HyMARC Seedling: "Graphene-Wrapped" Complex Hydrides as High-Capacity, Regenerable H_2 Storage Materials

Di-Jia Liu (Lead) and Lina Chong

Argonne National Laboratory

Qingfeng Ge (Sub)

Southern Illinois University

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Project ID ST136

Overview

Timeline

- Project start: Oct. 2016
- Phase I end: Sept. 2017
- Phase II end: Sept. 2019

Budget

- Total project requested: $1.114 Million
  - DOE share: $1 Million
  - Contractor share: $114 K
- Funding in FY2017 (Phase I)
  - DOE fund received: $ 250 K
  - DOE Fund Spent*: $ 100 K

* **As of 3/31/2017**

Barriers

- Barriers addressed
  A. System Weight and Volume
  B. System cost
  C. Efficiency
  D. Durability/Operability

Partners

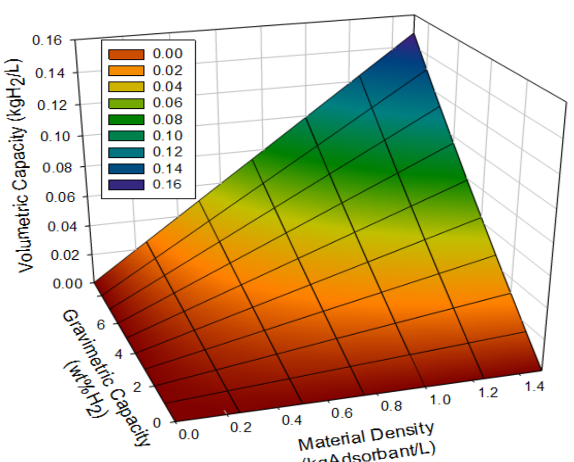
- Interactions/collaborations
  - Argonne National Laboratory (Lead)
  - Southern Illinois University (Subcontractor)
  - HyMARC (SNL, LLNL, LBNL)
  - NREL
  - Shanghai Jiao Tong University

Relevance - Current Challenges for Onboard Hydrogen Storage Technologies

DOE Hydrogen Storage Technology Target

Storage Parameter	Units	2020	Ultimate
System Gravimetric Capacity:	kWh/kg (kg H_2/kg system)	1.8 (0.055)	2.5 (0.075)
System Volumetric Capacity:	kWh/L (kg H_2/L system)	1.3 (0.040)	2.3 (0.070)
Storage System Cost	$/kWh net	10	8

Advantages & Challenges of Complex Hydride Storage Materials



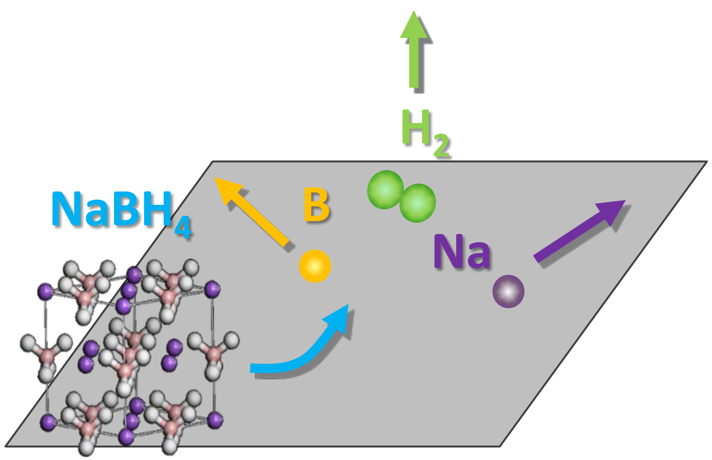
High Gr. capacity lessens the challenges on packing density

Advantages

- High gr. (10 ~14 wt.%) & vol. (0.08 ~0.15 kg/L) capacities
- Low storage pressure

Challenges

- Poor recyclability
- Poor H_2 Purity
- Poor DeH_2/ReH_2 Kinetics



Encapsulating deH_2 products is essential for regeneration

Relevance - Objective

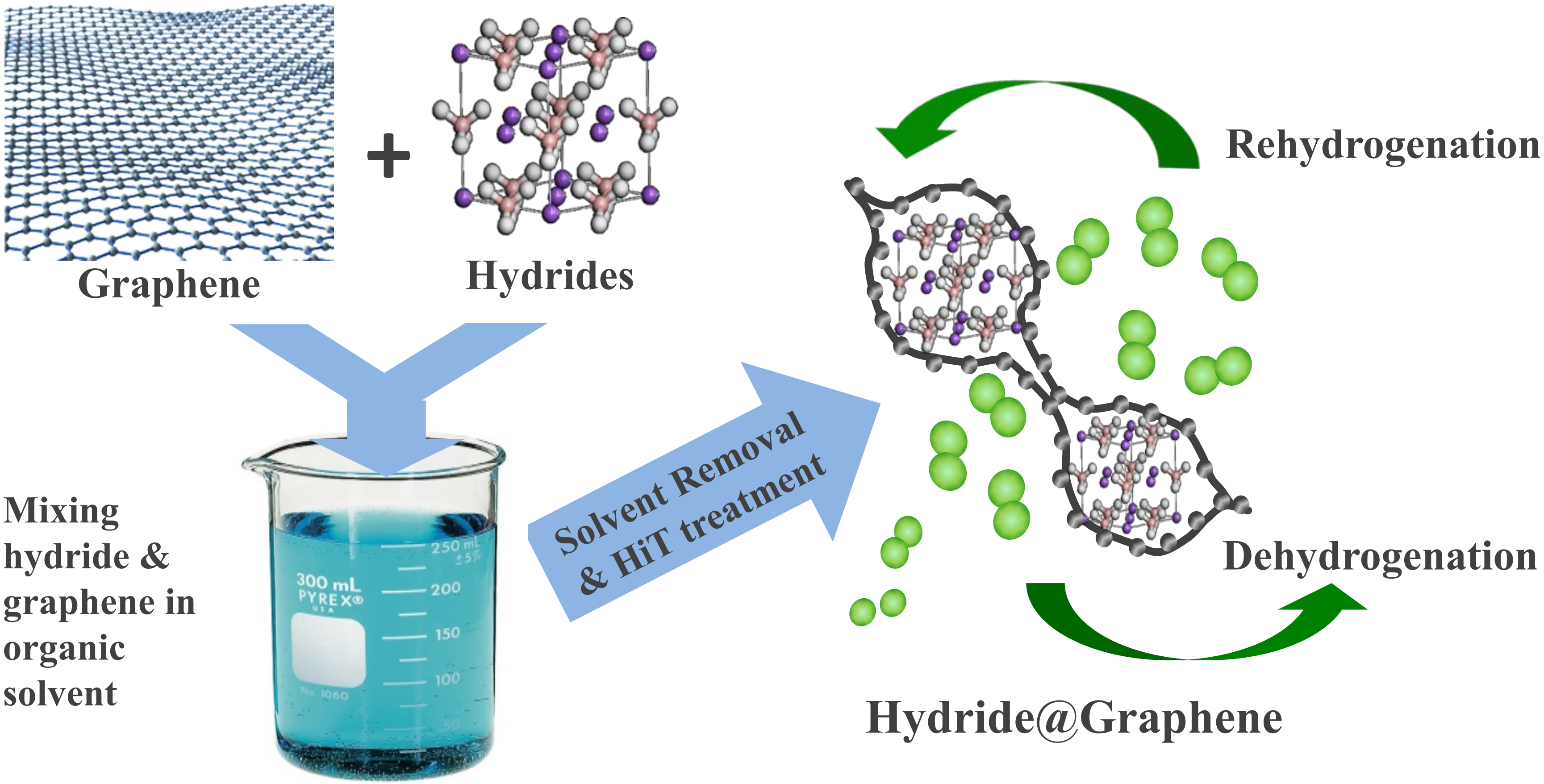
- ***Phase I –*** Deliver at least one "hydride@graphene" material with reversible total gravimetric capacity >8 wt% H_2 and total volumetric capacity >0.03 kg H_2/L at temperatures <400°C over at least five sorption/desorption cycles as validated by a DOE designated lab.
- ***Overall*** – To produce one or more hydride@graphene composite material with *regenerable / reversible* H_2 storage total gravimetric capacity >10wt.% and volumetric capacity greater than 0.055 kg H_2/L.

