The Center for Sustainable Nanotechnology

Transformations and Environmental Impact of Next-generation Energy Storage Materials

Robert Hamers
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http:/susnano.wisc.edu

Mission

The goal of the Center for Sustainable Nanotechnology is to develop and utilize a **molecular-level understanding** of **nanomaterial-biological interactions to enable development of sustainable, societally beneficial nanotechnologies**

Nanomaterials for clean water

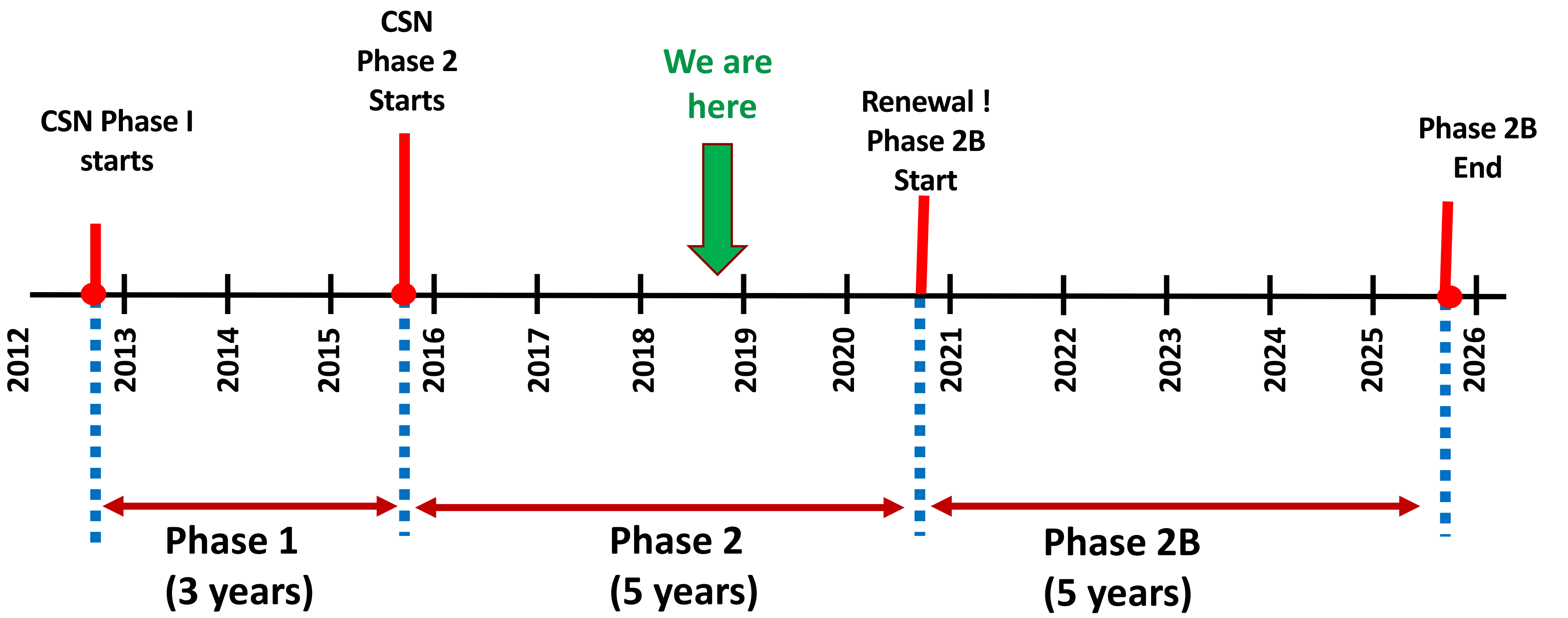
Nanomaterials for clean air

Nanomaterials for clean energy

Nanomaterials for sustainable agriculture

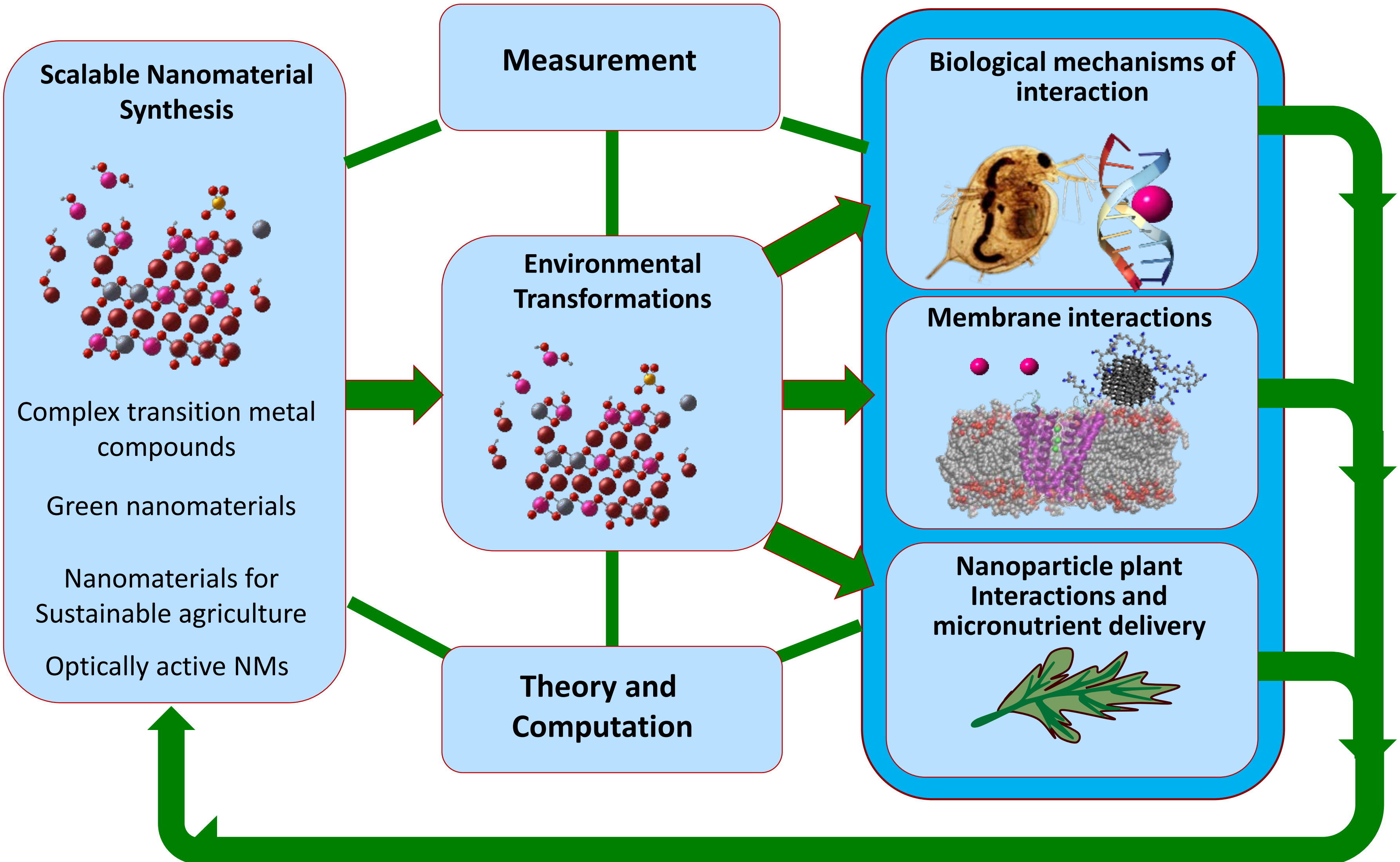
Air: www.air-duct-cleaning-denver.com/wp-content/uploads/2012/06/clean_air_blow.jpg
Water: lifesaverjerrycan.ca/

Timeline of the CSN



We are interested in forging partnerships with the European nano community

CSN Functional Areas



CSN Senior Investigators

Nanoparticle and Ligand Chemistry

Inorganic NPs

Robert Hamers

Metallic NPs

Catherine Murphy

NP-polymer composites

Howard Fairbrother

Quantum dots

Ze'ev Rosenzweig

Biological Chemistry

Bacterial models

Christy Haynes

Eukaryotic models

Rebecca Klaper

Cell chemistry

Galya Orr

Nano-agriculture

Jason White

Nano-plant interactions

Juan Pablo Giraldo

Physical & Analytical Chemistry

Analytical methodology

Vivian Feng

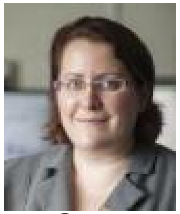
-Omics analysis

Erin Carlson

Environmental chemistry

Joel Pedersen

Computational Chemistry

Atomistic DFT

Sara Mason

Dynamics QM/MM

Qiang Cui

Multi-scale dynamics

Rigoberto Hernandez

Staff

Education & Outreach

Miriam Krause

Managing Director

Mike Schwartz

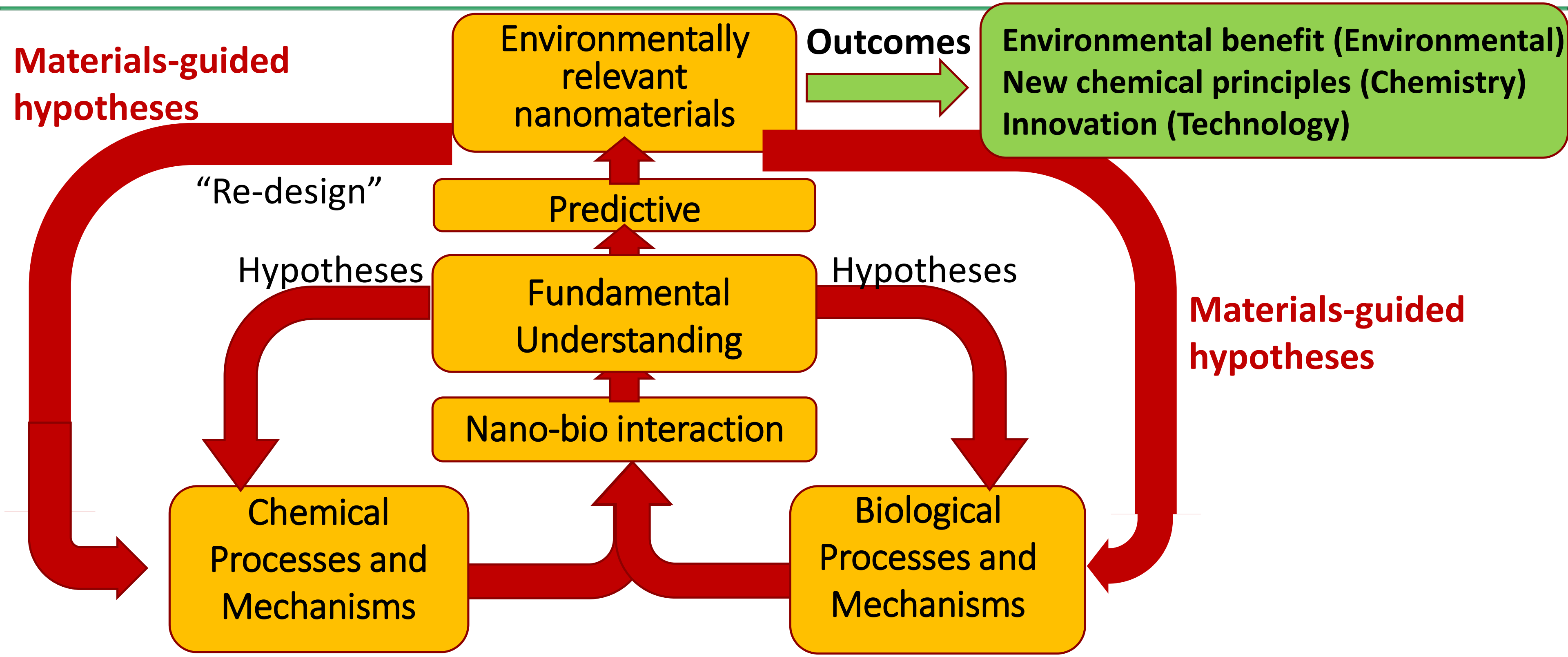
Assessment

Assessment Best practices

Lizanne DeStefano

Non-funded international collaborators: Thomas Frauenheim (Germany), Karen Lienkamp (Germany), Francesco Stellacci and Sylvie Roke (Switzerland), Thereza Soares (Brazil)

