HyMARC: A Consortium for Advancing Solid-State Hydrogen Storage Materials

HyMARC
Hydrogen Materials Advanced Research Consortium

Enabling **twice the energy density** for onboard H_2 storage

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BERKELEY LAB

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Overview (LBNL)

Timeline

Project start date: 09/21/2015
Phase I end date: 09/30/2018

Barriers addressed

- Lack of understanding of hydrogen physisorption and chemisorption (Barrier O)
- System weight and volume (Barrier A)
- Charge/discharge rate (Barrier E)

Budget

FY15 DOE Funding: $250K
FY16 DOE Funding: $590K
FY17 Planned DOE Funding: $870K
Total Funds Received: $1.710M (all years)

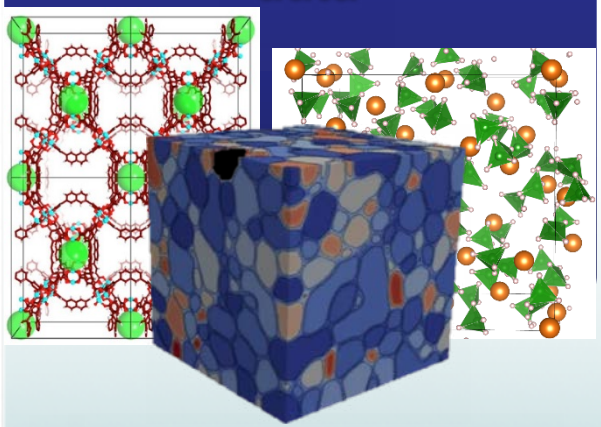
Team

Funded Partners:
Sandia National Laboratories (lead)
Lawrence Livermore National Laboratory

Relevance and Objectives

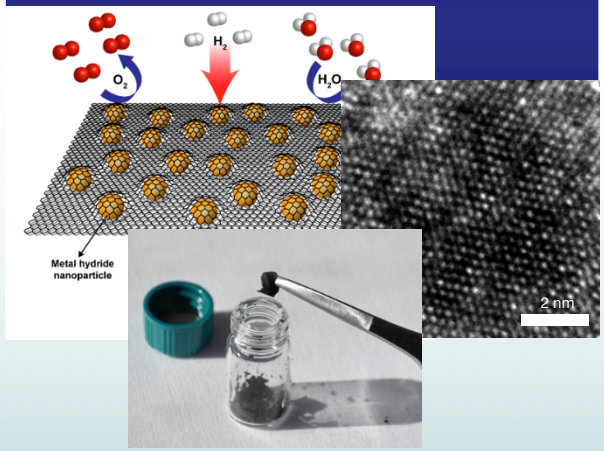
HyMARC will provide **community tools** and **foundational understanding** of phenomena governing thermodynamics and kinetics to enable development of solid-phase hydrogen storage materials

Theory, simulation, & data



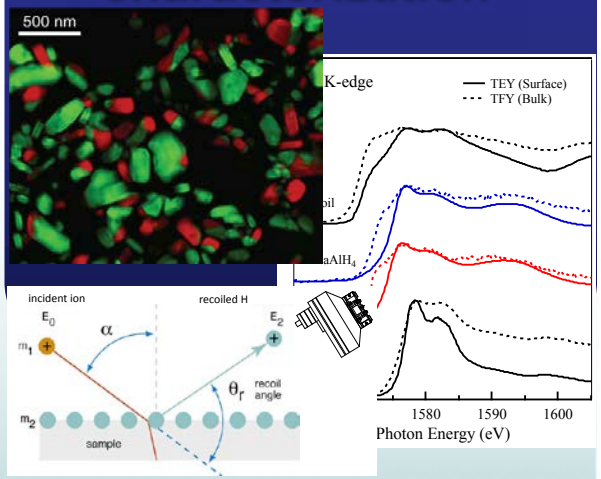
- Quantum Monte Carlo for sorbents
- **DFT and *ab initio* molecular dynamics for bulk/surface/interface chemistry**
- Classical MD & kinetic Monte Carlo for non-equilibrium transport
- Phase-field modeling for solid-state phase transformation kinetics
- **Computational spectroscopy**
- **Community software & databases**

Controlled synthesis



- Metal organic frameworks (MOFs)
- Hierarchical integrated bulk and nanoscale metal hydrides
- High-pressure synthesis
- **Functionalized carbon encapsulants and porous nanoconfining media**
- Sorbent suite for model testing and validation

In situ characterization



- **Ambient-pressure XPS**
- **Soft X-ray absorption and emission spectroscopy**
- **Electron microscopy and X-ray spectromicroscopy**
- Low-energy ion scattering for surface hydrogen detection

Relevance (LBNL-specific): Materials by Design Coupled with Advanced Characterization and Modeling

Project Objectives, overall:

- Focus on **light materials** and synthesis strategies with fine **control of nanoscale dimensions** to meet weight and volume requirements via encapsulation, confinement (A)
- Design **interfaces with chemical specificity** for thermodynamic and kinetic control (E) of hydrogen storage/sorption and selective transport
- Explore **novel storage concepts** and/or obtain **fundamental understanding** of "established" processes via known/idealized systems/materials (O)
- Develop in situ/operando **soft X-ray characterization** capabilities in combination with **first-principles simulations** to extract atomic/molecular details of functional materials and interfaces (O)
- Refine chemical synthesis strategies based on atomic/molecular scale insight from characterization/theory

Establish expertise and capabilities for the H_2 storage community

Relevance

FY17 Project Objectives:

- Develop more complete model for metal hydride-graphene interface based upon X-ray spectroscopy and theoretical modeling
- Translate insights from nanoscale Mg to higher capacity materials (e.g. $Mg(BH_4)_2$)
- Advance tools to enable in-situ X-ray spectroscopic experiments on buried interfaces in metal hydrides
- Develop synthesis to enable targeted extrinsic doping using graphene nanoribbon based systems
- Perform accurate simulations of high-pressure H_2 sorption in MOFs based upon information from CoRE database
- Share insights on nanoencapsulant expertise and in-situ X-ray spectroscopy to benefit D.J. Liu (ANL) seedling project – initially on graphene-wrapped $NaBH_4$
- Begin discussion with G. Severa (UHi) seedling project on etherates for $MgBH_4/MgB_2$ based on previous ether/BH_4 dissolution work

Technical Approach: Contributions of LBNL to HyMARC, Integration Across All Tasks, Access to All Labs

Tasks	LBNL Team:
2,3,4,5	**Jinghua Guo** (jguo@lbl.gov): X-ray synchrotron spectroscopy
2,3,4,5	**David Prendergast** (dgprendergast@lbl.gov): Computational spectroscopy
1,4	**Jeff Urban** (jjurban@lbl.gov): Phase transitions and nanoscale effects in hydrides
1,5	**Gabor Somorjai** (gasomorjai@lbl.gov): Functional sorbents
1	**Felix Fischer** (ffischer@lbl.gov): Functionalized graphene nanoribbons
6	**Maciek Haranczyk** (mharanczyk@lbl.gov): Materials genome for porous materials

Entire HyMARC Team accessing LBNL BES User Facilities

The Molecular Foundry (TMF):

- synthesis, characterization, and simulation of nanoscale materials/interfaces
- National Center for Electron Microscopy
- access to supercomputing (NERSC) through existing Foundry allocations

Advanced Light Source (ALS):

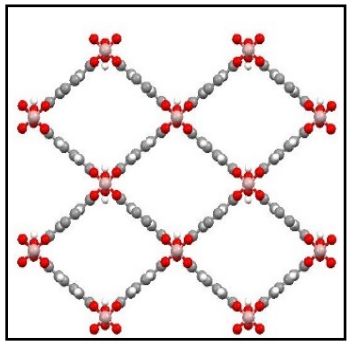
- Soft X-ray absorption/emission spectroscopies (XAS/XES) – in situ
- Ambient Pressure XPS
- Scanning Transmission X-ray Microscopy (STXM) and Ptychography

Active user projects at TMF and ALS and Approved Program Proposal @ ALS

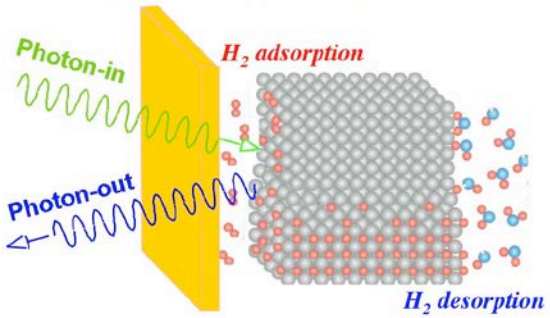
- partnership to foster a new soft X-ray H_2 storage user community

Technical Approach: Matched Novel Synthesis, Characterization, and Modeling for Storage Materials

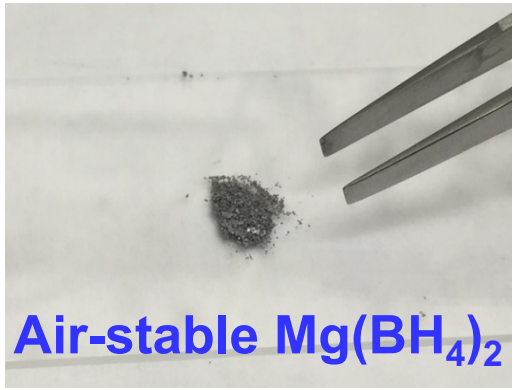
Theory & Design of Storage Materials



Characterization



Synthesis & Performance Evaluation



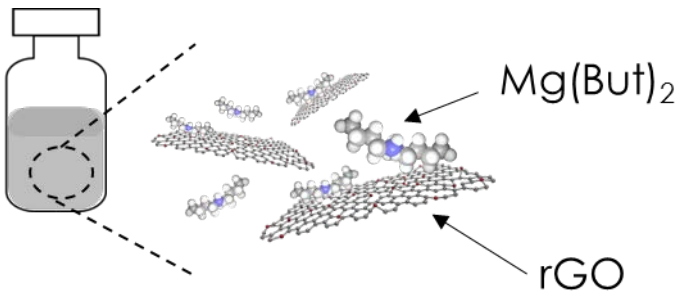
- Enabling approach: **user projects acquired for Molecular Foundry and ALS**
- Innovative synthetic routes to metal hydrides and hybrid nanoscale systems to reveal key phenomena governing H_2 release/absorption and motivate new H_2 storage materials
- Developing new acid/base concepts to modify the enthalpy of H_2 binding in sorbents
- Creating algorithms to enable computation of H_2 isotherms in framework materials
- *In-situ* spectroscopic and structural characterization techniques that establish the role of interfaces in controlling H_2-storage reaction mechanisms and pathways;
- Computational modeling of structure, chemistry and dynamics of interfaces and additives for nanoscale H_2 storage systems and interpretation of X-ray spectroscopy

Planned Milestones and Status: FY17 and FY18

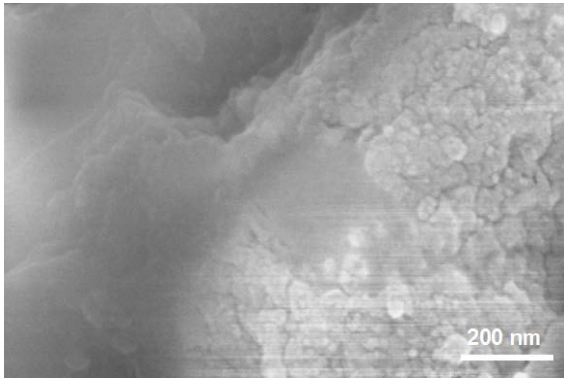
Milestone (revised)	Description	Status*
Q3 FY16	Demonstrate in-situ soft X-ray AP-XPS, XAS, XES tools, with sample heating	100
Q4 FY16	Identify hydride mobile species and diffusion pathways	100
Q4 FY16	Synthesize library of nanoparticles: 1 – 5 nm, 5 – 10 nm, >10 nm for one prototype hydride	100
12/31/17	Use QMC, DFT, and force fields to compute H_2 binding and select appropriate levels of theory for MOFs.	50
9/30/17	Sensitivity analysis of local binding and second-sphere effects	20
3/31/17 Go/No-go	Rank improvement strategies for sorbents. Decision criterion: select 2 with greatest potential for increasing $\Delta H°$	100
6/30/17	Modify LEIS instrument to enable laser-induced thermal desorption	100
9/30/17	Evaluate additive/composite strategies for improving effective ΔE	20
9/30/17	Prototype hydride surface and interface chemistry kinetic models	100

Accomplishment: Synthetic control over $Mg(BH_4)_2$ nanoparticle stability & phase - *Tasks 1,4 (Urban)*

Solution-phase synthesis to control the phases of $Mg(BH_4)_2$ stablized by rGO (~250nm flakes)

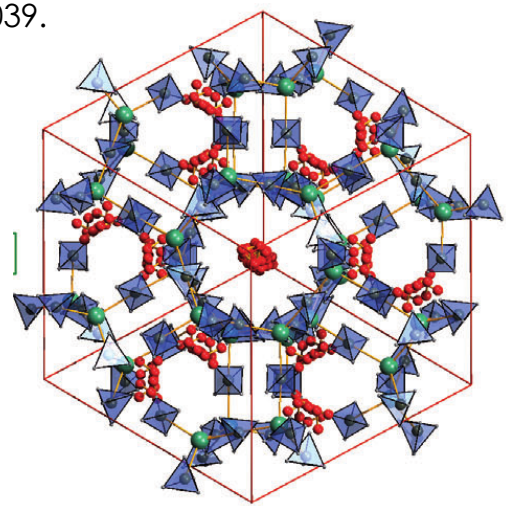


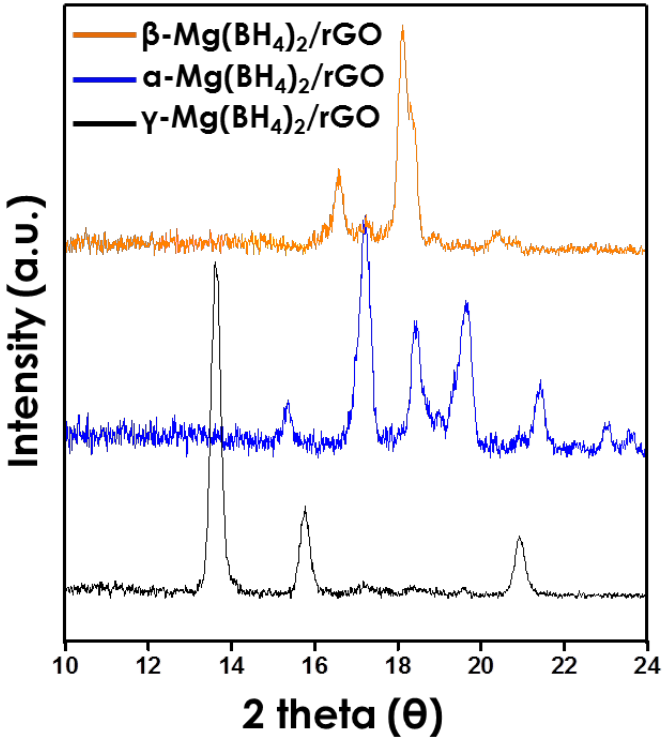
$Mg(BH_4)_2$ NPs < 50 nm



Zanella *et al. Inorg. Chem.* **2007**, *46*, 9039.