Potential Advantages of Hydride@Graphenes & Their Impact to Technology Barriers

- ***System Weight and Volume*** – Hydride@Graphenes have potential to reach both gravimetric and volumetric based on theory and preliminary experimental data
- ***System Cost*** – Hydride@Graphene is based on robust, solution based chemistry, scalable for industrial production.
- ***Efficiency*** – Hydride@Graphenes could significantly improve DeH_2/ReH_2 kinetics and temperatures compared to bulk hydrides.
- ***Durability/Operability*** – Hydride@Graphenes show promise to improve DeH_2/ReH_2 regenerability with cleaner hydrogen.

Approach – Complex Hydride Encapsulated by Graphene "Hydride@Graphene"

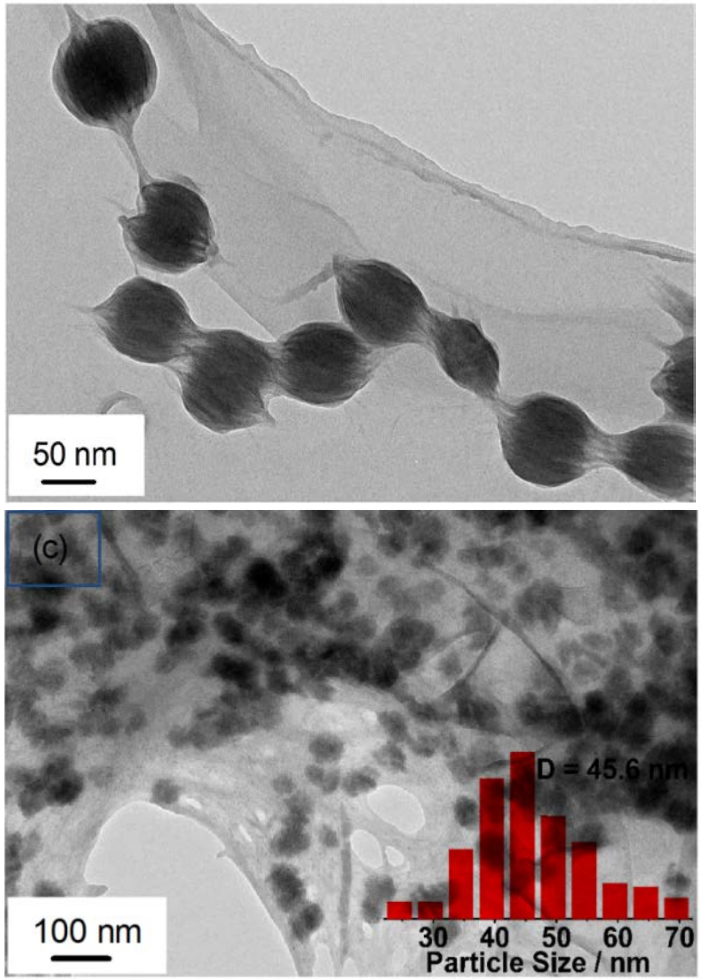
Concept developed through collaboration between Shanghai Jiao Tong U. & Argonne



1. "NaBH4 in 'Graphene Wrapper': Significantly Enhanced Hydrogen Storage Capacity and Regenerability through Nano-encapsulation", L. Chong, X. Zeng, W. Ding, D-J Liu and J. Zou, Advanced Materials, **2015**, 27, 5070–5074
2. "Wrapped by graphene": An efficient way to achieve high capacity, reversible hydrogen storage through nanoencapsulated hydride, J. Zou, L. Chong, D-J Liu, X. Zeng, L. Peng, W. Ding, *Science*, **2016**, *351* (6278), 1223, Special issue

Approach -Advantages of Hydride@Graphene

$NaBH_4$@Graphene



- Improved DeH_2/ReH_2 recyclability
  - Retention of DeH_2 byproducts facilitates hydride recovery during ReH_2
- Improved DeH_2/ReH_2 kinetics
  - Interaction between hydride and structurally conformable graphene and size control lead to lower DeH_2/ReH_2 temperatures
- Improved gravimetric capacity
  - Light weight, high surface area of graphene adds less parasitic weight
- Improved hydrogen purity
  - Only hydrogen can shuttle through graphene, reducing the release of byproducts to H_2 stream

Approach - Development Strategy

Hydride@Graphene Exploration (ANL)	Characterization & Optimization (ANL/HyMARC/HySCORE)	Modeling & Simulation (SIU/HyMARC)
▪ Refining existing and exploring new hydride@ graphene syntheses through rational design ▪ Structure characterization ▪ Post synthesis treatment	▪ H_2 storage capacity & reversibility measurements ▪ DeH_2/ReH_2 kinetics measurement ▪ Surface/structural property characterizations	▪ Computational guidance on size-dependent DeH_2/ ReH_2 activation energy ▪ Computational guidance on dopant catalytic effect

- New hydride@graphenes with enhanced H_2 storage capacities
- Reducing graphene usage in hydride@graphene for higher capacities
- Lowering DeH_2/ReH_2 temperatures through hydride crystallite size control
- Improving DeH_2/ReH_2 kinetics through interaction with graphene & additives
- Exploring the intrinsic storage capacity of graphene

Collaboration with HyMARC and leveraging existing experimental/ theoretical capabilities are essential to the project success!