Molecular approach to safer nanomaterials



Processes:
Redox-mediated dissolution
"Controlled Release"
Acquisition of coatings (coronas)
NP core transformations

Properties:
Composition
Size
Shape
Surface properties
Mechanical properties

Processes

Uptake
Metal toxicity
Mechanical disruption
Resistance

Properties
Single- vs. multicellular
Gram + vs. Gram –
Cell membrane chemistry
Natural ecosystem
Genomic information

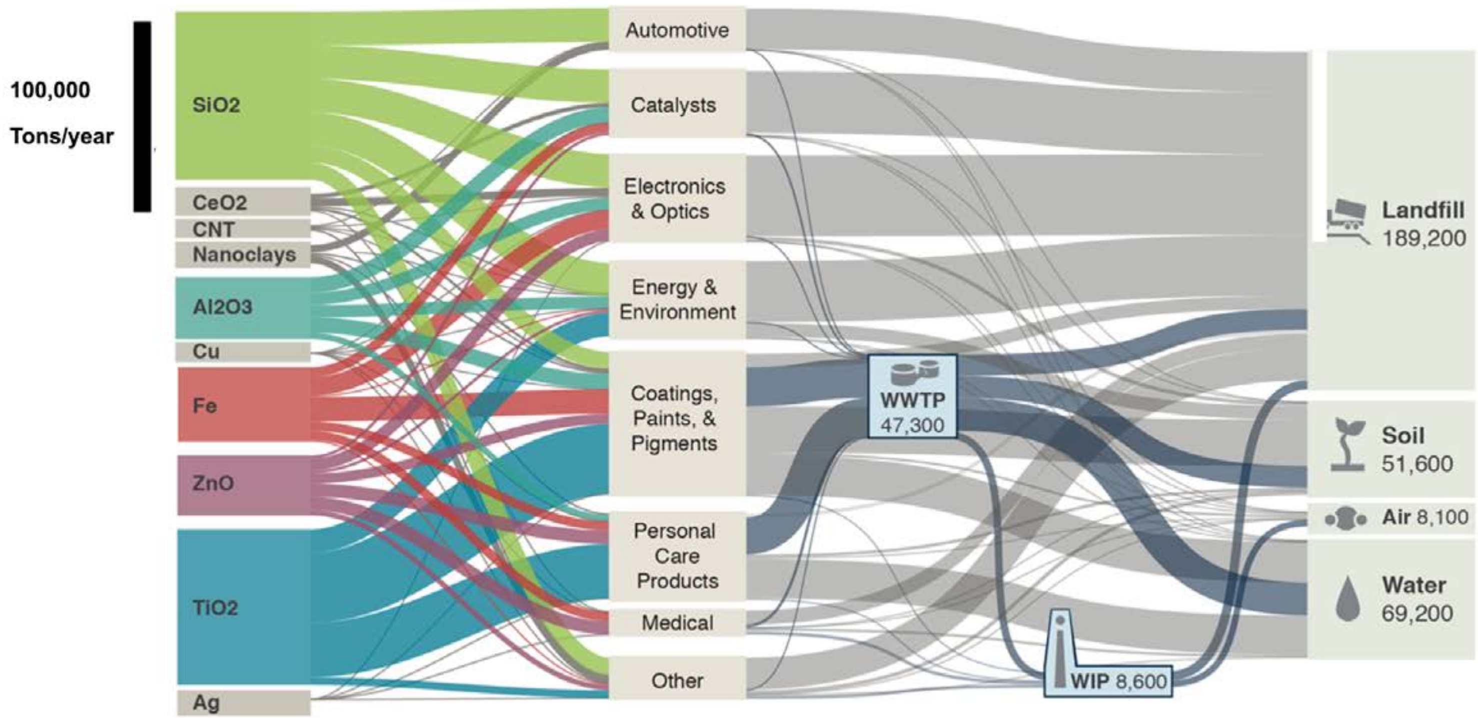
Choosing classes of nanoparticles for CSN Study

1) Potential for environmental impact, adverse of beneficial
   - Volume of manufacture/use
   - Potential for release into the environment
   - Potential for biological impact if released

2) Potential for new, fundamental chemical understanding, especially chemistry extending beyond the CSN

3) Potential to impact technology and/or society (Innovation)

Nanomaterial production and disposal, 2010



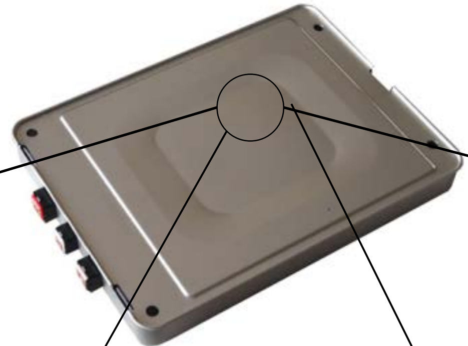
- Simple, single-component systems
- Chemical stable (except Ag, ZnO, Cu)
- Many are naturally present in the environment (already adapted)

But what technologically relevant materials are on the horizon ?

The Center for Sustainable Nanotechnology

Arturo Keller, et al., Environ. Sci. Technol. Lett. 2014, 1, 65−70

Energy Storage Materials: Emerging Nanomaterials



Grid-level storage

Consumer electronics

Transportation

Energy storage is increasingly an important part of our societal landscape and our energy future

Image: Forbes.com
Electric Vehicles Initiative. "Global EV Outlook. Understanding the Electric Vehicle Landscape to 2020."

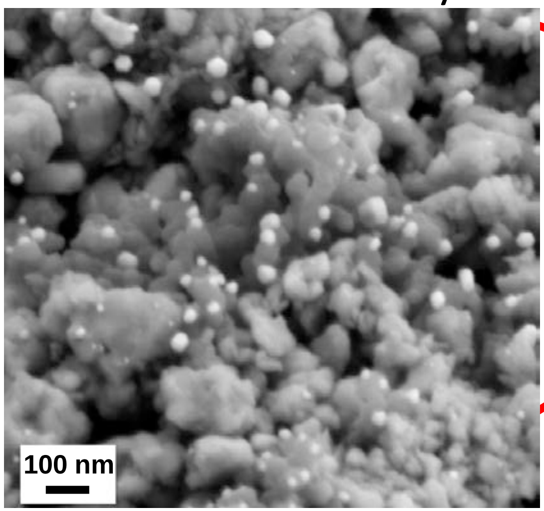
Nanomaterials in Energy Storage

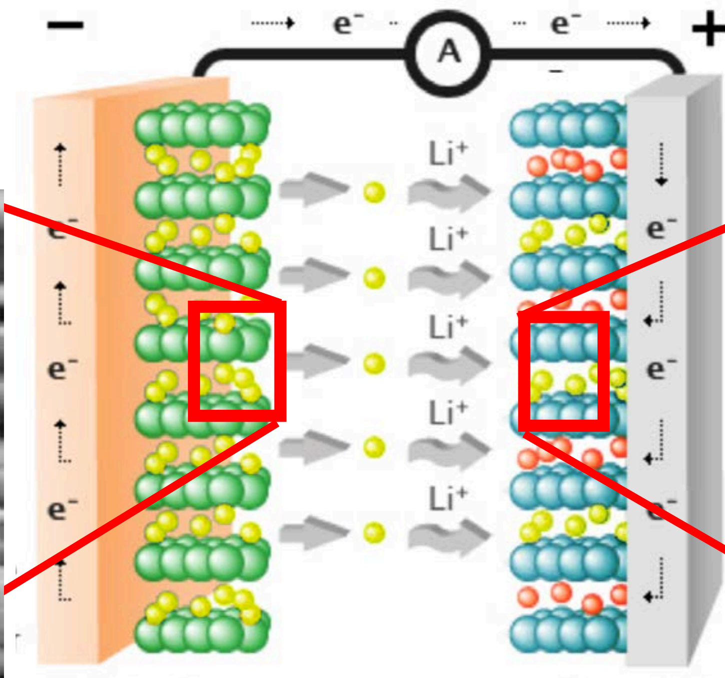
Anode
Negative electrode
C (graphite)
→ Nano-silicon alloys

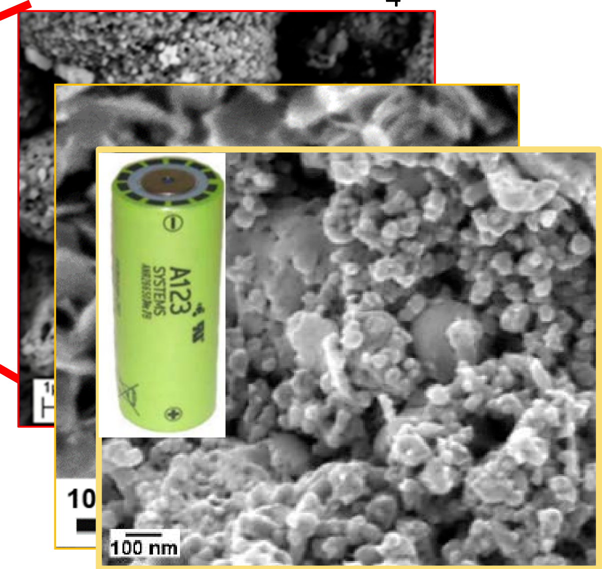
$C + Li^+ + e^- \rightarrow LiC_6$

$LiCoO_2 \rightarrow Li^+ + e^- + CoO_2$

Cathode
Positive electrode
$LiCoO_2$
→ $LiNi_xMn_yCo_{1-x-y}O_2$
→ $LiFePO_4$





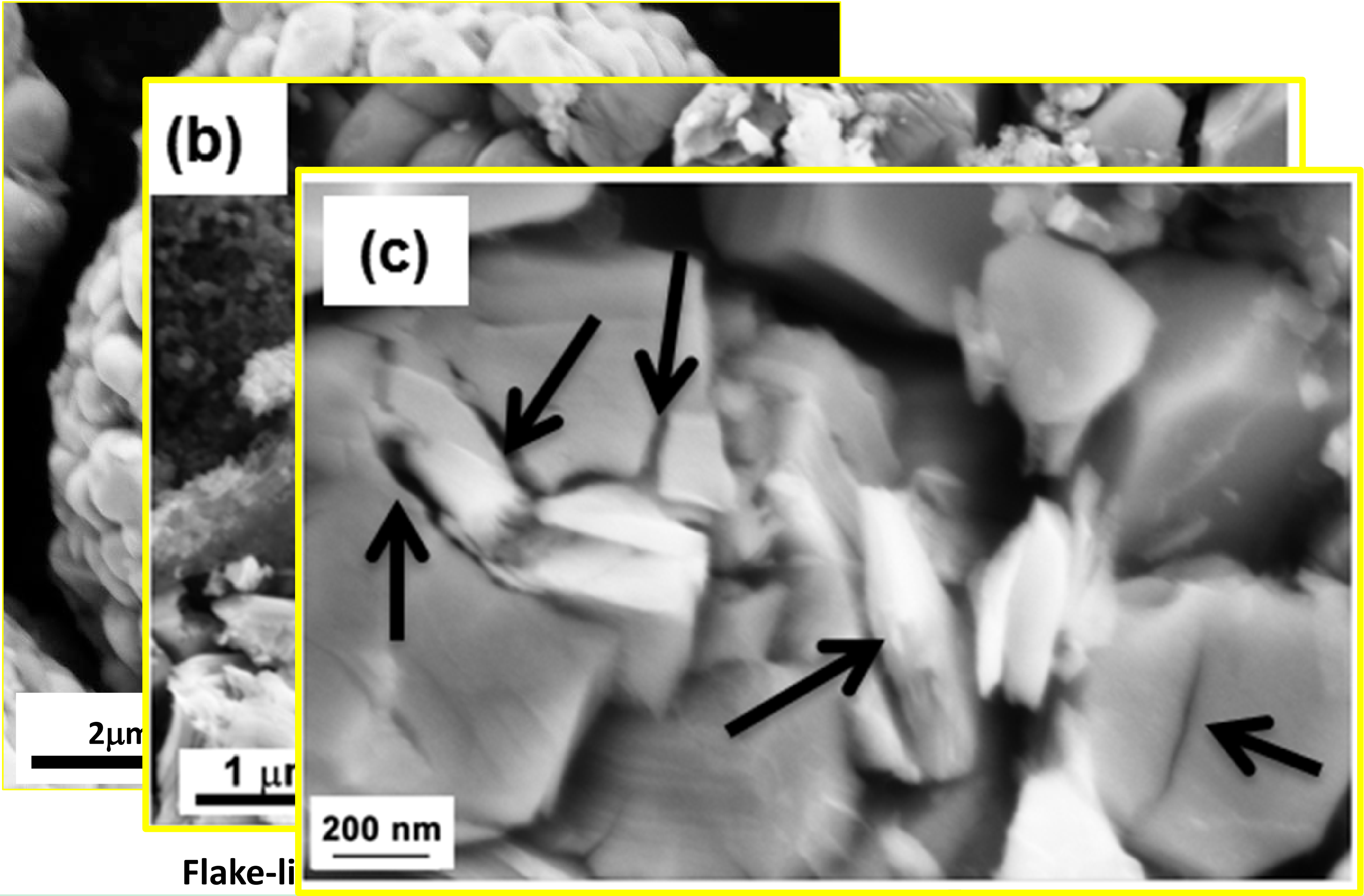


- Compositional changes driven by **cost, sustainability**
- Electrode nanostructuring driven by:

  Improving mechanical integrity (volumetric expansion)

  Improving rate performance (electrical conductivity, Li^+ transport)

In situ formation of nanoparticles from current-generation commercial materials



Flake-li

Complex Transition Metal Oxides: Ubiquitous Nanomaterials

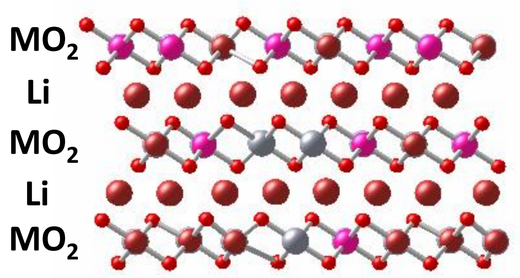
Consumer electronics

$LiCoO_2$

Transportation

~84 pounds/car

$LiNi_xMn_yCo_{1-x-y}O_2$



$LiNi_xMn_yCo_{1-x-y}O_2$

2^+, 4+ 4^+ 3^+

Ni^{4+} Co^{3+} unstable in water

Proton-induced metal release

$LiCoO_2 + 2H^+ \rightarrow Li^+ + 2OH^- + Co^{3+}$

Redox chemistry: Water oxidation

$Co^{3+} + H_2O \rightarrow Co^{2+} + \cdot OH + H^+$

$4\ Co^{3+} + 2H_2O \rightarrow 4\ Co^{2+} + O_2 + 4H^+$

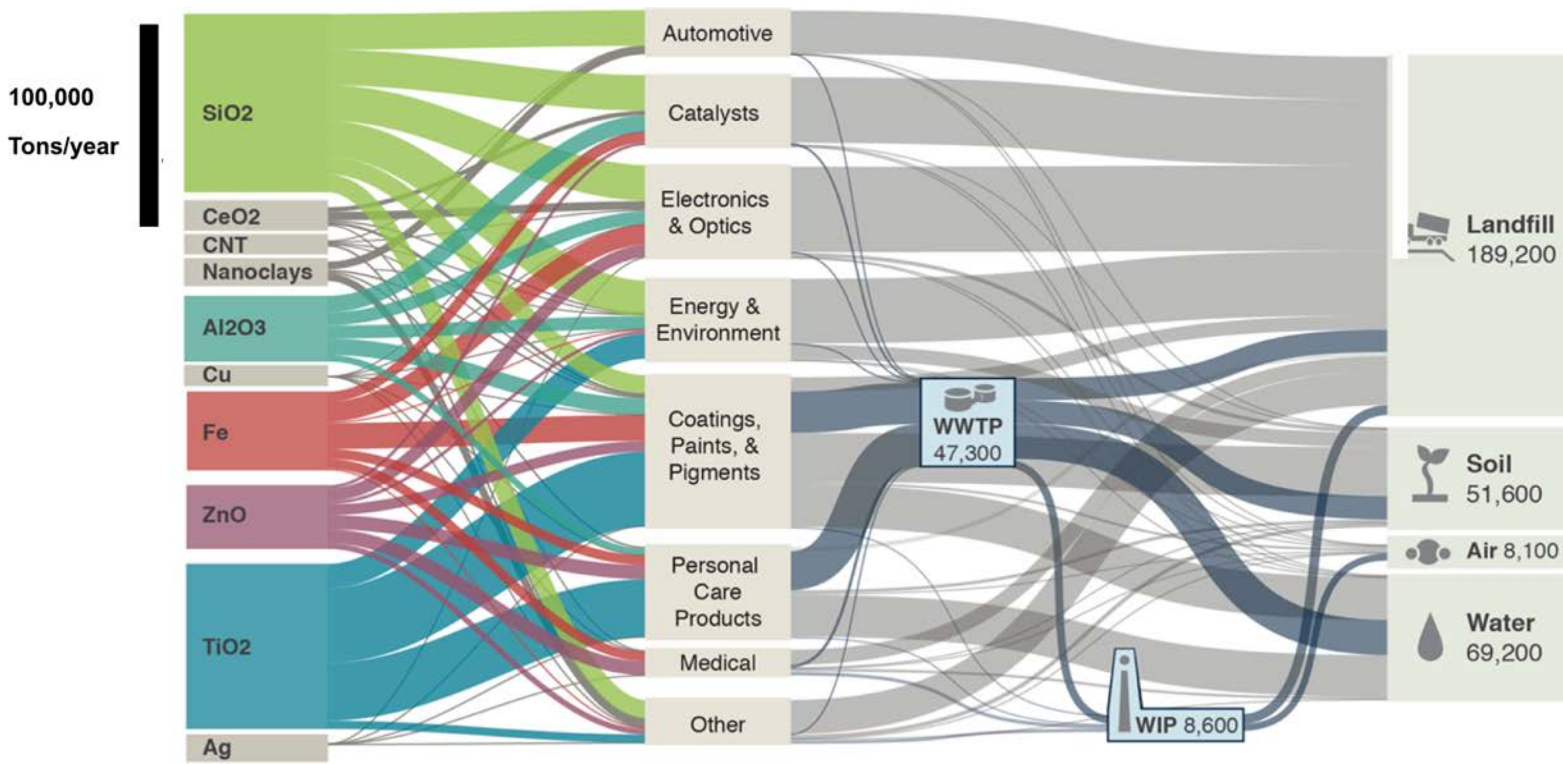
- **Multiple oxidation states drives new chemistry:**
- **Large-scale production volumes drives environmental risk**

$LiCoO_2$ and $LiNi_xMn_yCo_{1-x-y}O_2$ are emergent, reactive nanomaterials produced in amounts of potential environmental significance

- Production of 75,000 tons 2015; >500,000 tons/year est. ~ 2020
- <5% of Li-ion batteries are recycled (2017): No national infrastructure for recycling
- High-valence metals have unique catalytic properties and high reactivity Co^{3+}, Ni^{4+}
- Known inherent toxicity associated with Ni, Co, Mn

Nitta, eta l., Materials Today **2015**, *18*, 252
NMC production: Olivetti, *et al*., Joule **2017**, *1*, 229
Nano-CeO_2: Cassee, et all, Crit. Rev. Toxicol. **2011**, *31* , 213
$LIMO_2$ catalysts: Yi Cui, et al. Nature Comm. 5:4345
https://www.chemistryworld.com/news/battery-builders-get-the-cobalt-blues/3008738.article

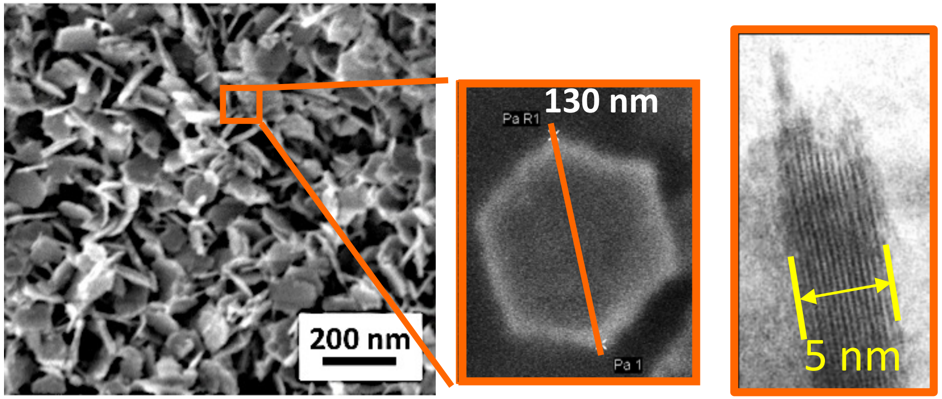
How do these materials stack up ?

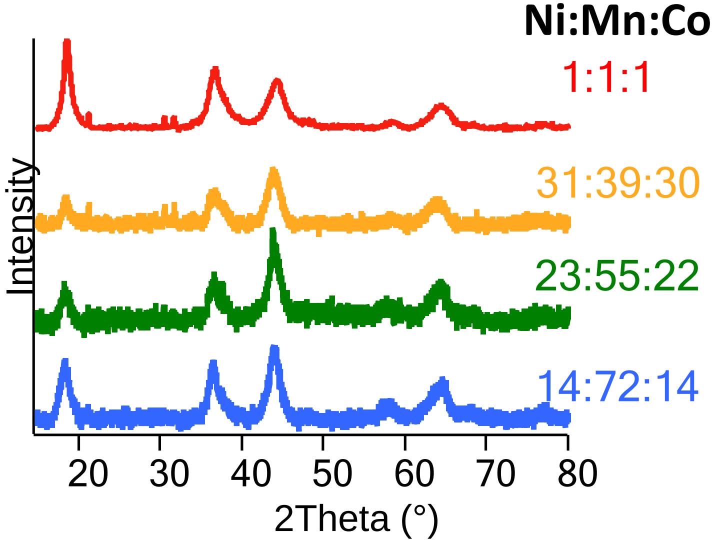


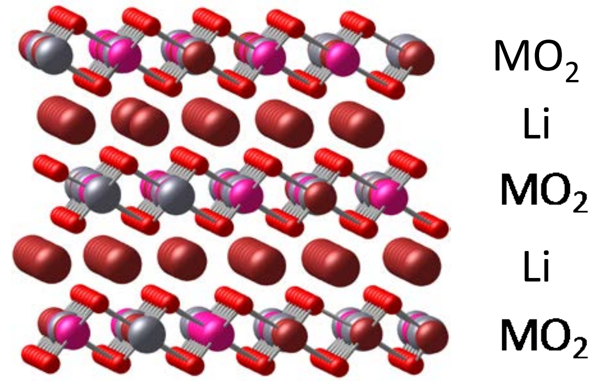
Manufactured quantities of complex metal oxides may drarf the amounts of other oxide materials in the next few years.