Phase determination by PXRD





14.9 at% H

dense phases:

- **α (117 g H_2/L)**
- **β (113 g H_2/L)**

porous phase:

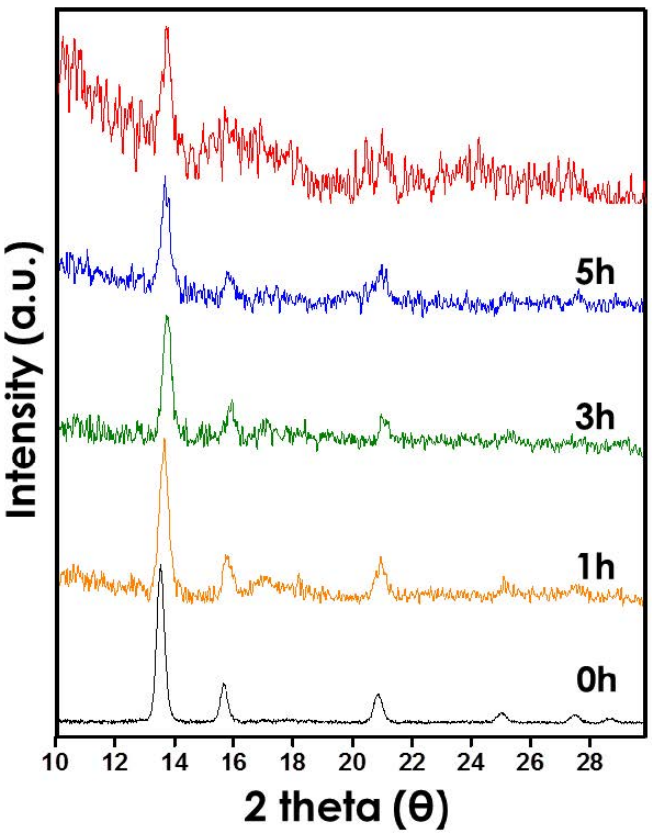
- **γ (82 g H_2/L), up to +3 at% H physisorbed**

Filinchuk *et al. Angew. Chem.* **2011**, *123*, 11358.

Accomplishment: Air stability in γ-$Mg(BH_4)_2$/rGO – *Tasks 2,3,4 (Urban)*

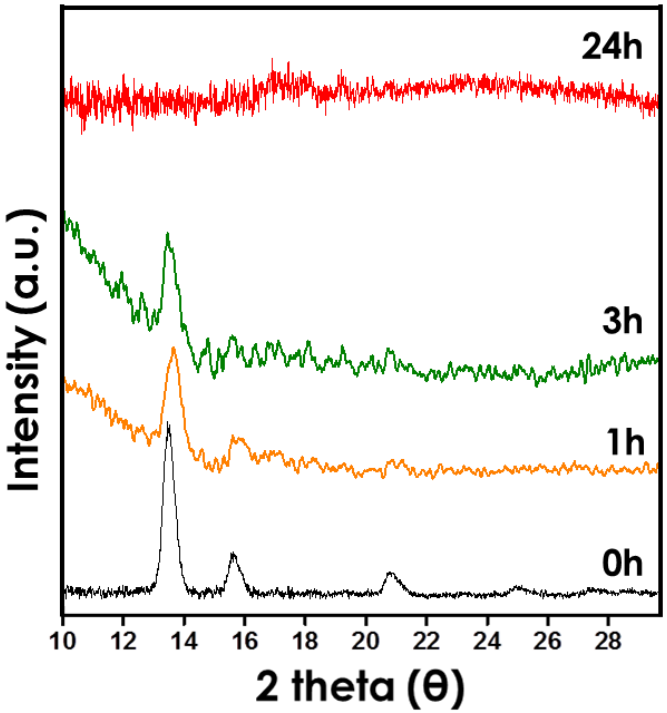
Enhanced air stability of γ-$Mg(BH_4)_2$/rGO vs. γ-$Mg(BH_4)_2$

γ-$Mg(BH_4)_2$/rGO



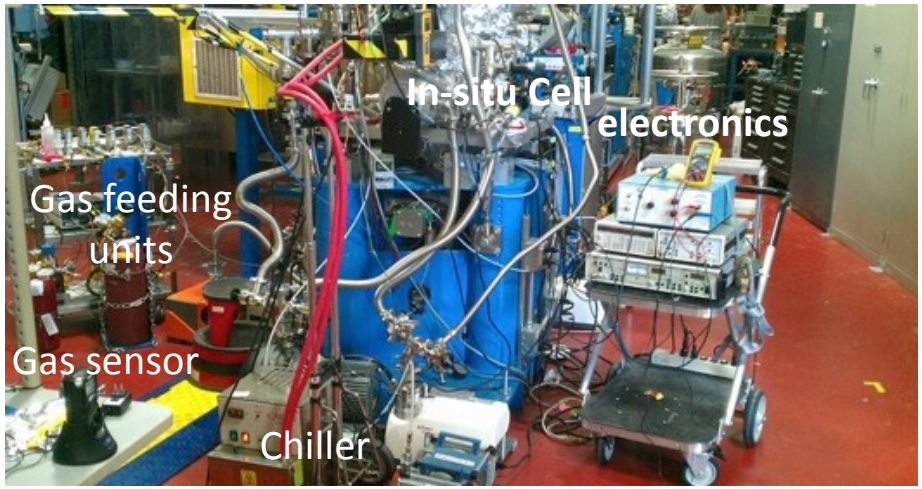
* All $Mg(BH_4)_2$/rGO samples are measured under air

γ-$Mg(BH_4)_2$

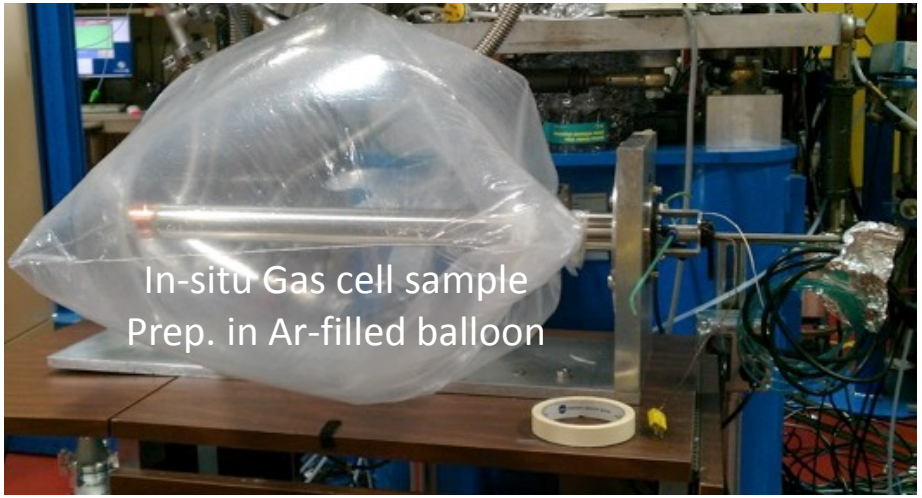


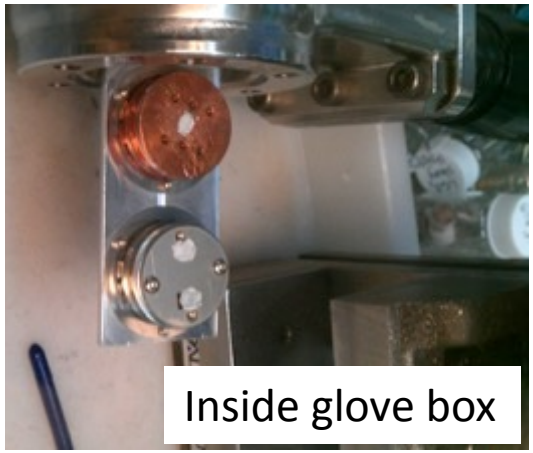
* $Mg(BH_4)_2$ sample at 0h is measured with capillary tube

Accomplishment: in-situ characterization capability at the ALS – *Tasks 1-5 (Guo)*

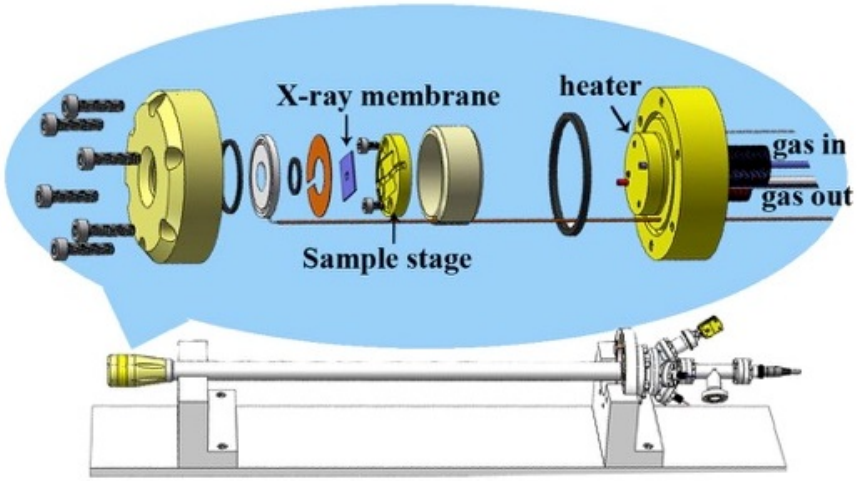


Vacuum suitcase





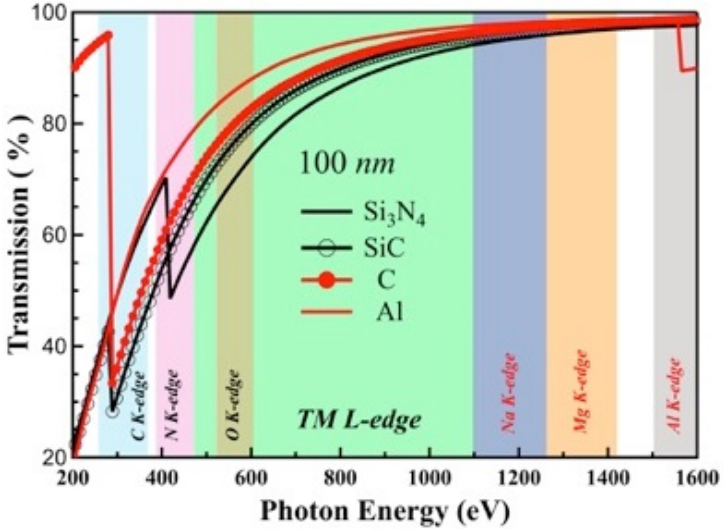
Accomplishment: in-situ H_2 gas cell for X-ray beam-line – *Tasks 1-5 (Guo)*

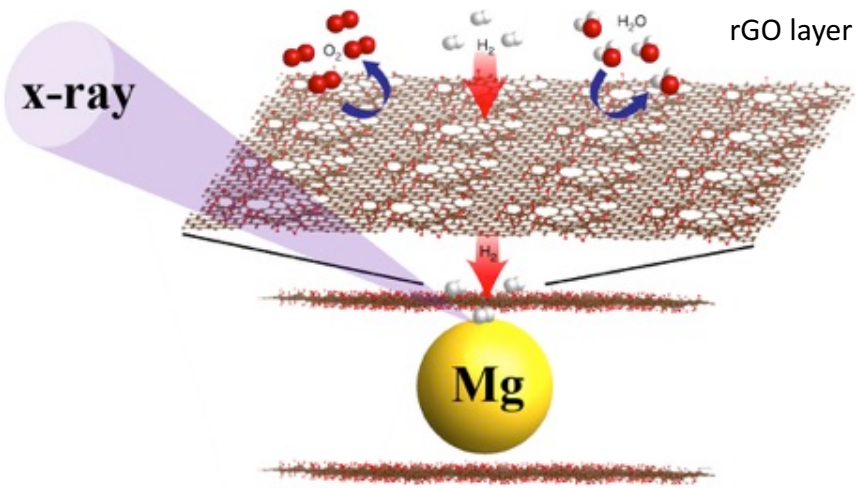


Specification:

- *A few bars environment*
- R.T. to 300°C
- Better gas-sealing, ideal for dehydrogenation process

