2016 Basic Research Needs for Synthesis Science for Energy Relevant Technology Workshop

CHAIRS:

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DOE Office of Basic Energy Sciences

BESAC reports highlight the challenges and opportunities of synthesis science

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- *"Mastering Hierarchical Architectures and Beyond-Equilibrium Matter"*
- *"Beyond Ideal Materials and Systems: Understanding the Critical Roles of Heterogeneity, Interfaces, and Disorder"*

  - Challenges at the Frontiers of Matter and Energy: Transformative Opportunities for Discovery Science

- *"How do we design and perfect atom- and energy-efficient synthesis of revolutionary new forms of matter with tailored properties"*

  - Directing Matter and Energy: Five Challenges for Science and the Imagination

Importance of synthesis science reflects historical link between new materials and new technologies

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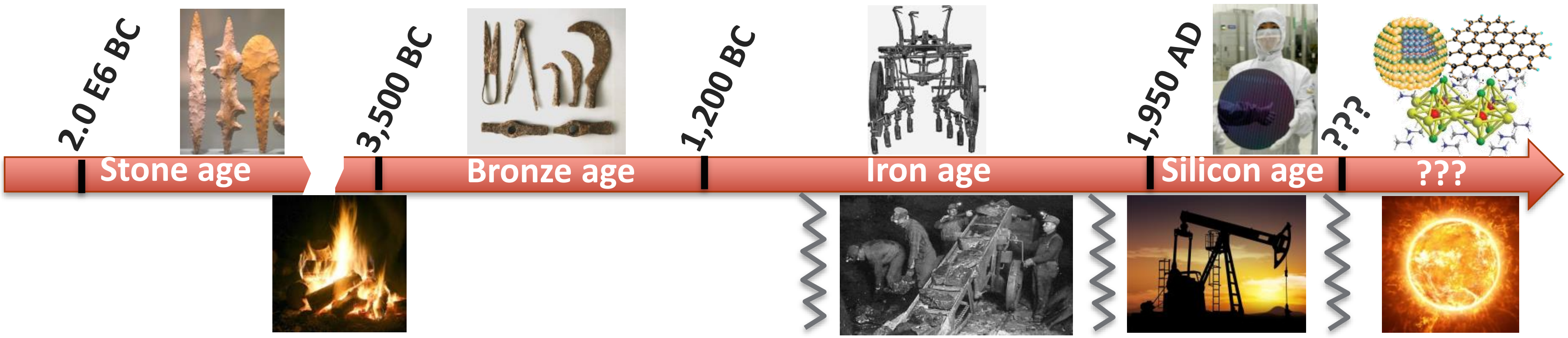

Major recent discoveries

- Conducting polymers (1982)*
- High T superconductors (1986)*
- Buckyballs, C_{60} (1985)*
- Dye-sensitized solar cells (1990)#
- Carbon nanotubes (1991)$
- Quantum dots (1992)$
- GaN semiconductors (1993)*,#
- Magnetoresistive materials (1995)#
- Graphene (2004)*

Unsung heroes

- Carbon fiber composites (1960s)
- High Si alumino-Si zeolites (1980s)
- Pt-group catalysts (1980s)
- Transparent conducting oxides(1980s)
- Rare earth phosphors (1980s)
- Lithium ion conductors (1984)
- Metal organic frameworks (1995)
- Bismuth chalcogenides (1997)
- Hybrid perovskites (2009)

* Nobel Prize $ Kavli Prize   #Millenium Prize

Adapted from T. Cheetham's Plenary talk

Advancing synthesis science is also critical to realizing the vision of MGI

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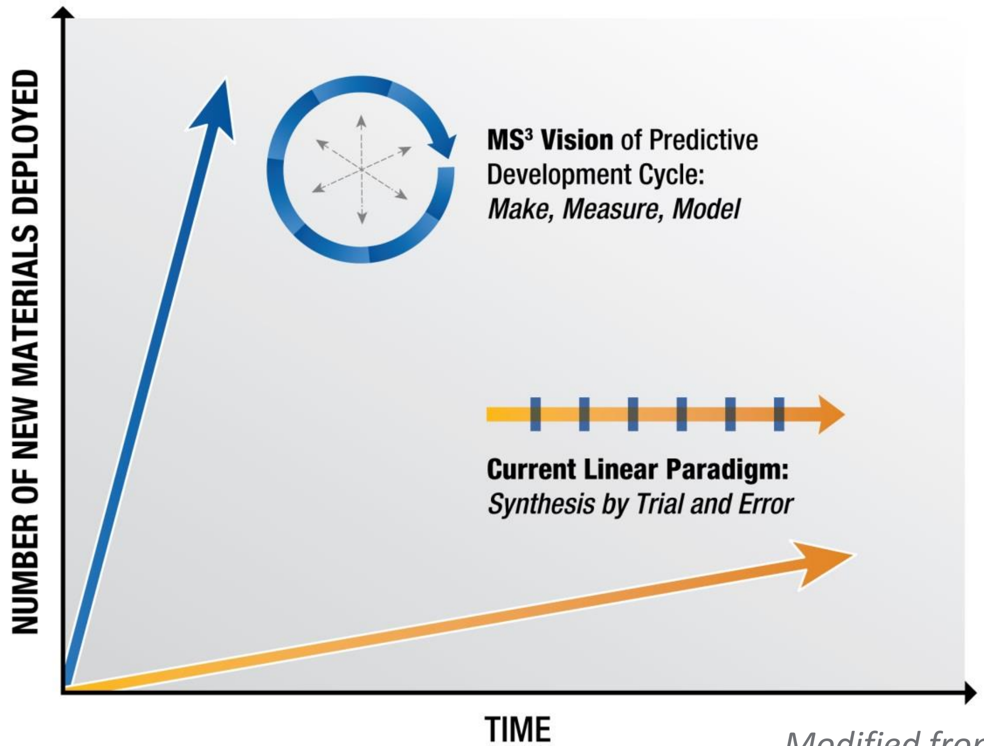
"Accelerating the pace of discovery and deployment of advanced material systems will … be crucial to achieving global competitiveness in the 21st century."

