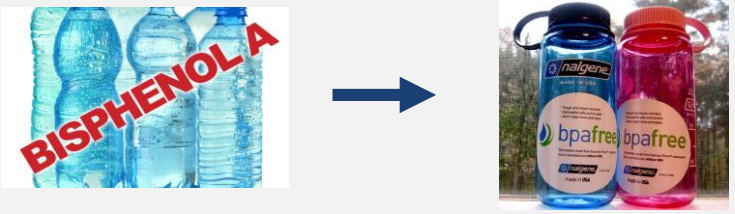


TiO_2 and ZnO nanoparticle sunscreens

Emerging Technology Concerns and Risks

Regrettable Substitution

The replacement of a toxic chemical by one with unknown (maybe greater) toxic effects



Public Perception Risk

Public concern and over-regulation can effectively kill nascent industries

How do we ensure emerging nanomaterials don't suffer the same fate, while maintaining functional performance?

Zimmerman and Anastas, Science, 201

Limiting Nanomaterial Risk

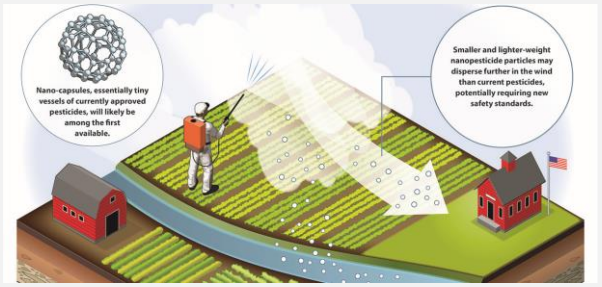
RISK = HAZARD x EXPOSURE

Can be limited through encapsulation or capture techniques, but difficult to completely eliminate

f(material, surrounding environment)

