Life Cycle Issues for Scalable Nanomanufacturing of CNT-enabled Products

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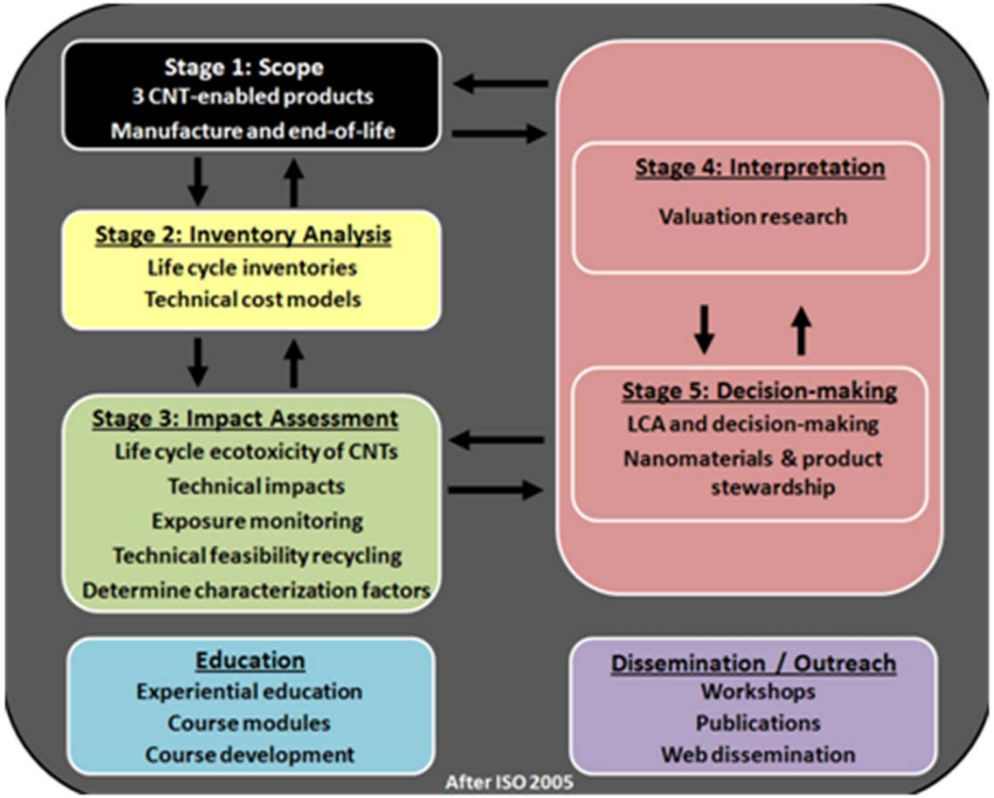
Northeastern University

How can we ensure nanomanufacturing processes and products remain safe for workers, consumers and the environment?

How can industry develop new technologies in a responsible, sustainable manner?

NSF SNM: Designing and Integrating LCA Methods for Nanomanufacturing Scale-up



Isaacs, Bosso, Busnaina, Cullinane, Eckelman, Sandler : **Northeastern**
Mead, Bello: **U Mass Lowell**
Zimmerman: **Yale**
Nash: **Harvard**

- NSF Scalable Nanomfg Award **#1120329**
- Lead Institution: NEU
- Collaborators at Yale, Harvard, UMass Lowell
- Project focuses on applications with CNTs
  - Composites (EMI shielding)
  - Batteries
  - Sensors

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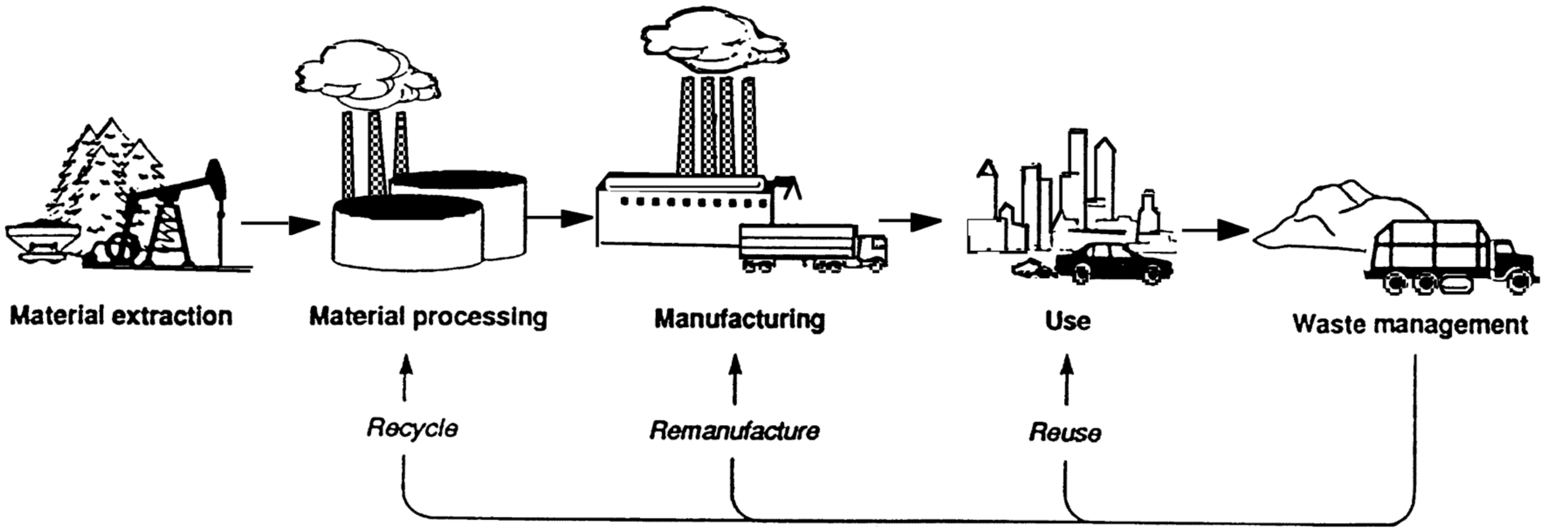
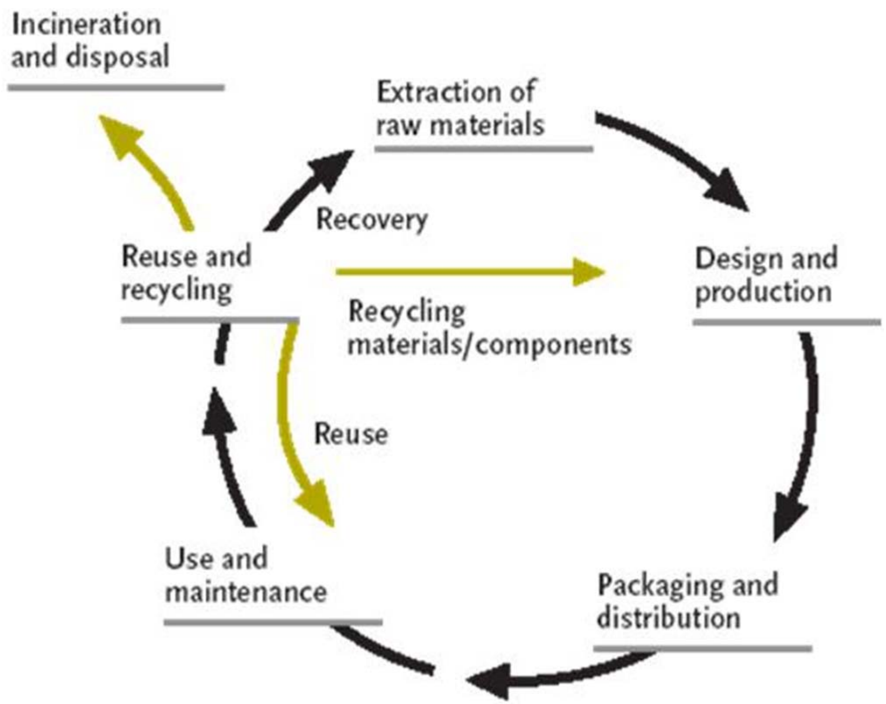
Utilizes Life Cycle Assessment

- Methodology to evaluate the environmental effects and potential impacts of…
  - Product
  - Process
  - Activity
- From raw materials acquisition through production, use and disposal



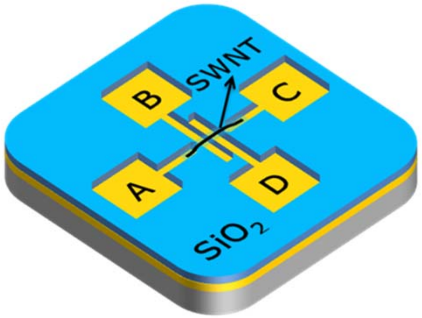
Nano-Enabled Product Lifecycle



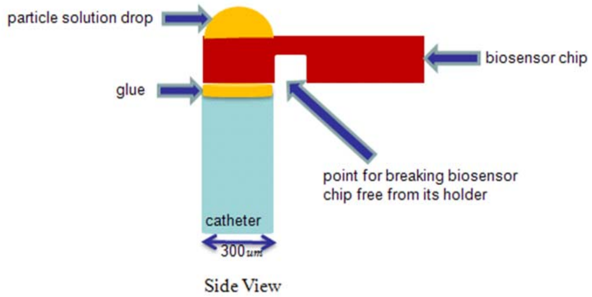
- Where do nano-enabled products contact people?
- Where would nano products contact the environment?
- Any means for estimating quantities at points of contact?