- Materials Genome Initiative (MGI) for Global Competiveness, 2012 OSTP report



Modified from MGI report

Discovery alone no longer ensures leadership

Focus is on developing a predictive science of synthesis

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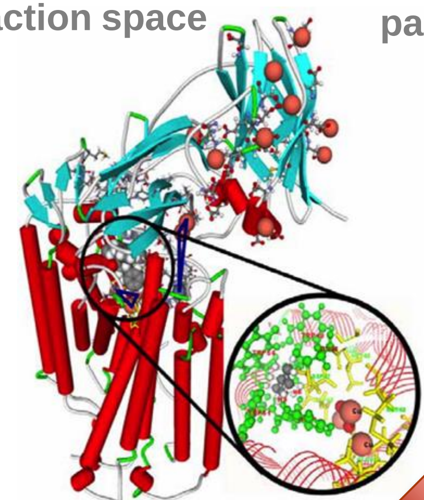
Bioinspired catalyst

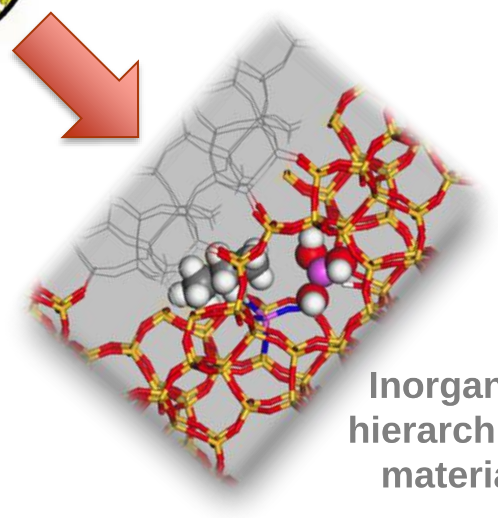
Constrained reaction space

Proton transport pathways



Uniquely determined locations of multi-functional active sites

Channels for delivery of reactants



Inorganic hierarchical material

The science of design: ***Knowing where to put the atoms to achieve a targeted function***

The science of synthesis: ***Knowing how to get the atoms where they need to go to obtain a targeted structure***

Charge to the Workshop

"Identify basic research needs and priority research directions in synthesis science with a focus on new, emerging areas with the potential to leapfrog current capabilities and impact future energy technologies. The workshop will identify the scientific opportunities and new frontiers associated with both existing and novel synthetic processes that will enable predictive synthesis of energy relevant matter via assembly of atoms, molecules, clusters, nanoparticles, and other constituents. This research is essential to realizing the opportunities identified in the recent BES Advisory Committee report on Challenges at the Frontiers of Matter and Energy: Transformative Opportunities for Discovery Science. This report concluded that further progress towards the transformative opportunities will require specific, targeted investments in synthesis science, specifically the ability to make the materials and architectures that are envisioned."

85 researchers participated in five topical and two crosscutting panels

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Panel 1: Mechanisms of synthesis under kinetic and thermodynamic controls
Tori Forbes (University of Iowa)
Mercouri Kanatzidis (Northwestern University)

Panel 2: Establishing the design rules for supramolecular and hybrid assemblies
Uli Wiesner (Cornell University)
Ting Xu (University of California, Berkeley)

Panel 3: Interface-defined matter
Sarah Tolbert (University of California, Los Angeles)
Michael Zaworotko (University of Limerick)

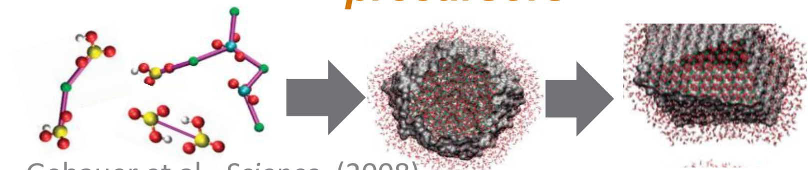
Panel 4: Crystalline matter: Challenges in discovery and directed synthesis
Julia Chan (University of Texas, Dallas)
John Mitchell (ANL)