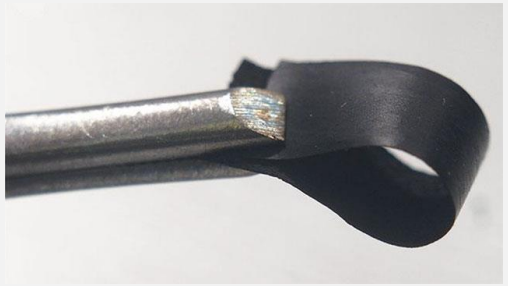
Nano-replacement exposure

Sprayed into the environment



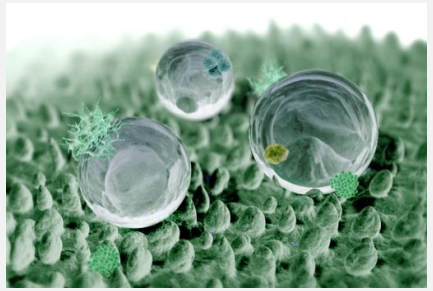
Nano-metal/metal oxide nanopesticides

Abrasion-based release of NPs



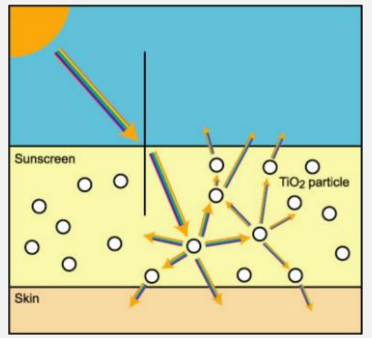
Carbon nanotube plastic composites

Washing clothes releases NPs into water



Nano-enabled clothing fibers

Washes off body into water while swimming

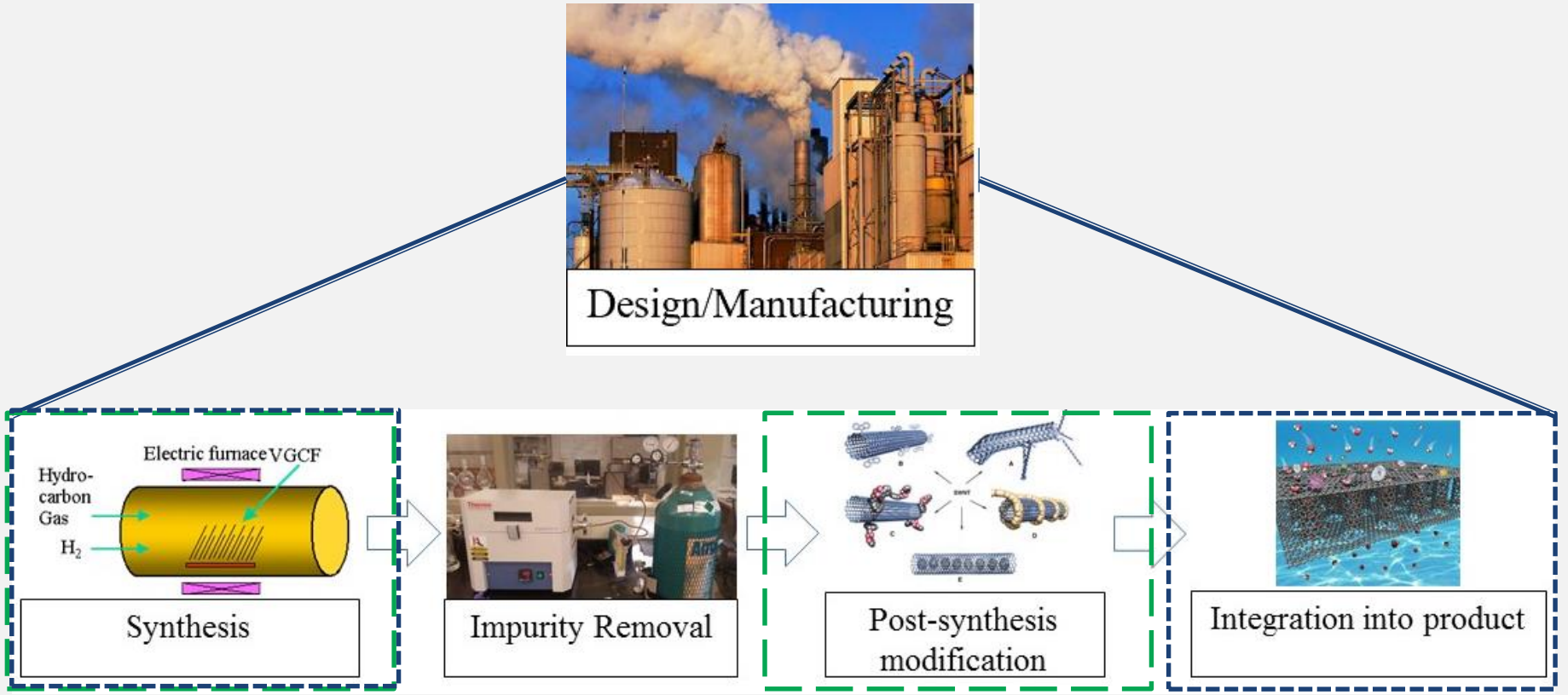


TiO_2 and ZnO nanoparticle sunscreens

Safe by Design: Limiting Nanomaterial Risk

We must aim to make our nanotechnologies Safe By Design to reduce or eliminate hazard

Nano-Enabled Device Design/Manufacture

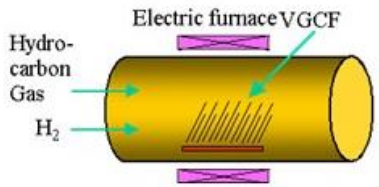


1. **How do we select a safe (yet functional) ENM "type" for use in our products, especially as toxic chemical replacements?**

2. **How do we design the ENM itself to limit risk, while maintaining performance?**

