Life Cycle Issues for Scalable Nanomanufacturing of CNT-enabled Products

Jacqueline Isaacs
Associate Director, Center for High-rate Nanomanufacturing
Northeastern University, Boston MA

The 10th U.S.-Korea Forum on Nanotechnology
Boston, MA USA
October 15-16, 2013
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

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

Isaacs, Bosso, Busnaina, Cullinane, Eckelman, Sandler: Northeastern
Mead, Bello: U Mass Lowell
Zimmerman: Yale
Nash: Harvard
Methodology to evaluate the environmental effects and potential impacts of:

- Product
- Process
- Activity

From raw materials acquisition through production, use and disposal
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**

Busnaina and Somu, Northeastern University
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

- **Mixing**
- **Coating & Drying**
- **Calendaring**
- **Cutting**
- **Assembly**
- **Filling**
- **Sealing**
- **Forming & Testing**

**Materials:**
- CNT
- NMP
- Anode AM
- Cathode AM
- Carbon Black
- PVDF
- Al Sheet
- Cu Sheet
- Separator
- Electrolyte

**Environmental Conditions:**
- High Protection Environment Desired
- Clean Room Environment

**Center for High-rate Nanomanufacturing**
## CHN Toolbox
Connects Research to Applications

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

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

<table>
<thead>
<tr>
<th>ENERGY</th>
<th>kWh</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.073657</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>INPUT MATERIAL</th>
<th>g/chip</th>
</tr>
</thead>
<tbody>
<tr>
<td>ethanol (200 proof)</td>
<td>15.78</td>
</tr>
<tr>
<td>Lithium Manganese Oxide Powder</td>
<td>0.1</td>
</tr>
<tr>
<td>Gold Chip</td>
<td>0.5576</td>
</tr>
<tr>
<td>N2 Gas</td>
<td>10.324</td>
</tr>
<tr>
<td>ethylene glycol</td>
<td>0.446</td>
</tr>
<tr>
<td>deionized water</td>
<td>5163.95</td>
</tr>
<tr>
<td>disposable lab materials (plastic and paper</td>
<td>10.48</td>
</tr>
<tr>
<td>MWCNT</td>
<td>0.00112</td>
</tr>
<tr>
<td>INPUT TOTAL</td>
<td>5201.639</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>OUTPUT MATERIAL</th>
<th>g/chip</th>
</tr>
</thead>
<tbody>
<tr>
<td>mixed wastewater to treatment</td>
<td>5174.364</td>
</tr>
<tr>
<td>hazardous waste</td>
<td>16.276</td>
</tr>
<tr>
<td>emissions to air</td>
<td>10.324</td>
</tr>
<tr>
<td>MWCNT</td>
<td>0.00112</td>
</tr>
<tr>
<td>OUTPUT TOTAL</td>
<td>5200.964</td>
</tr>
</tbody>
</table>
Nanobattery Cathode Characterization Results

SimaPro Software: Nanobattery Cathode Labscale Fabrication

Analyzing 1 p ‘CNT Lithium-ion Battery’; Method: Eco-indicator 99 (H) V2.06 / Europe EI 99 H/H / Characterization
Nanobattery Cathode Normalized Results

Cathode normalized result indicate three greatest contributors:

- Respiratory inorganics
- Land use
- Fossil fuels

Hakimian and Isaacs, Northeastern University
Results do not indicate effect of CNTs due to limited toxicological information...

Same issues as in 2007, 2009...
Table 1. Past Studies of CNT Aquatic Toxicity for Selected Organisms

<table>
<thead>
<tr>
<th>type</th>
<th>genus species</th>
<th>test type</th>
<th>test details</th>
<th>reported as 5–100 mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>bacteria</td>
<td>E.coli, P. aeruginosa, S. aureus, B.subtilis</td>
<td>membrane integrity</td>
<td>reported as 5–100 mg/L</td>
<td></td>
</tr>
<tr>
<td>protozoa</td>
<td>Styloynchia mytilis</td>
<td>uptake and growth</td>
<td>inhibition</td>
<td></td>
</tr>
<tr>
<td>algae</td>
<td>Pseudokirchneriella subcapitata</td>
<td>growth inhibition</td>
<td>mortality</td>
<td></td>
</tr>
<tr>
<td>copepods</td>
<td>Anomia tasmaniens</td>
<td>fertilization/molting</td>
<td>mortality</td>
<td></td>
</tr>
<tr>
<td>daphnia</td>
<td>Daphnia magna</td>
<td>LC50</td>
<td>sublethal IC-25 value</td>
<td></td>
</tr>
<tr>
<td>hydra</td>
<td>Hydra attenuata</td>
<td>sublethal morphological</td>
<td>change</td>
<td></td>
</tr>
<tr>
<td>fish</td>
<td>Onchorhynchus mykiss</td>
<td>respiratory toxicant</td>
<td>reported as 0.1–0.5 mg/L</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Danio rerio</td>
<td>bioaccumulation</td>
<td>reported as 240 mg/L for MWNT</td>
<td></td>
</tr>
</tbody>
</table>