Applications Using CNTs

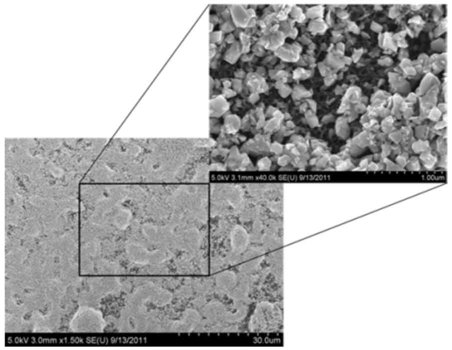
- SWNT Switch



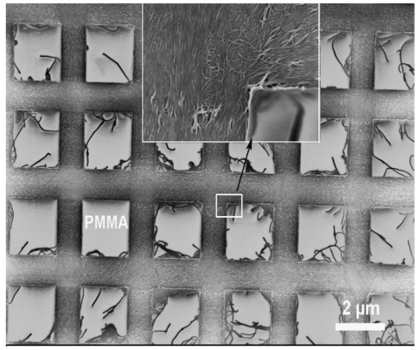
- Sensors



- Batteries



- EMI-Shielding



Batteries Background

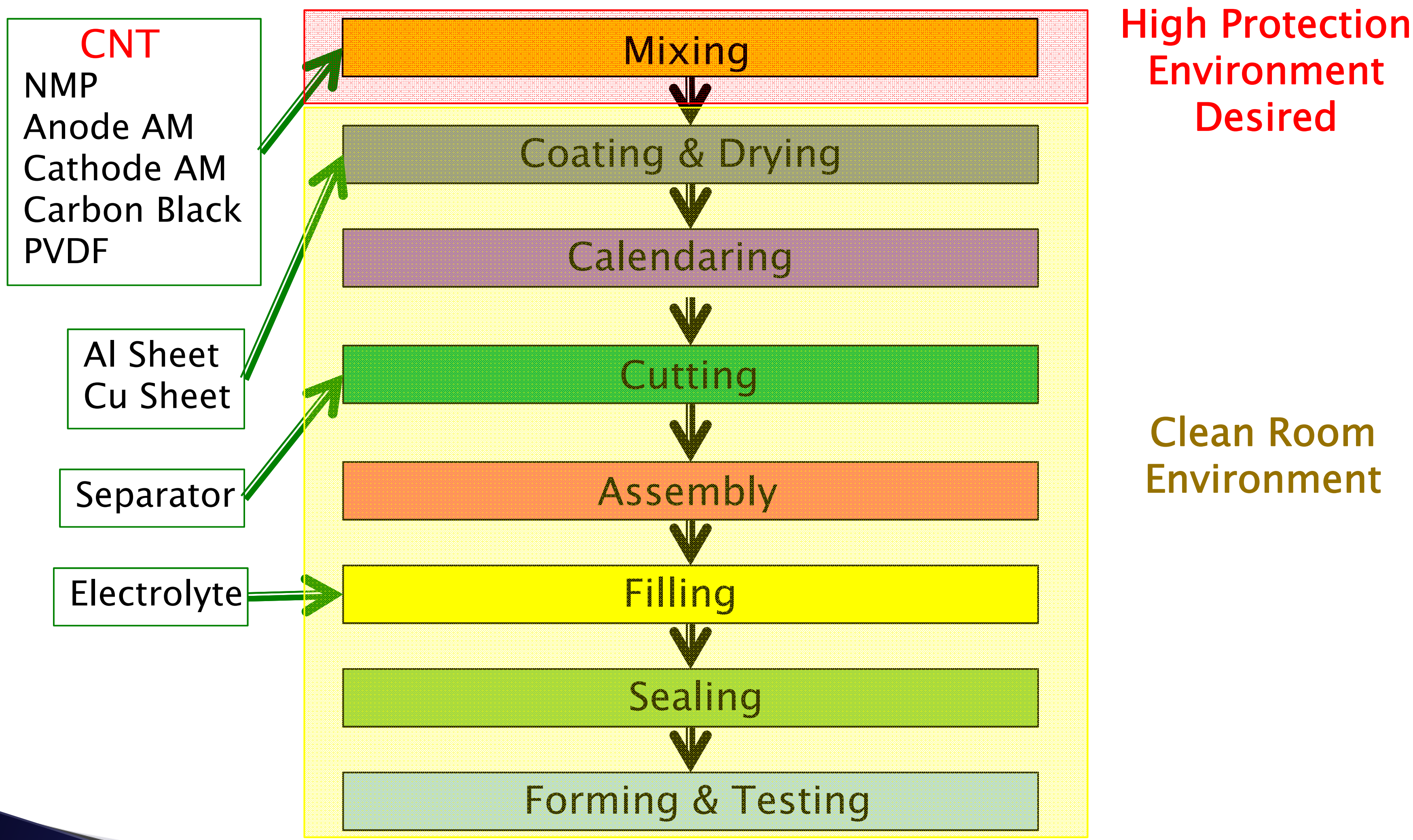
1. Components of batteries

- Cathodes
- Anodes
- Separator and electrolyte

2. Batteries classification

- Primary or non-rechargeable
- Secondary or rechargeable

Process Flow Chart – CNT Enabled LiMnO Battery



CHN Toolbox
Connects Research to Applications

Templates	Nanoelements	Assembly Processes	Transfer Processes	Substrates	Applications
Microwires template	Nanoparticles	Electrophoretic 2-D and 3-D	Direct transfer (no functionalization)	Silicon	SWNT switch for memory devices
Nanowires templates	Carbon nanotubes (SWNTs and MWNTs)	Chemical Functionalization	Direct transfer with chemical functionalization	Polymer	Polymer-based Biosensors
Nanotrench template	Conductive polymers (PANi)	Electrophoretic and chemical functionalization	No transfer needed	Metal	Nanoparticle-based Biosensors
Template-free	Polymer blends	Dielectrophoretic 2-D and 3-D	Reel-to-reel transfer		SWNT Batteries
Damascene Template	Fullerenes	Convective	Switchable functionalization		Photovoltaics
	Acenes	Convective interfacial			SWNT Chem Sensors
	Graphene	Self assembly			EMI Shielding

Process Flow for CNT Cathode/Anode

Templates	Nanoelements	Assembly Processes	Transfer Processes	Substrates	Applications
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	Acenes	Convective interfacial			SWNT Chem Sensors
	Graphene	Self assembly			EMI Shielding

Shah, Kotz, Somu and Busnaina, Northeastern University

Life Cycle Inventories for CNT Cathodes

1- Material preparation
2- Cutting the Aluminum
3- Treating the surface
4- Preparing CNT solution
5- Directed assembly (Spinning)
6- Inspection
7- Electrophoresis assembly
8- Clean up
9- Additional layer MWCNT
10- Inspection
11- Additional layer LiMnO

ENERGY	kWh
	1.073657
INPUT MATERIAL	**g/chip**
ethanol (200 proof)	15.78
Lithium Manganese Oxide Powder	0.1
Gold Chip	0.5576
N2 Gas	10.324
ethylene glycol	0.446
deionized water	5163.95
disposable lab materials (plastic and paper	10.48
MWCNT	0.00112
INPUT TOTAL	5201.639

OUTPUT MATERIAL	g/chip
mixed wastewater to treatment	5174.364
hazardous waste	16.276
emissions to air	10.324
MWCNT	0.00112
OUTPUT TOTAL	5200.964