Panel 5: Emerging approaches to synthesis at all length scales
Jonah Erlebacher (Johns Hopkins University)
Julia Laskin (PNNL)

Cross cutting Panels:
***In situ* characterization** - Simon Billinge (Columbia University)
Theory and simulation - Giulia Galli (University of Chicago)

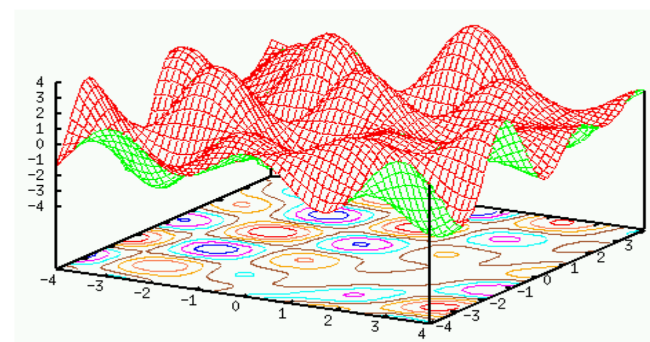
Panel 1: Mechanisms of synthesis under kinetic and thermodynamic controls

- Elucidate, model, and classify fundamental pathways of materials formation



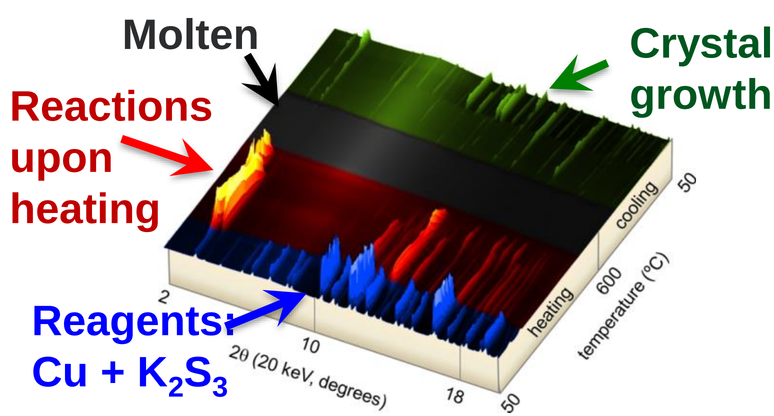
Gebauer et al., *Science,* (2008)
Dimechelis et al., *Nature Comm*. (2011)

- Advance thermodynamic characterization of energy landscapes and multi-variable phase diagrams, including both stable and kinetically stabilized materials



http://fourier.eng.hmc.edu/e161/lectures/NeuralNetworks/node5

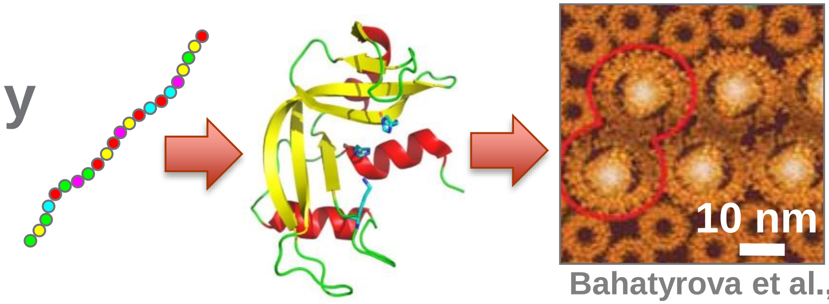
- Integrate *in-situ* characterization and theoretical approaches to understand reaction dynamics at multiple length and time scales



Shoemaker et al., *Proc. Natl. Acad. Sci. U. S. A.*(**2014**)

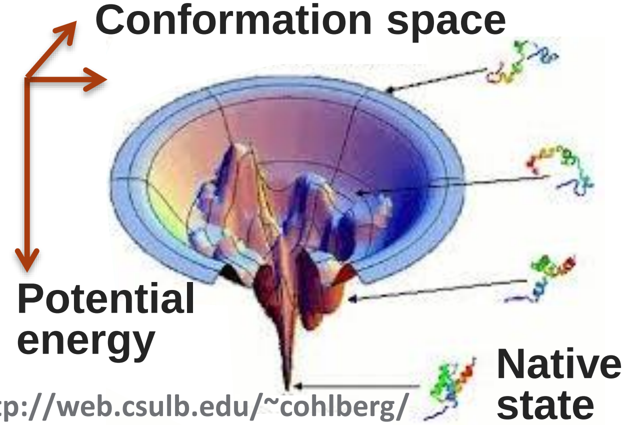
Panel 2: Establishing the design rules for supramolecular and hybrid assemblies

- Enable programmable assembly via synthesis of information-encoded building blocks