Table 2. CNT Fate and Transport Parameters for LCA Scenarios

<table>
<thead>
<tr>
<th>parameter</th>
<th>unit</th>
<th>worst case</th>
<th>realistic</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>fraction of CNTs released to</td>
<td>1.0</td>
<td>0.002</td>
<td>1.42</td>
<td></td>
</tr>
<tr>
<td>environment</td>
<td>g mol⁻¹</td>
<td>1 × 10⁻⁵</td>
<td>1 × 10⁻⁵</td>
<td>53</td>
</tr>
<tr>
<td>molecular weight</td>
<td>1 × 10⁻⁵</td>
<td>1 × 10⁻⁵</td>
<td>21.54</td>
<td></td>
</tr>
<tr>
<td>octanol–water partition coeff. K Ow</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>organic carbon–water partition coeff.</td>
<td>L kg⁻¹</td>
<td>1 × 10⁻²⁰</td>
<td>1 × 10⁻⁷</td>
<td>55</td>
</tr>
<tr>
<td>Henry’s law coeff. 25 °C, K H</td>
<td>Pa kg mol⁻¹</td>
<td>1 × 10⁻²⁰</td>
<td>1 × 10⁻²⁰</td>
<td>46</td>
</tr>
<tr>
<td>solubility in deionized water (25 °C)</td>
<td>mg L⁻¹</td>
<td>2 × 10⁻⁴</td>
<td>2 × 10⁻³</td>
<td>5657</td>
</tr>
<tr>
<td>dissolved carbon–water partition coeff.</td>
<td>L kg⁻¹</td>
<td>1 × 10⁻³</td>
<td>1 × 10⁻³</td>
<td>52</td>
</tr>
<tr>
<td>suspended solids–water partition coeff.</td>
<td>L kg⁻¹</td>
<td>1 × 10⁻¹</td>
<td>1 × 10⁻¹</td>
<td>52</td>
</tr>
<tr>
<td>sediment–water partition coeff. K sp</td>
<td>L kg⁻¹</td>
<td>1 × 10⁻¹</td>
<td>1 × 10⁻¹</td>
<td>52</td>
</tr>
<tr>
<td>oil–water partitioning coeff. K pg</td>
<td>L kg⁻¹</td>
<td>1 × 10⁻³</td>
<td>1 × 10⁻³</td>
<td>52</td>
</tr>
<tr>
<td>aggregation and settling</td>
<td>%</td>
<td>0</td>
<td>90</td>
<td>42</td>
</tr>
<tr>
<td>degradation rate in air</td>
<td>s⁻¹</td>
<td>1 × 10⁻²⁰</td>
<td>1 × 10⁻²⁰</td>
<td>6</td>
</tr>
<tr>
<td>degradation rate in water</td>
<td>s⁻¹</td>
<td>1 × 10⁻²⁰</td>
<td>1 × 10⁻²⁰</td>
<td>6</td>
</tr>
<tr>
<td>degradation rate in sediment</td>
<td>s⁻¹</td>
<td>1 × 10⁻²⁰</td>
<td>1 × 10⁻²⁰</td>
<td>6</td>
</tr>
<tr>
<td>degradation rate in soil</td>
<td>s⁻¹</td>
<td>1 × 10⁻²⁰</td>
<td>1 × 10⁻²⁰</td>
<td>6</td>
</tr>
<tr>
<td>bioaccumulation factor in fish/biota, BAF fish</td>
<td>L kg⁻¹</td>
<td>5 × 10³</td>
<td>5 × 10⁻²</td>
<td>46.58</td>
</tr>
</tbody>
</table>

Based on a density of 1.3 g cm⁻³ and a length of 100 nm.

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

Product Stewardship Issues

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?

“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

Nash, Harvard University
Bosso, Northeastern University
Applications Using CNTs

- SWNT Switch
- Sensors
- Batteries
- EMI-Shielding/Composites
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
- Batteries
- Sensors
- EMI-Shielding/ Composites
Impacts from CNT-Sensor Fabrication

Porte, Bosso and Isaacs, Northeastern University

Siavoshi, Yilmaz, Somu and Busnaina, Northeastern University

Image of the in-vivo biosensor (0.1 mm x 0.1 mm) after animal testing
Process Flow Diagrams

**Chemical sensors**

- PMMA Deposition & Baking (Protecting Layer)
- Dicing the Wafer into Chips
- Cleaning (Removal of PMMA Protecting Layer)
- Etching (Plasma Surface Treatment)
- Lithography for Trenches
- SWNTs Assembly Using the Dip-coater
- Cleaning (Removal of PMMA Layer)
- Lithography for Contact Leads
- Metal Deposition (Au or Ti)
- Lift-off (Removal of PMMA + Part of Metal)
- Functionalization

**Biosensors**

- Clean Wafer
- Dry Wafer
- Film Deposition - 2nm Cr
- Re-clean Wafer
- Oven Bake
- Film Deposition - 75 nm SU-8
- Bake Wafer 65 degrees
- Bake Wafer 95 degrees
- Clean Spinner
- Pattern Photoresist (SU-8)
- Film Deposition, 45 nm Gold (Au)
- Film Deposition - PMMA
- Bake Wafer with PMMA
- Film Patterning E-beam Lithography
- Develop SU-8
Comparative Impact Assessment

Assessment Input

- Conventional Chemical Sensor (Metal Oxide)
  - Processes unique to metal oxide semiconductor sensor fabrication
- Next Generation Chemical Sensor (Carbon Nanotube, CNT)
  - Same manufacturing foundation: Silicon microchip (IC) CMOS Process
  - Processes unique to carbon nanotube sensor fabrication (ex. manufacture and functionalization of CNTs)

Assessment Output

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

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

Pasquinni and Zimmerman, Yale University
Eckelman, Northeastern University
End-of-Life Issues for Nanosensors

- Do standard practices for medical waste hold for CNTs?
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...

Inventory collection and estimations through the lifecycle will provide data for influence diagrams and help prioritize subsequent research needs.
Nanomaterial Releases Through the Value Chain

Adapted from Wiesner, 2011 ICEIN Plenary Talk
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?
Social Justice Issues

Regulation and Economic Development

Enviro-Economic Assessment

EHS Monitoring and Screening

Engineering Performance

Integrated Systems Approach Required for Appropriate and Efficient Commercialization

- 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