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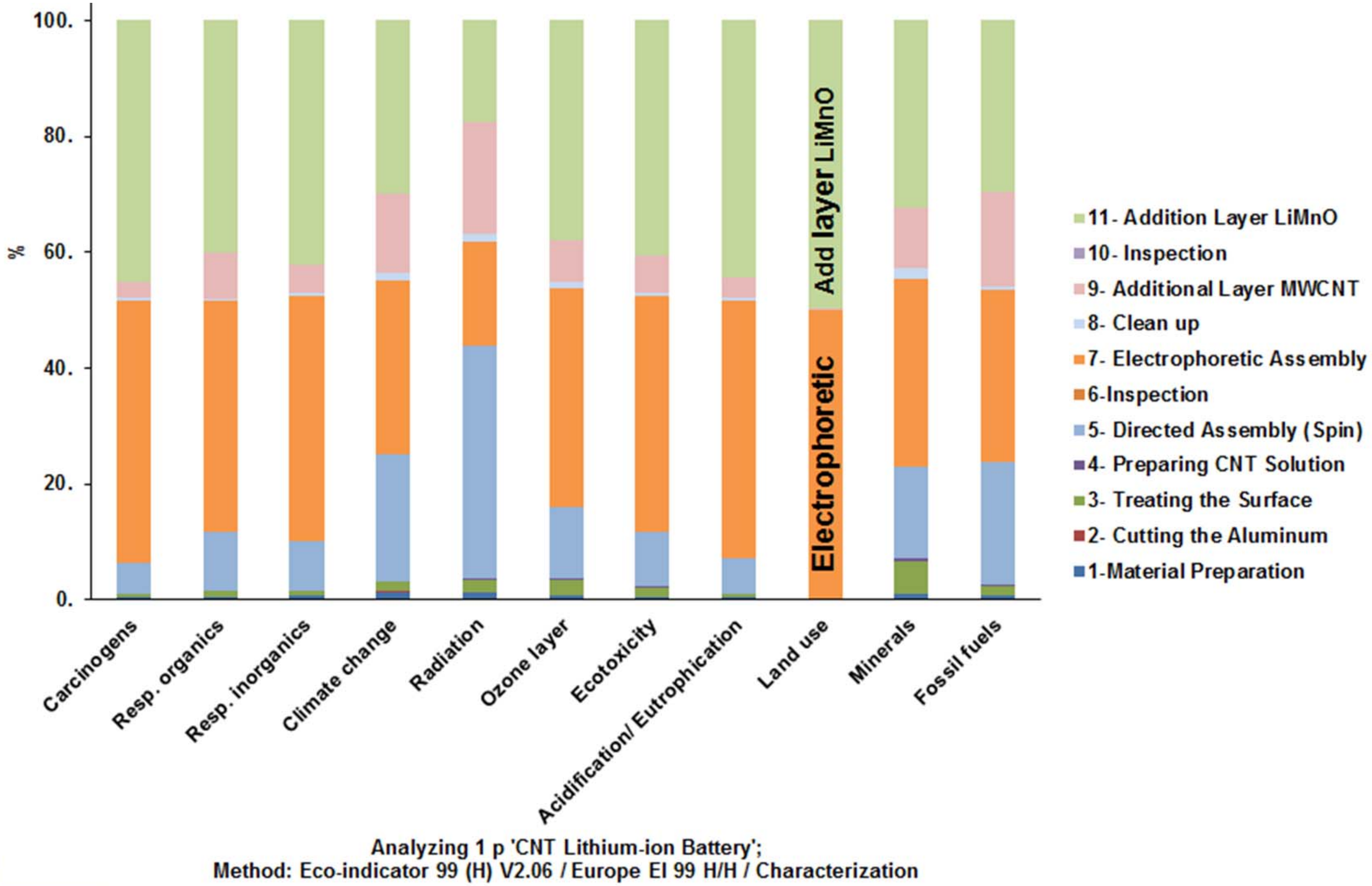
Nanobattery Cathode Characterization Results

SimaPro Software: Nanobattery Cathode Labscale Fabrication



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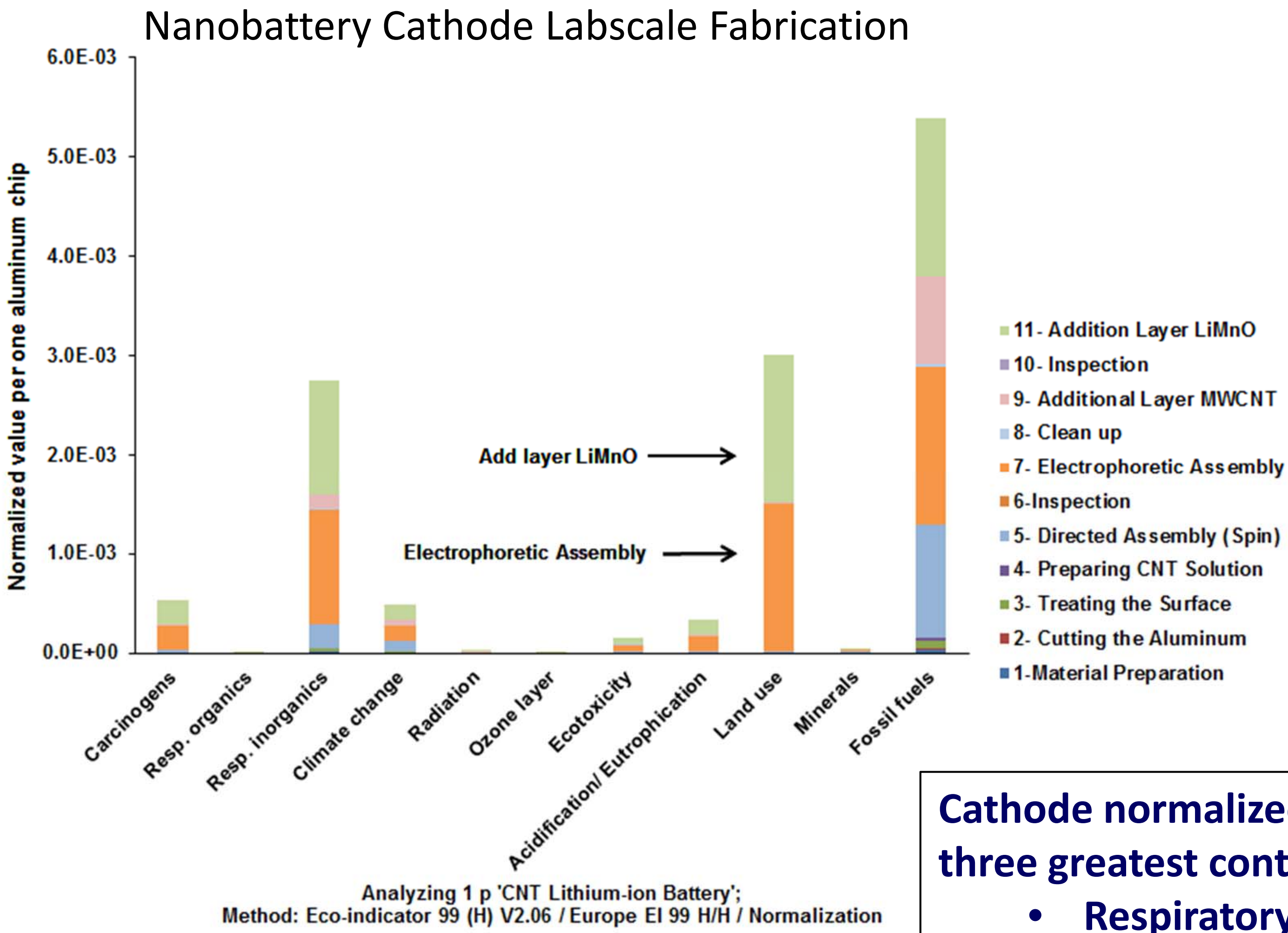
Nanobattery Cathode Normalized Results



Cathode normalized result indicate three greatest contributors:

- **Respiratory inorganics**
- **Land use**
- **Fossil fuels**

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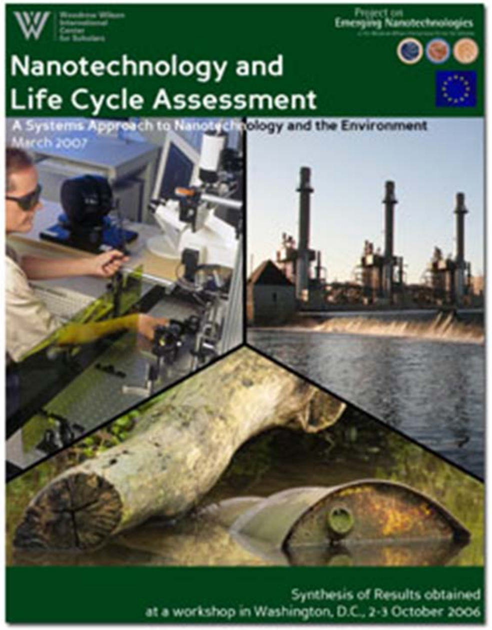
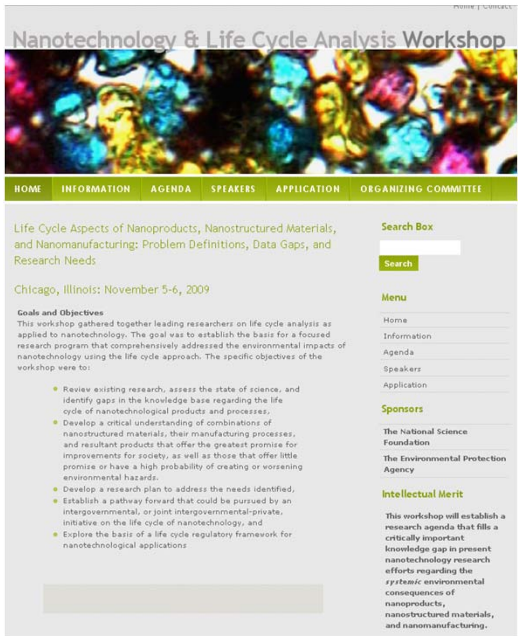
Hakimian and Isaacs, Northeastern University

Results do not indicate effect of CNTs due to limited toxicological information…

Same issues as in 2007, 2009…





CNT Ecotoxicity Characterization Factors Predicted

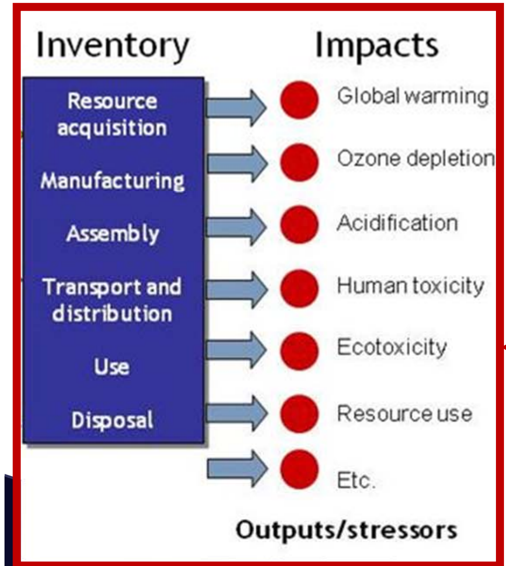
Table 1. Past Studies of CNT Aquatic Toxicity for Selected Organisms

type	genus species	test type	test details
bacteria	*E.coli, P. aeruginosa, S. aureus, B.subtilis*	membrane integrity	reported as 5–100 mg/L
protozoa	*Stylonychia mytilus*	uptake and growth inhibition	
algae	*Pseudokircheriella subcapita*	growth inhibition	sublethal, IC-25 value
copepods	*Amphiascus tenuiremis*	mortality	concentration of 10 mg/L gives 35% mortality SWNT; 20% for purified
	Amphiascus tenuiremis	fertilization/molting	concentration of 1 mg/L gives No Observed I SWNT
daphnia	*Daphnia magna*	LC50	reported as 2.4–15 mg/L
hydra	*Hydra attenuata*	sublethal morphological change	reported as 1–10 mg/L
fish	*Oncorhynchus mykiss*	respiratory toxicant	reported as 0.1–0.5 mg/L
	Danio rerio	hatching delay	240 mg/L for MWNT

Table 2. CNT Fate and Transport Parameters for LCA Scenarios

parameter	unit	worst case	realistic	ref
raction of CNTs released to environment		1.0	0.002	1,42
nolecular weight[a]	g mol^{-1}	1×10^5	1×10^5	53
ctanol–water partition coeff. K_{OW}		1×10^5	1×10^0	21,54
rganic carbon–water partition coeff. K_{OC}	L kg^{-1}	1×10^{-20}	1×10^7	55
Henry's law coeff. 25 °C, K_H	Pa kg mol^{-1}	1×10^{-20}	1×10^{-20}	46
olubility in deionized water (25 °C)	mg L^{-1}	2×10^4	1×10^1	56,57
lissolved carbon–water partition coeff., K_{DOC}	L kg^{-1}	1×10^{-20}	1×10^3	52
uspended solids–water partition coeff., Kp_{SS}	L kg^{-1}	1×10^{-20}	1×10^3	52
ediment–water partition coeff., Kp_{Sd}	L kg^{-1}	1×10^{-20}	1×10^3	52
oil–water partitioning coeff., Kp_{Sl}	L kg^{-1}	1×10^{-20}	1×10^3	52
ggregation and settling	%	0	90	42
legradation rate in air	s^{-1}	1×10^{-20}	1×10^{-20}	6
legradation rate in water	s^{-1}	1×10^{-20}	1×10^{-20}	6
legradation rate in sediment	s^{-1}	1×10^{-20}	1×10^{-20}	6
legradation rate in soil	s^{-1}	1×10^{-20}	1×10^{-20}	6
bioaccumulation factor in fish/biota, BAF_{fish}	L kg^{-1}	5×10^3	5×10^{-2}	46,58

[a]Based on a density of 1.3 g cm^{-3} and a length of 100 nm.



$$CF = EF * FF * XF$$

Characterization Factor

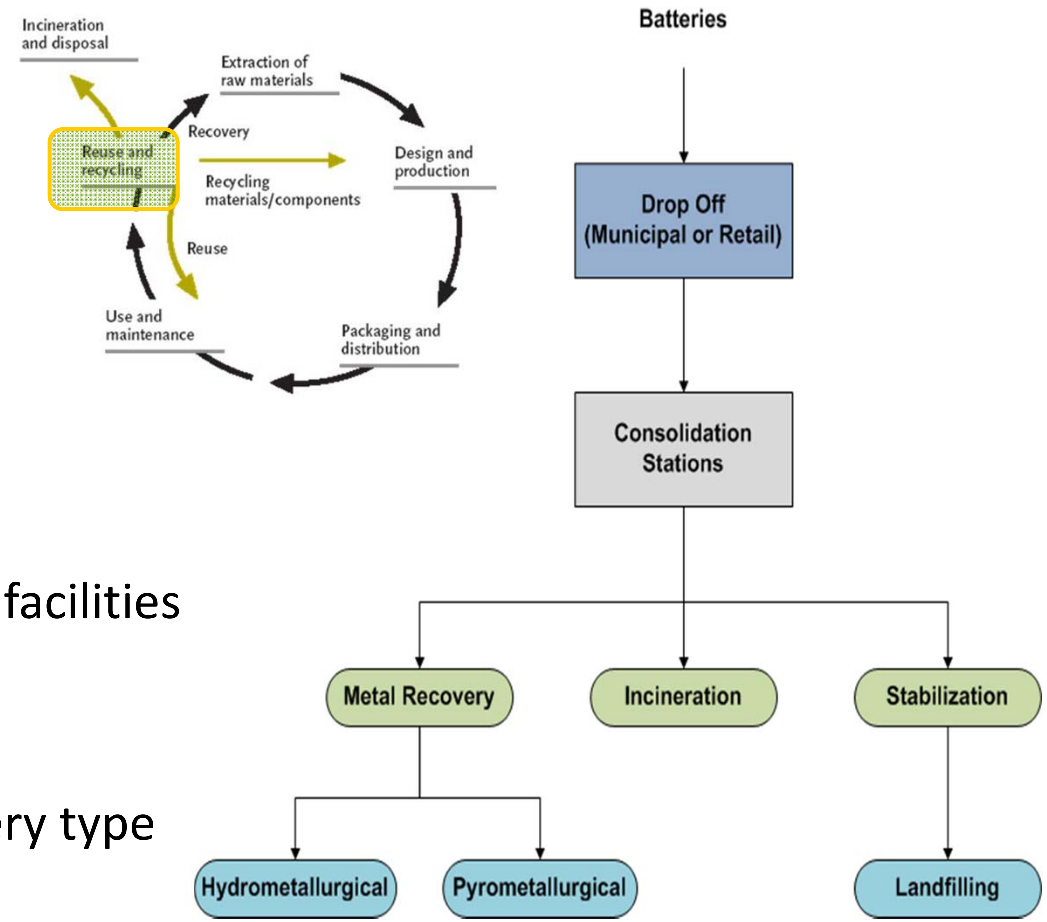
Effect, Fate, Exposure

Eckelman, Mauter, Isaacs, and Elimelech, New Perspectives on Nanomaterial Aquatic Ecotoxicity: Production Impacts Exceed Direct Exposure Impacts for CNTs, Enviro Sci Tech, 2012