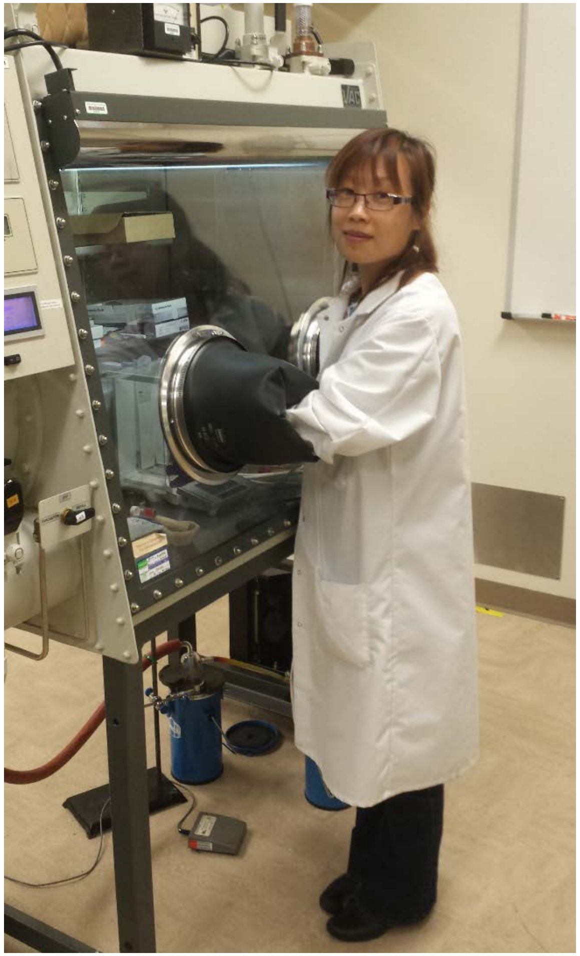
Approach – Phase I Milestones/Go-NoGo Decision

Month/ Year	Milestones/Go-NoGo DP	Milestone Status
June/17	Regenerable DeH_2/ReH_2 storage capacity of > 8 wt.%	Storage capacities ranging from 9 wt.% to 7.4 wt.% achieved during six DeH_2/ReH_2 cycles
Sept/17	To produce sufficient quantity MgH_2@graphene as precursor for binary hydride@graphenes	To be started.
Sept/17	To complete structural & capacity characterization for modified $NaBH_4$@graphene	TPD, TGA, XRD, FTIR experiments are completed for the first batch of $NaBH_4$@graphene
Sept/17	Deliver a "hydride@graphene" with reversible total gr. capacity >8 wt% H_2 and total vol. capacity >0.03 kg H_2/L at T<400°C over 5 sorption/desorption cycles	To be delivered to a DOE designated lab for validation after initial measurement at ANL.

The focus of Phase I is to produce and demonstrate a hydride@graphene with reversible capacity of 8 wt.%.

Accomplishment - Update Since Project Inception

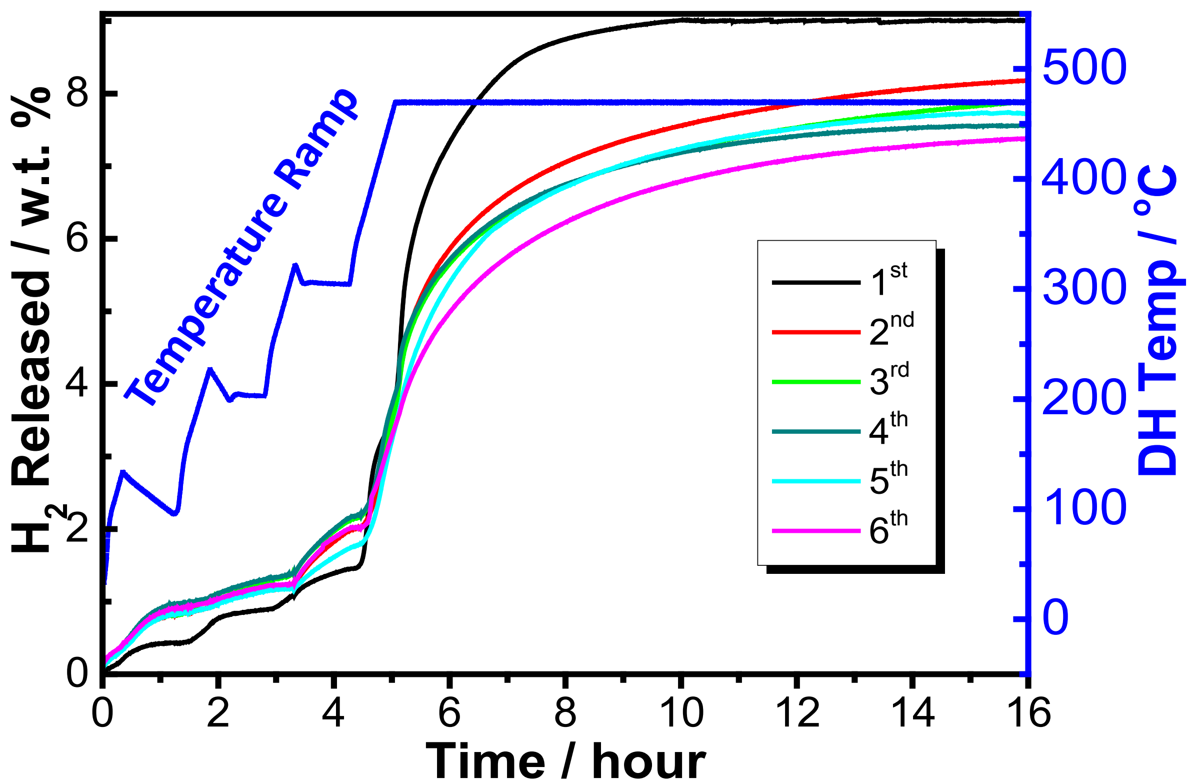
- New postdoc recruited and started in Jan, 2017
- Eight batches of $NaBH_4$@Graphene samples were synthesized.
- Dehydrogenation and rehydrogenation capacities and kinetics were measured and the capacity of 7.4 ~ 9 wt.% were observed
- Several characterizations including TPD, TGA, XRD, FTIR were performed on $NaBH_4$@graphene versus $NaBH_4$; insightful information on graphene-promoted DeH_2/ReH_2 recyclability and kinetics were obtained
- Preliminary computational simulations over hydride@graphene were carried out at SIU
- A number of collaborations with HyMARC team were initiated



Accomplishment - Multiple Dehydrogenation (DeH_2) Cycles over $NaBH_4$@Graphene Demonstrated