X-ray membrane transmission

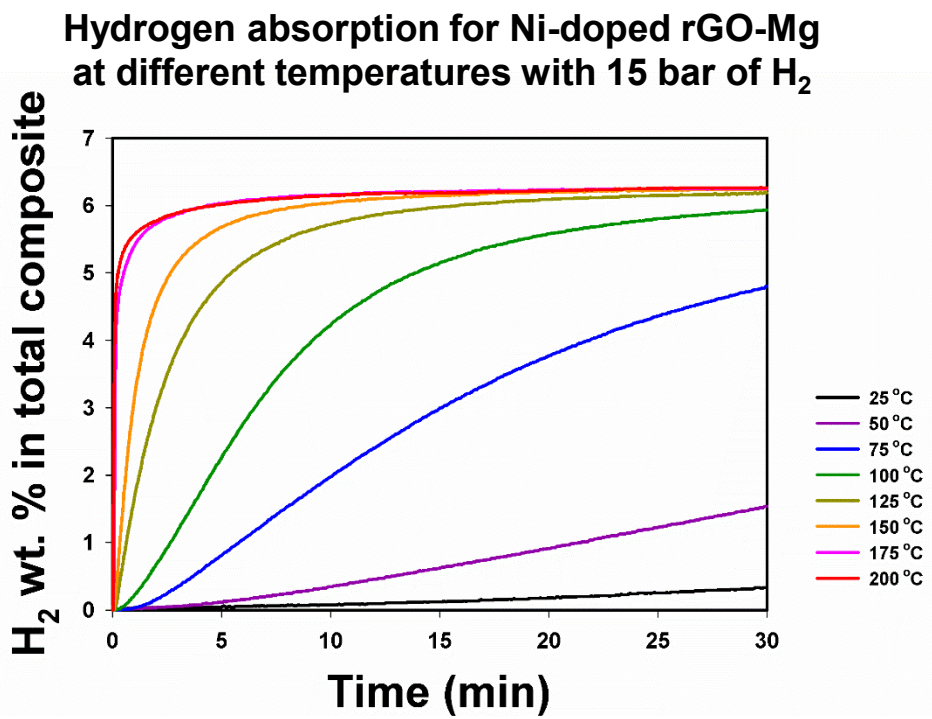


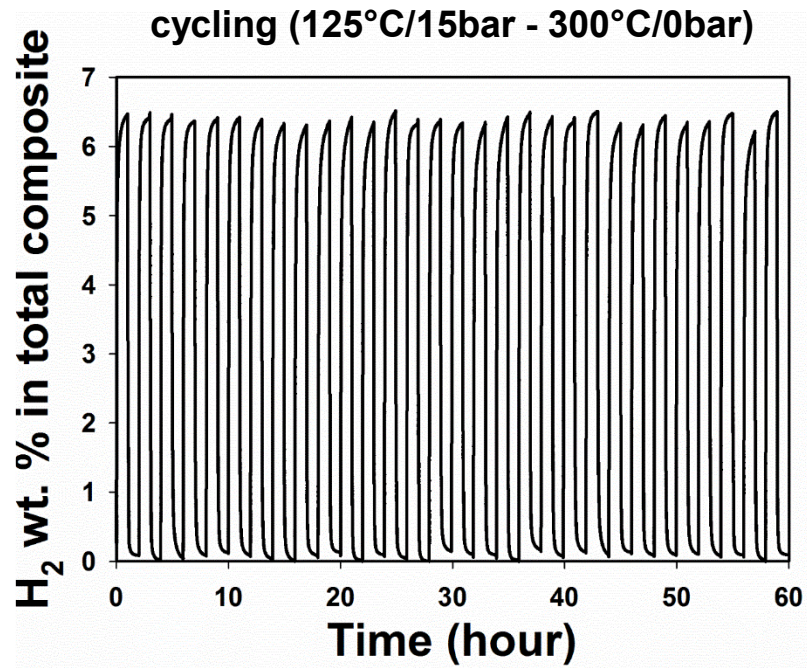


Courtesy: Eun Seon Cho

Accomplishment: 3d-Transition Metal (TM) doped rGO-Mg absorbs H_2 at 1 bar and as low as 75° C - *Tasks 4,5 (Urban, Klebanoff)*

5 mol.% TM dopants increase hydrogen sorption rates without sacrificing the high hydrogen capacity of rGO-Mg.



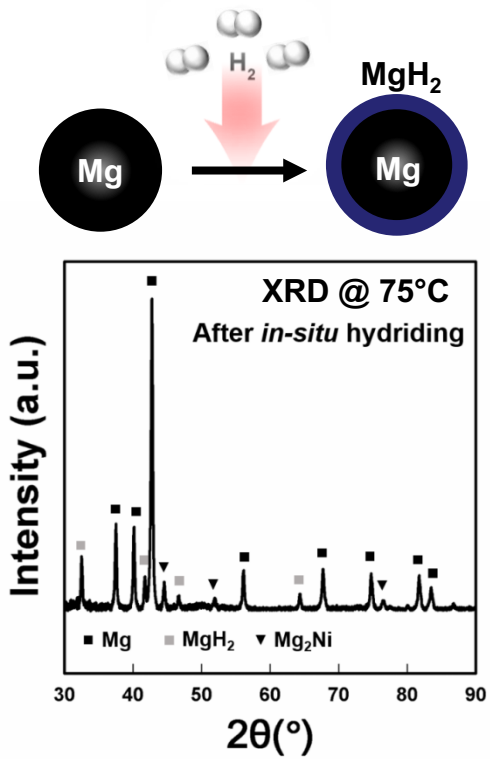


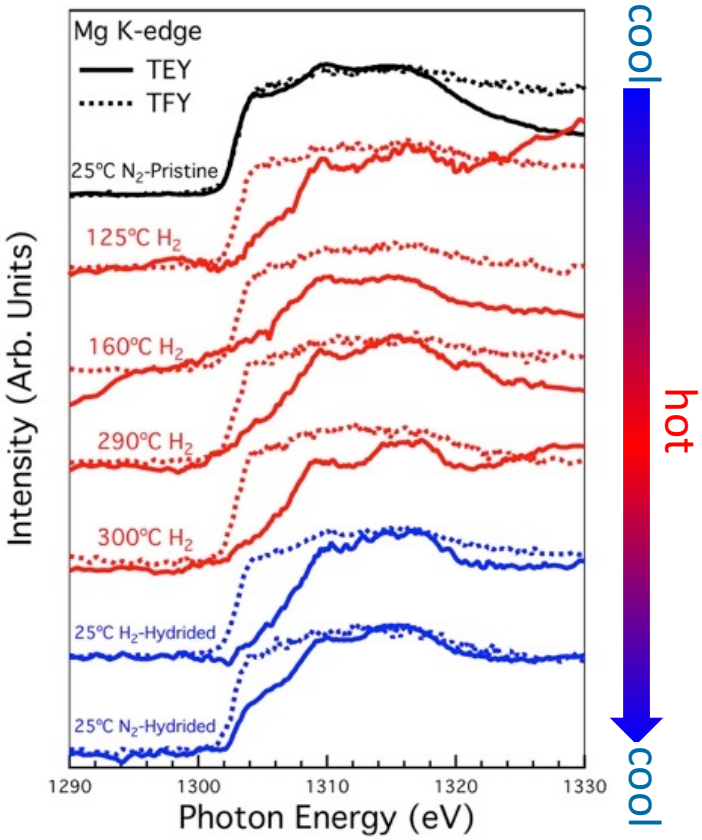
- Different kinetics were observed depending on the dopants.
- Ni-doped rGO-Mg is fairly reproducible in further cycles with highly enhanced kinetics.

E.S.Cho et al, *submitted*

Accomplishment: Observation (*In-Situ* XAS) of hydride formation at 1 bar (Ni-doped rGO-Mg) – *Task 5 (Guo, Lee, Urban, Klebanoff)*

We can observe hydride formation *in-situ* at a pressure of 1 bar





Shift of Mg K-edge to higher energy indicates that the surface forms a hydride – even at the relatively low pressure of 1 bar!

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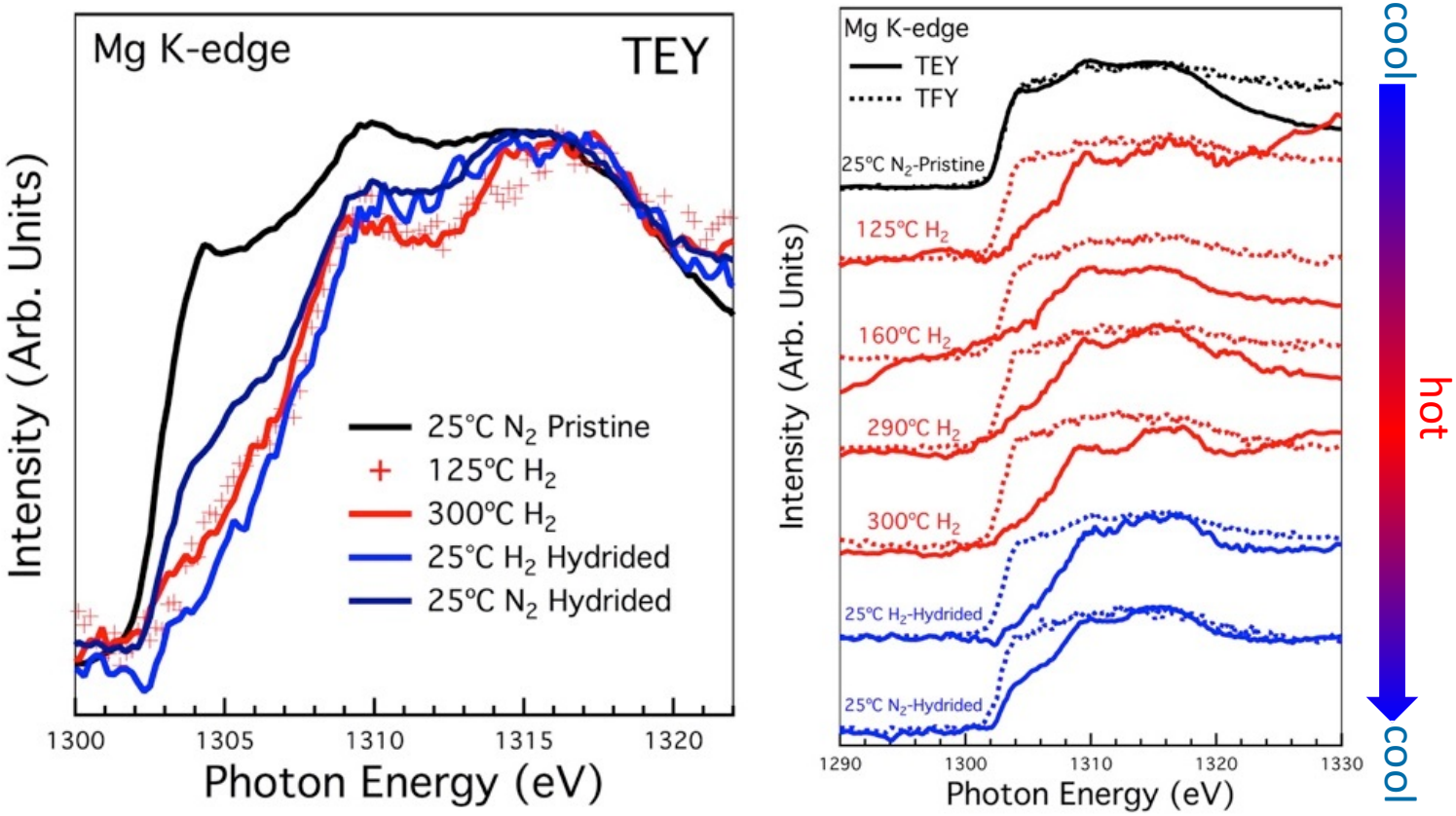