End-of-Life Alternatives for Batteries

Alternatives for final disposition:

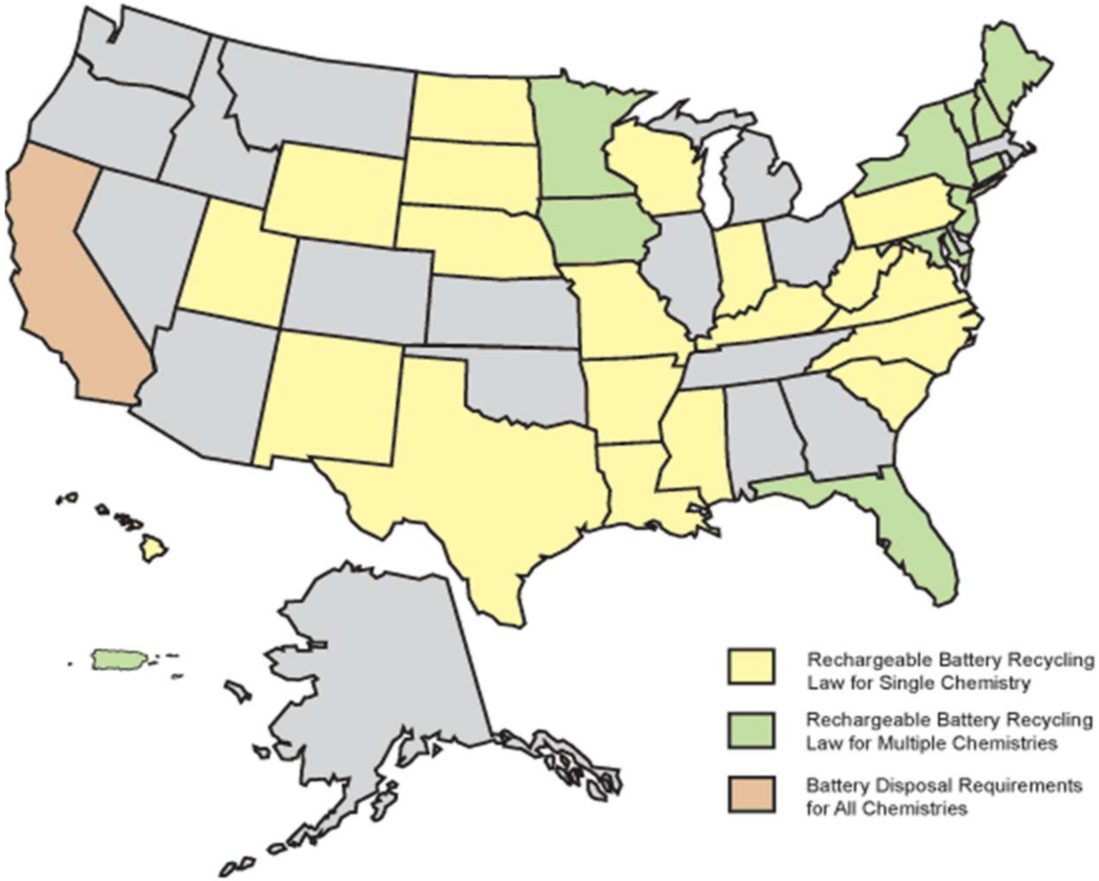
- Landfill
  - Most household batteries
  - 87% of all waste batteries
- Stabilization
  - Prior to landfill
  - Not used in general
- Incineration
  - Municipal waste combustion facilities
- Recycling
  - High temperature processes
  - Percentage depends on battery type



Espinoza and Isaacs, Northeastern University

Recycling Laws for Batteries

- Rechargeable Battery Recycling Corporation
- Single Chemistry (Lead-Acid)
- Multiple Chemistries (Lead-Acid and Ni-Cd)
- California includes primary batteries
- Recovery of (Ni, Co, Mn) for steel production (secondary feedstock)



Source: Recycling Laws Map http://www.call2recycle.org/recycling-law-map/

Product Stewardship Issues

"Product stewardship calls on those in the product life cycle—manufacturers, retailers, users, and disposers—to share responsibility for reducing the environmental impacts of products."

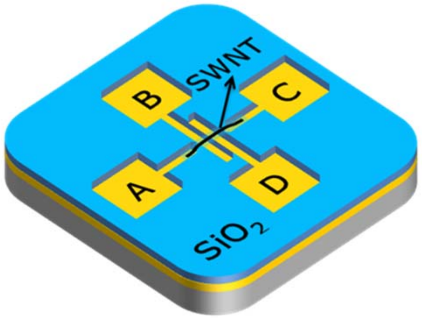
US Environmental Protection Agency

1. Can nano-enabled products be handled appropriately using the same stewardship collection infrastructure developed for other products, or must manufacturers provide some form of special handling for products containing nano?
2. Does mixing of recyclate from nano-enabled products impact markets for recycled materials?
3. Does the collection of nano-enabled products pose particular challenges to household waste facilities run by municipalities in terms of costs, worker health and safety, or public perception?

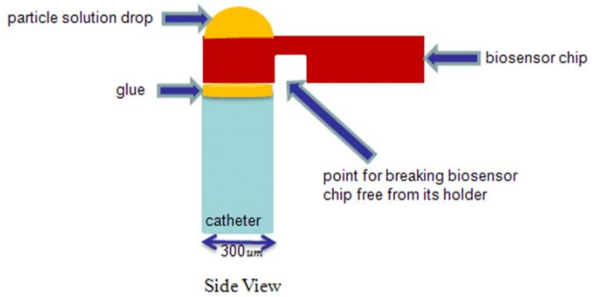
Nash, Harvard University
Bosso, Northeastern University