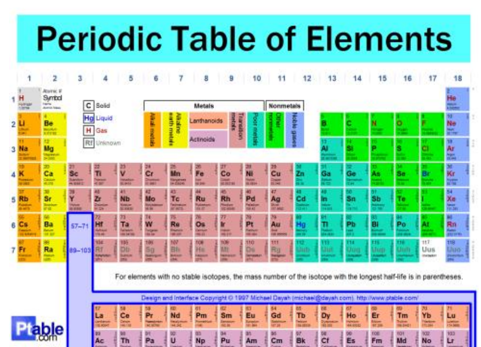
Bahatyrova et al., *Nature* (2004)

- Identify and navigate energy landscapes to achieve functional hierarchical assemblies



http://web.csulb.edu/~cohlberg/

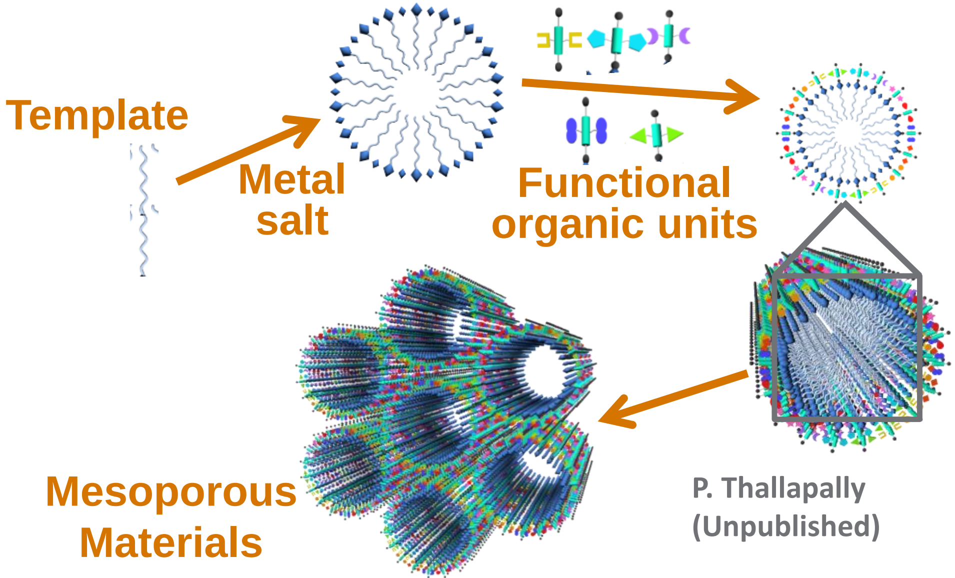
- Develop robust synthetic strategies based on *sustainable* energy relevant materials and processes



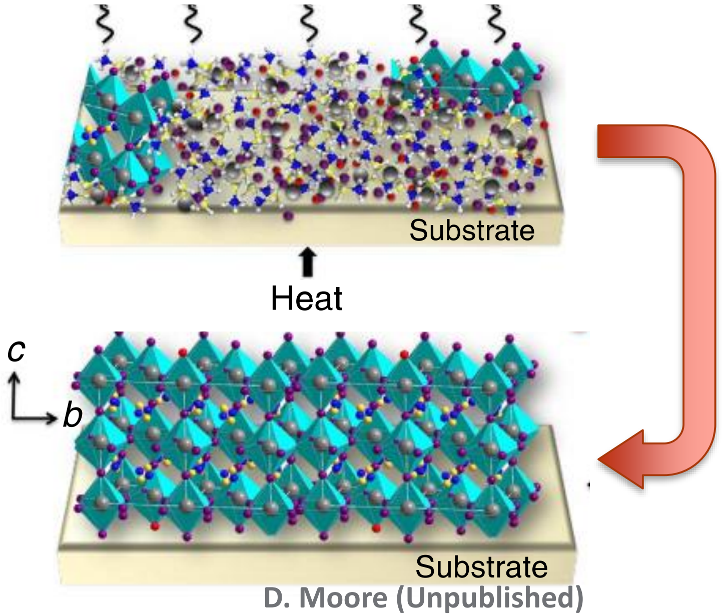
http://www.ptable.com

Panel 3: : Interface-defined matter

- Achieve synthesis of multifunctional hierarchical materials by design with precise controlled over interfacial structure and composition across all scales



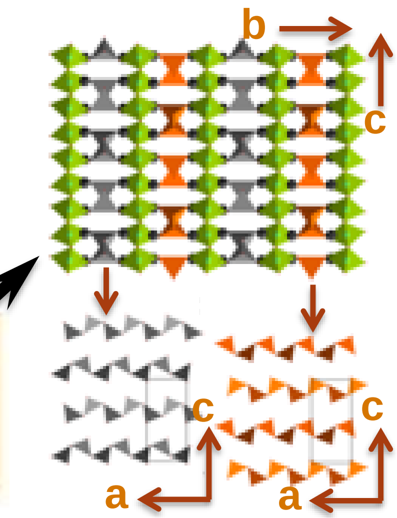
- Understand and accurately predict pathways and barriers to exploit interfaces as drivers of synthesis for both stable and metastable materials