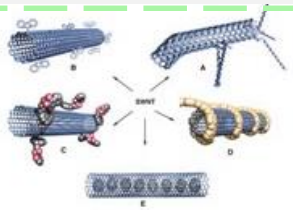
Nano-Enabled Device Design/Manufacture

Design/Manufacturing

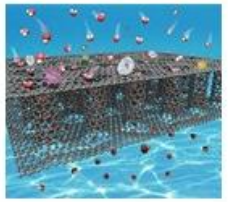


Synthesis

Impurity Removal



Post-synthesis modification



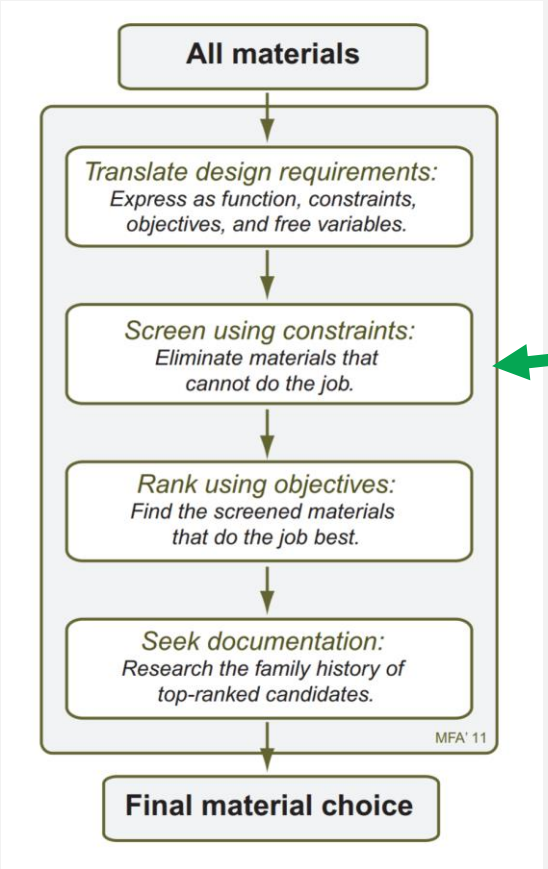
Integration into product

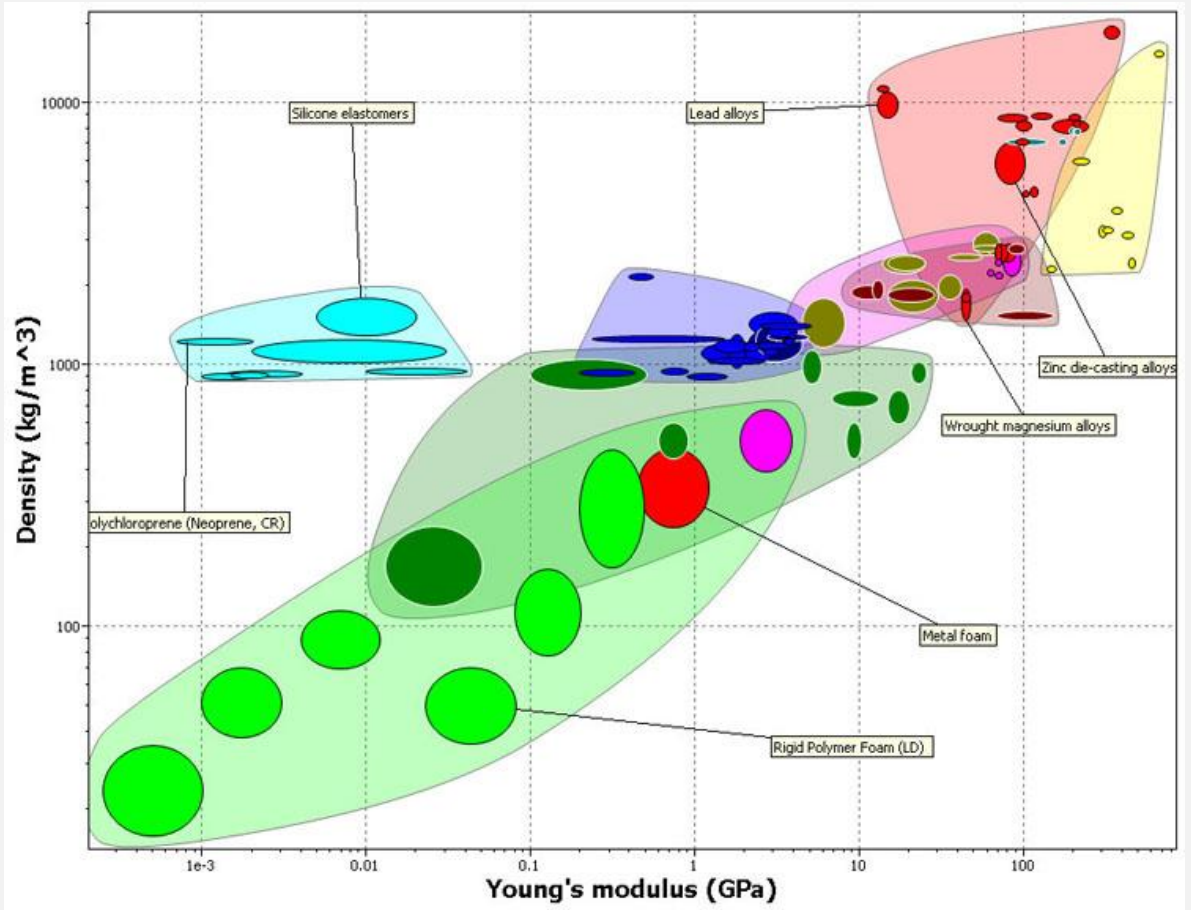