Applications Using CNTs

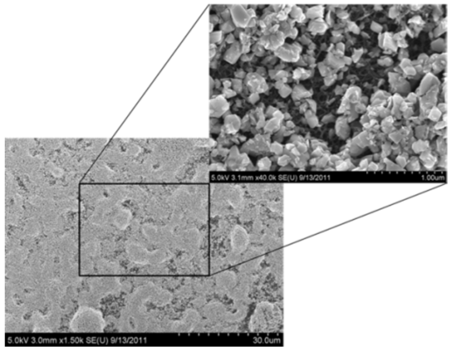
- SWNT Switch



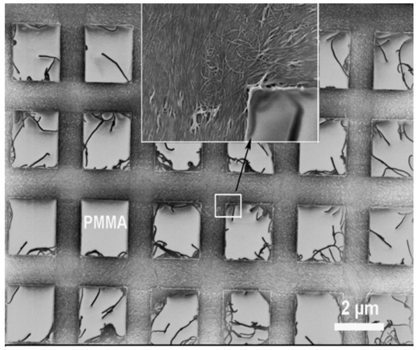
- Sensors



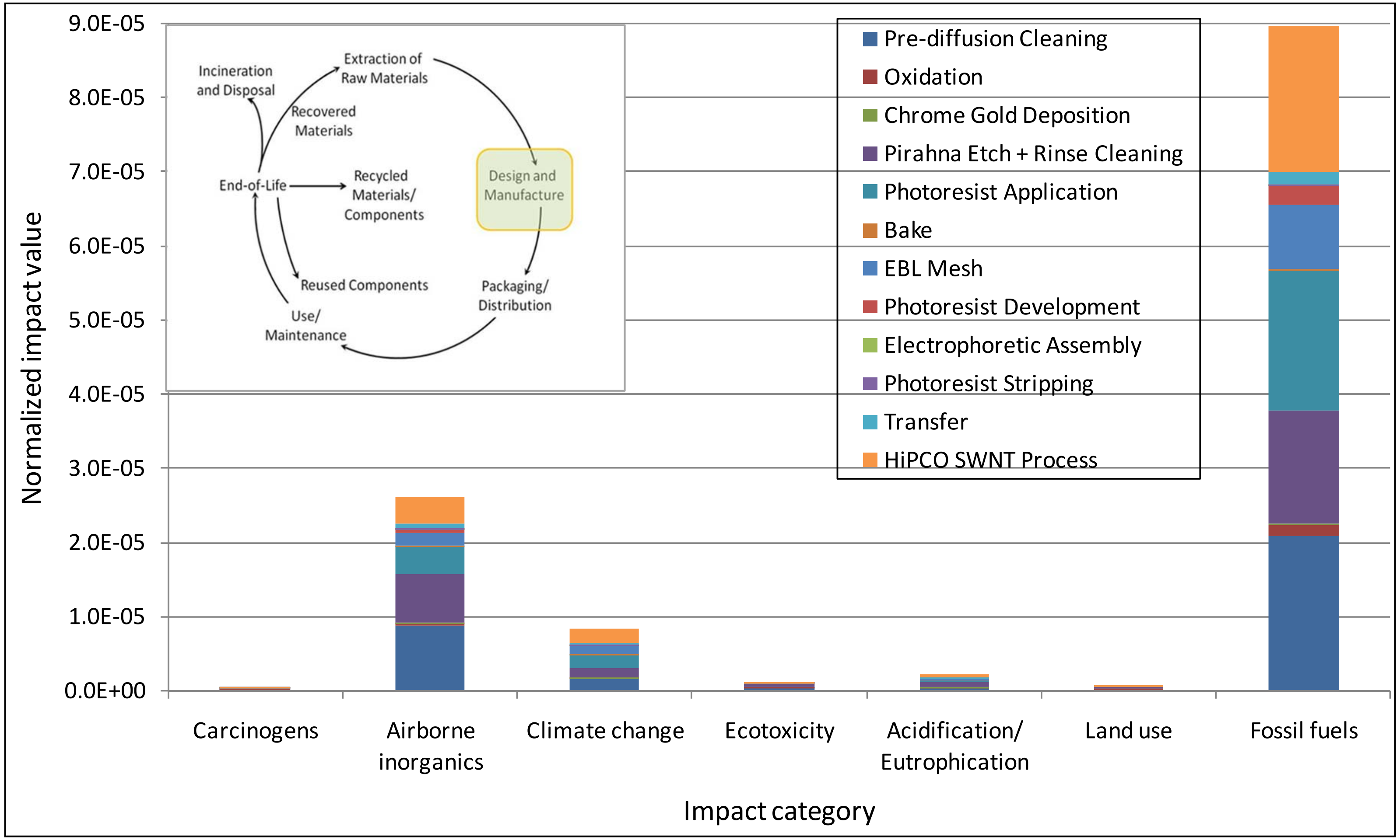
- Batteries



- EMI-Shielding/ Composites



Impacts for CNT-Composite Fabrication



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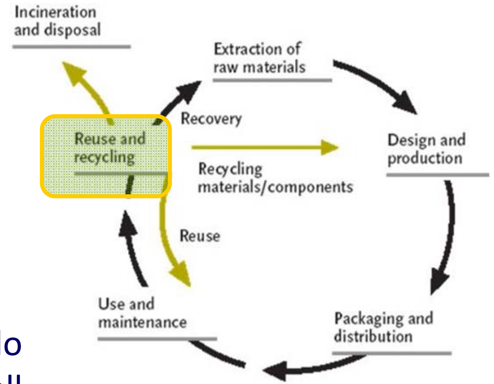
Dahlben and Isaacs, Northeastern University

Recycling at EOL for CNT-Polymers

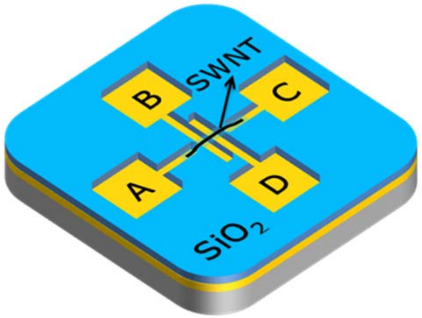
- Sustainability infers need for recycling strategies for both manufacturing scrap and post-consumer waste
- Determine effect of molding cycles on recyclate properties
  - thermal and/or mechanical degradation?
  - chemical and physical changes?
  - decrease in final properties?
- Determine maximum number of cycles to maintain the level of quality for secondary materials
- Assess potential for worker exposure during recycling processes, such as machining and grinding



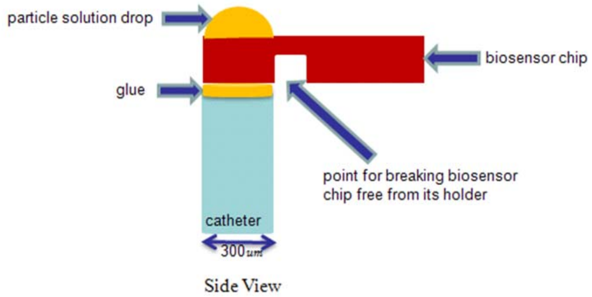
Zhang, Mead and Bello
University of Massachusetts Lowell