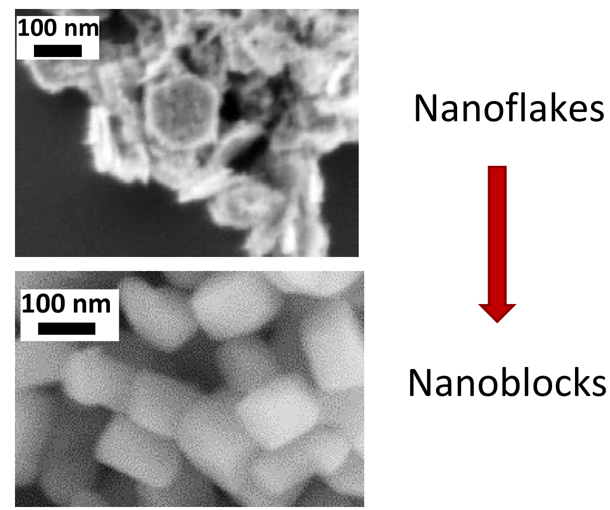
Arturo Keller and Anastasiya Lazareva, Env. Sci. Tech. Lett. 2013, 1, 65-70

Synthesis of 2D complex oxides $LiNi_yMn_zCo_{(1-y-z)}O_2$ (NMC)





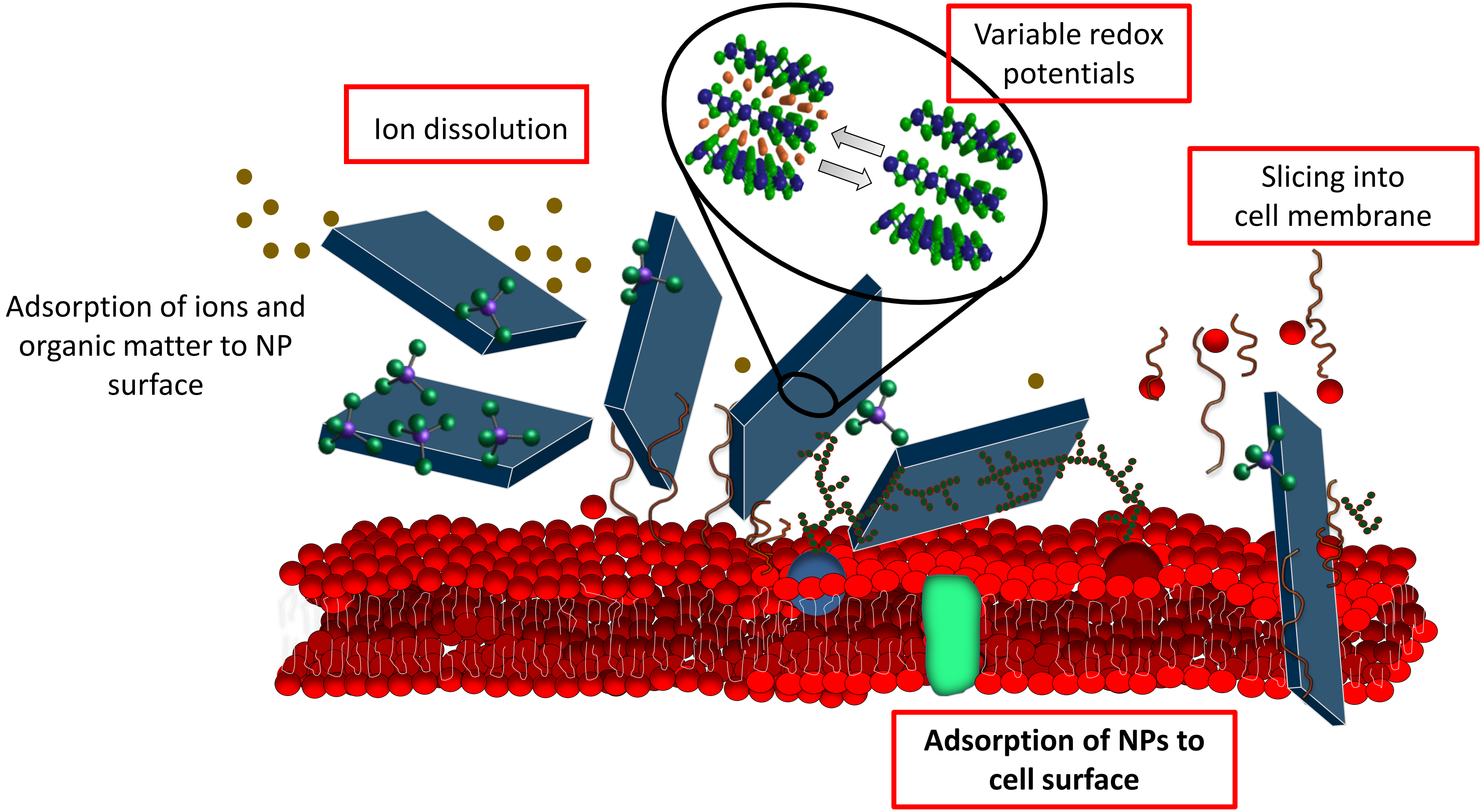




Chemical synthesis allows tuning composition and shape of nanomaterials to test underlying structure-property relationships

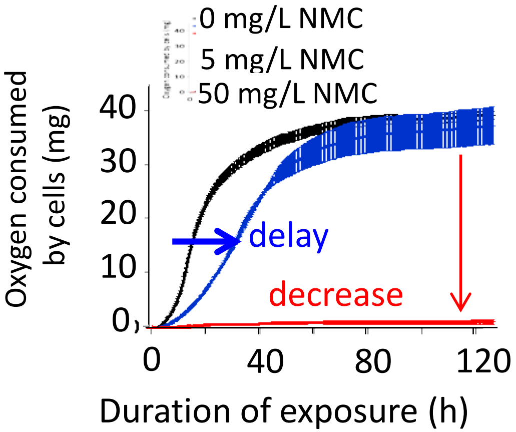
Hang, Gunsolus, …, **Pedersen, Haynes, Hamers**, *Chem. Mater.* **2016**, *28,* 1092-1100.

Possible mechanisms of interaction?



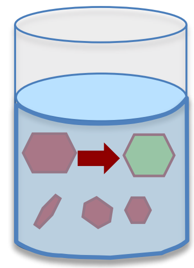
NMC biological impact dominated by indirect processes

Respirometry with *S. oneidensis*



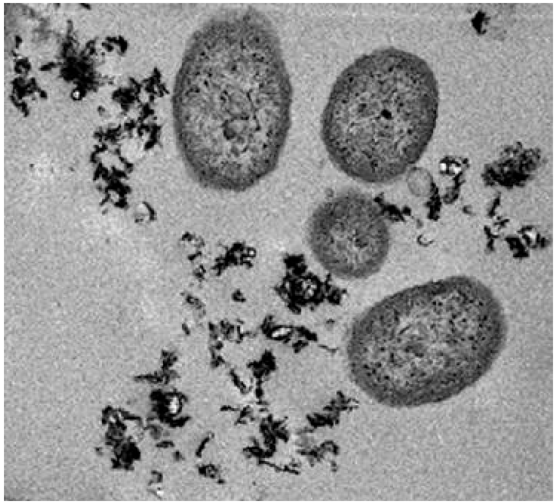
Li $Ni_{0.33}Mn_{0.33}Co_{0.33}O_2$

Biological impact



Nanoparticle transformation

But no Direct association

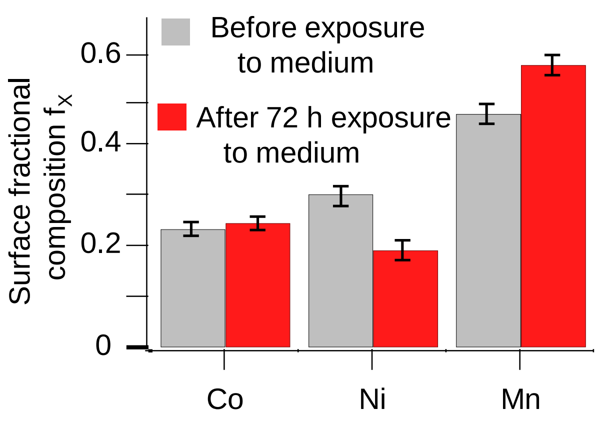


- *Reactive* nanomaterials can induce biological impact without direct *physical* association with cell membranes
- *Chemical* interactions alone can generate response

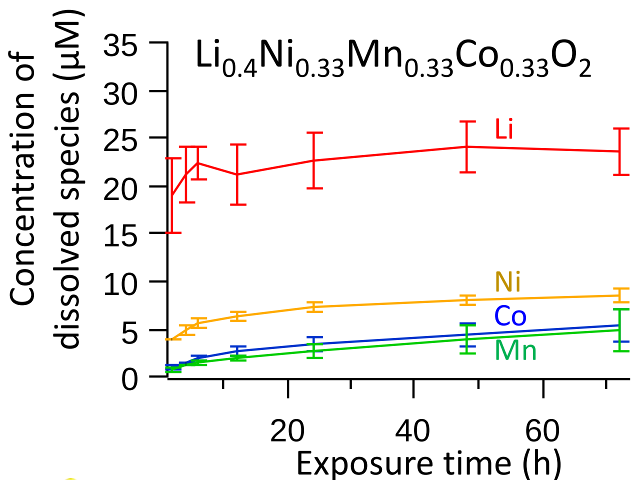
Hang, Gunsolus, Wayland, Melby, Mensch, Hurley, **Pedersen, Haynes, Hamers**, *Chem. Mater.* **2016**, *28,* 1092-1100.