Panel 4: Crystalline matter: Challenges in discovery and directed synthesis

- **Mastering the science of crystal synthesis**
  - Development and understanding of new properties-directed synthetic routes and growth techniques, emphasizing extreme regimes

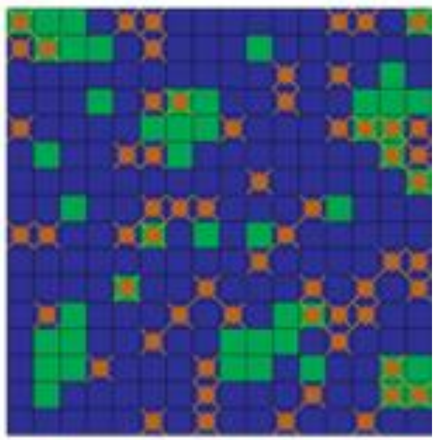
New high pressure $Ca_2Co_2O_5$ phase



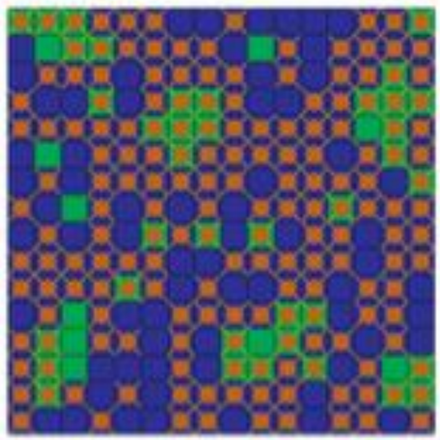
Zhang et al., *Chem. Mater.* (2014)

- **Exploring Hierarchies of Crystalline Complexity**
  - Exposing new properties of materials by moving beyond average structures to materials with defects and disorder by design across scales

Low Fe



Fe-Rich



Multiferroic enabled by mixed-site crystal

R O FeO_6

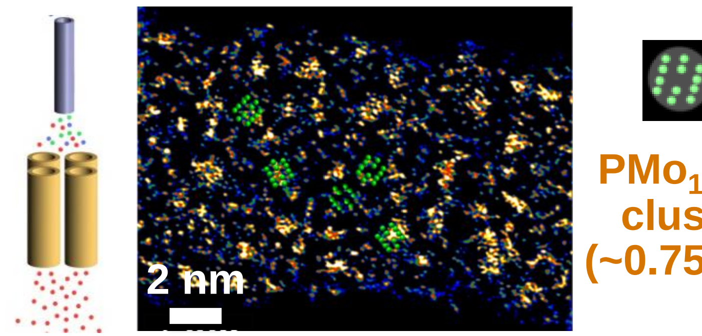
Mandal et al. *Nature* (2015)

Panel 5: Emerging approaches to synthesis at all length scales

- **Far From Equilibrium Synthesis**
  - Navigate kinetic pathways in systems driven far from equilibrium
  - Understand and predict interface and defect dynamics in systems under high thermodynamic gradients

Mangolini et al., *Nano Lett.*, (2005)

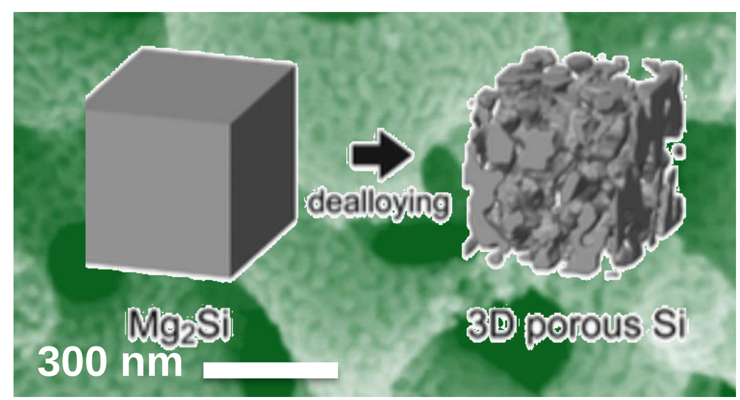
- **Complex Hybrid Materials**
  - Synthesis of composite nanoscale materials by creating interfaces between dissimilar components (phases, structures, molecules)



$PMo_{12}O_{40}$ cluster (~0.75 nm)

Prabhakaran et al. *Nat. Commun.* (2016)