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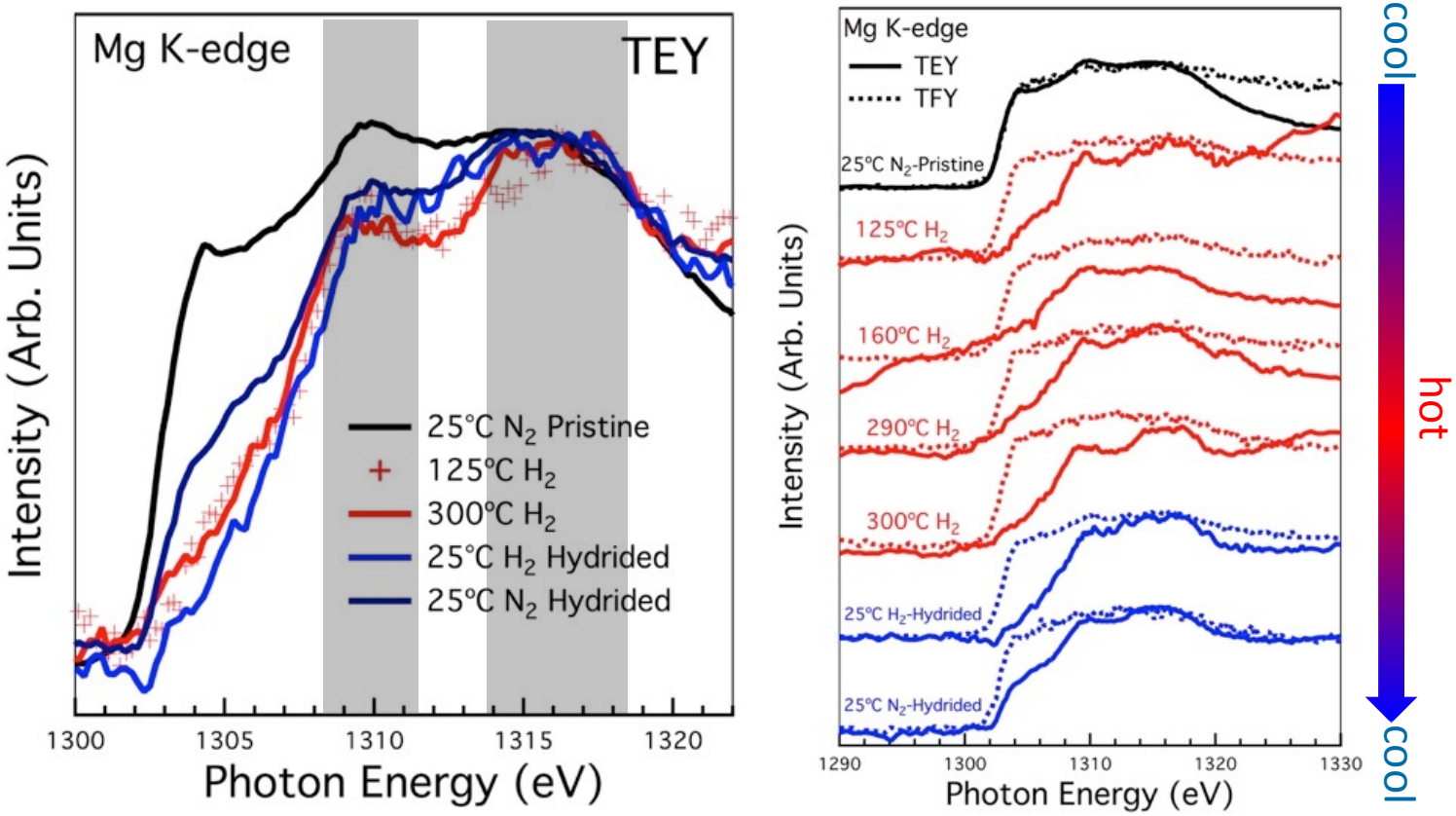
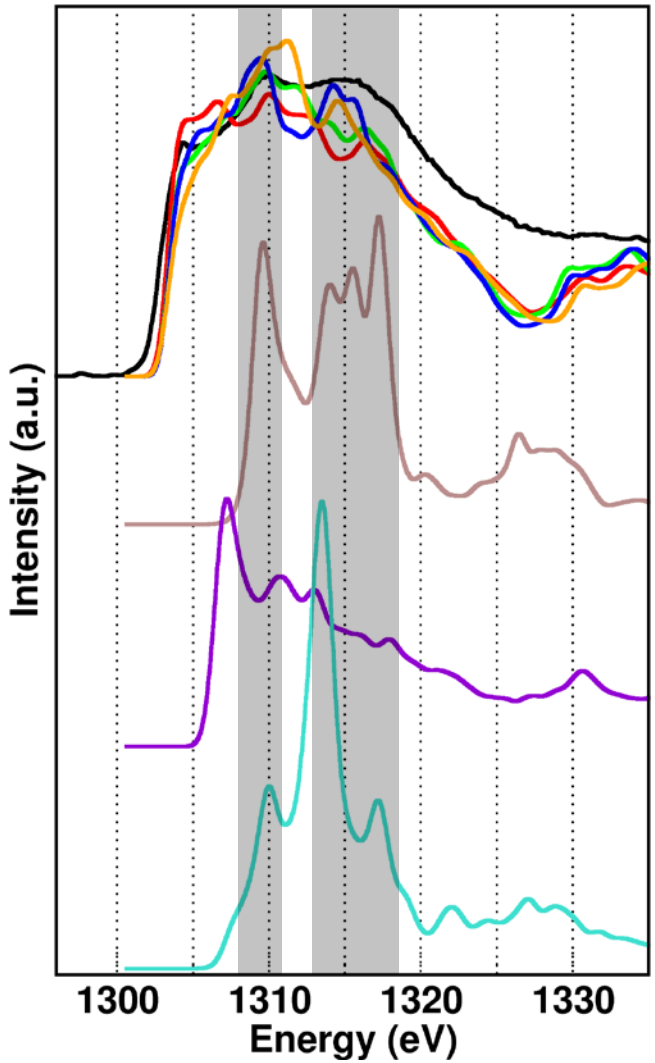


Additional peaks not expected for Mg metal or hydride…

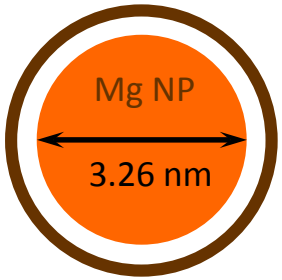
Accomplishment: DFT simulations and XAS interpretation consistent with slight oxidation at Mg-graphene interface – *Task 4 (Prendergast)*



- TEY RT (Exp. before hydrogenation)
- Mg metal
- Graphene/MgO/Mg
- Graphene/Mg(OH)/Mg
- Graphene/Mg(OH)-disso/Mg
- MgO Ref.
- MgH_2 Ref.
- $Mg(OH)_2$ Ref.

Model encapsulated oxidation

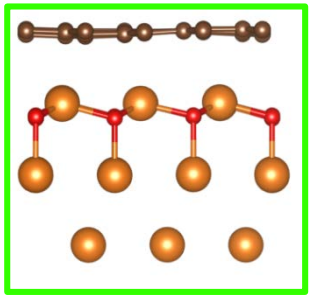
graphene oxide (C:O ~ 2:1)

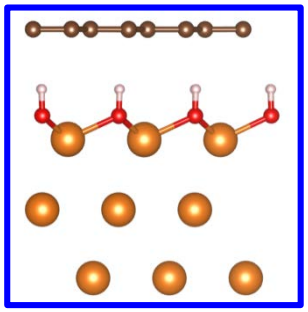


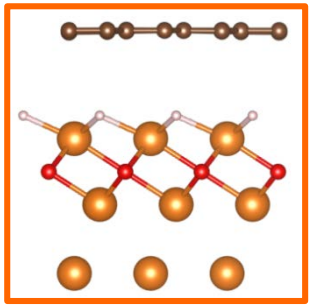
Oxygen in GO forms hydroxyls (edges) and epoxides (basal plane).

Hypothesis: transfer inner O to Mg surface

O:Surface Mg ≈ 1:1 for ~3nm NPs



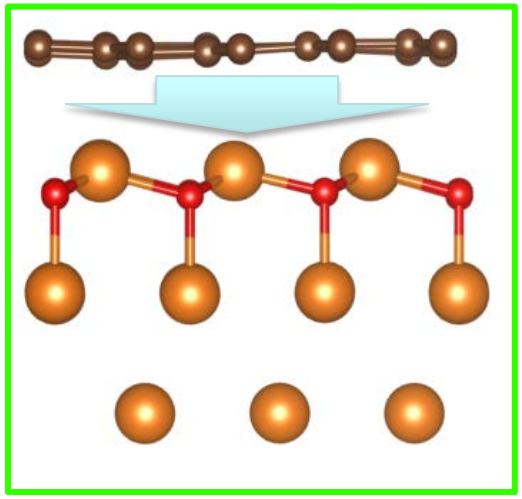




L. F. Wan et al, *in preparation*

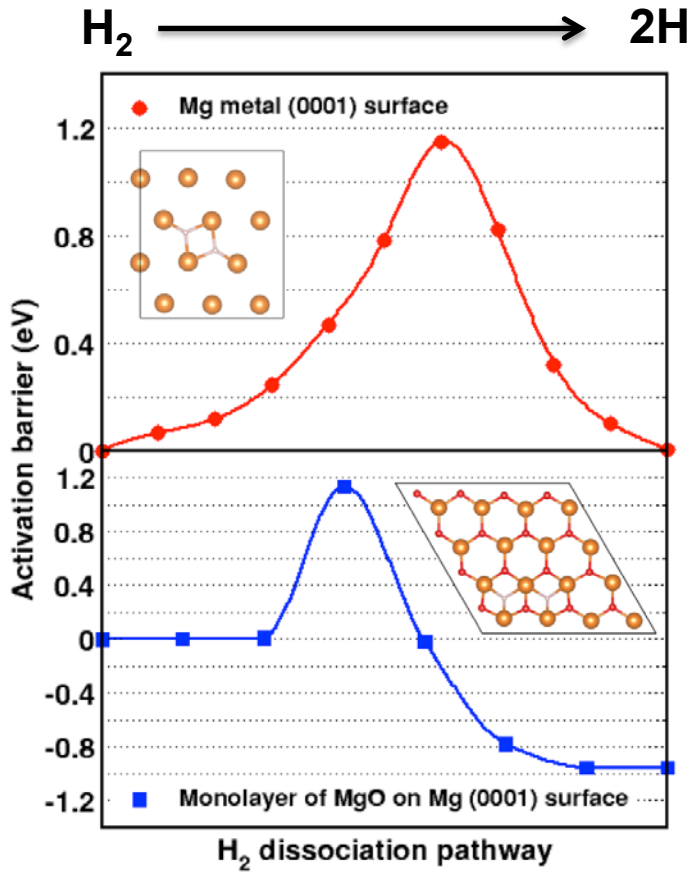
Accomplishment: DFT simulations indicate surprising functional advantages of Mg interfacial oxidation – *Task 4 (Prendergast)*

Oxidized surface enhances graphene attraction to NP



3.6Å on Mg → 2.9Å on MgO/Mg

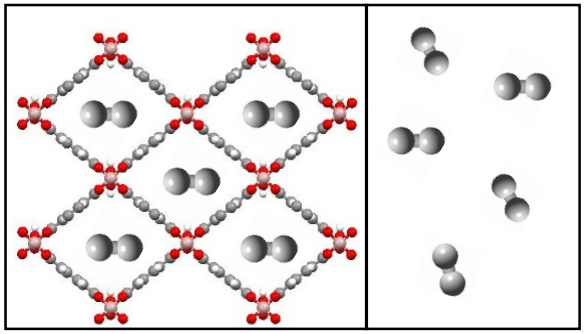
H_2 dissociation enhanced on oxidized surface



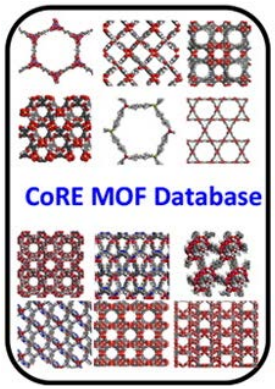
L. F. Wan et al, *in preparation*

Accomplishment: Methodology to compute H_2 adsorption sampling across large MOF database; Sensitivity to H_2 parameters – *Task 6 (Haranczyk)*

Jeff Camp, Vitalie Stavila, David Prendergast, and Maciej Haranczyk



GCMC
constant μ,V,T
variable number of
H_2 adsorbates



Simulation inputs:

1. Structures: MOF framework coordinates + H_2 geometry
2. Energetics: potentials for H_2 – MOF and H_2– H_2 interactions
3. Equation of state:
   - Fugacity coefficients
   - Absolute adsorption → excess adsorption conversion

Simulation outputs:
excess and absolute adsorption isotherms

Structures models from our Computation-Ready Experimental MOF database[1]

H_2 potentials: 3-site and 5-site models that include dispersion and electrostatic interactions

NIST hydrogen equation of state[2] and Peng-Robinson equation of state compared to NIST reference data for H_2 densities and fugacities[3]

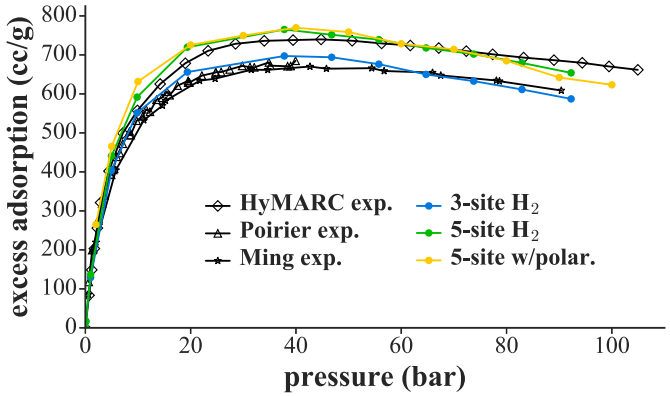
1. Chung, Y. G.; Camp, J.; Haranczyk, M. et al., Computation-ready, experimental metal-organic frameworks: A tool to enable high-throughput screening of nanoporous crystals. *Chemistry of Materials* **2014**, *26*, 6185-6192.
2. Lemmon, E. W.; Huber, M. L.; Leachman, J. W., Revised standardized equation for hydrogen gas densities for fuel consumption applications. Journal of Research of the National Institute of Standards and Technology **2008**, *113*, 341.
3. Zhou, L.; Zhou, Y., Determination of compressibility factor and fugacity coefficient of hydrogen in studies of adsorptive storage. Int J Hydrogen Energ **2001**, *26*, 597-601.

Accomplishment: GCMC simulations accurate up to high-P at 77K – Task 6 (Haranczyk)

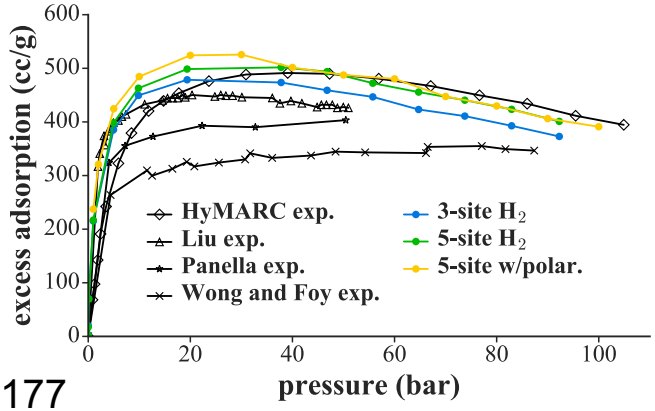
J. Camp
M. Haranczyk

Predictions vs. Experiment (Stavila/HyMARC and lit. data)

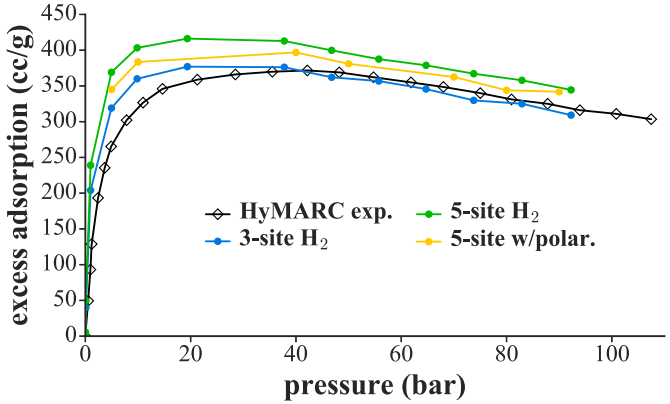
MOF-5



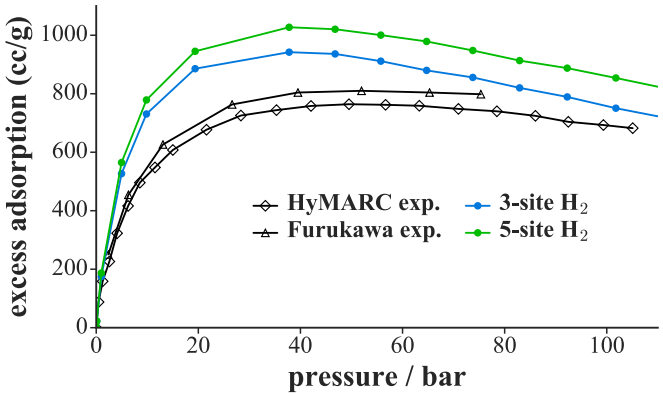
HKUST-1



ZIF-8



MOF-177



⇒ ***GCMC calculations can be used to accurately predict the hydrogen adsorption isotherms in MOFs with and without open metal sites at 77 K***

⇒ *manuscript in progress*

Response to 2016 AMR Reviewer Comments

"Project Weaknesses"

- Possibility of too much overlap with ST-129 on carbon-coating H_2 storage materials
  - The carbon coating efforts in ST-129 are a completely different approach.
- Lack of specifics w.r.t. how it will interact with the Characterization and Validation team
  - In situ hydride formation from XAS and theoretical investigations to understand the origins and role of partial surface oxidation
- Justification of materials selection is lacking
  - Our focus is on viable materials such as $Mg(BH_4)_2$. Prior Mg work used as a model system for validation of methods and theory.
- Project appears "too defocused"
  - We have worked to highlight the merits of HyMARC's approach in all presentations.