1. **How do we select a safe (yet functional) ENM "type" for use in our products, especially as toxic chemical replacements?**

2. **How do we design the ENM itself to limit risk, while maintaining performance?**

A Framework For Safe and Sustainable Nano-Selection

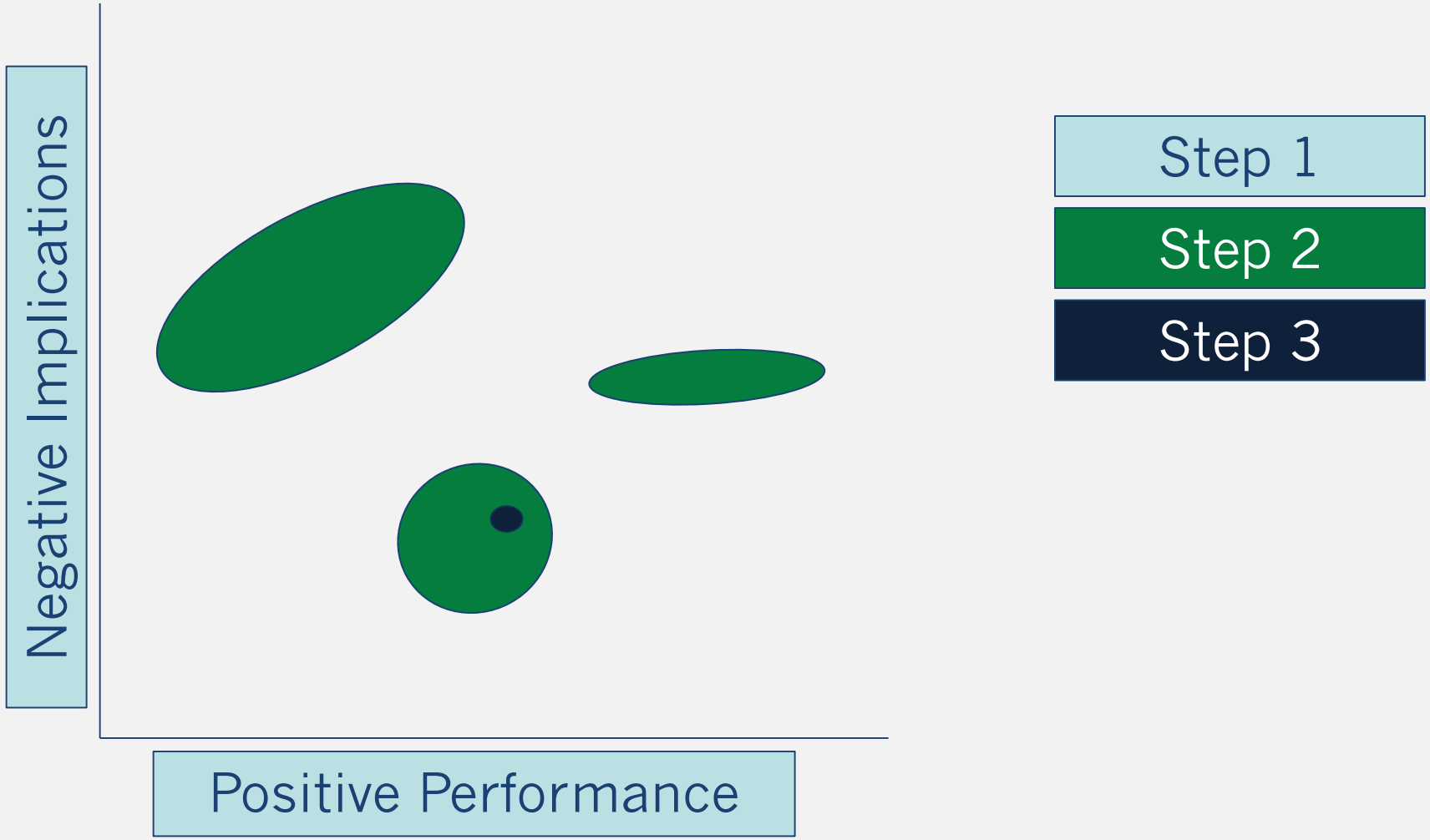
Inspired by the Ashby Material Selection Strategy (AMSS)