Multiple DeH_2 Cycles Over a $NaBH_4$@Graphene Composite

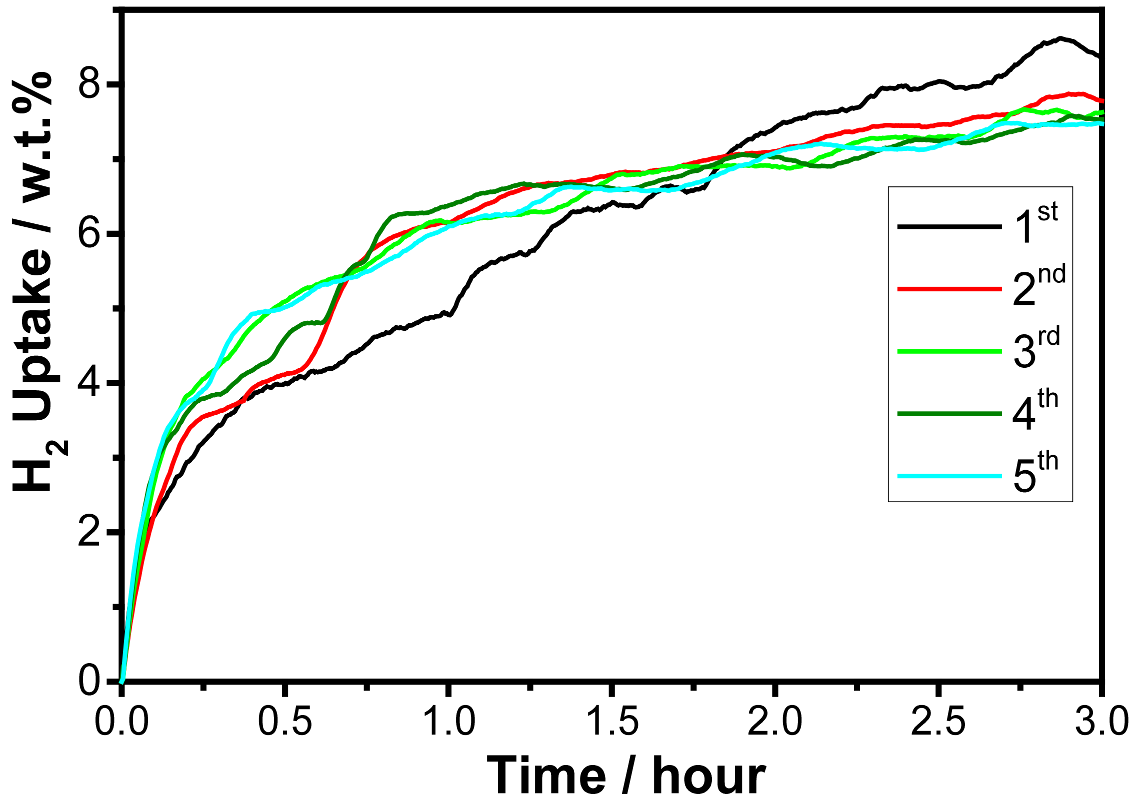
Theoretical capacity = 9.1 w.t.% (86%$NaBH_4$ + 14% Graphene)



- Regenerable H_2 discharge was shown over 6 temperature programmed release cycles
- The first cycle demonstrates nearly 100% hydrogen discharge from $NaBH_4$@Graphene composite

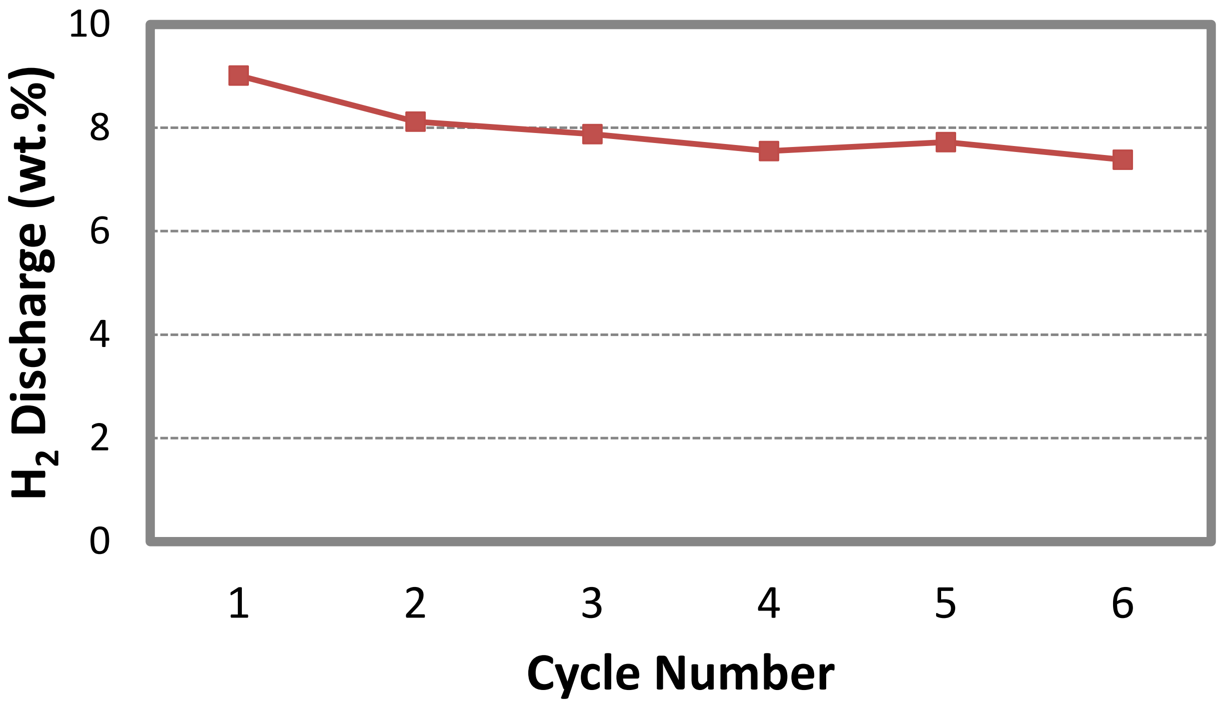
Accomplishment - Multiple Rehydrogenation (ReH_2) Cycles Between DeH_2 over $NaBH_4$@Graphene Shown

Multiple ReH_2 Between DeH_2 Cycles of $NaBH_4$@Graphene Composite



- One-step rehydrogenation at 350 °C under 4 MPa H_2 leads to recovery of majority hydride in graphene

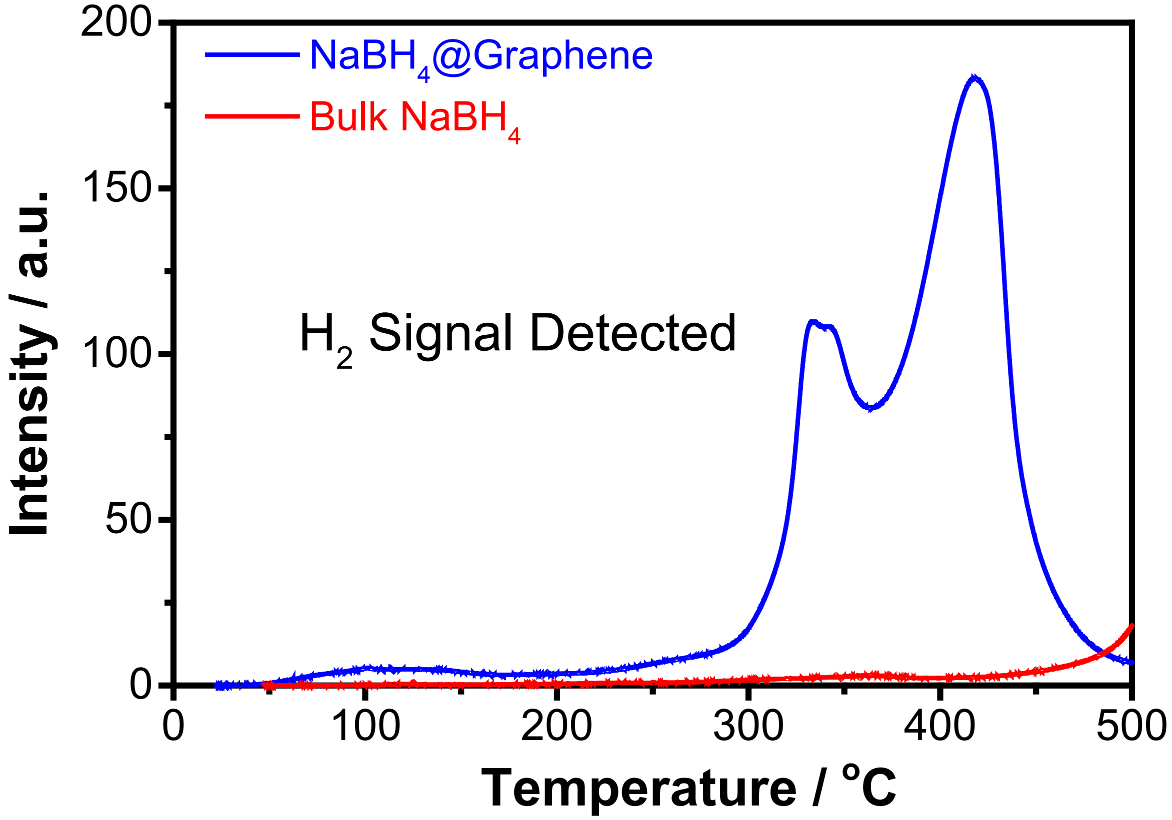
Accomplishment - High Fraction of Hydride Regeneration over $NaBH_4$@Graphene Achieved