"Recommendations for additions/deletions to project scope"

- The team should identify the test/validation platform demonstrated by each material system
  - We have clarified which aspects of material properties, i.e. thermodynamics, internal interfaces, etc., we are addressing.
- The project should remove three research areas: metal hydride encapsulation, Lewis acid on silica templates, and plasmonics
  - We argue that metal hydride encapsulation is important. The Lewis acid on silica templates work is completed. The plasmonics work is important and we are making an effort to justify it's merit.
- The project should drop the aluminosilicate materials effort.
  - Done.

Collaborations

- HySCORE team (Long, UC Berkeley; Gennett, NREL)
- Godwin Severa, U of Hawaii (seedling project) – *molecular dynamics simulations of BH_4/etherate coordination of Mg*
- D.J. Liu, ANL (seedling project) – *initial discussions of X-ray spectroscopic characterization of $NaBH_4$ NPs in graphene*
- Agiltron, Inc. Scale up of encapsulated metal hydrides via SBIR
- Aaron Thornton (CSIRO Australia) and Berend Smit (UC Berkeley/EPFL)
- University of Cape Town (South Africa) – *in-situ* time-resolved XRD of GNR-Mg composites

Remaining Challenges and Barriers

- Achieve phase purity and size control in synthesis of encapsulated $Mg(BH_4)_2$ materials
- Incorporate theoretical insights on graphene-hydride interface into advanced synthesis of these materials
- Increasing operating parameter range for in-situ XAS cell to better match hydriding conditions (currently 1 bar, low-T)
- Assess possibility of accurately modeling sorption in MOFs ab initio (vs. relying on database parameters)
- Understanding coordination/reactivity of $Mg(BH_4)_2$ with oxide and graphene interfaces
- Mechanistic theoretical understanding of the role of etherates in $Mg(BH_4)_2/MgB_2$ with G. Severa, UHi (seedling)
- In-situ X-ray characterization of complex hydride/graphene nanoparticles with D.J. Liu, ANL (seedling)

Proposed Future Work

- Further develop *in-situ* XAS cell for operating at higher temperatures (500° C) and higher H_2 pressure (up to 10 bar)
- *In-situ* study of $MgBH_4$ NPs wrapped by rGO in the dehydrided condition – Task 4
- Mechanistic understanding of enhanced kinetics for functionalized N/O-GNR-MgNP composite
- Determination of reversible hydrogen storage capacity, absorption and desorption kinetics and thermodynamics in cGNR-AlNP composites with characterization and optimization of synthesis (control of Al_2O_3 shell) – Task 4
- $LiAlH_4$ and $NaAlH_4$ under nanostructuring, doping and mechanistic H_2 activation – Task 1
- Collaboration with Sandia on $Mg(BH_4)_2$ and the addition of catalytic additive – Task 5
- Derive protocol to perform simulations of hydrogen adsorption in large MOF database (incl. open metals) without empirical parameters (*ab initio* isotherms)
- In-situ XAS for NaBH4 in graphene from DJ Liu, ANL (seedling)
- MD and rxn kinetic calculations for $Mg(BH_4)_2/MgB_2$-etherate for G. Severa, UHi (seedling)

Any proposed future work is subject to change based on funding levels.

Technology Transfer Activities (optional)

- Agiltron, Inc. collaborating with Urban in Phase 1 SBIR relating to scale up of encapsulated metal hydrides
- HyMARC presented research at annual Tech Team meeting
- 2 new patents, and 3 new records of invention filed in the past year.

Any proposed future work is subject to change based on funding levels.

Summary

- Synthetic-control over various phases of $Mg(BH_4)_2$ NPs in rGO with increased air stability
- Development of *in-situ* H_2 XAS capability at ALS for absorption/desorption experiments
- *In-situ* XAS measurements of Ni-doped rGO-Mg up to H_2 pressure of 1 bar
- Understanding of presence and advantages of interfacial oxidation in rGO-Mg based on DFT calculations
- Demonstrated ability to model high-pressure H_2 storage in metal-organic framework adsorbents using classical GCMC, and verified the simulations using experiments run within HyMARC
- Initial discussions and calculations with seedling projects (Liu, ANL and Severa, UHi)

HyMARC Collaboration and Funding Partners

Sandia National Laboratories

Lawrence Livermore National Laboratory

HyMARC

Hydrogen Materials Advanced Research Consortium

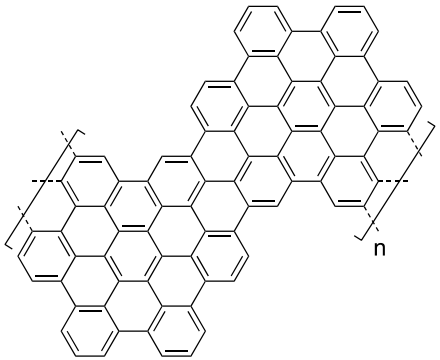
Enabling **twice the energy density** for onboard H_2 storage

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

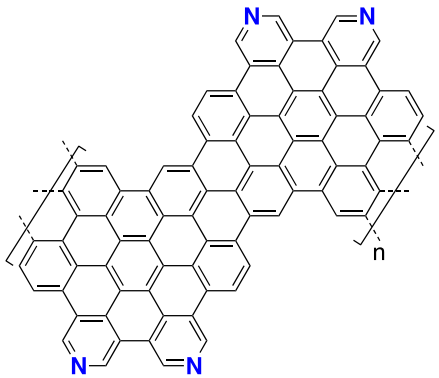
BERKELEY LAB
Lawrence Berkeley National Laboratory

Technical Back-Up Slides

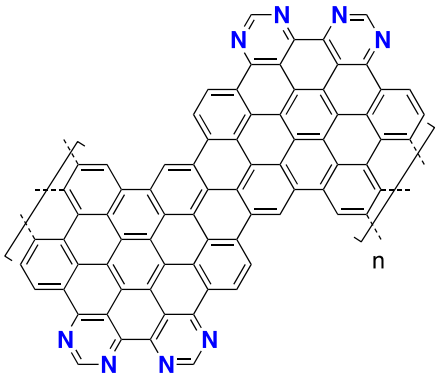
Accomplishment: Synthetic graphene analogs with similar air stability to rGO – *Task 4,5 (Fischer, Urban)*



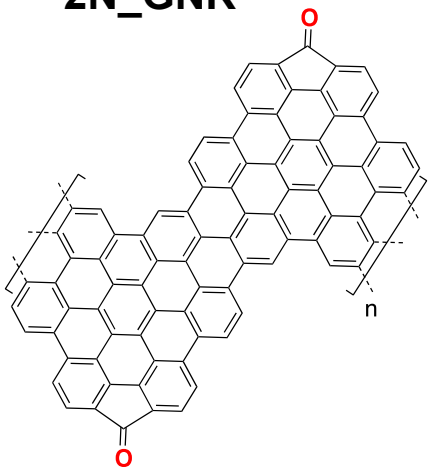
C_GNR



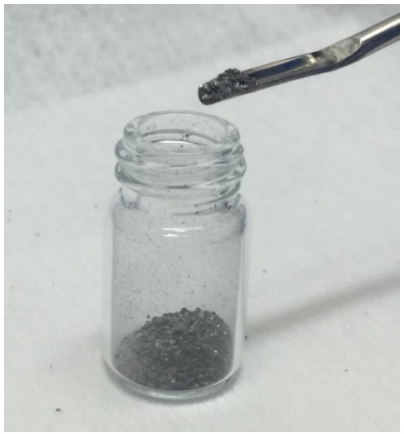
2N_GNR



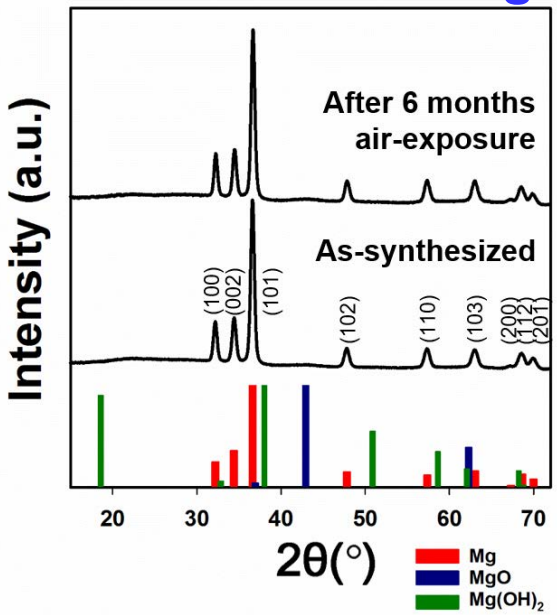
4N_GNR



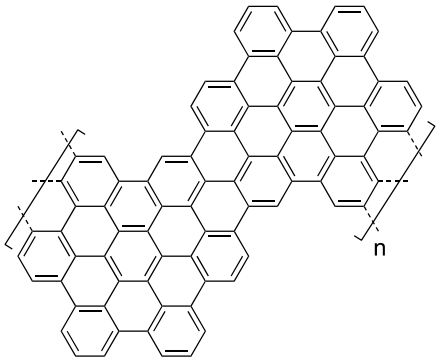
ke_GNR



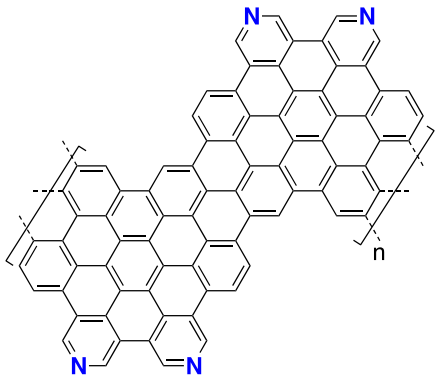
Air-stable GNR-Mg



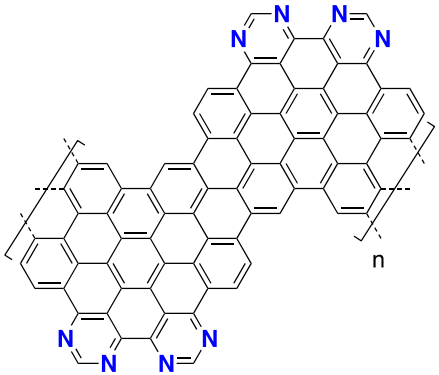
Accomplishment: Functionalization-dependent hydrogen absorption & desorption kinetics in GNR-Mg – Task 4,5 (Fischer, Urban)