NMC Nanomaterials Transform in Aqueous Media

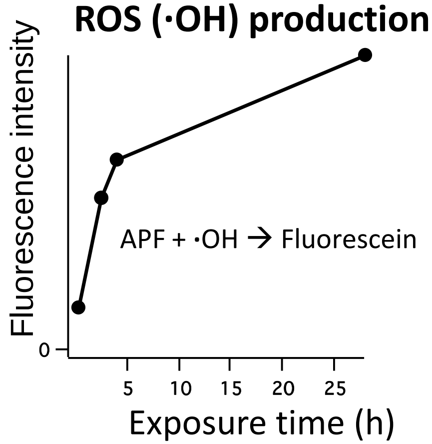
XPS: Nanoparticle composition

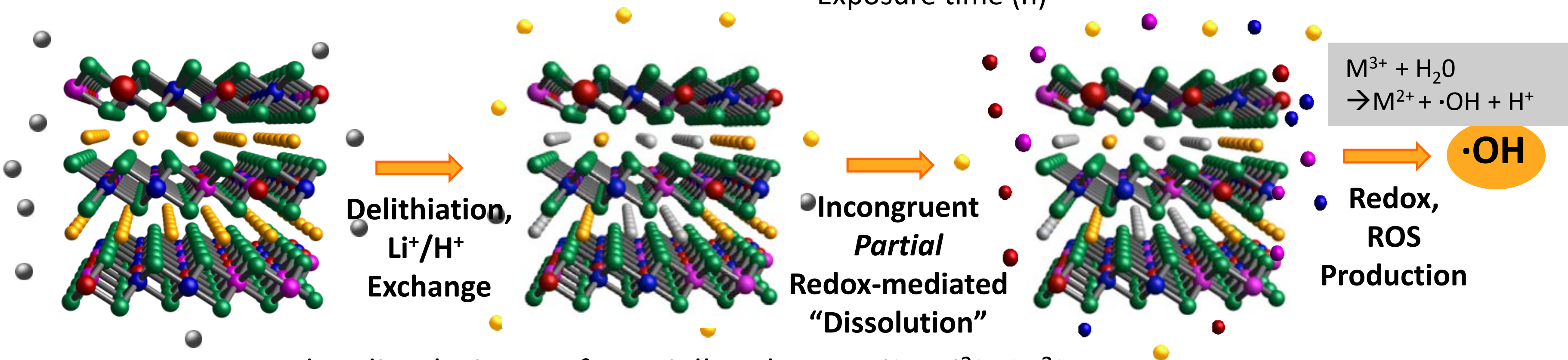


ICP-OES: Ions released



Fluorescence: ROS (·OH) production



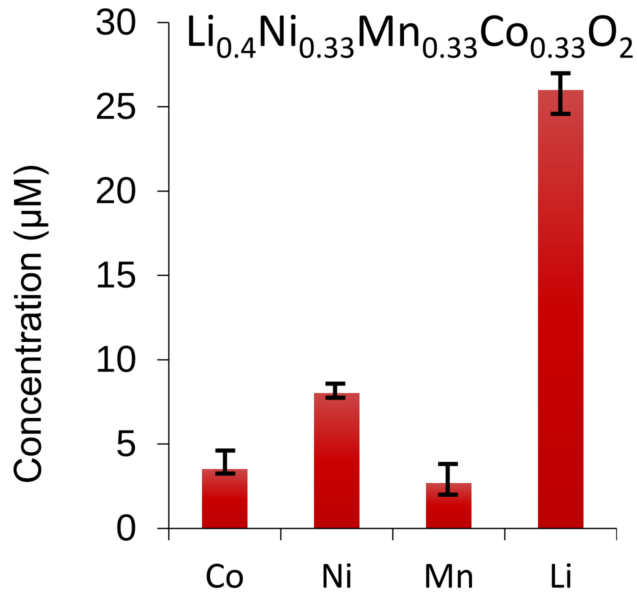


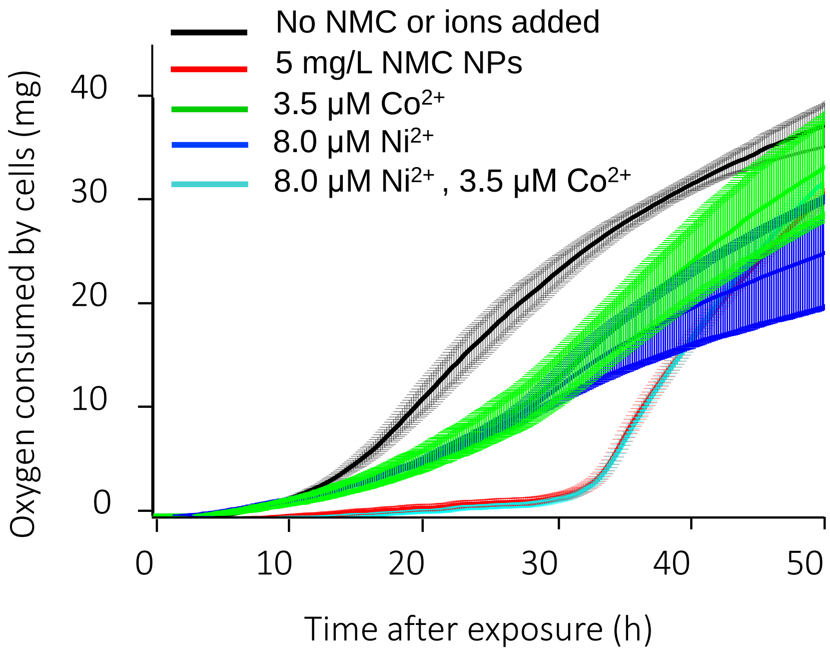
- Incongruent redox dissolution preferentially releases Li^+ , Ni^{2+}, Co^{2+}
- Transformed nanoparticles are Mn-rich, depleted in Li, Ni, and Co, but *stable*.
- NMC continually produces hydroxyl radicals (ROS)

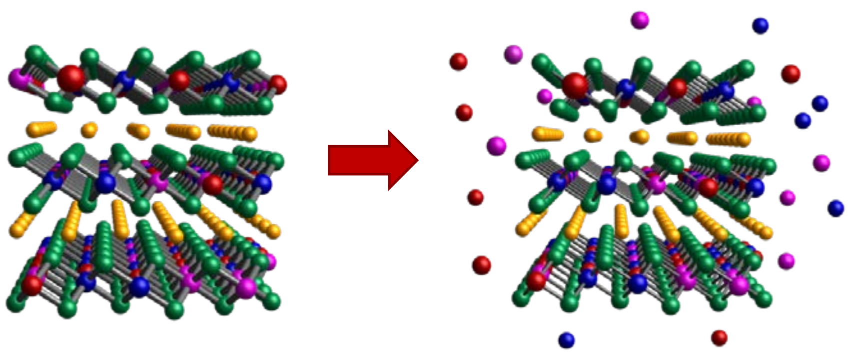
Is toxicity from the released ions, from the transformed NPs, or from the ROS ?

Hang, Gunsolus, Wayland, Melby, Mensch, Hurley, **Pedersen, Haynes, Hamers**, *Chem. Mater.* **2016**, *28,* 1092-1100.

Mechanism: Released Ions *vs.* Transformed Carcasses *vs.* ROS





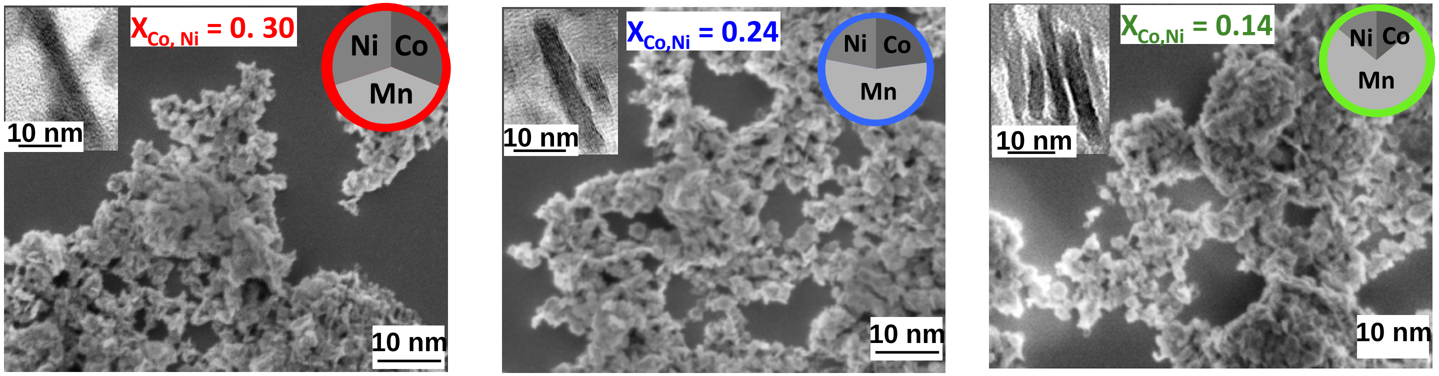


- Biological response can be recapitulated using free Co^{2+}, Ni^{2+}
- Indirect mechanism due to metals
- ROS not dominant mechanism

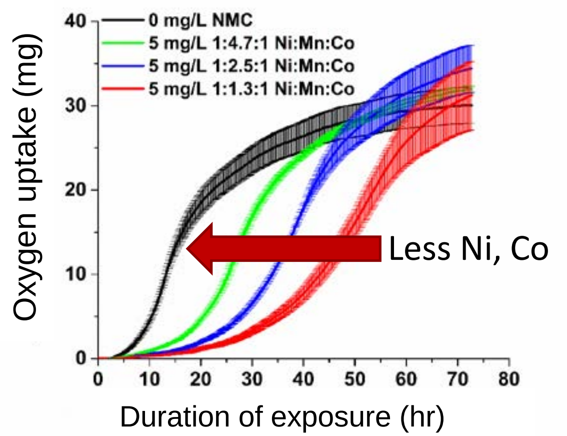
Hang, Gunsolus, Wayland, Melby, Mensch, Hurley, **Pedersen, Haynes, Hamers**, *Chem. Mater*. **2016**, *28,* 1092-1100.

Can we re-design MMC nanomaterials to reduce biological impact?

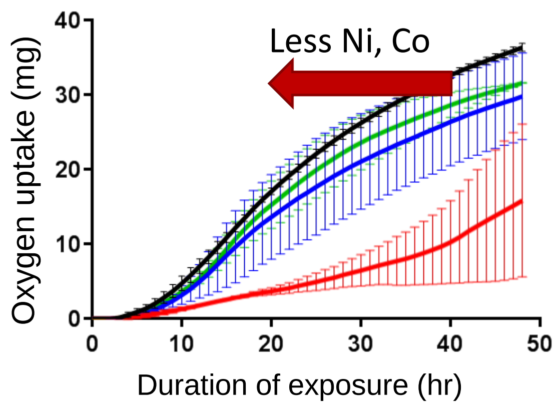
We can tune the composition of NMC materials over a broad range with constant morphology



S. oneidensis

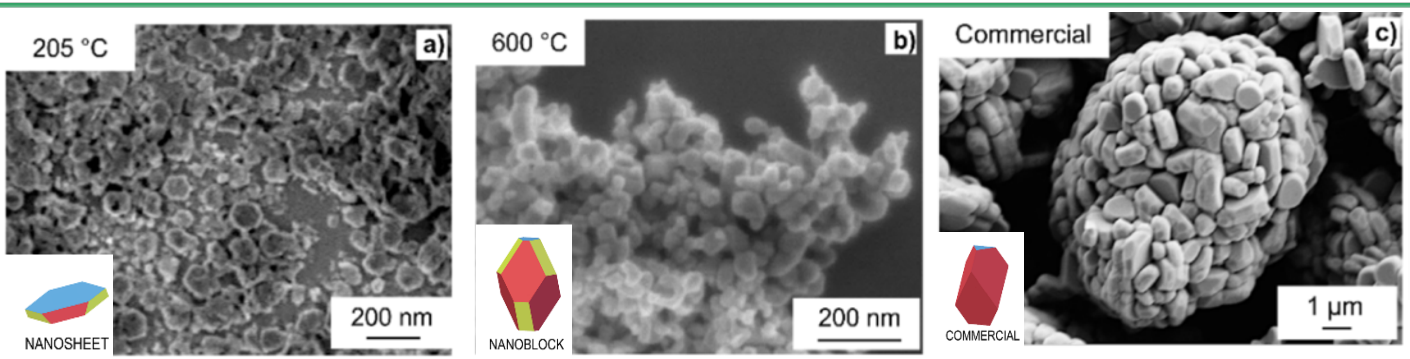


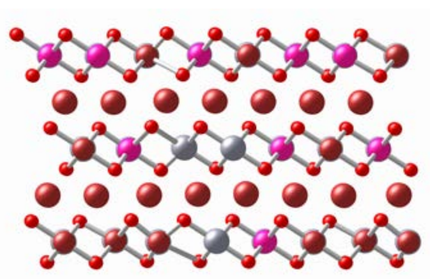
B. subtilis

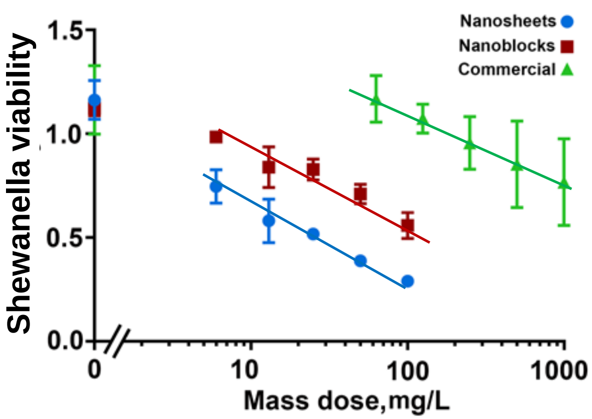


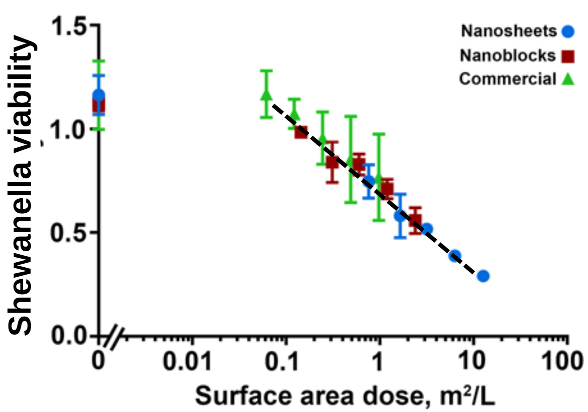
"Redesign" by altering stoichiometry impacts biological response..but does not eliminate it

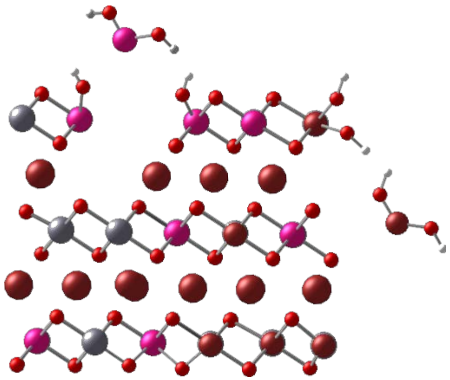
How does distribution of exposed crystal planes alter biological impact ?