Cycle #	1	2	3	4	5	6
H2 Discharge (wt.%)	9.01	8.12	7.88	7.55	7.72	7.38
% to Theoretical Value	99%	89%	86%	83%	85%	81%

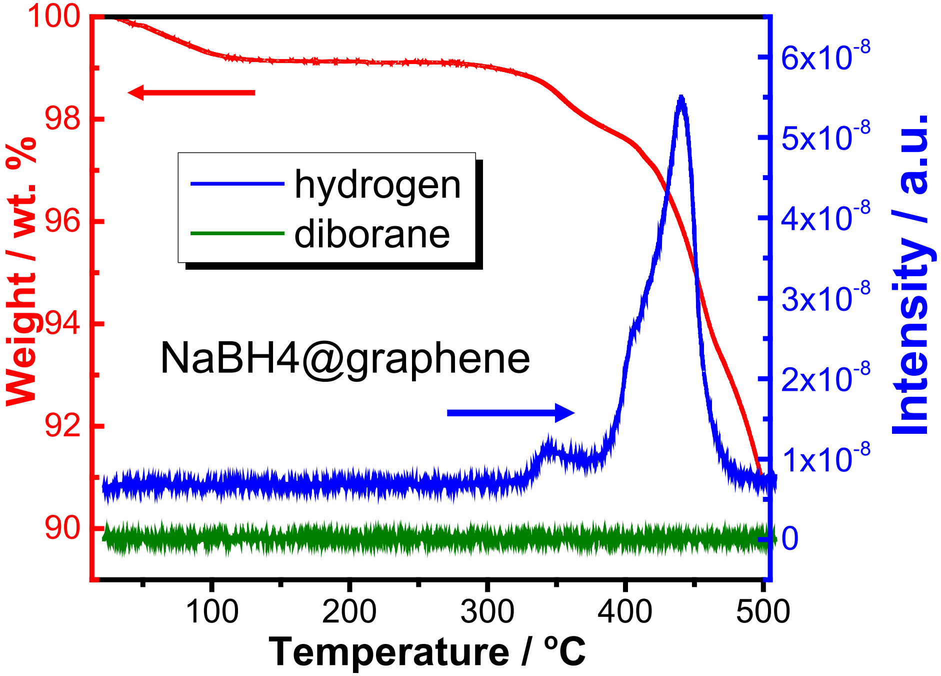
> 80% of hydride in $NaBH_4$@graphene was regenerated during multiple DeH_2/ReH_2 cycles

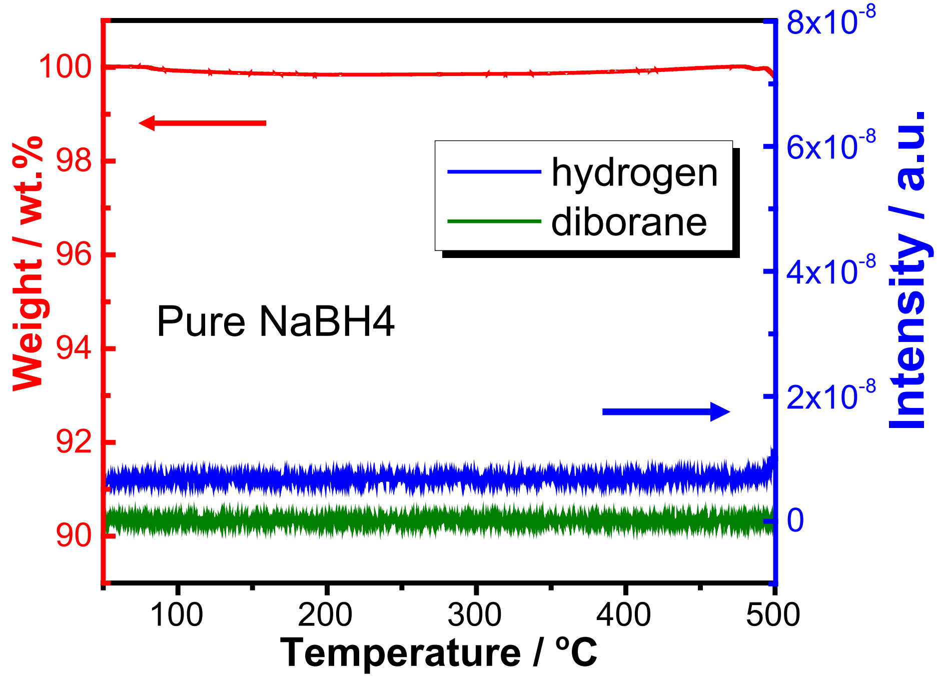
Accomplishment – Temperature Programmable Desorption (TPD) Showed Lower DeH_2 Temperature over $NaBH_4$@Graphene



- TPD experiment showed a significant reduction of hydrogen discharge temperature in $NaBH_4$@Graphene over bulk $NaBH_4$
- A very low hydrogen release temperature (~50 °C) was observed for $NaBH_4$@Graphene, its root cause is yet to be identified