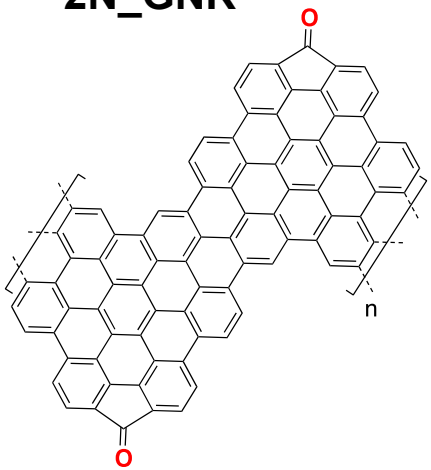
C_GNR



2N_GNR

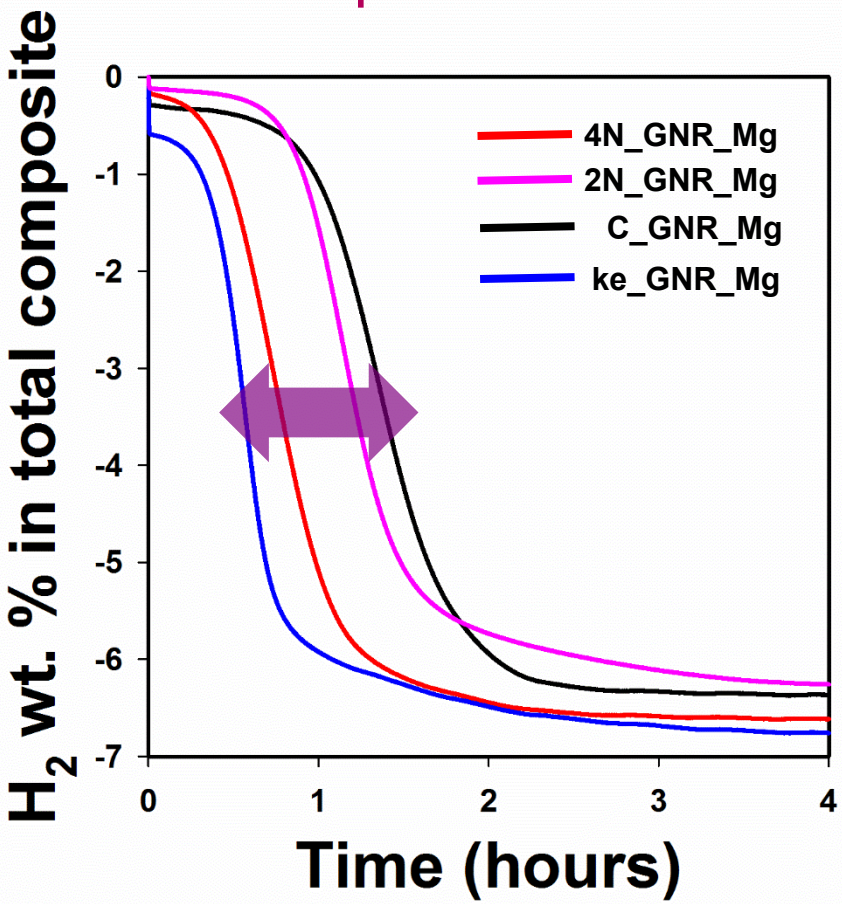


4N_GNR



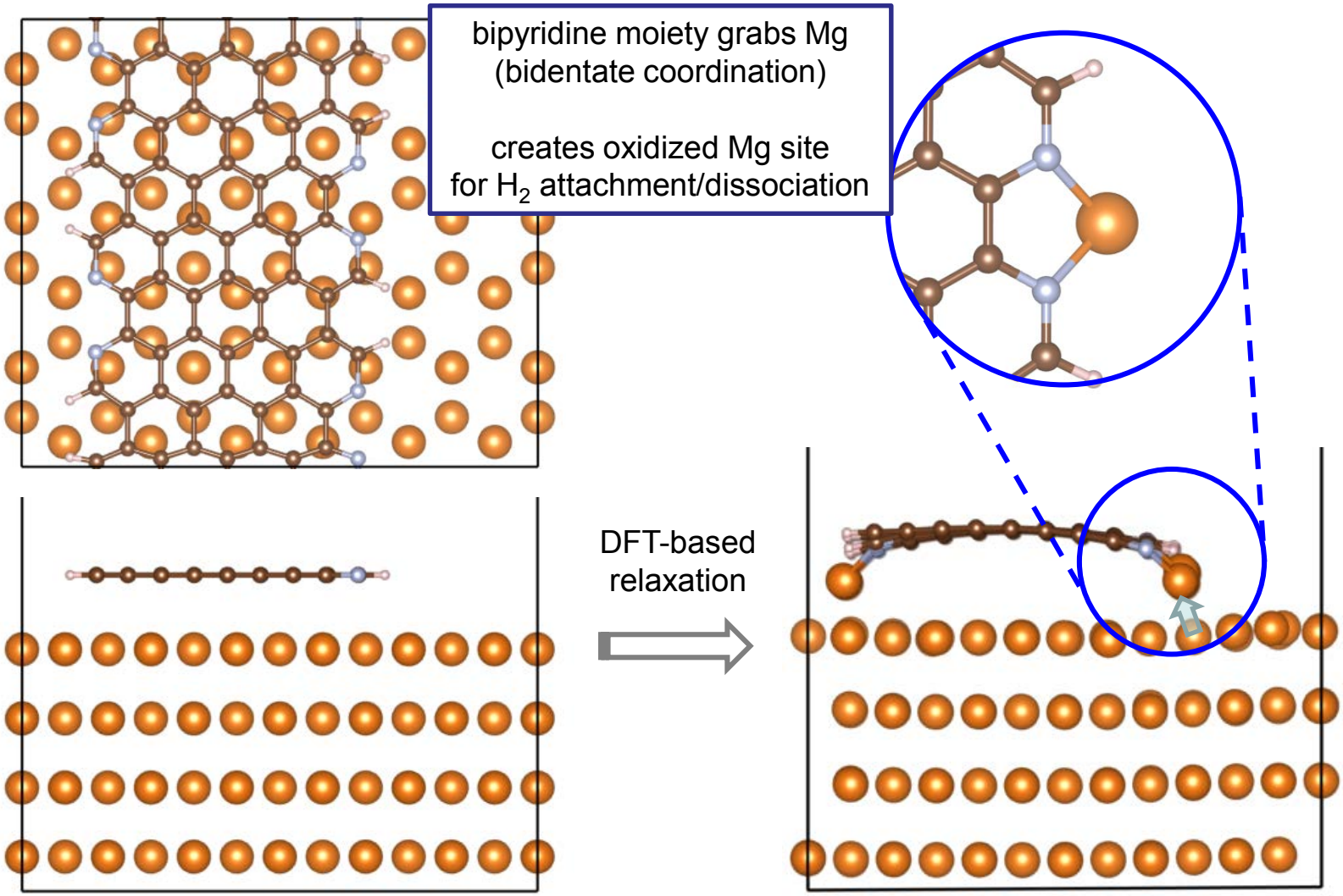
ke_GNR

Desorption at 300 ºC



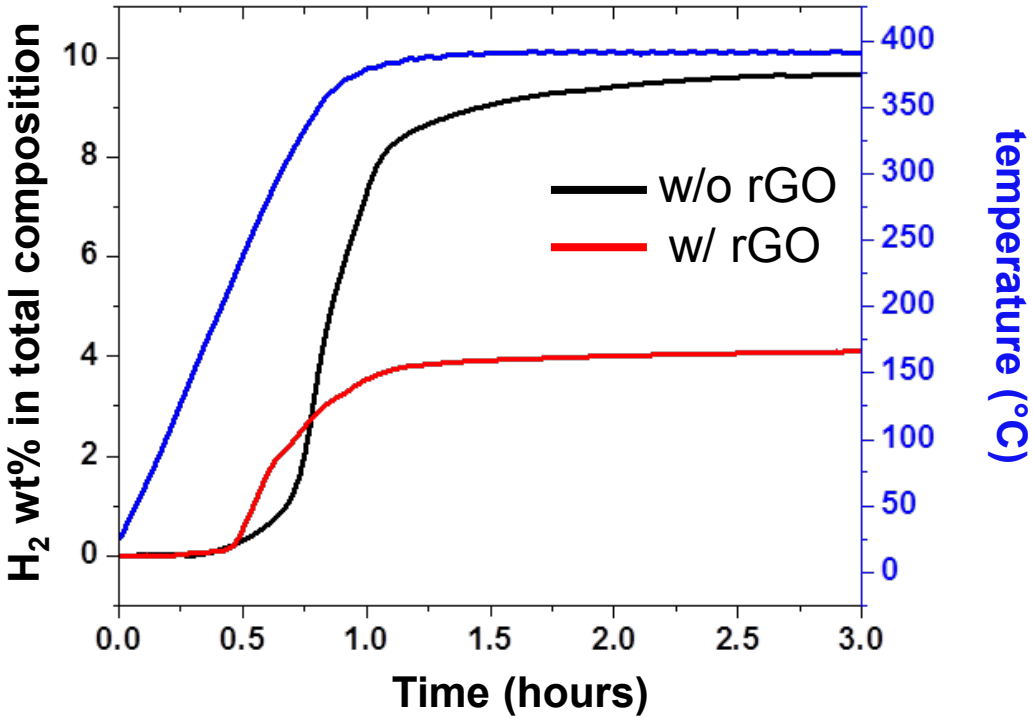
E.S.Cho et al, *in preparation*

Accomplishment: DFT simulations show N-functionalized GNR enhances activity of Mg NP surface – Task 4,5 (Prendergast, Fischer, Urban)



L. F. Wan et al, *in preparation*

Accomplishment: Hydrogen Desorption Kinetic Changes in γ-$Mg(BH_4)_2$ Nanocrystals with rGO – *Tasks 2,4 (Urban)*



- Different kinetics and hydrogen capacity were observed.

- $Mg(BH_4)_2$ **w/o rGO** shows a high hydrogen capacity (9.6 wt%)
- $Mg(BH_4)_2$ **w/ rGO** shows significantly higher rate of hydrogen release

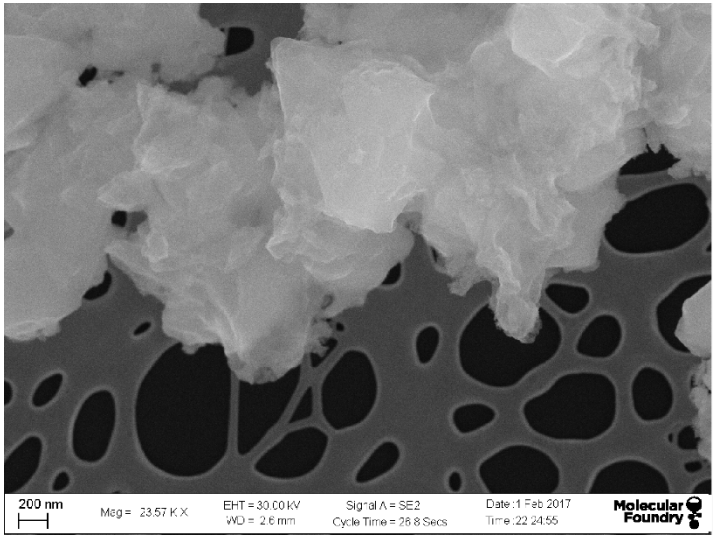
Ligand-Free Synthesis of Stabilized Aluminum Nanoparticle GNR Composite Materials

- **Synthesis**

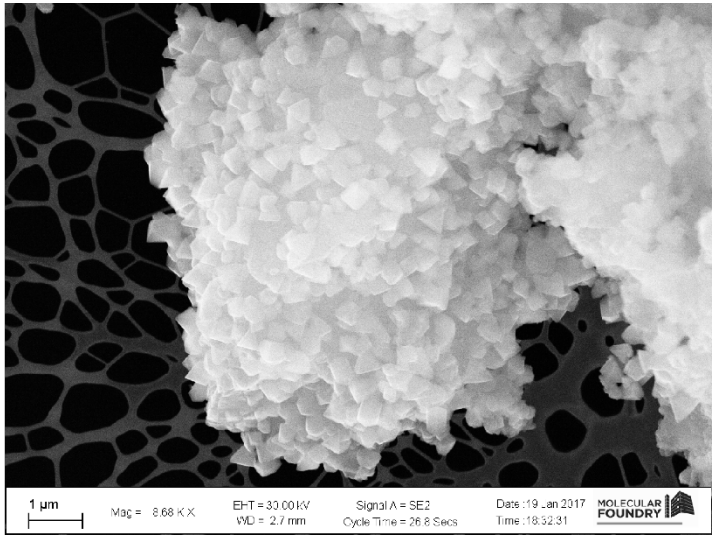
$$AlH_3{\bullet}NMe_2Et \quad + \quad \text{c}\mathbf{GNR}\text{s} \xrightarrow[\text{24 °C, 12 h}]{\text{Ti(O}^{i}\text{Pr)}_4\text{, toluene/Et}_2\text{O}} \text{c}\mathbf{GNR}\text{-AlNP}$$

- **Morphology of nanodisperse Al depends on the structure of the GNRs**

without c**GNR**s amorphous Al_2O_3

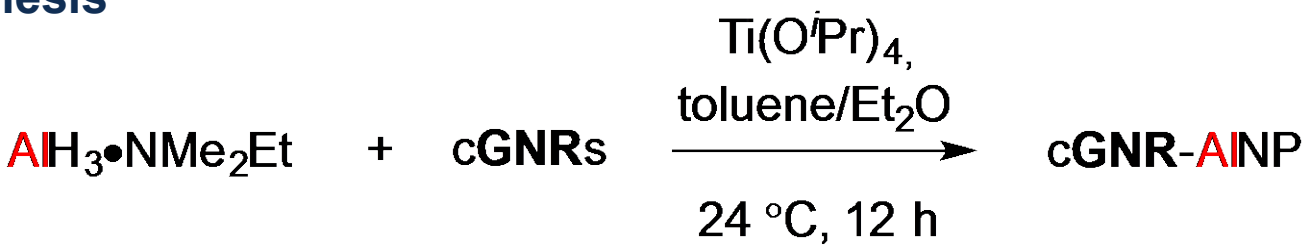


with c**GNR**s crystalline AlNPs



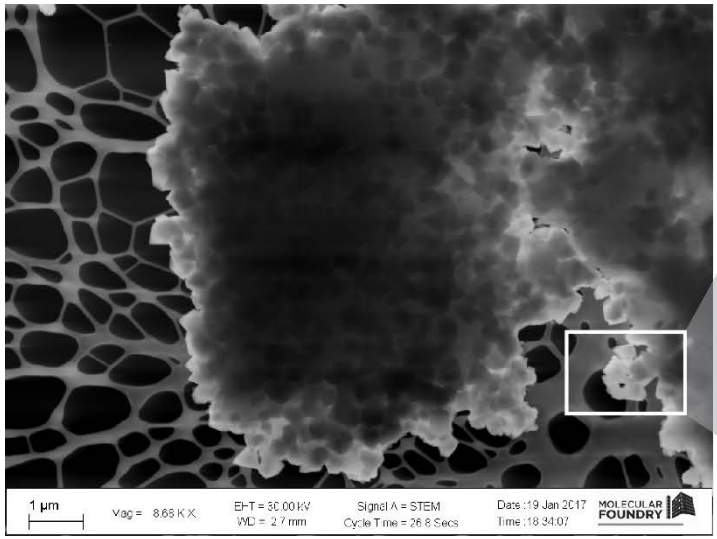
Ligand-Free Synthesis of Stabilized Aluminum Nanoparticle GNR Composite Materials