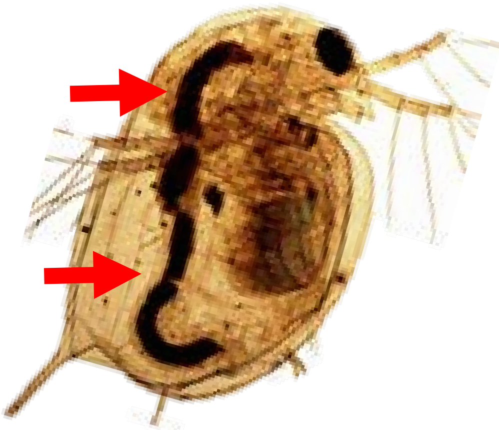
Distribution of exposed crystal planes has negligible impact on release, biological impact

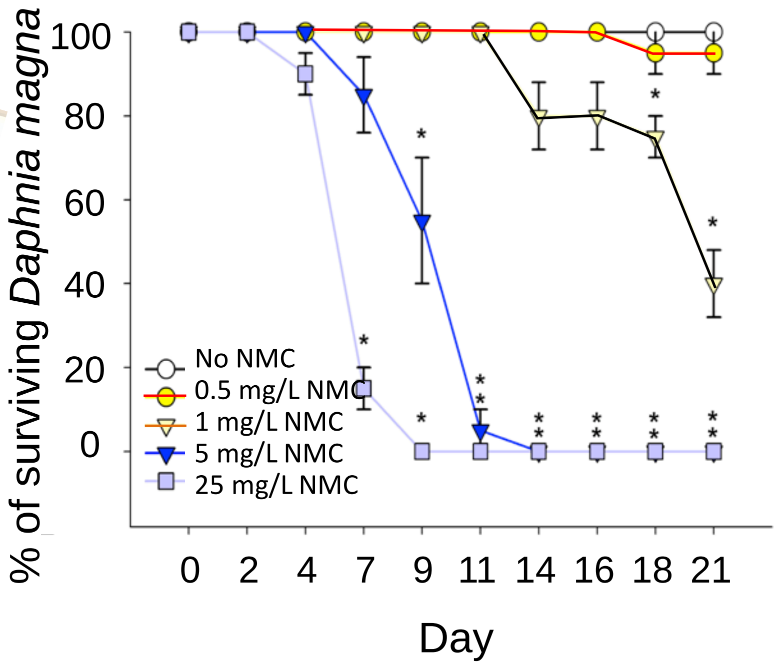
→ Critical step in metal release occurs "late" in the kinetic mechanism; e.g., $M(OH)_2$ species

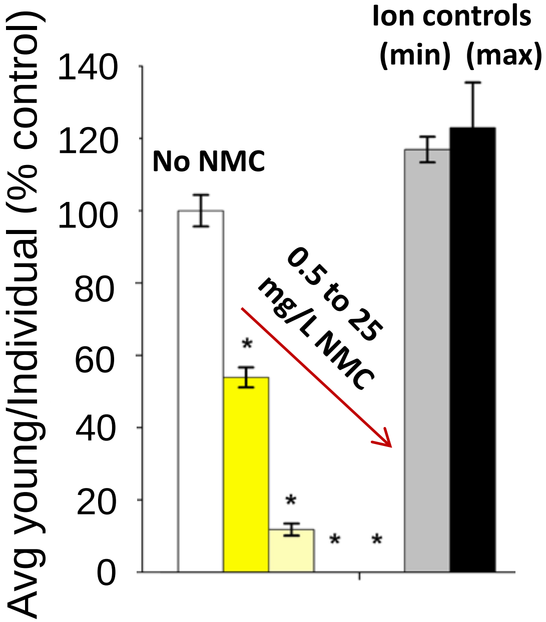
Predictive ability as a function of nanoparticle size, bridge lab to commercial materials

Hang, Hudson-Smith, **Haynes, Hamers**, *ACS Appl. Nanomater.* 2018

Nanoparticle-specific effects: NMC ($LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$) with *Daphnia magna*





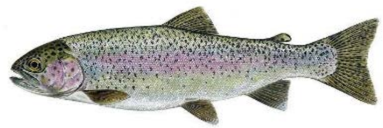


- Daphnids ingest NMC; particles also stick to exterior membranes
- Chronic studies showed significant impacts on *Daphnia magna* survival and reproduction at 1 mg/L NMC and higher.
- **Unlike bacterial cells, nanoparticle-induced biological impact in *Daphnia* cannot be recapitulated using free ion equivalents**

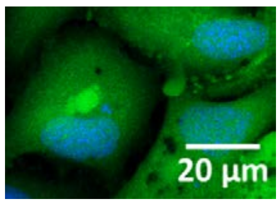
--> Biological impact isn't only about redox-dissolution and release of metal ions…

Up and down the complexity ladder

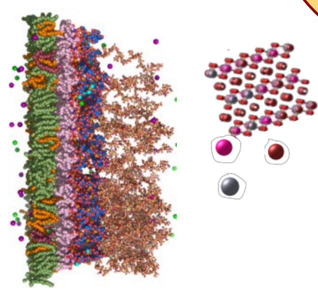
Multicellular Organisms



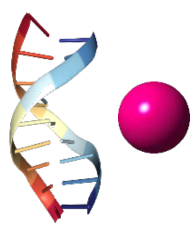
Single Cells



Model cell membranes

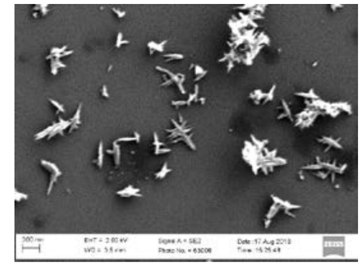


Single molecules

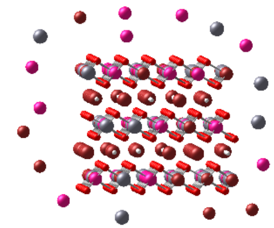


Fundamental Physico-chemical Interactions

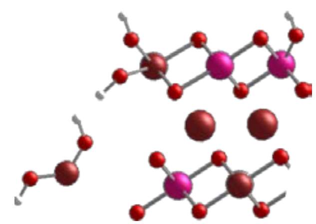
Engineered Nanoparticles



Environmental transformations



Atomistic thermodynamics and mechanisms



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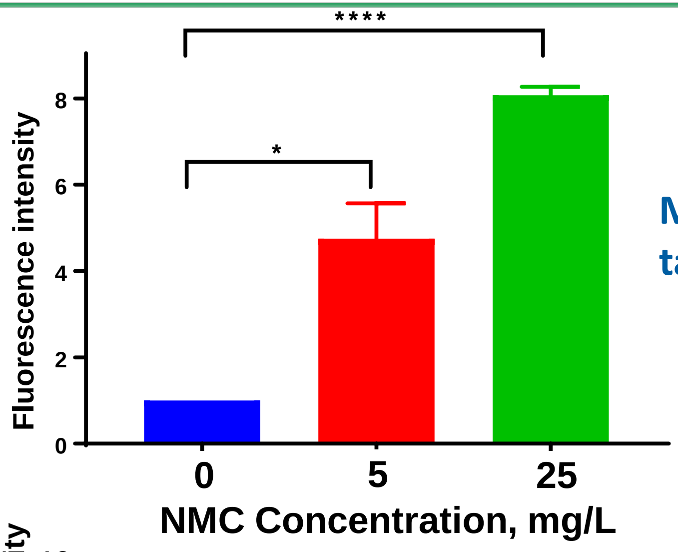
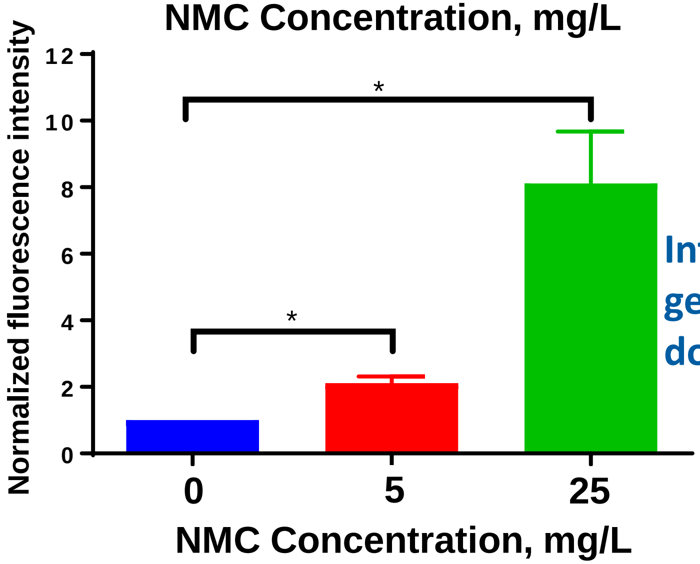
Computationally driven synthesis

Molecular impacts to *B. subtilis*

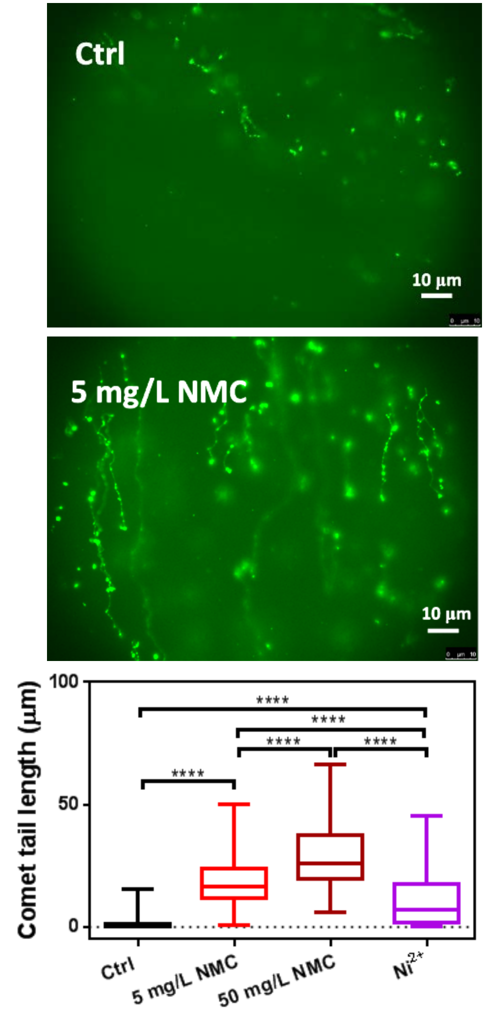


Metal ions (Ni^{2+} and Co^{2+}) taken up by cells



Intracellular ROS generated by NMC in a dose-dependent manner

"Comet Assay" (DNA Damage)



Metal ions induce intracellular ROS formation, induce DNA damage

The Center for Sustainable Nanotechnology

Vivian Feng, Augsburg College

Hoang, …**Hamers**, **Haynes**, **Feng**, *In Preparation*

Not all nanomaterials are alike: transition metal oxide chemistry

Proton-initiated metal release

$LiCoO_2 + 2H^+ \rightarrow Li^+ + 2OH^- + Co^{3+}$

Oxidation of water

$Co^{3+} + H_2O \rightarrow Co^{2+} + \cdot OH + H^+$

$4\ Co^{3+} + 2H_2O \rightarrow 4\ Co^{2+} + O_2 + 4H^+$

What is the mechanism by which complex transition metal oxides release TM ions ?