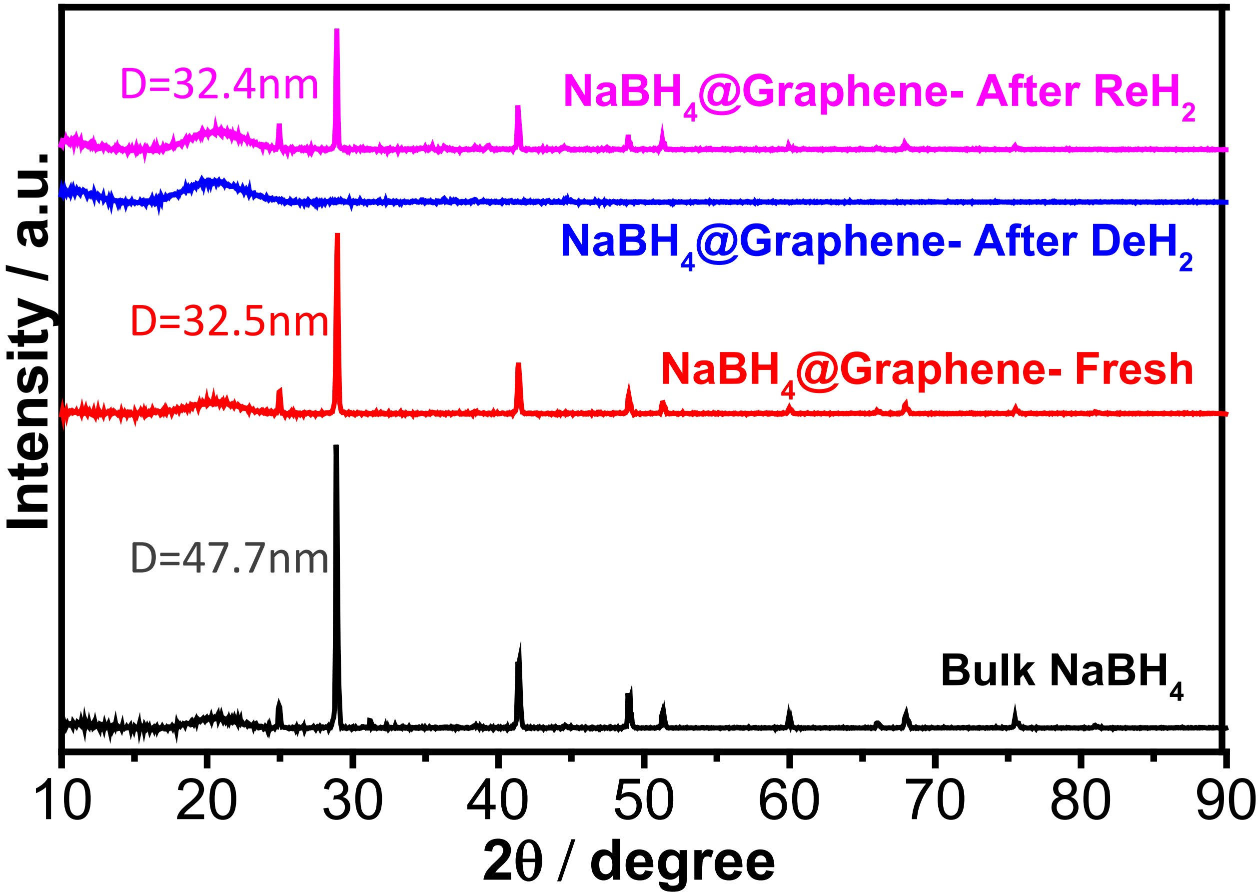
Accomplishment – Thermogravimetric Analysis (TGA) Confirmed Decrease of DeH_2 Temperature over $NaBH_4$@Graphene





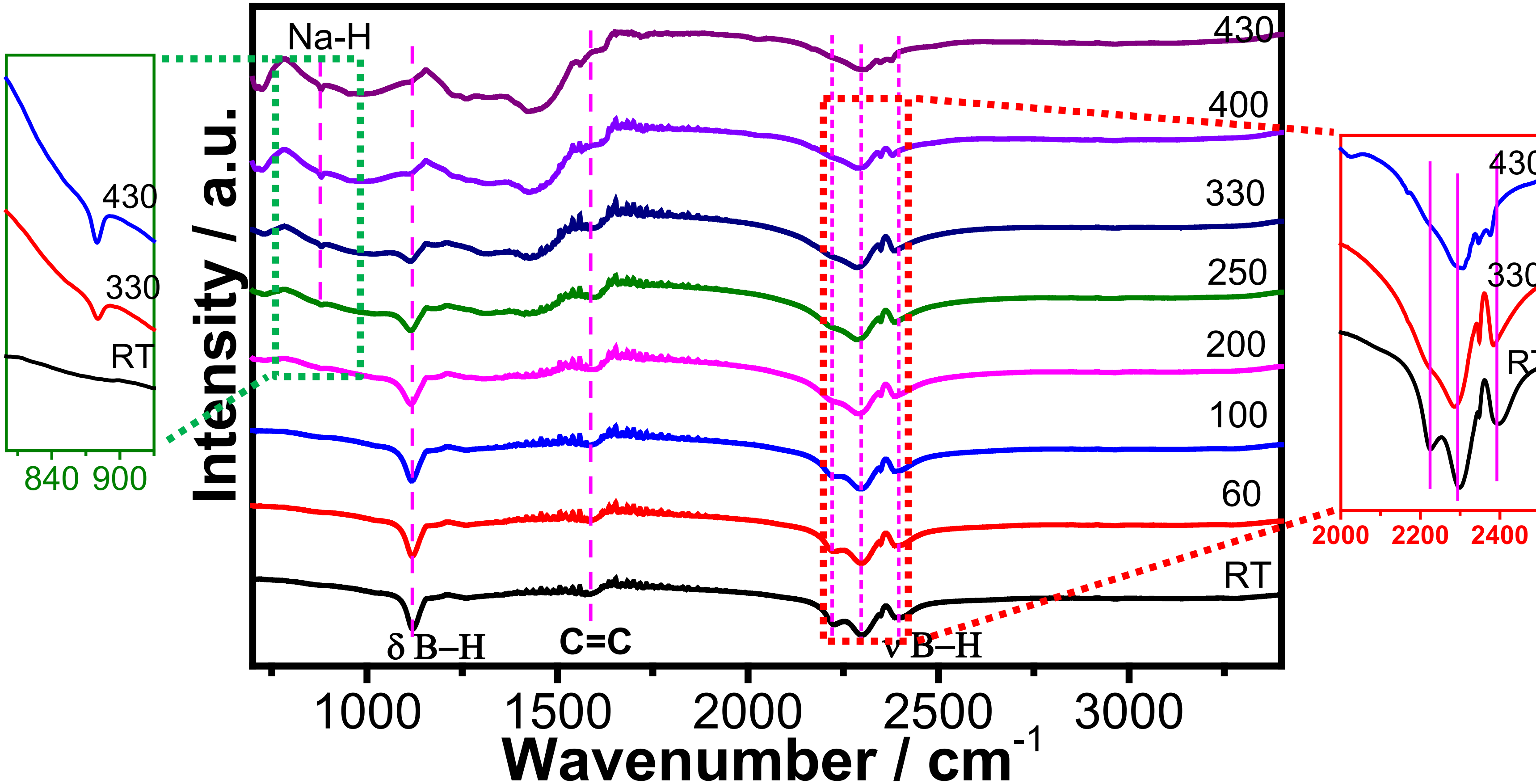
- Weight loss for $NaBH_4$@graphene matches that obtained from volumetric measurement. Weight loss at < 100 °C was again observed
- No appreciable weight loss for bulk $NaBH_4$ was observed, indicating the hydrogen release was promoted by graphene
- No other gas product such as diborane were observed