- **Synthesis**

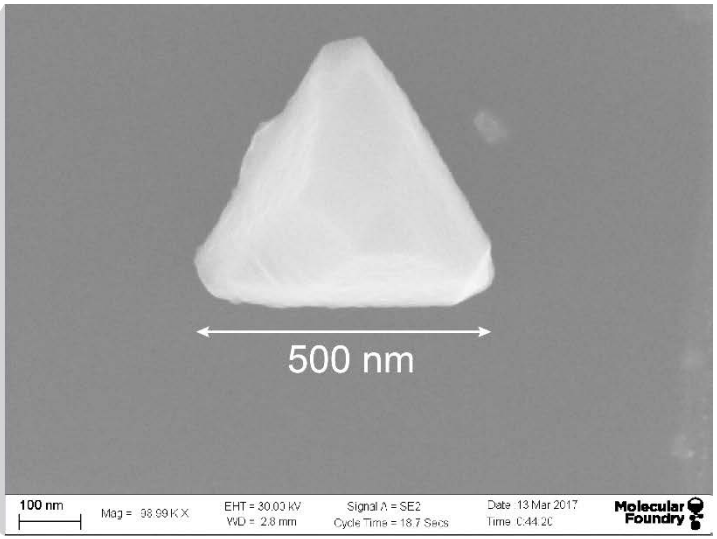


- **cGNR coated AlNPs crystallize in tetrahedral morphology**

STEM reveals clusters of discrete tetrahedral AlNPs

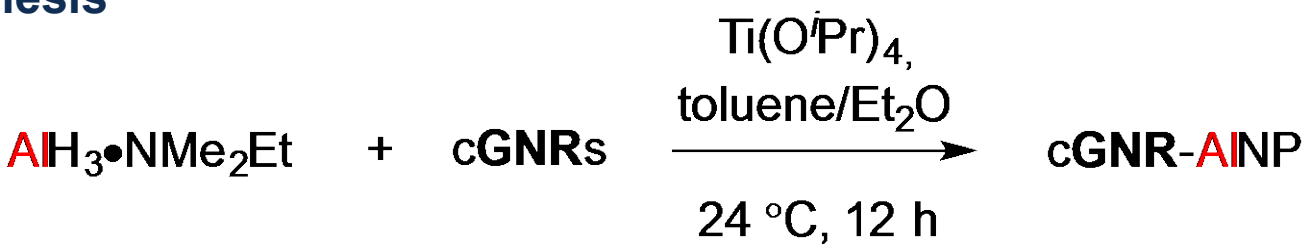


Sonicated samples show largely individual AlNPs



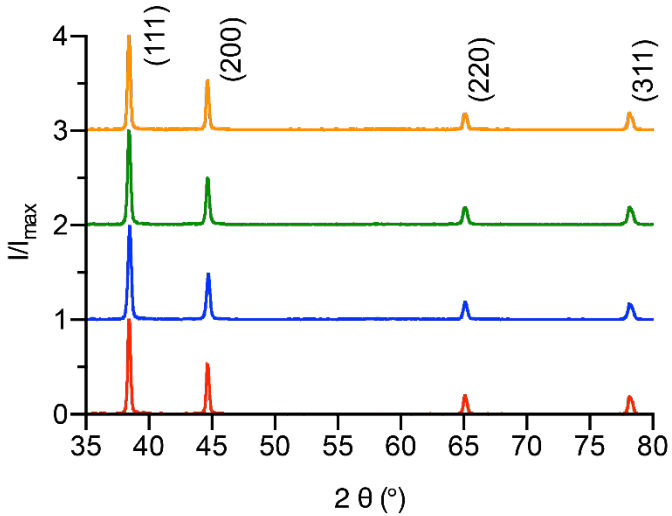
Ligand-Free Synthesis of Stabilized Aluminum Nanoparticle GNR Composite Materials

- **Synthesis**

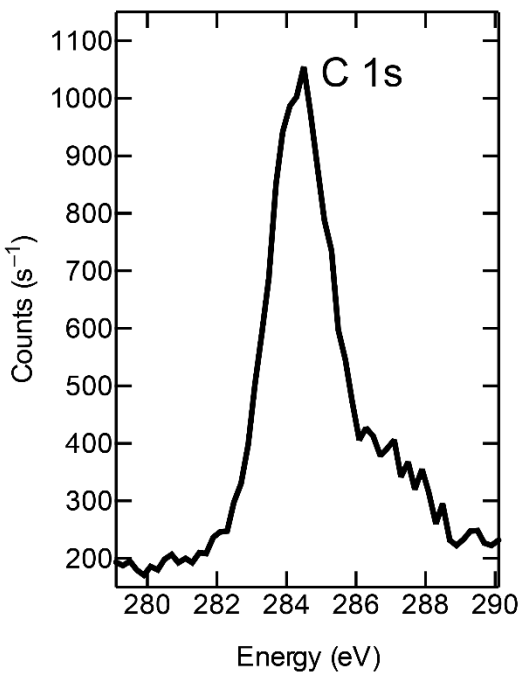


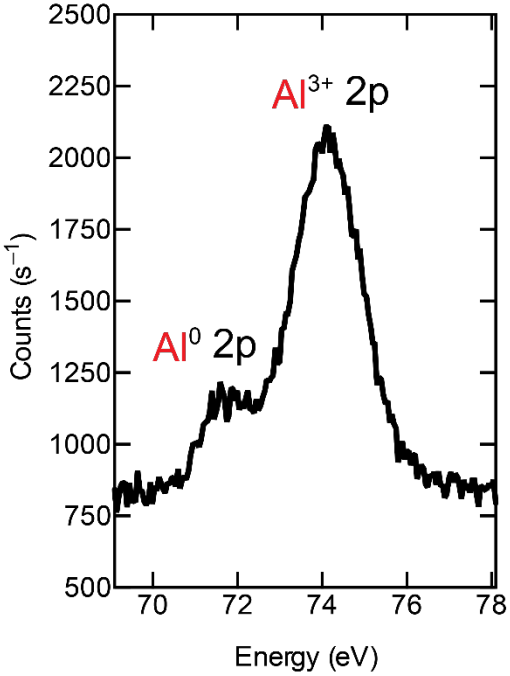
- **Characterization**

PXRD shows diffraction pattern of metallic Al



XPS shows AlNP are coated with thin Al_2O_3 layer

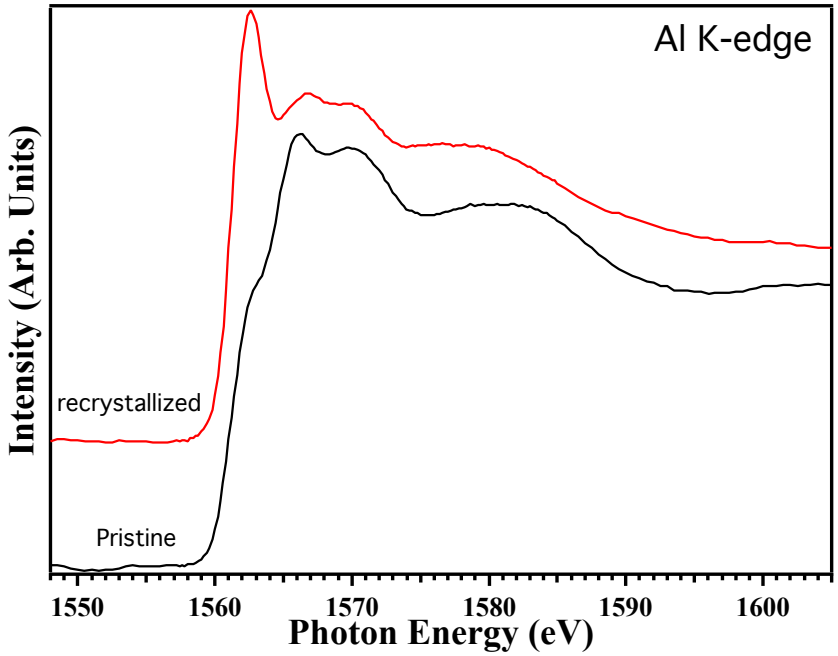


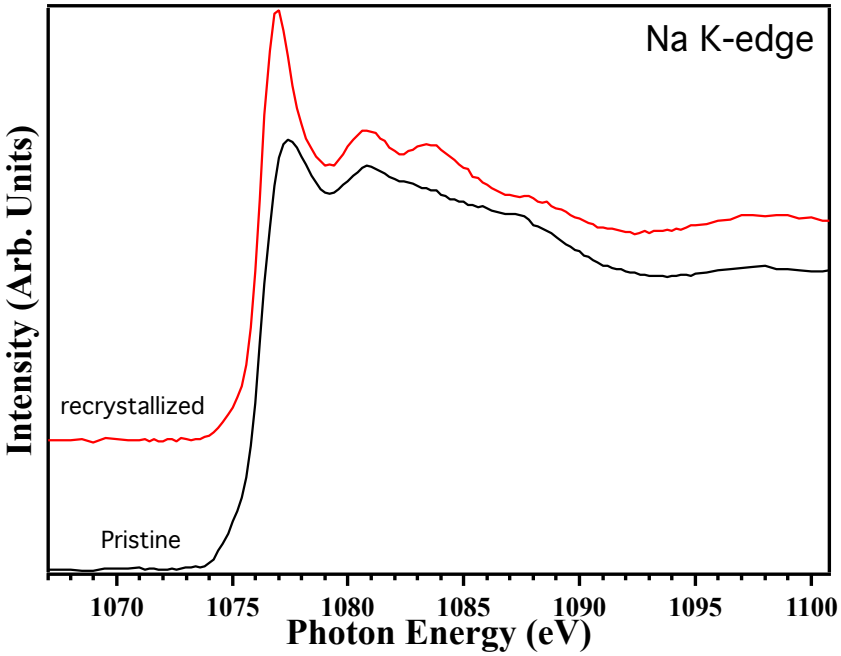


Accomplishment #3b: XAS characterization of pure samples

Task 1 (Vitalie Stavila, SNL), Task 3 (Rob Kolasinski, SNL)

- *Recrystallized $NaAlH_4$ XAS spectra show a sharp x-ray absorption peak (high purity/less oxidized) from the samples newly synthesized by Sandia group.*
- *Settle down the controversial issue in the previous literature*

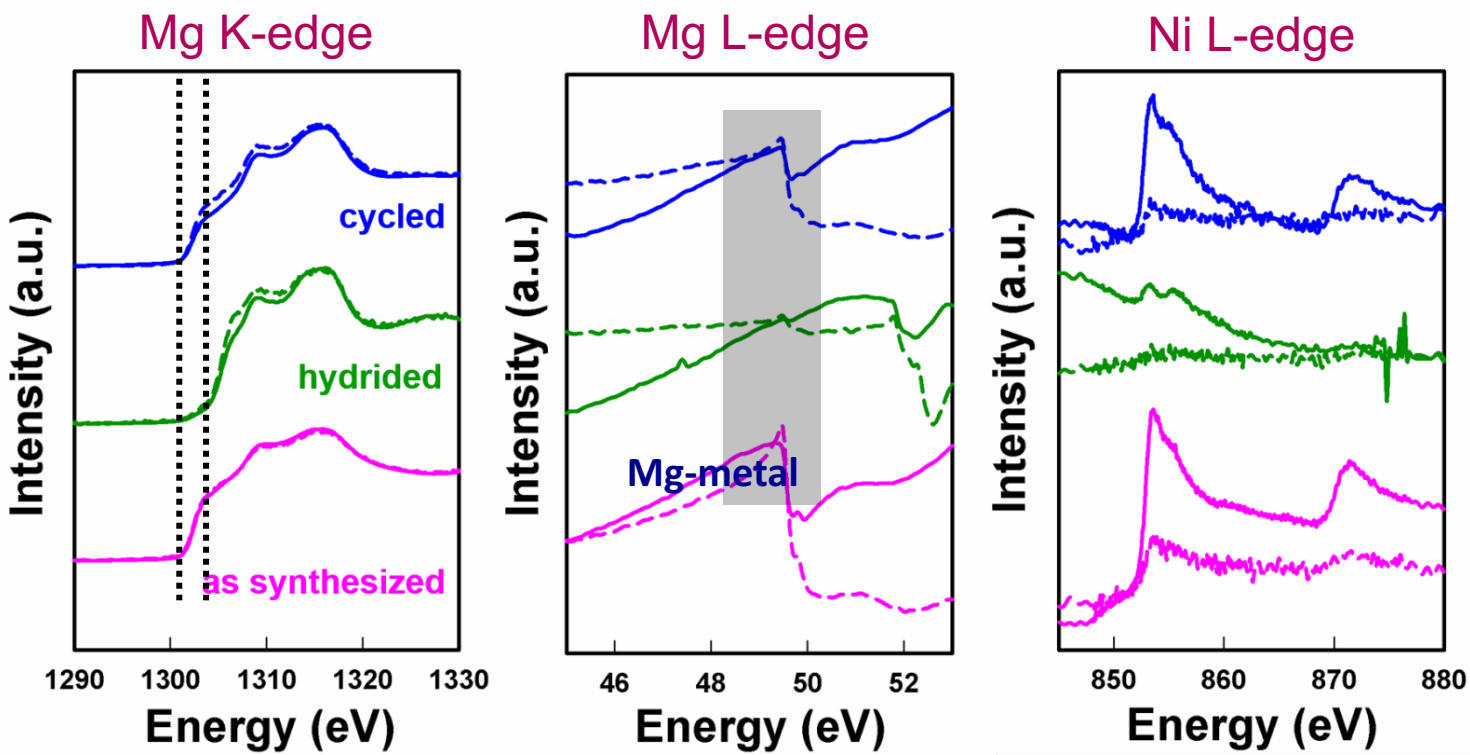




Accomplishment #3c: XAS of Ni-doped rGO-Mg
Task 5 (Lennie Klebanoff, SNL)