Why are different metals released at different rates ? (Ni>Co>Mn)

Why does "dissolution" stop and not continue, even thought metal concentrations are much lower than solubility product limits

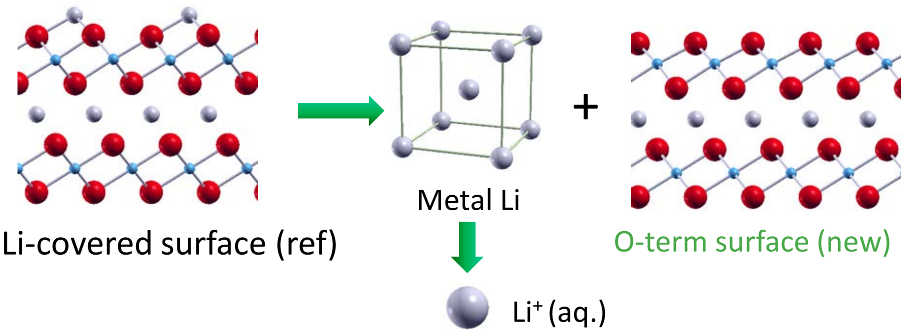
Does distribution of exposed crystal planes matter (NP shape)?

How do complex oxides transform?
Hess's Law Approach: DFT + Solvent Ion Model

$$\Delta G = \Delta G_1 + \Delta G_2$$

- ΔG_1 is the DFT-computed free energy
- ΔG_2 is tabulated from experimental results

$\Delta G_1 =$



$$\Delta G_2 = \Delta G^0_{SHE} - n_e e U_{SHE} - 0.0591\, n_H\, pH + 0.0257 \ln \alpha\, [H_x AO_y^{z-}]$$

Reference to SHE — # of e- & Potential — # of H+ & pH — Activity & Concentration

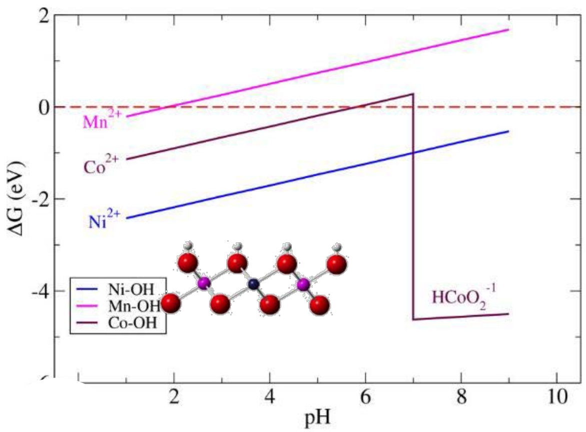
Robust method takes into account experimentally tunable parameters…
enabling more connections between theory, experiment

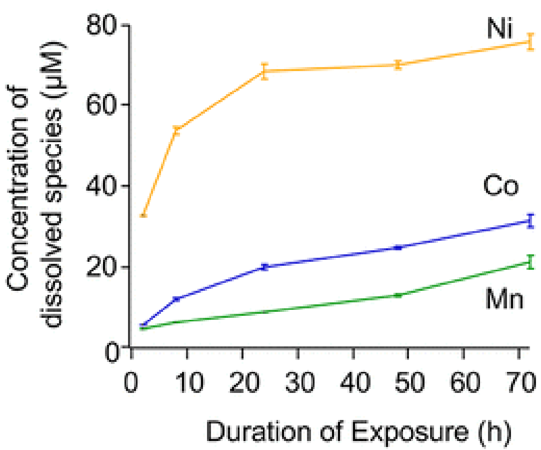
XSEDE Extreme Science and Engineering Discovery Environment

GBRV high-throughput pseudopotentials

Computational results provide atomistic insights into mechanisms

Dissolution Modeled by Removing HO-M





A closer look…

	$LiCoO_2$	333-NMC	252-NMC	171-NMC	
ΔG_1	11.49	9.73	7.74	6.78	Lattice energies
ΔG_2	-9.68	-9.68	-9.84	-9.84	Solvation
ΔG_{tot}	1.81	0.05	-2.11	-3.06	

Most stable → **Least stable**

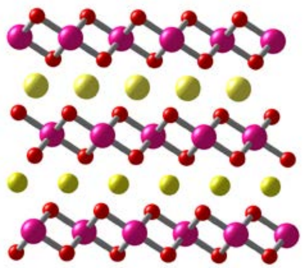
Key Results:
Mn will dissolve pH < 1.9
Co will dissolve pH < 5.9
Ni will dissolve 2 < pH < 9
@ pH = 6, Ni > Co > Mn, Consistent with experiment!

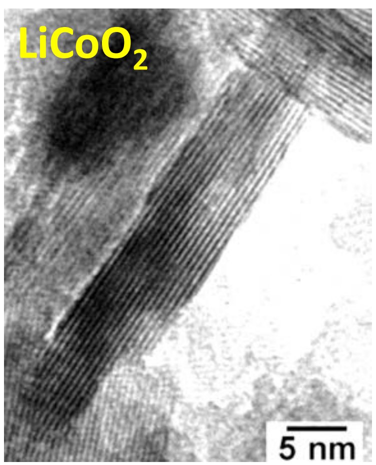
- **Trend in materials composition are driven by differences in lattice energies**
- **Thermodynamic free energy of metal releas is Ni>Co>Mn, in agreement with experimental trends**
- **Free energies of release decrease as lithiation decreases (self-limiting reaction)**

Hang, Hudson-Smith… **Haynes, Hamers,** *ACS Appl. Nanomater*. 2018
Bennett, **…Hamers, Mason,** *Environ. Sci. Technol.* 2018

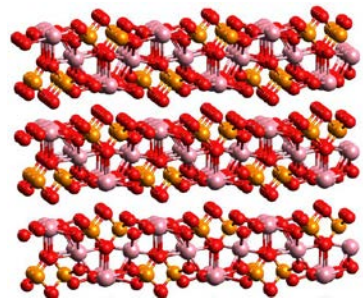
Beyond oxides: Phosphates, hydroxyphosphates

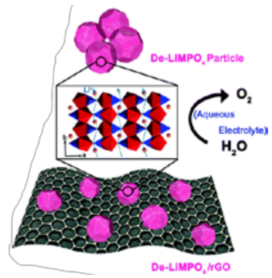
Oxides





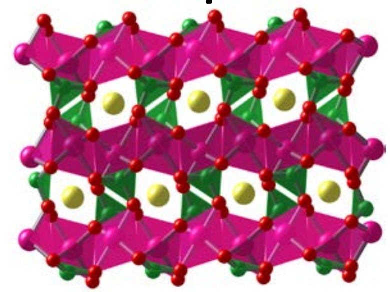
Phosphate adsorption
Hydroxy-phosphates

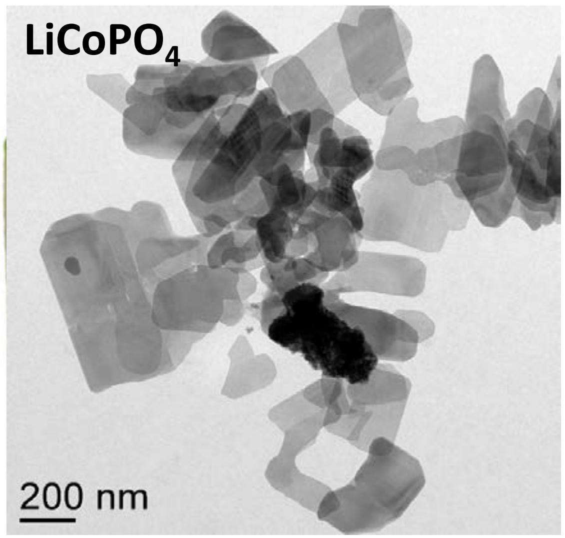




CoP- Hydrogen Evolution (CCI-Solar)[1]
CoPi Oxygen Evolution (Nocera)[2]
Tunable $LiMPO_4$ catalysts(M=Co, Fe,…)[3]

Phosphates

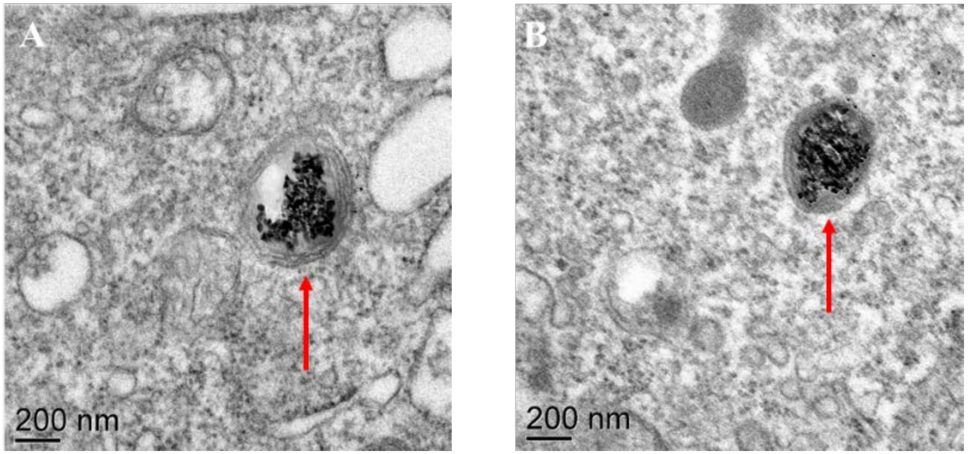




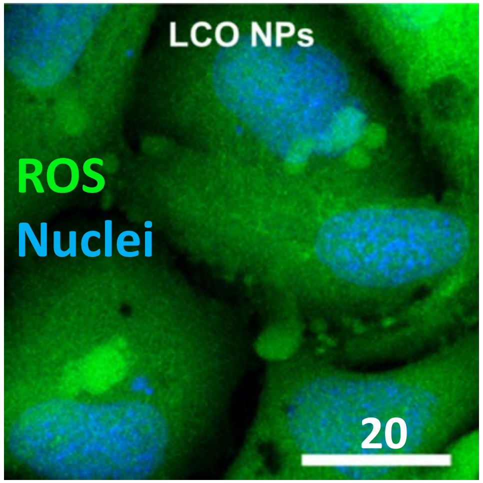
What is the role of the anion in controlling NP behavior?
Long-term transformations: Do oxides and phosphates converge to hydroxyphosphates?
What other matrix effects are important in controlling longer-term transformations of NM?

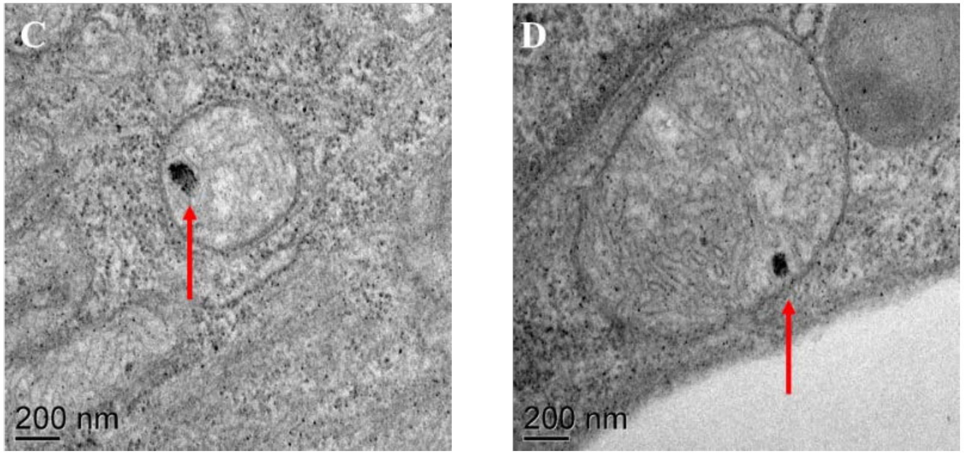
[1] Callejas, Lewis, Schaak, Lewis. Ang. Chem., 2014, 53, 5427.
[2] Nocera, et al, J. Am. Chem. Soc. 2010, 132, 13692-13701.
[3] Yi Cui, et al., Energy Environ. Sci., 2015, 8, 1719