Applications Using CNTs

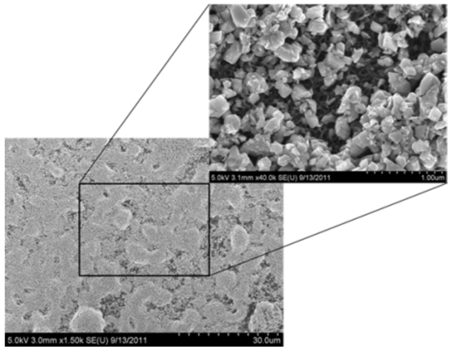
- SWNT Switch



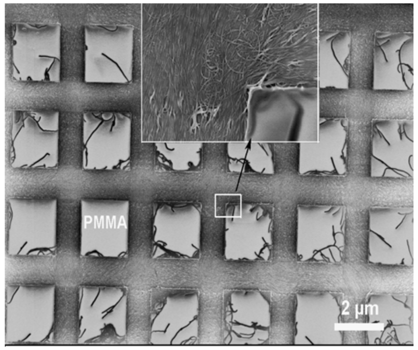
- Sensors



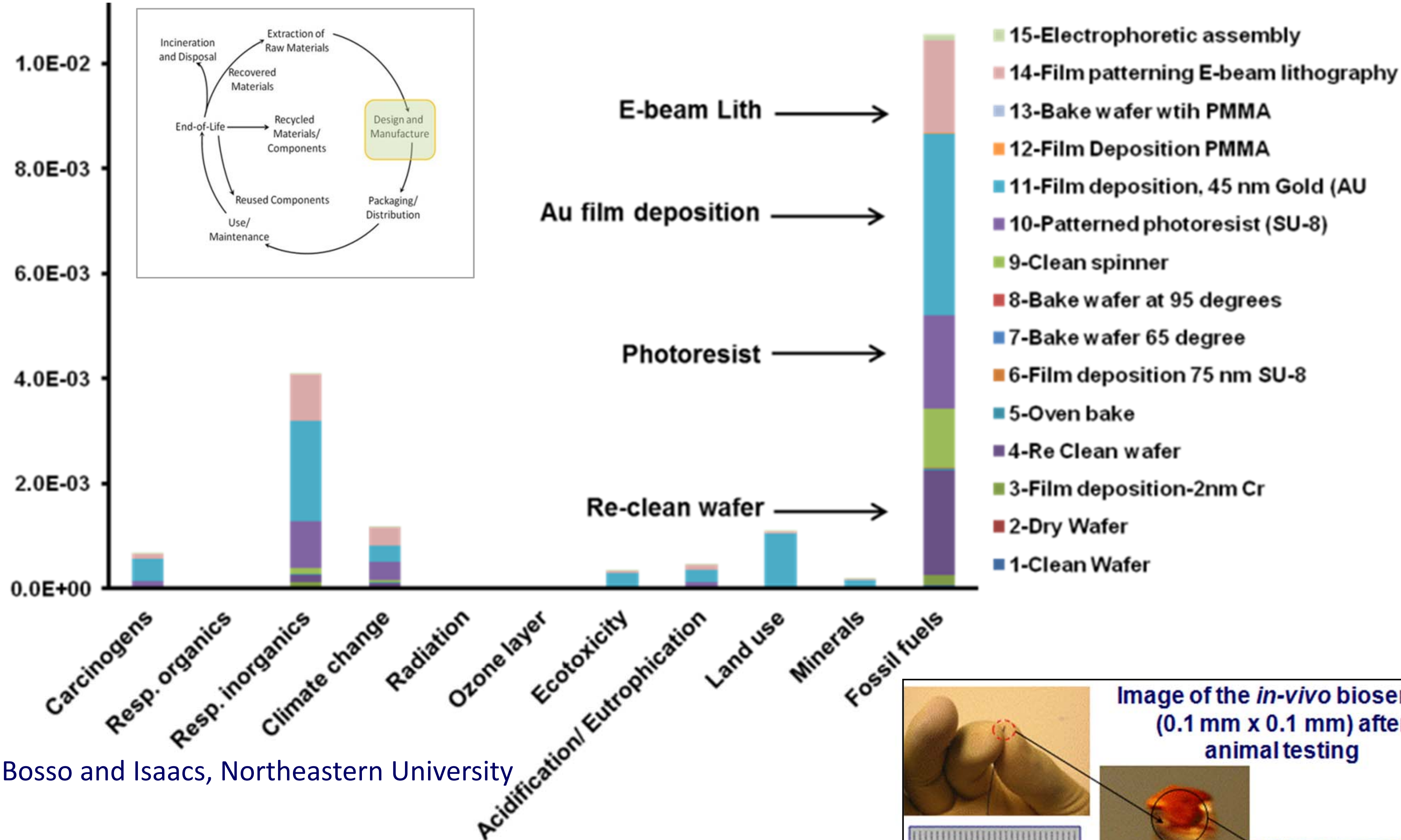
- Batteries



- EMI-Shielding/ Composites



Impacts from CNT-Sensor Fabrication



Porte, Bosso and Isaacs, Northeastern University

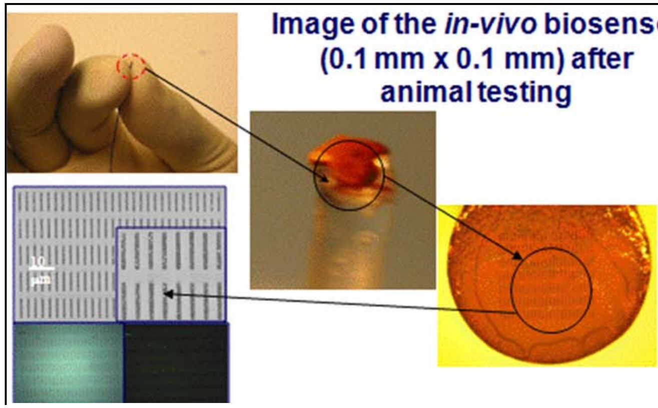


Image of the *in-vivo* biosensor (0.1 mm x 0.1 mm) after animal testing

Siavoshi, Yilmaz,
Somu and Busnaina,
Northeastern University

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Process Flow Diagrams

Chemical sensors

1. PMMA Deposition & Baking(Protecting Layer)
2. Dicing the Wafer into Chips
3. Cleaning(Removal of PMMA Protecting Layer)
4. Etching(Plasma Surface Treatment)
5. Lithography for Trenches
6. SWNTs Assembly Using the Dip-coater
7. Cleaning(Removal of PMMA Layer)
8. Lithography for Contact Leads
9. Metal Deposition(Au or Ti)
10. Lift- off(Removal of PMMA+ Part of Metal)
11. Functionalization

Biosensors

1. Clean Wafer
2. Dry Wafer
3. Film Deposition- 2nm Cr
4. Re-clean Wafer
5. Oven Bake
6. Film Deposition- 75 nm SU-8
7. Bake Wafer 65 degrees
8. Bake Wafer 95 degrees
9. Clean Spinner
10. Pattern Photoresist (SU-8)
11. Film Deposition, 45 nm Gold(AU)
12. Film Deposition- PMMA
13. Bake Wafer with PMMA
14. Film Patterning E-beam Lithography
15. Develop SU-8

Comparative Impact Assessment

Conventional Chemical Sensor (Metal Oxide)	VS	Next Generation Chemical Sensor (Carbon Nanotube, CNT)

Assessment Input

Processes unique to *metal oxide* semiconductor sensor fabrication	Same manufacturing foundation: Silicon microchip (IC) CMOS Process	Processes unique to *carbon nanotube* sensor fabrication (ex. manufacture and functionalization of CNTs)

Proposed Advantages:

- Lower Detection Limits
- Enhanced Selectivity
- Lower Operational Temperature
- Low operation energy consumption
- Small Size
- Longer Lifetime

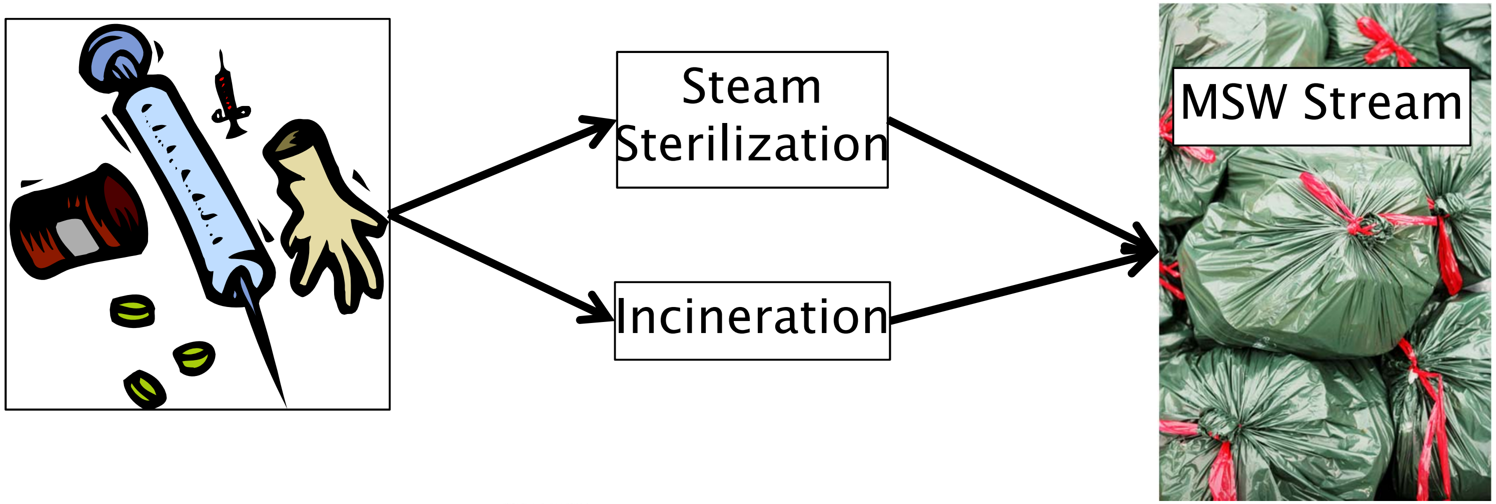
Assessment Output

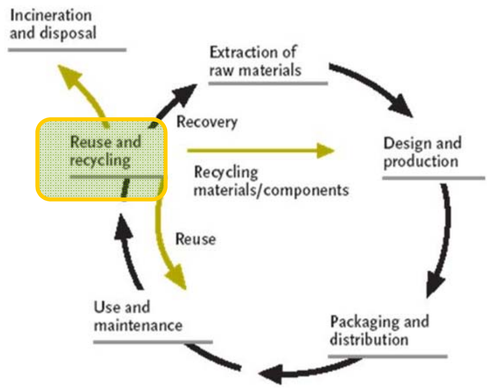
- Comparative environmental and human health impacts throughout the life cycle
- Will focus on human toxicity, ecotoxicity, global warming potential, fossil fuels

Pasquinni and Zimmerman, Yale University
Eckelman, Northeastern University

End-of-Life Issues for Nanosensors

- Do standard practices for medical waste hold for CNTs?