Accomplishment - X-ray Diffraction (XRD) Demonstrated Recovery of Hydride Crystallites in $NaBH_4$@Graphene after ReH_2



- XRD showed regeneration of crystalline hydride after rehydrogenation
- Hydride crystallite size in $NaBH_4$@graphene was reduced slightly compared to bulk hydride estimated based on Scherrer equation

Accomplishment - *In situ* FTIR Showed Reduction of B-H Band During DeH_2 over $NaBH_4$@Graphene

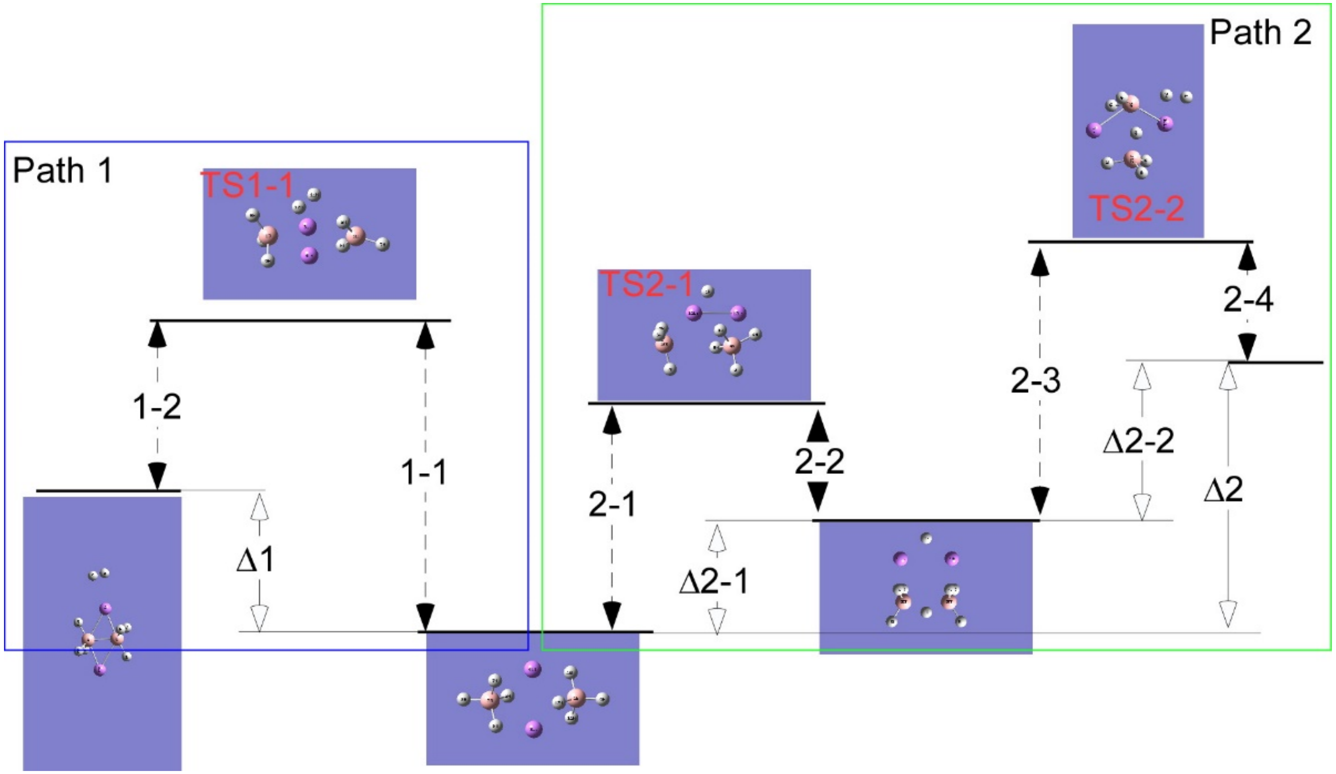


- *In situ* FTIR showed the loss of vibration peak associated with B-H and appearance of peak associated with Na-H as the temperature rose
- No other major chemical residual was found

Accomplishment – Computational Modeling Identified Two DeH_2 Pathways for Hydride@Graphene

Quantum Mechanical/Molecular Mechanical Calculation of $(MBH_4)_2$@Graphene

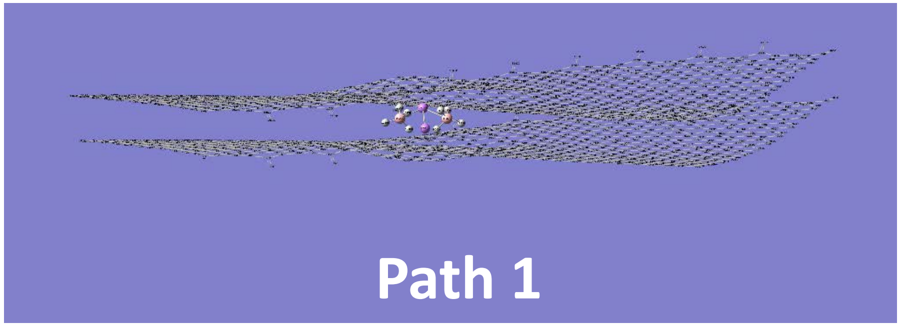
(M = Li, Na, K…, # of carbon used for graphene = 1928)

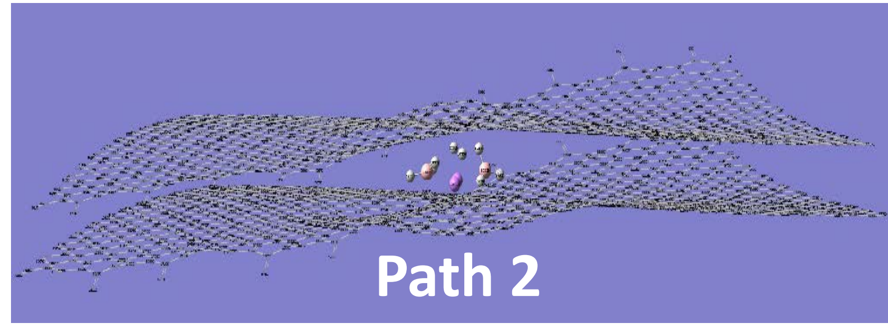


Path - 1

Path - 2

Accomplishment - Modeling Results Showed Limited Decreases of DeH$_2$ Barriers for Hydride@Graphene





	Path 1			Path 2						
	1-1	1-2	Δ1	2-1	2-2	Δ2-1	2-3	2-4	Δ2-2	Δ2
$LiBH_4$	443.5	294.4	149.1	222.2	88.6	133.6	269.5	36.3	233.2	366.8
$LiBH_4$(Encap)	302.2	153.6	148.6	221.1	77.2	143.9	271.9	114.5	157.3	301.2
$NaBH_4$	407.7	222.0	185.6	229.8	96.4	133.4	267.4	215.1	52.3	185.6
$NaBH_4$(Encap)	388.7	208.9	179.8	220.3	84.1	136.1	267.9	219.4	48.5	184.6
KBH_4	418.6	210.7	207.9	259.1	100.4	158.7	252.6	203.4	49.2	207.9
KBH_4(Encap)	489.0	279.8	209.2				249.0	214.1	34.9	