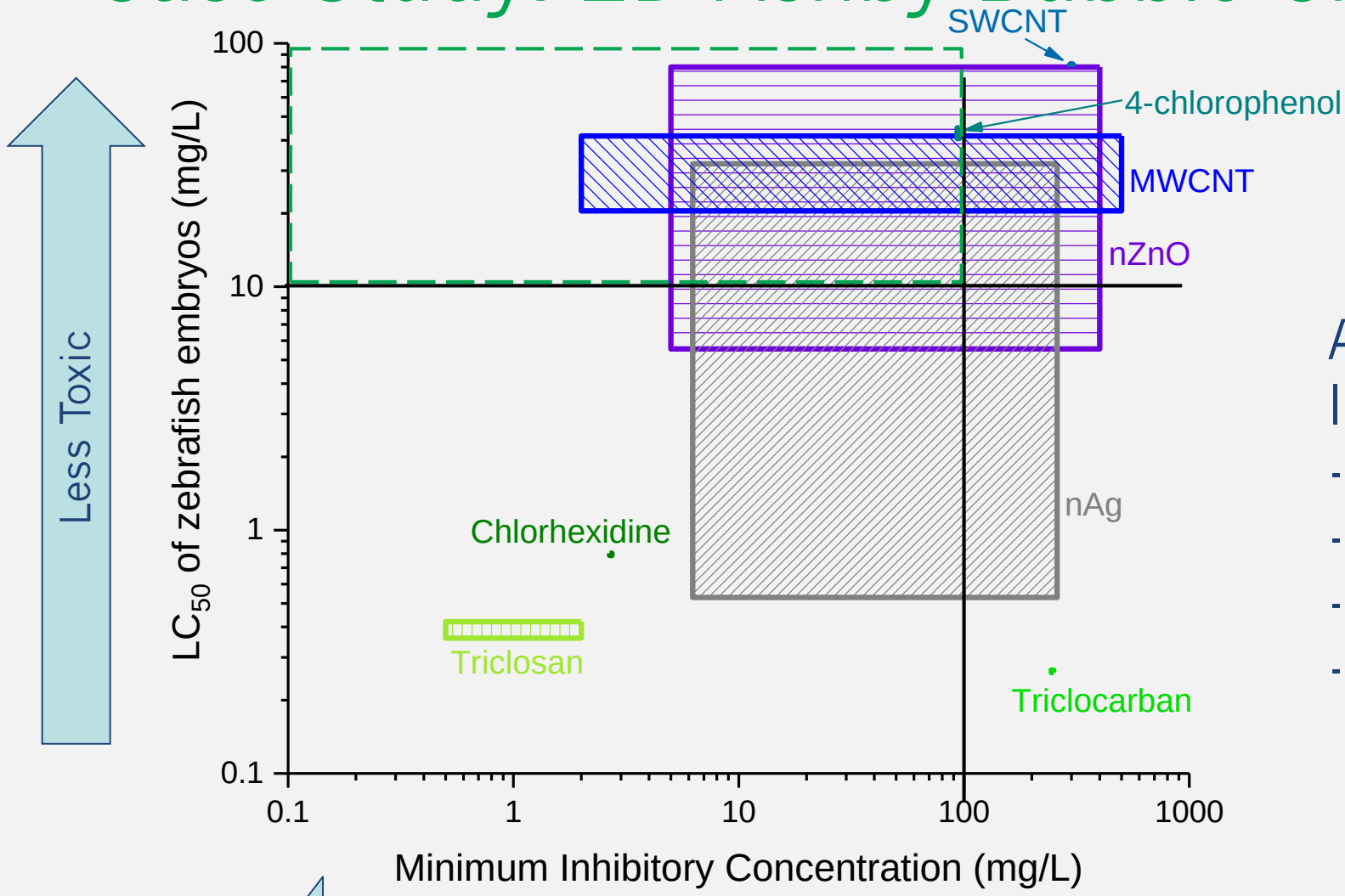


Ashby, "Materials and the Environment", 2009

Developing Responsible Nanomaterial Selection Charts



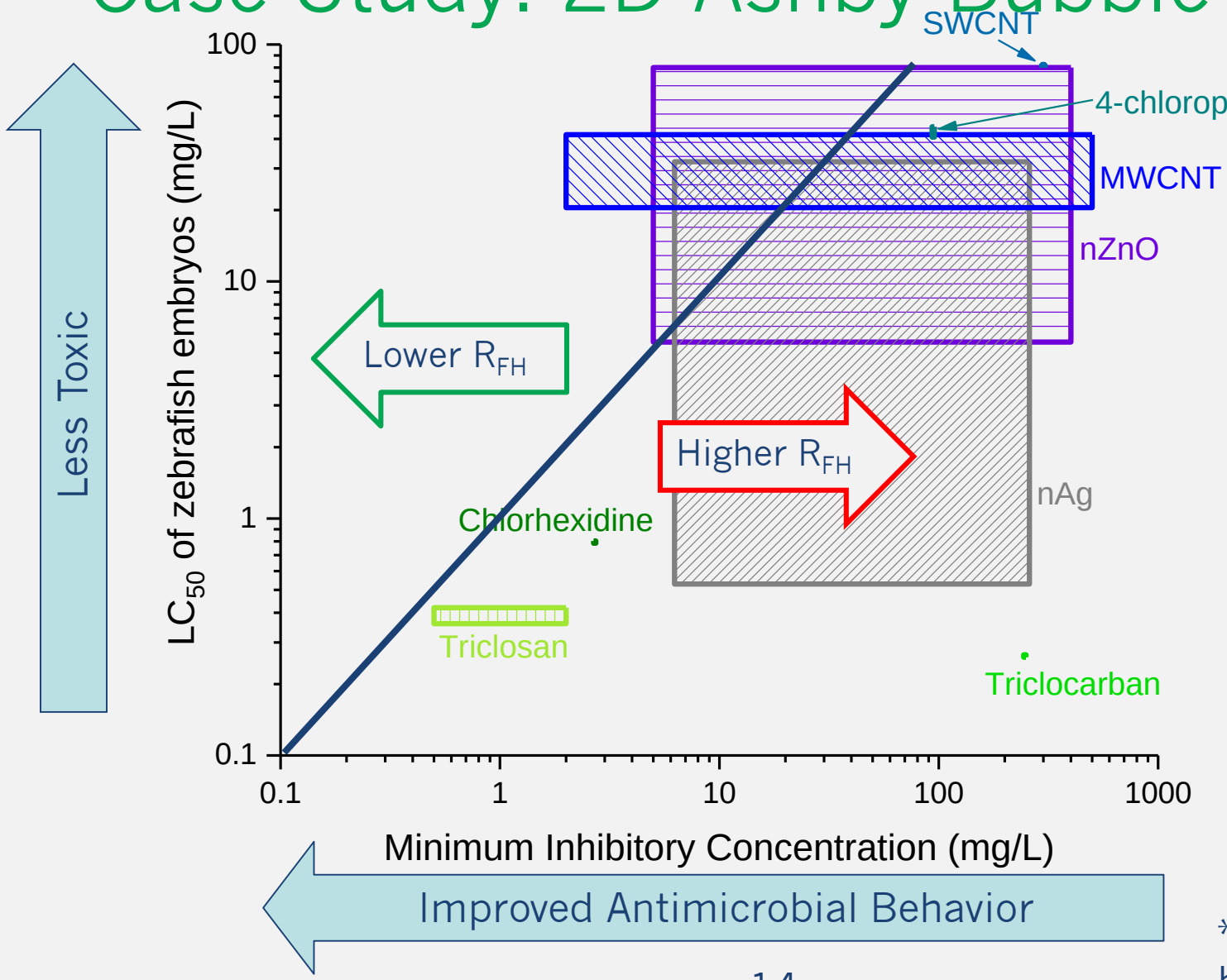
Case Study: 2D Ashby Bubble Charts



Applying constraints leaves only:

- MWCNT
- nAg
- nZnO
- 4-chlorophenol

Case Study: 2D Ashby Bubble Charts



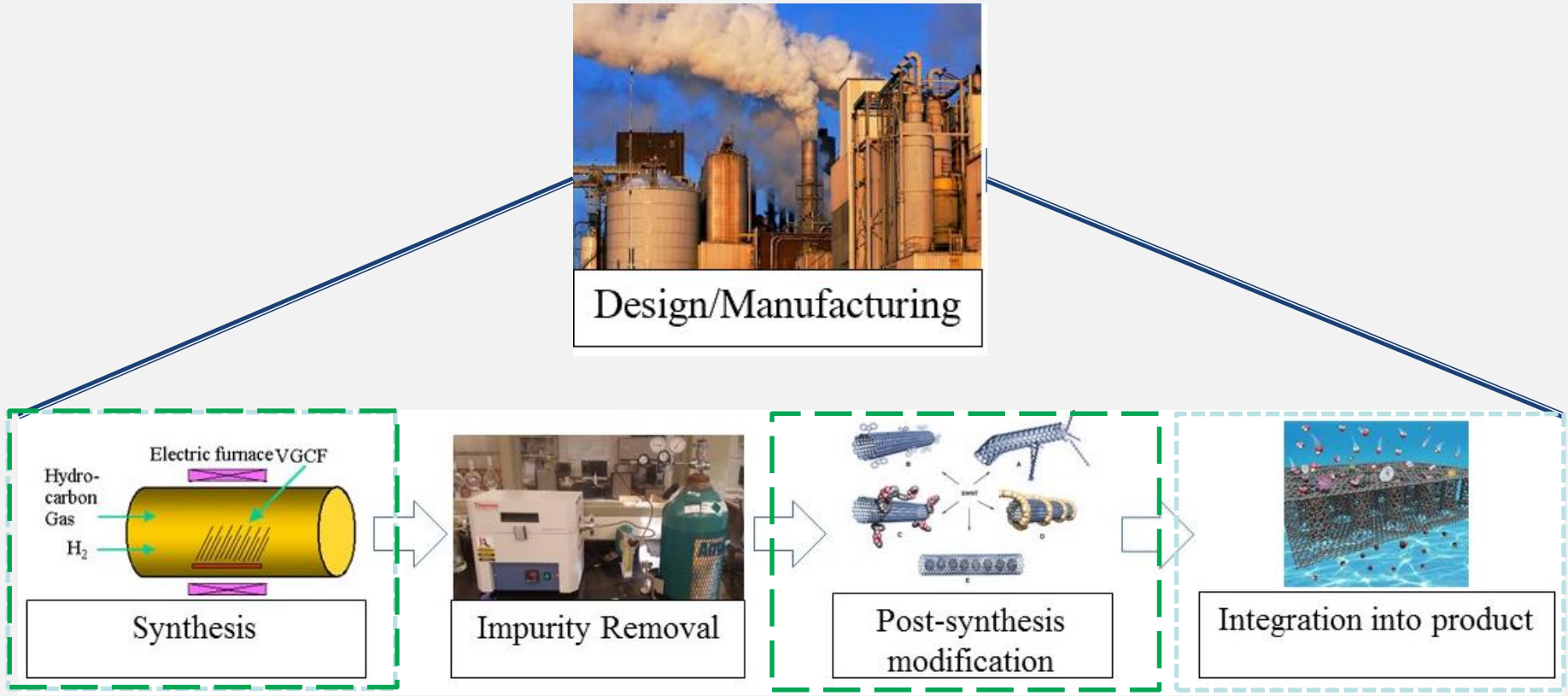
$$R_{FH} = \frac{\text{Hazardous Impacts}}{\text{Functional Performance}}$$