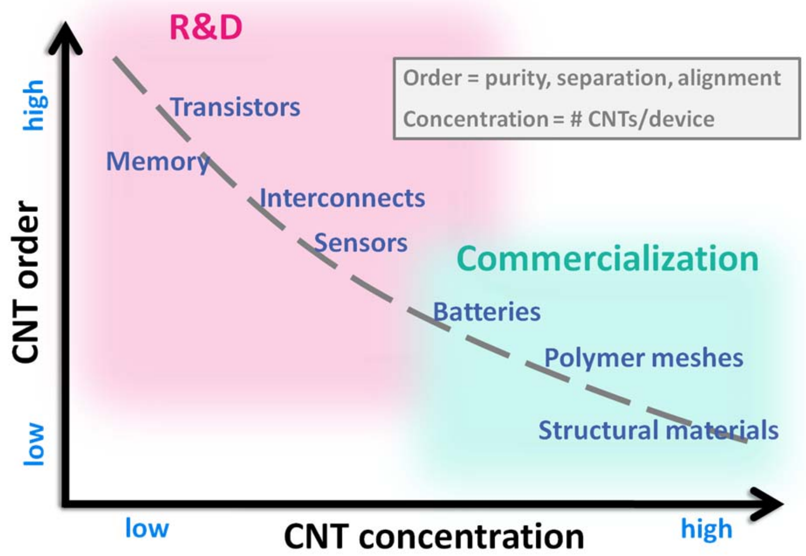




Walker and Bosso, Northeastern University

Inventory Collection Offers Value

- Process-based inventory collection applied to lab-scale fabrication of CNT applications
- Scale-up estimates allow approximation of possible CNT releases by series of nano-enabled products
  - Manufacturing
  - Use
  - End-of-Life decommission
- Opportunity to reduce environmental footprint of nano-fabrication
  - Greener design…
  - Early intervention…



Modified from J. Hart (2006), WTEC CNM Workshop Proceedings

Inventory collection and estimations through the lifecycle will provide data for influence diagrams and help prioritize subsequent research needs.

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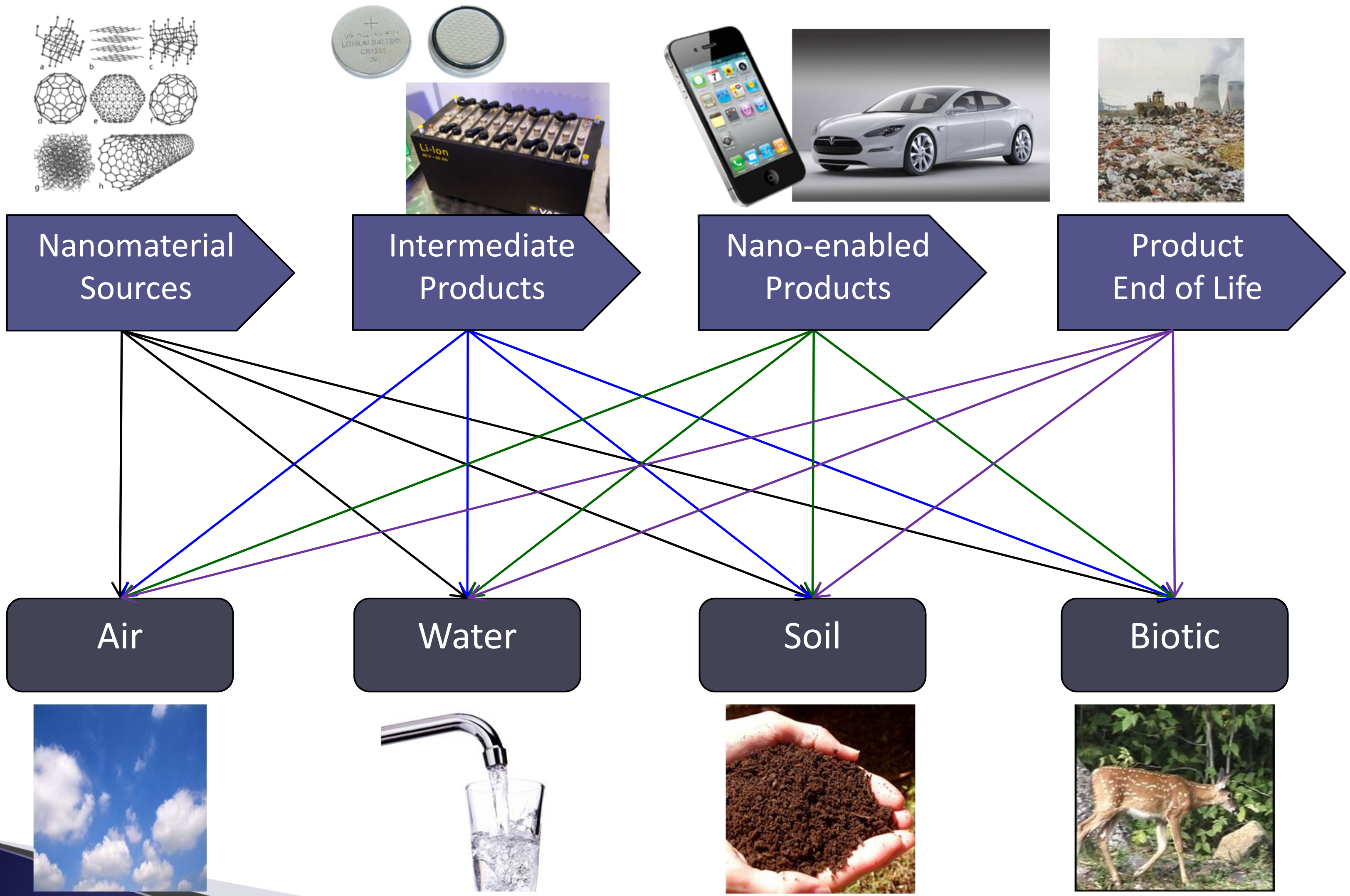
Nanomaterial Releases Through the Value Chain



Adapted from Wiesner, 2011 ICEIN Plenary Talk

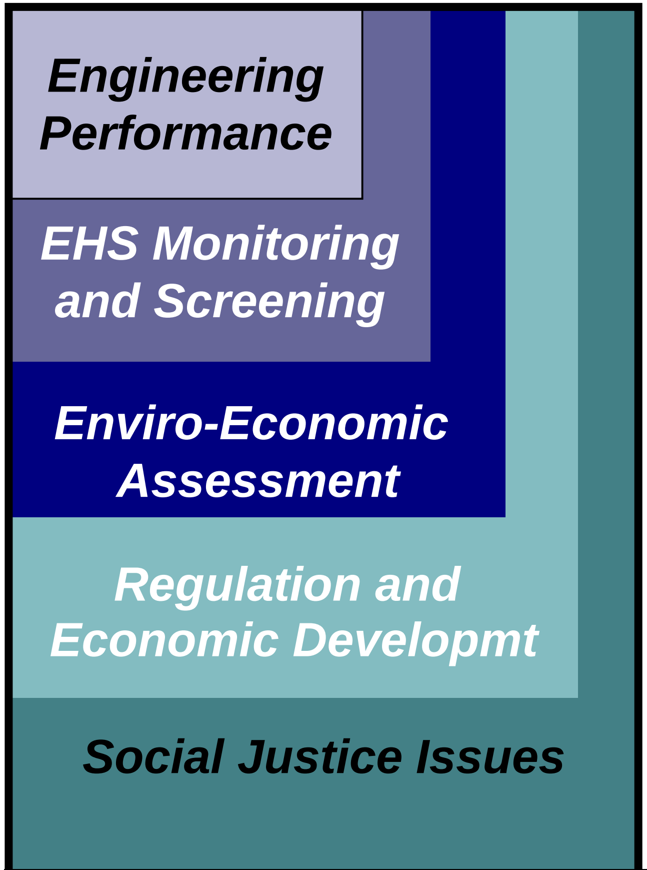
Finding the Balance Between Social & Technical

- Materials scarcity?
- Energy increase for raw mat'l production?
- Energy reduction during manufacture?
- Energy reduction during product use?
- Dissipation issues at End-of-Life?

System analysis needed to inform decisions --
But system can become quite broad and includes the social context into which the technology evolves…

Can the interdisciplinary community learn to bridge the gap?

Sustainable Process/Product Development



- Create technological feasibility
- Determine best safety practices and screening methods for nanomaterials
- Evaluate EHS /economic tradeoffs and impact of possible releases
- Promote informed policymaking
- Advocate productive public discourse

Integrated Systems Approach Required for Appropriate and Efficient Commercialization

Acknowledgements

Center for High-rate Nanomanufacturing

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University of New Hampshire

Museum of Science

UMASS LOWELL

YALE

HARVARD

National Science Foundation
WHERE DISCOVERIES BEGIN

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http://www.northeastern.edu/chn/