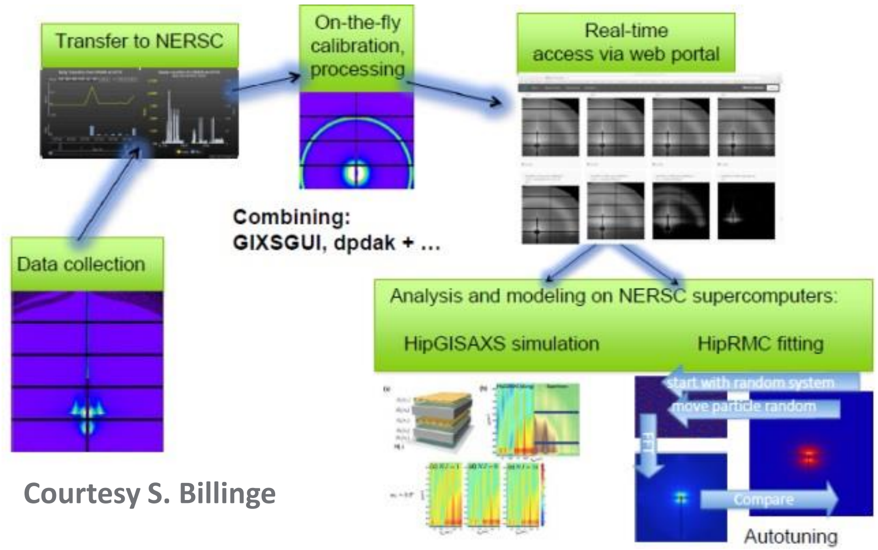
- **Hierarchical Control During Materials Synthesis and Processing**
  - Simultaneous control of structure at nano, meso- & macroscale
  - Enable kinetic or thermodynamic trapping of intermediates



Qi et al. *Nano Lett.* (2013); Wada et al., *J. Power. Sources* (2016)

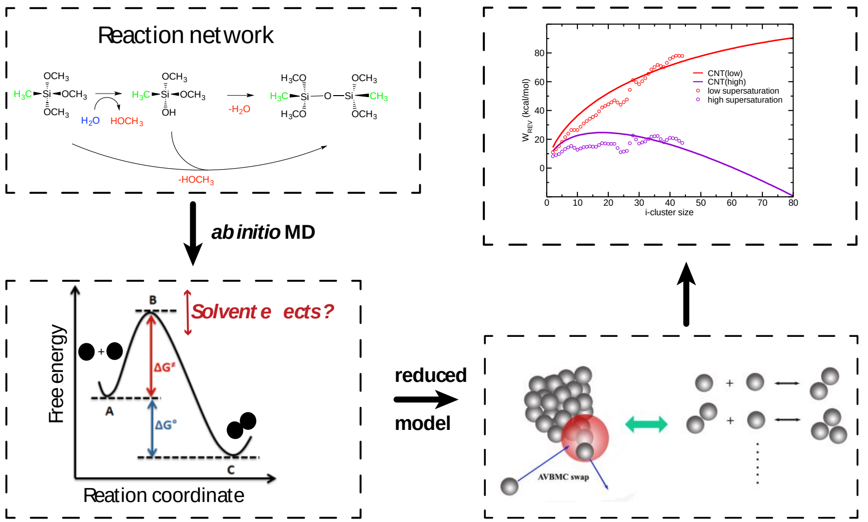
Crosscutting panels: 1) *In situ* characterization and 2) Theory and simulations

- **Enable identification and control of synthetic pathways**
  - **Develop *in situ* characterization tools that match length/time-scales and sensitivities required to understand synthesis mechanisms**
  - **Make *in situ* tools straightforward to use and widely available.**



Courtesy S. Billinge

- **Enable prediction of pathways and ensemble outcomes of synthesis that can direct processes on the fly**
  - **Develop sampling methods to simulate atomistic phenomena**
  - **Develop coarse-grain approaches to link atomistic results to long length/time scale outcomes**
  - **Achieve accurate description of heterogeneous reactive interfaces**



Broad agreement time is right due to opportunities for fundamental understanding created by recent advances in characterization and simulation

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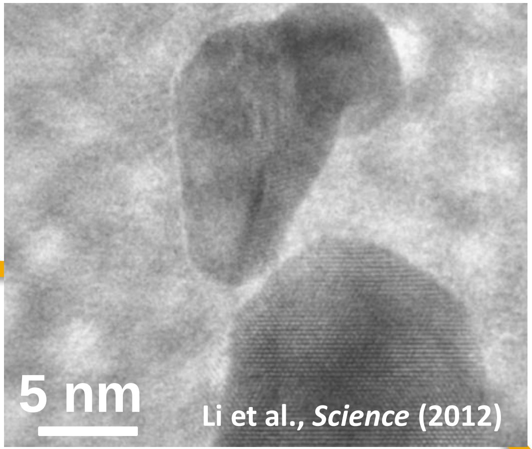
- Electron microscopy
- X-rays and neutrons
- Scanned probes
- Laser spectroscopy
- On-the fly data analytics

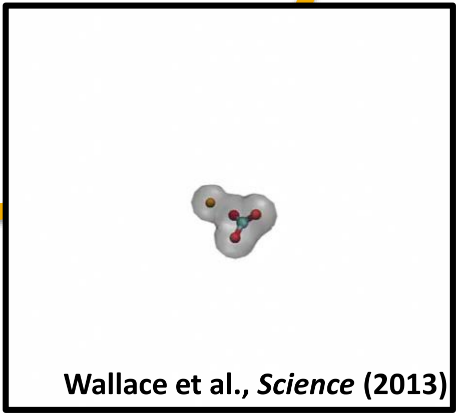


Li et al., *Science* (2012)

Understand reaction dynamics at multiple length and time scales

Courtesy E. Chan.