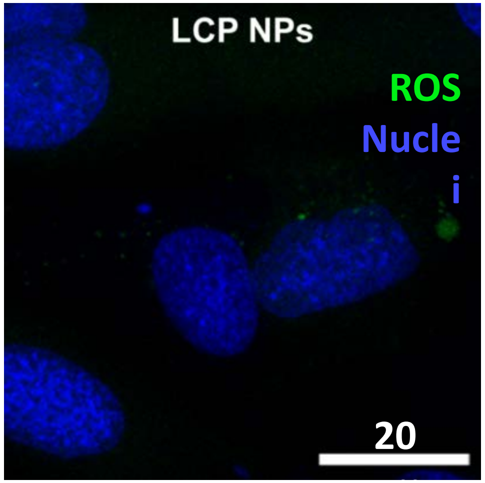
$LiCoO_2$ and $LiCoPO_4$ NPs are taken up by gill epithelial cells



Lithium cobalt oxide (LCO) in organelles



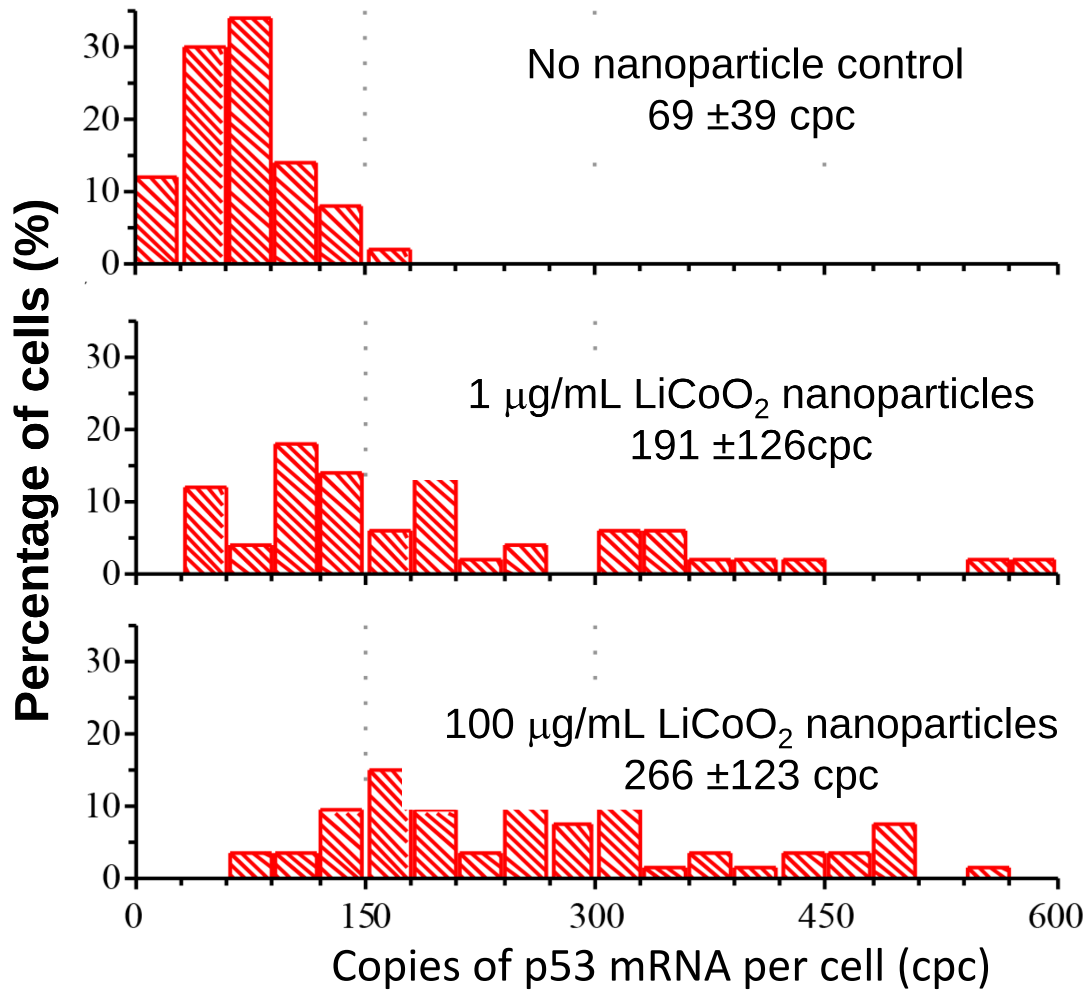




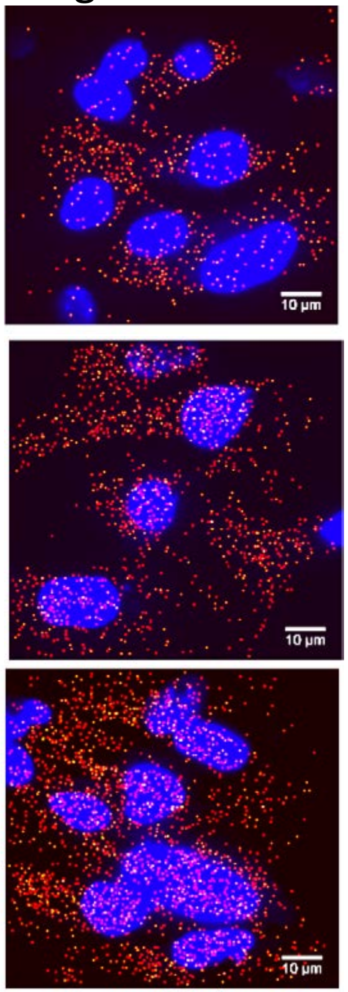
Lithium cobalt phosphate ($LiCoPO_4$) in organelles

Melby,… **Hamers**, **Orr**, *Submitted*

$LiCoO_2$ alters gene expression in gill epithelial cells



Single-cell FISH



$LiCoO_2$ nanoparticles increase expression of p53

E. Melby, et al., Nanotoxicology, in press

What materials has the “nanomaterials” team identified as high priority?:

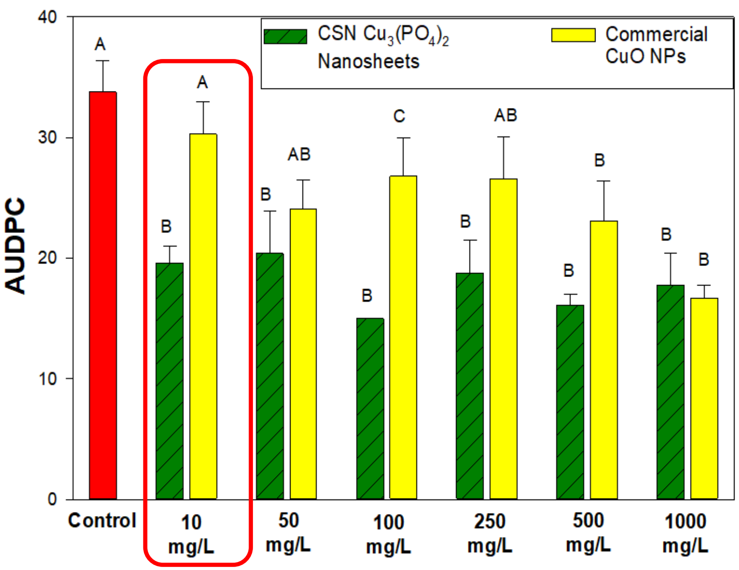
2. Nanomaterials for application in agriculture Enhancing global food production

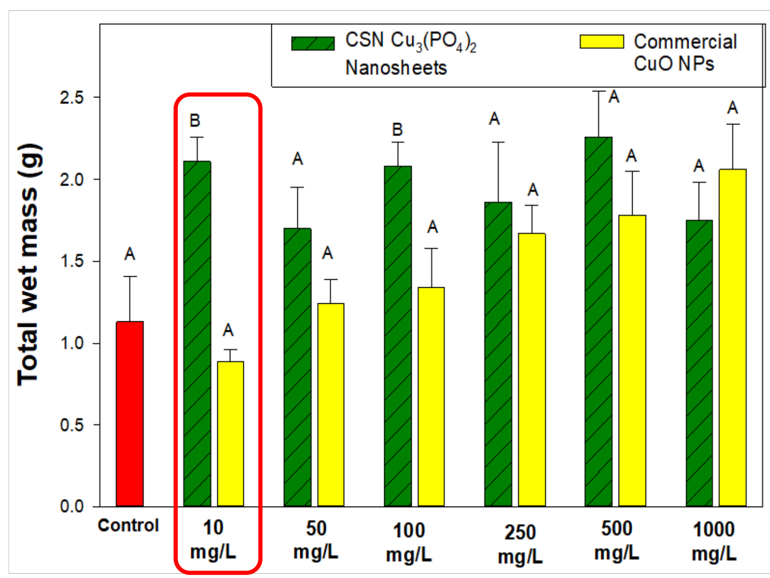
- **Broader theme:** “Controlled release”: Using chemical principles to control chemical transformation and release of elements at will
- **Sustainability:** More effective application of elements of interest, reduced application in areas that are not effective.

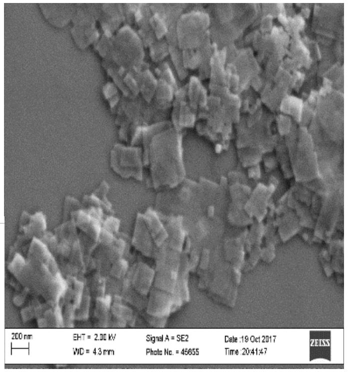
- Copper-based compounds
  - CuO, $Cu_3(PO_4)_2$
  - CuZnO, mixed-valence $Cu_xZn_yAl_zO$ (“controlled release”)
- Nanodiamond
- Carbon dots
- Nitrogen, Phosphorus-containing NPs.
- Biologically derived polymeric NPs (nanocellulose,..)

$Cu_3(PO_4)_2$ Nanosheets to Suppress Disease

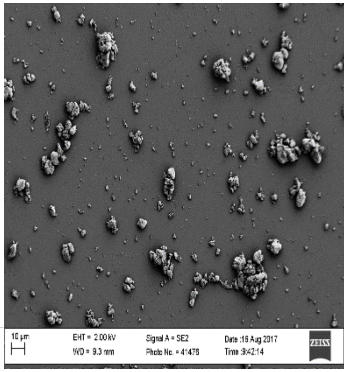
- Foliar application, watermelon, using *Fusarium* infested soils.
- $Cu_3(PO_4)_2$ nanosheets promote growth and inhibit disease more effectively than commercial CuO NPs.







$Cu_3(PO_4)_2$ Nanosheets



Commercial CuO NPs

Borgatta et al. 2018. *ACS Sustain. Chem. Eng.* In preparation.

Summary

Surface and Bulk Chemical Transformations of Li_xCoO_2 and $Li_xNi_yMn_zCo_{(1-y-z)}O_2$ nanoparticles control biological impact

- incongruent dissolution, and production of ROS, leaving behind Mn-rich transformed particles.
- In bacteria, impact mostly controlled by transition metal ions released into medium

  → "Redesign" based on chemical composition partially successful in reducing response
- In eukaryotes (Daphnia, trout gill cells) effects *cannot* be recapitulated using free 2+ ions, showing *nanoparticle-specific* effects

  → Direct observation of DNA damage (bacillus) and genetic changes (Daphnia)

  → $LiCoO_2$ and $LiCoPO_4$ nanoparticles are taken up into trout gill cells but elicit very different responses. Oxidation state may be a crtitcal variable in NP toxicity.
- Computational studies are providing insights into how materials transform

Complex transition metal oxides are a frontier area for nano-safety

Redox-mediated dissolution	ROS production	Metal complexation	Surface adsorption	Transformed NPs

Acknowledgements

Christy Haynes (Minnesota)

Vivian Feng (Augsburg)

Rebecca Klaper (UWM)

Sara Mason (U. Iowa)

Erin Carlson (Minnesota)

Joel Pedersen

Galya Orr (PNNL)

Eric Melby (PNNL)

Liz Laudadio (UW-Madison)

Mimi Hang (UW-Madison)

Joe Bennett (U. Iowa)

Joe Buchman (Minnesota)

Natalie Hudson-Smith
Minnesota)

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The Center for Sustainable Nanotechnology is a Center for Chemical Innovation, which is funded by the National Science Foundation under Grant No. CHE-1503408

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DOI: 10.1021/acs.est.8b02324