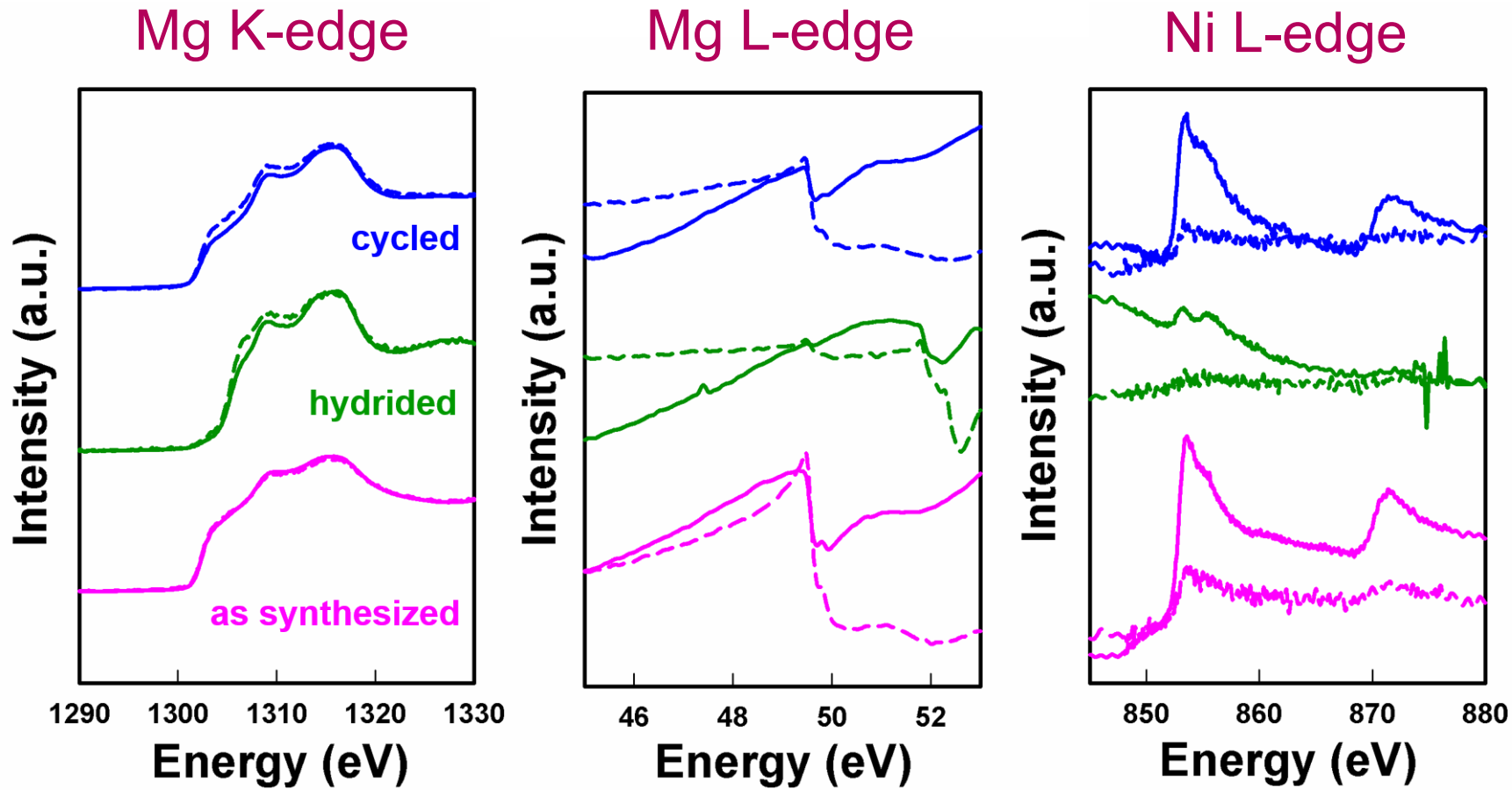
***Ex-Situ* XANES highlights the signature of hydride formation**

Solid lines indicate surface state (total electron yield) and dashed lines indicate bulk state (total fluorescence yield)



Hydride formation shifts the Mg K-edge to higher energy

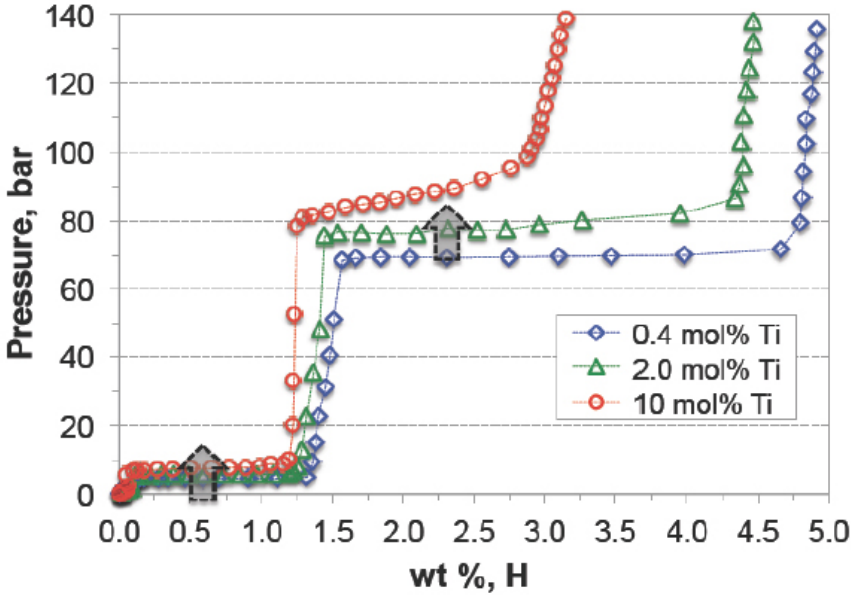
X-ray Absorption Spectroscopy (XANES) for Ni-doped rGO-Mg



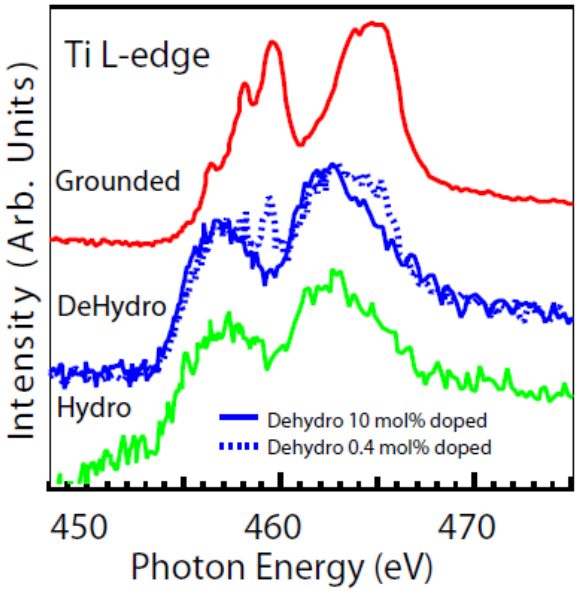
E.S.Cho et al, *submitted*

Accomplishment #3e: XAS of Ti doped $NaAlH_4$

Task 5 (Lennie Klebanoff, SNL)



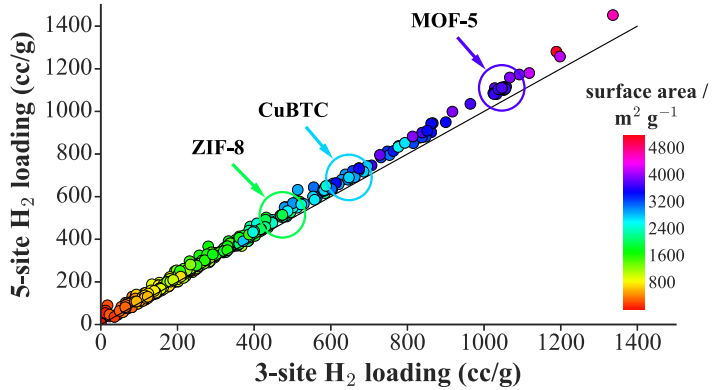
Increasing the concentration of $TiCl_3$ in $NaAlH_4$ leads to increased plateau pressures

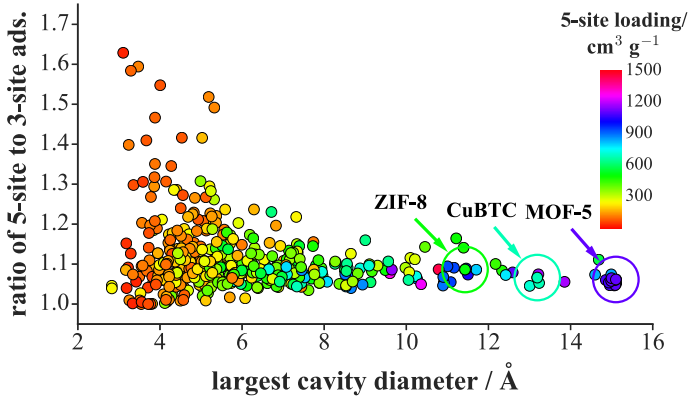


XAS spectra of $TiCl_3$ grounded mixing and Ti doped $NaAlH_4$

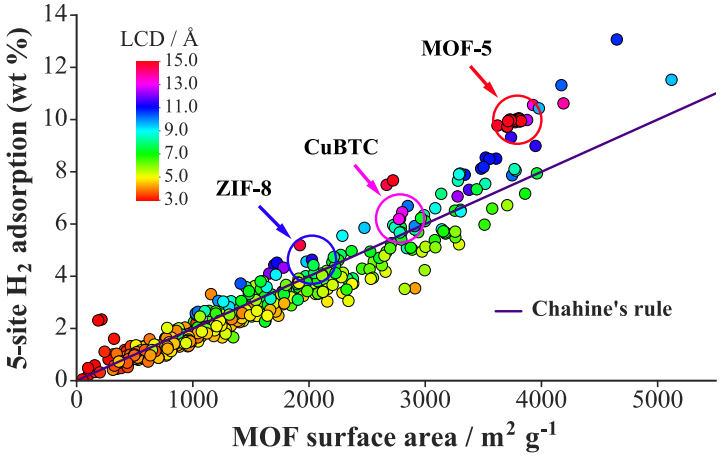
High-throughput GCMC studies at 100 bar, 77 K

H_2 potential:





Chahine's rule:



Results from high-throughput GCMC on ~500 MOF structures generally in agreement with Chahine's rule of **1 wt% H_2 loading per 500 m^2/g surface area**

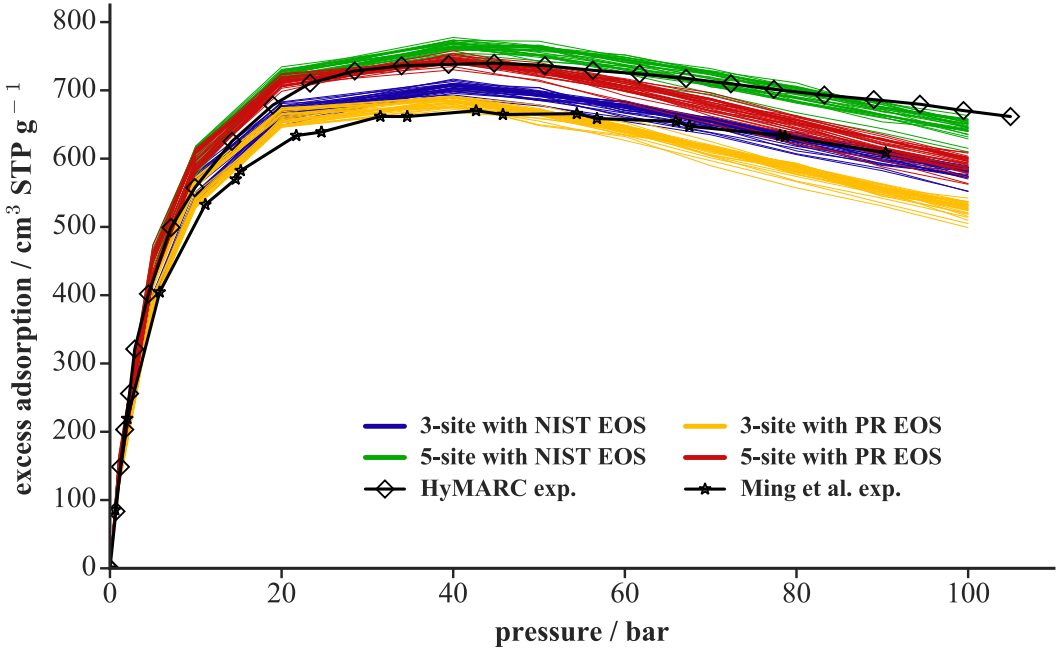
The commonly used Peng-Robinson equation of state gives excess H_2 loadings ~ 7% too low at 100 bar, 77 K

⇒ *New capability*

⇒ ***5-site potential gives approx. 10% higher hydrogen loadings than 3-site H_2 potential***

⇒ ***The deviation is larger for MOFs with small pore sizes***

Simulations of H_2 adsorption in MOF-5



16 different MOF-5 structures with slightly different lattice constants, atomic positions

- Both experimental and DFT optimized representations, 32 structures total

Two H_2 potentials used in concert with two H_2 equations of state

32×2×2=128 independent GCMC simulations

Two sources of high quality experimental data

⇒ ***Up to 20% variance in excess adsorption at 100 bar hydrogen using different reasonable simulation inputs***

⇒ ***Simulations and experiments can be considered to be in agreement within a somewhat broad "band of uncertainty"***

⇒ *manuscript in progress*

Research Introduction

Gerome Melaet – Gabor Somorjai – Task5

Goals: Study the effects of catalytic additives on the hydrogen storage capacity in high surface area (i.e. 10^2-10^3 m^2/g) mesoporous and/or microporous supports and thermodynamic (heat of adsorption, etc.) using catalytic-like additives

Strategy: Use of mesoporous and microporous silica based samples and study the H_2 adsorption under isobar/isotherm conditions

Project objectives:
Samples preparation with additives such as: acid sites, metal-oxide interface

Synthetic Strategy:

Aluminum grafting of mesoporous silica support

- Substitution of Al in SiO_2 structure: Slurry of $AlCl_3$ with pure SiO_2 support in ethanol overnight (RT)
- Sample is then washed with $NH_4NO_{3\,(aq)}$ to obtained the H^+ form

Metal nanoparticles are produced by colloidal method

- Platinum precursor is dissolved in diols solution + NaOH
- Temperature is increased, allowing for the reduction of Pt and formation of nanoparticles
- PVP is added to cap the particles and avoid sintering