- Generalizable systems
- Defined P, T, μ_i
- Extreme fields and fluxes
- Robotics

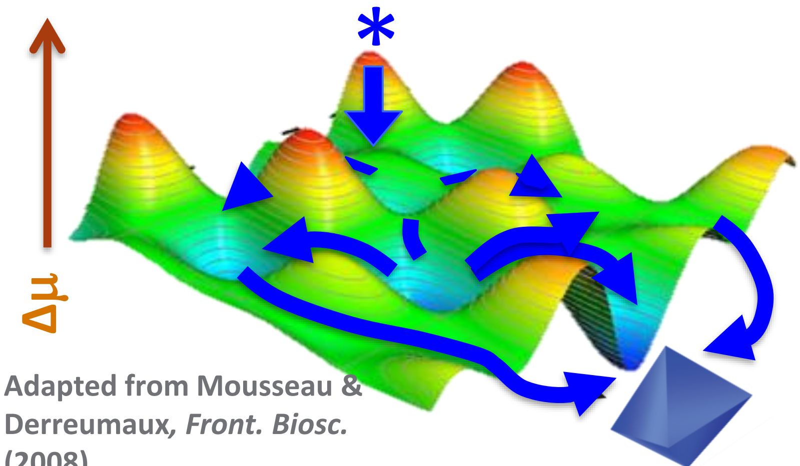


Wallace et al., *Science* (2013)

- Connecting length scales
- High-throughput sampling
- Theory development
- Towards exascale

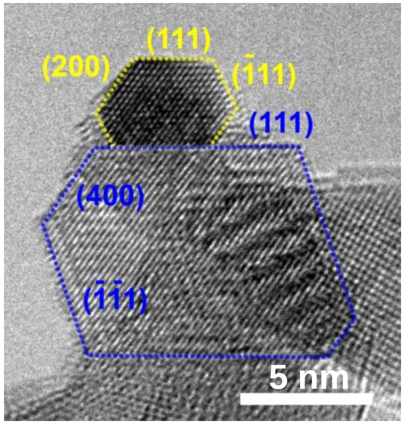
Theme 1: Understanding mechanisms, pathways and intermediates seen as key to achieving control

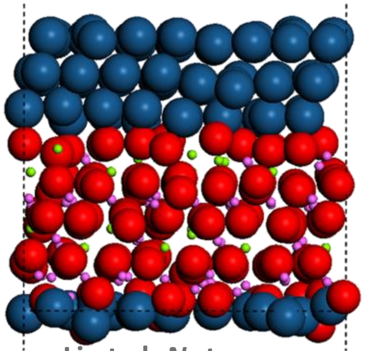
Complex landscapes; far from equilibrium



Adapted from Mousseau & Derreumaux, *Front. Biosc.* (2008)

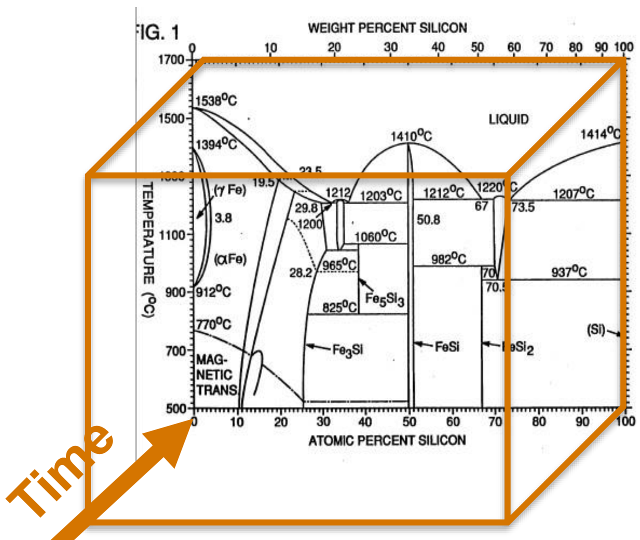
Interface-directed synthesis



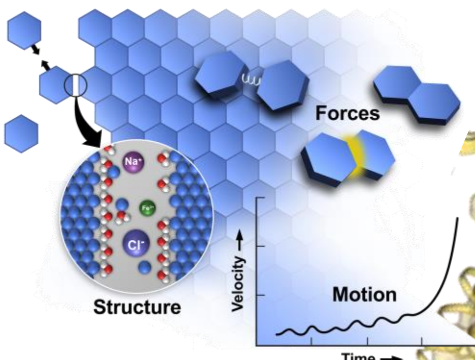


Li et al. *Nature Comm.* (2013)