- **Modeling shows only minor reduction of transition state barriers and overall reaction enthalpies for graphene encapsulated $NaBH_4$ in both reaction paths**
- **Major change in experimentally observed kinetics may be due to other effect**

Collaborations

- **HyMARC** – Computational modeling (solid mechanics) on encapsulated hydrides (in planning with Lawrence Livermore National Lab)
- **HyMARC** – Synchrotron X-ray absorption spectroscopic study on hydride under reaction (in planning with Lawrence Berkeley National Lab)
- **HyMARC** – Molecular Foundry for hydride synthesis optimization (in planning with Lawrence Berkeley National Lab)
- **HyMARC** – Collaborative investigations on the graphene promoted kinetics in hydrides (monthly meeting, Sandia National Lab)
- **HySCORE** – Hydrogen storage capacity certification (National Renewable Energy Lab, to be submitted)
- **Southern Illinois University** – Project subcontractor on the computational modeling (work initiated)
- **Shanghai Jiao Tong University** – Graphene/catalyst material exchange.

Proposed Future Work

Phase I

- Continue to increase overall H_2 storage capacity in $NaBH_4$@graphene through optimizing hydride/graphene ratio
- Improve DeH_2 and ReH_2 kinetics in $NaBH_4$@graphene through catalysis
  - Metal complex as added catalyst
  - Graphene defect / hetero-element incorporation as catalyst
- Continue to improve fundamental understanding of DeH_2 and ReH_2 mechanism through computational modeling and advanced characterization (collaborating with HyMARC)
- Initiate synthesis on binary complex hydrides encapsulated by graphene

Phase II

- Exploring new complex hydride@graphene with higher theoretical capacities
- Lowering DeH_2 and ReH_2 temperature and increase rate through the catalytic additives and hydride size control by synthesis
- Investigating DeH_2 and ReH_2 mechanism through advanced characterization & modeling to guide the design and improvement of hydride@graphene
- Engineering downselected hydride@graphene for transportation application

Summary

- Regenerable hydrogen storage capacities between 8.1 wt.% to 7.4 wt.% were demonstrated during six dehydrogenation/rehydrogenation cycles over $NaBH_4$@Graphene.
- Dehydrogenation/rehydrogenation kinetics and recyclability of $NaBH_4$ were significantly improved through "graphene wrapping". Further improvement is still necessary and underway.
- A variety of structural characterizations confirmed the regeneration of hydride micro-crystallites assisted by graphene in the rehydrogenation cycle.
- Release of low level hydrogen at near ambient temperature was observed. Better understanding of the root cause could be important in improving dehydrogenation kinetics.
- Computational modeling for hydride@graphene was initiated.
- Several collaborations with HyMARC are underway.

Acknowledgement

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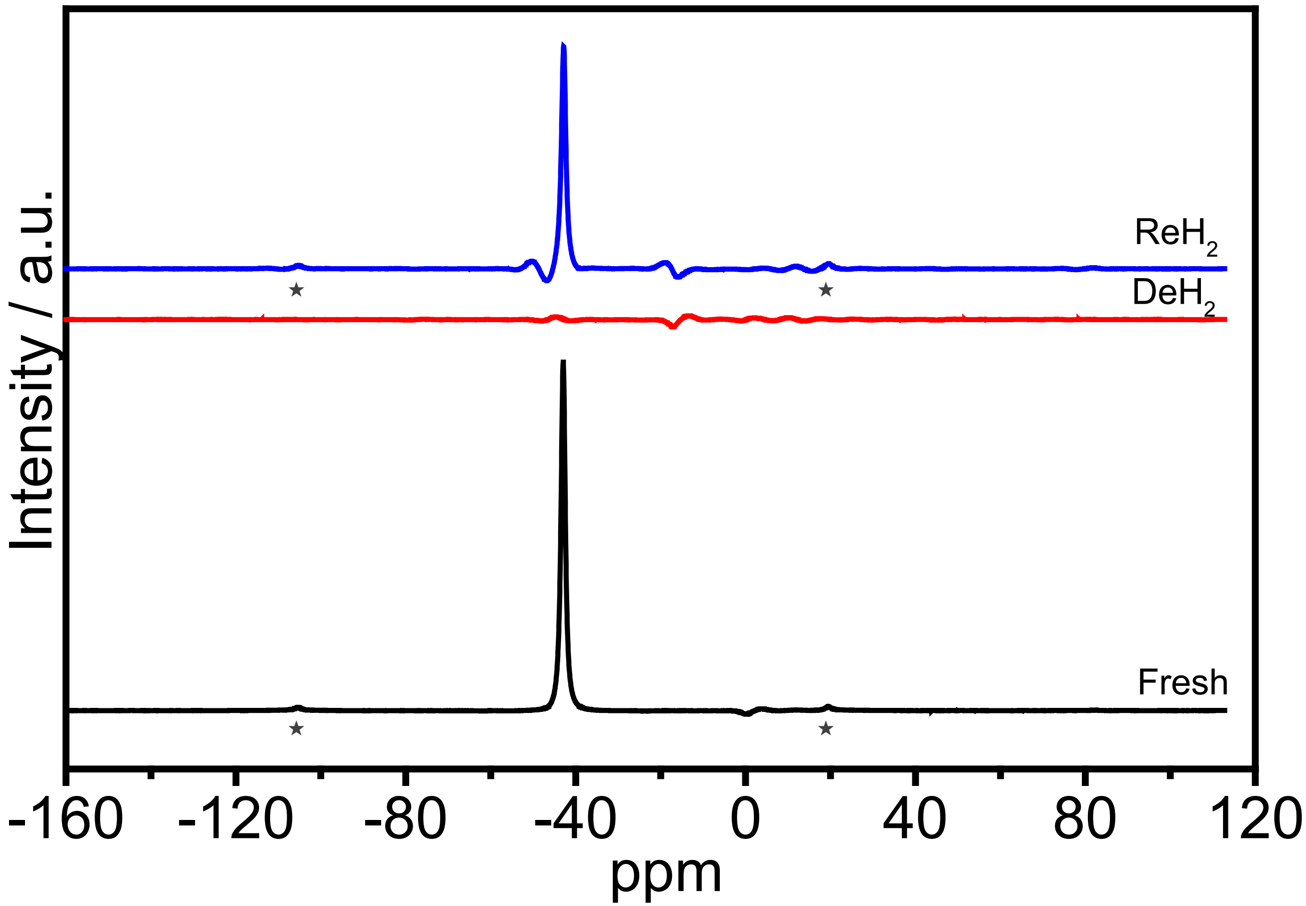
- Project Manager: Jesse Adams

- Hydrogen Storage Program Manager: Ned Stetson

ADDITIONAL SLIDE

Accomplishment - Recent NMR Result

11B MAS-NMR spectra



Asterisks indicate spinning sidebands