Low R_{FH} = Good
High R_{FH} = Bad

$R_{FH} = 1 \rightarrow$ MIC = LC_{50}

*Based on Impact-Benefit Ratio by Gilbertson et. al, ES&T, 2014

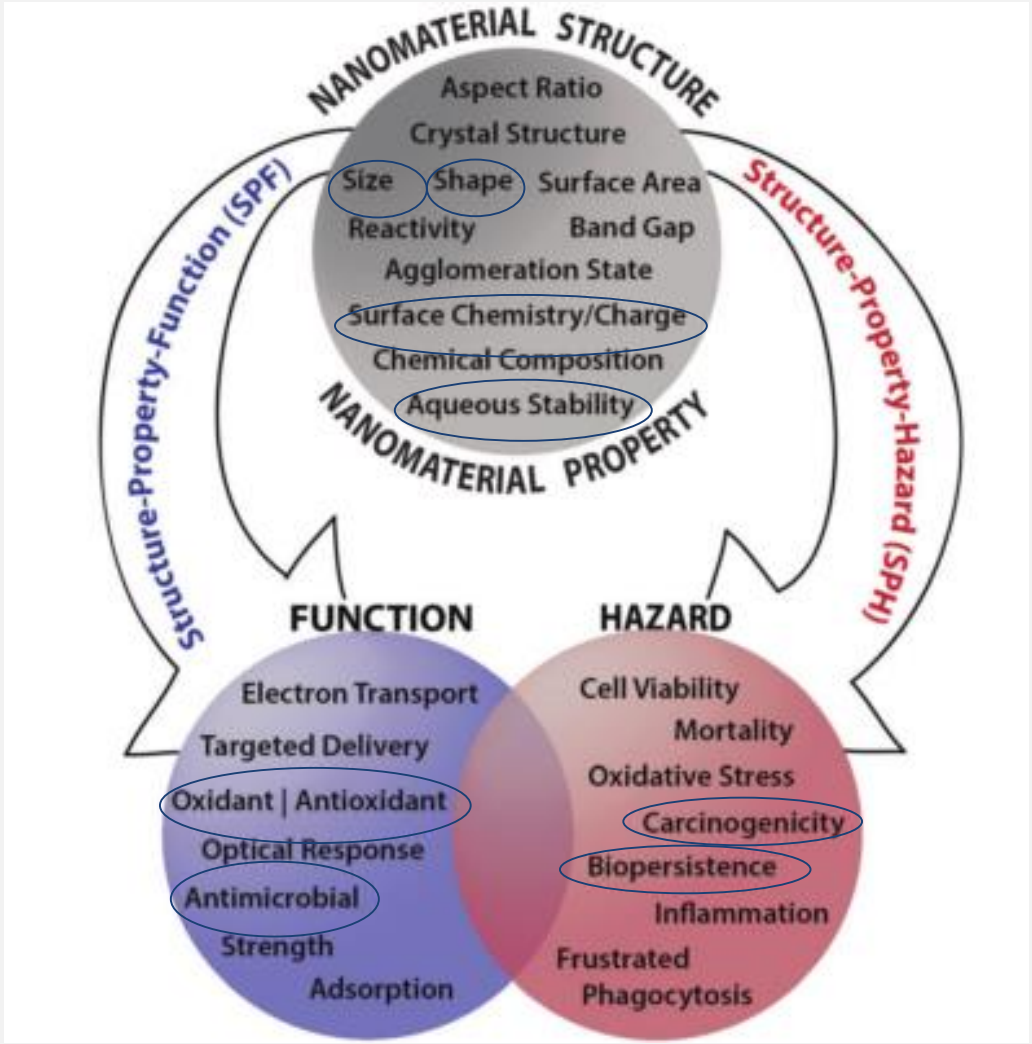
Nano-Enabled Device Design/Manufacture



1. **How do we select a safe (yet functional) ENM "type" for use in our products, especially as toxic chemical replacements?**

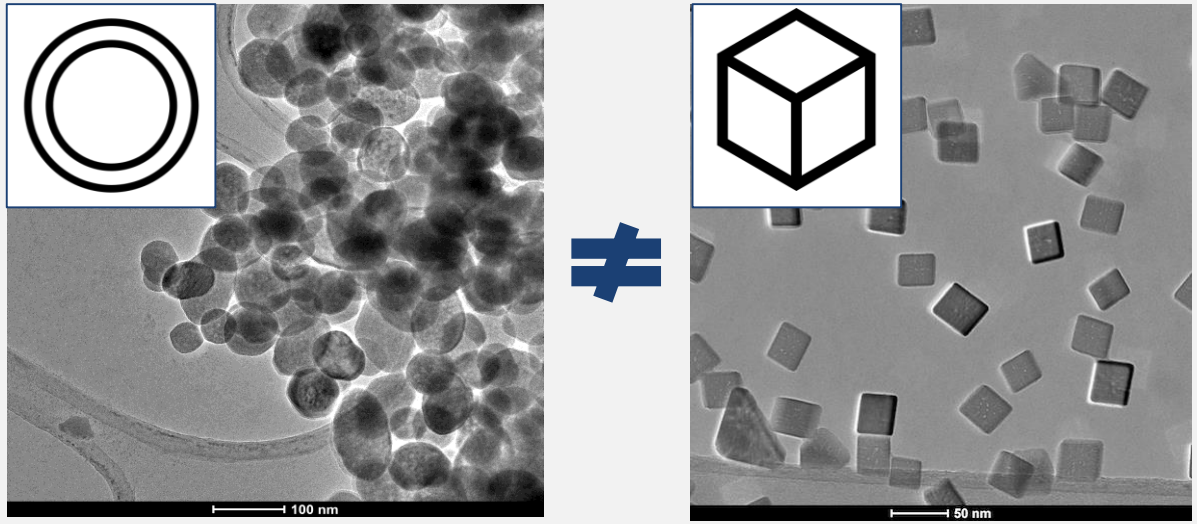
2. **How do we design the ENM itself to limit risk, while maintaining performance?**

Structure-Property-Function-Hazard Relationships (SPFH)



Modified from: Gilbertson et al., Chem Soc Rev, 2015

Triclosan = Triclosan



n-α-Fe_2O_3 ≠ n-α-Fe_2O_3

Images supplied by Holly Rudel, Yale University

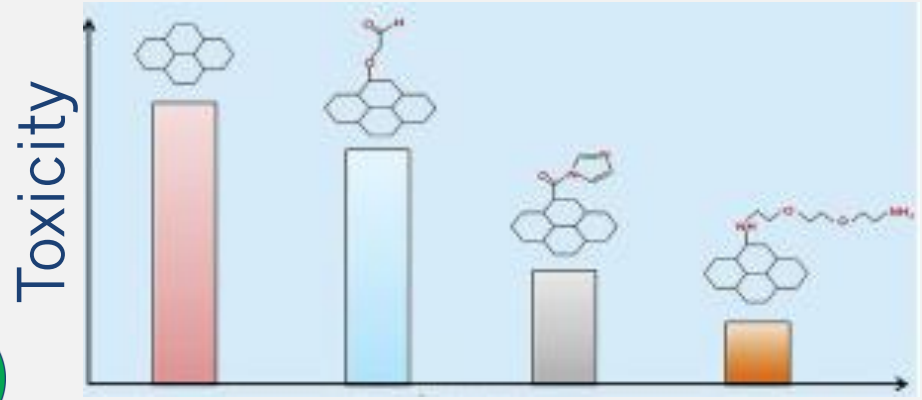
Size

Example **TiO_2 NPs with endothelial cells**

Modified from: Liao et al., Env Tox, 2019

Surface Functional Groups

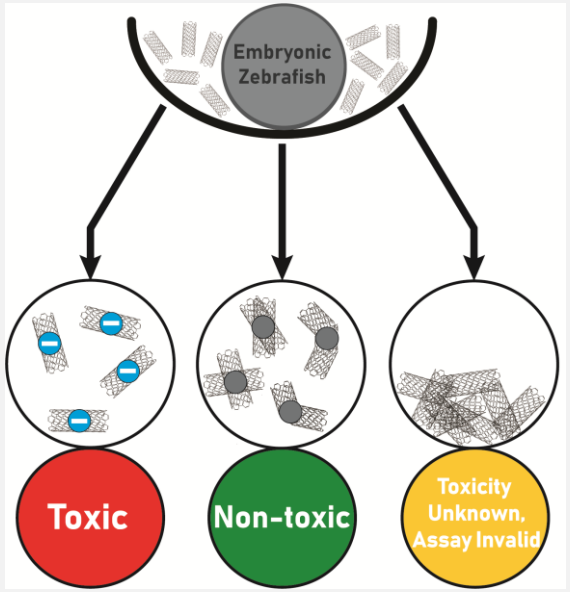
Example **Graphene with *Daphnia magna***