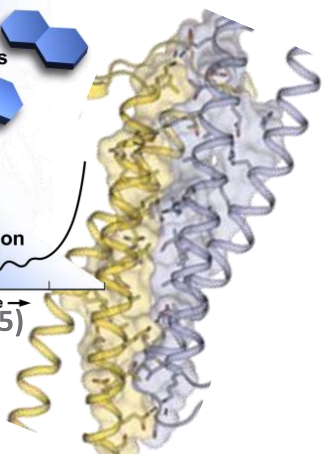
Complex and evolving chemistry



Assembly of higher-order species



De Yoreo et al., *Science*, (2015)



Gonnen et al., *Science* (2015)

Theme 2: Hierarchical materials comprise a key opportunity space in all areas of synthesis

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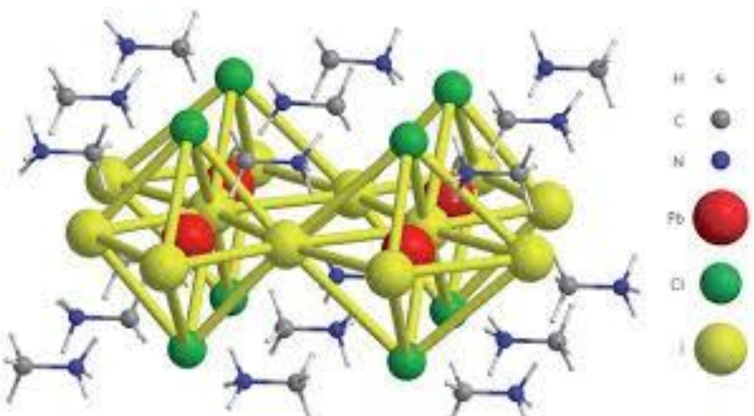
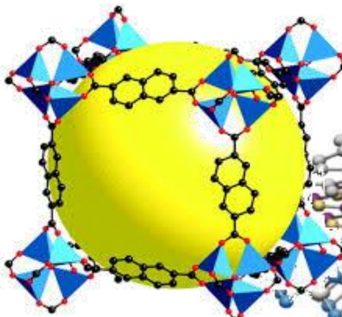
Hybrid crystal systems

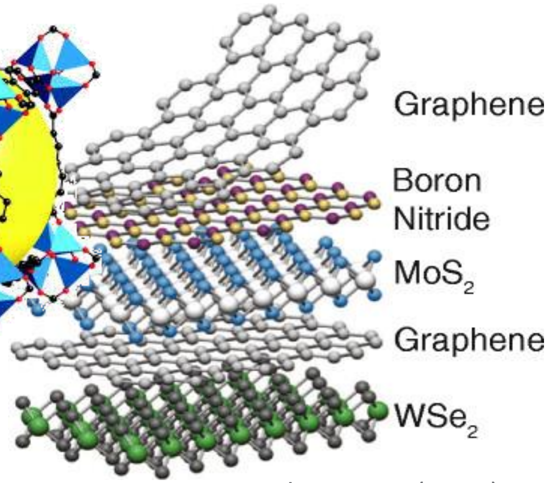


Loi & Hummelen, *Nature Comm.* (2013)

Interface engineering

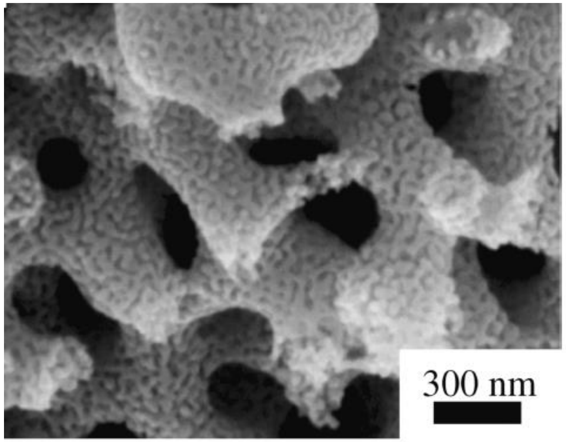


Hallian et al..
Nature (1999).

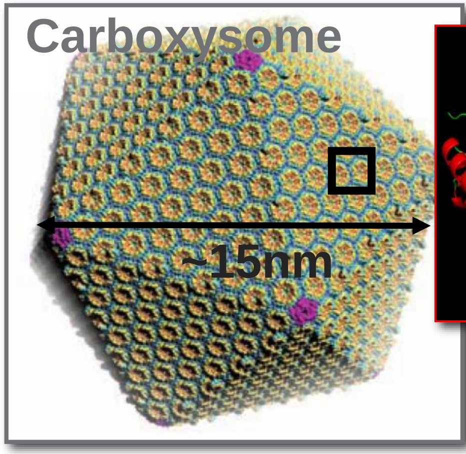


Geim et al., *Nature* (2013)

Additive/subtractive processes



Self-assembled systems



C.A. Kerfeld et al., *Science* (2005)

Theme 3: Synthesis of new materials will always remain a voyage of discovery

- **Current opportunities are consequence of exploring new materials spaces**
- **Theory and simulation will not be able to predict *a priori* how to make new materials with novel properties for many years to come**
- **Opportunities for transformational discoveries lie in extreme conditions, complex chemistries, information-rich molecules, and interfacial systems**