Modified from: Liu et al., Env Poll, 2018

Surface Charge/Aggregate State

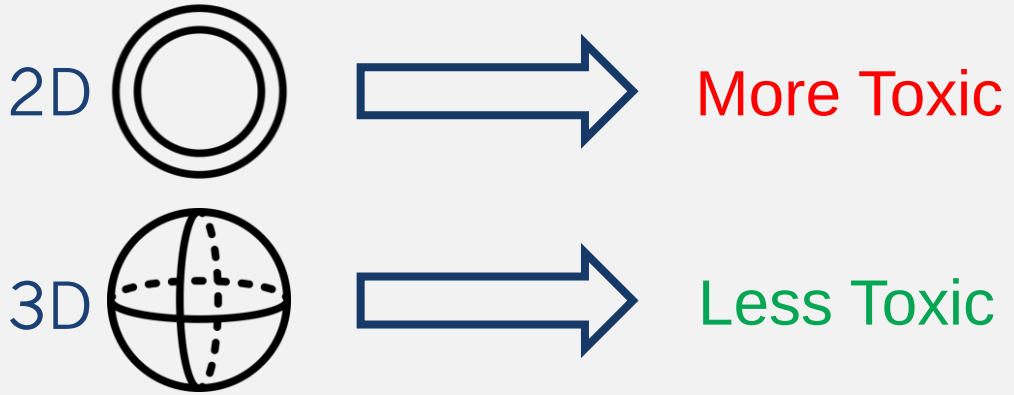
Example **MWCNTs with embryonic zebrafish**



Modified from: Falinski et al., Carbon, 2019

Shape

Example **Ag NPs with embryonic zebrafish**



Modified from: Abramenko et al., J Haz Mat, 2018

Size

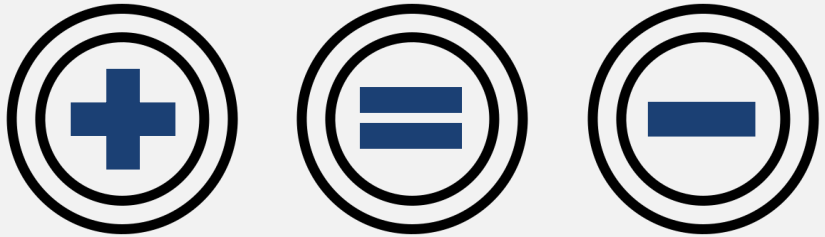
Example **α-Fe_2O_3 NPs for Cr(IV) sorption**

Increasing Sorption

Modified from: Xiao et al., App Surf Sci, 2015

Surface Charge/Aggregate State

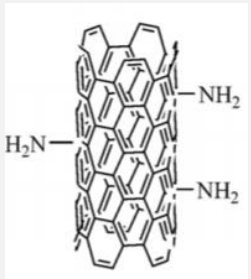
Example **Charged Ag NPs for *S. aureus* inactivation**



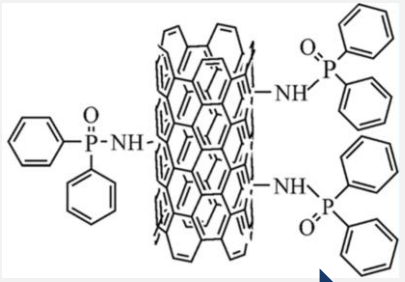
Improved Inactivation

Surface Functional Groups

Example **CNTs for flame retardant fabrics**



vs.



Flame Retardancy

Modified from: Xing et al., App Mat Int, 2016

Shape

Modified from: Abbaszadegan et al., J Nano, 2015

Example **Al_2O_3 NPs for conductive fibers**

nanoplatelet nanorod nanofibre nanoflake

Conductivity

Modified from: Falinski et al., Nat Nano, 2018

Impact-Benefit Ratio

Nano-Enabled Products

$$\text{Impact-Benefit Ratio (IBR)} = \frac{\text{Upstream Impacts}}{\text{Downstream Benefits}}$$

< 1 ✓ Pursue Development and Implementation
Realization of downstream benefits outweigh production impacts

= 1 Net Neutral Impact

> 1 ✗ No Added Value, Redesign
Production impacts outweigh realization of downstream benefits

Gilbertson et. al, ES&T, 2014

Safe by Design

- Eliminate **hazard** early in the design process, not just exposure
  - Select nanomaterial classes for nano-enabled products based on performance *and* negative implication metrics
    - Synthesis and Material Integration
  - Design physicochemical structure of nanoparticles to minimize Impact-Benefit Ratio
    - Synthesis and Post-synthesis Modifications

Questions?

email: mark.falinski@yale.edu