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HyMARC research efforts on nanoscale metal hydrides

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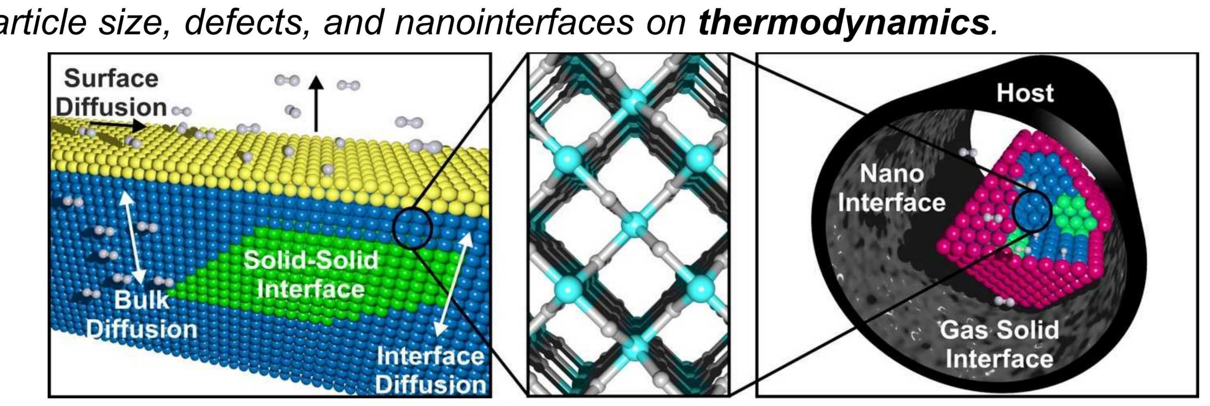
Overview

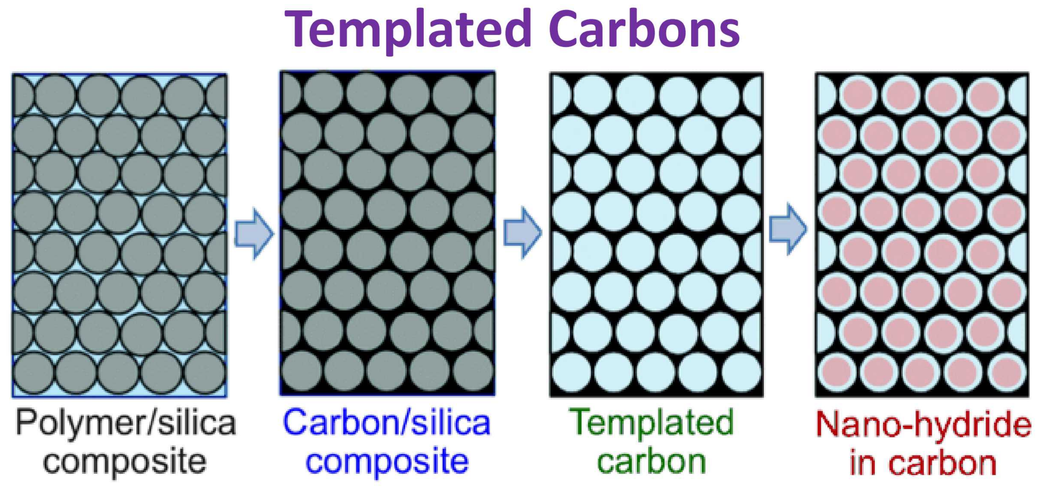
Nanostructuring has become a promising strategy for enhancing hydrogen storage properties of metal hydrides. Nanostructured and nanoscale hydrides can strongly influence the thermodynamics and kinetics of hydrogen absorption and desorption by modifying the reaction pathways and increasing the rate-limiting reaction rates. Additionally, the materials at the nanoscale offer the possibility of tailoring technical parameters independently of their bulk counterparts.

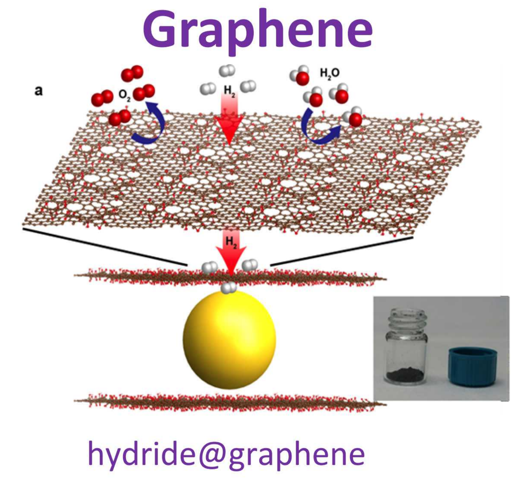
Objective: *Use nanostructuring to improve* ***kinetics****, alter* ***reaction pathways****, and study the effects of particle size, defects, and nanointerfaces on* ***thermodynamics****.*



Schneemann, A.; White, J.L.; Kang, S.Y.; Jeong, S.; Wan, L.F.; Cho, E.S.; Heo, T.W.; Prendergast, D.; Urban, J.J.; Wood, B.C.; Allendorf, M.D.; Stavila, V. "Nanostructured Metal Hydrides for Hydrogen Storage." *Chem. Rev.*, **2018**, *118*, 10775-10839.

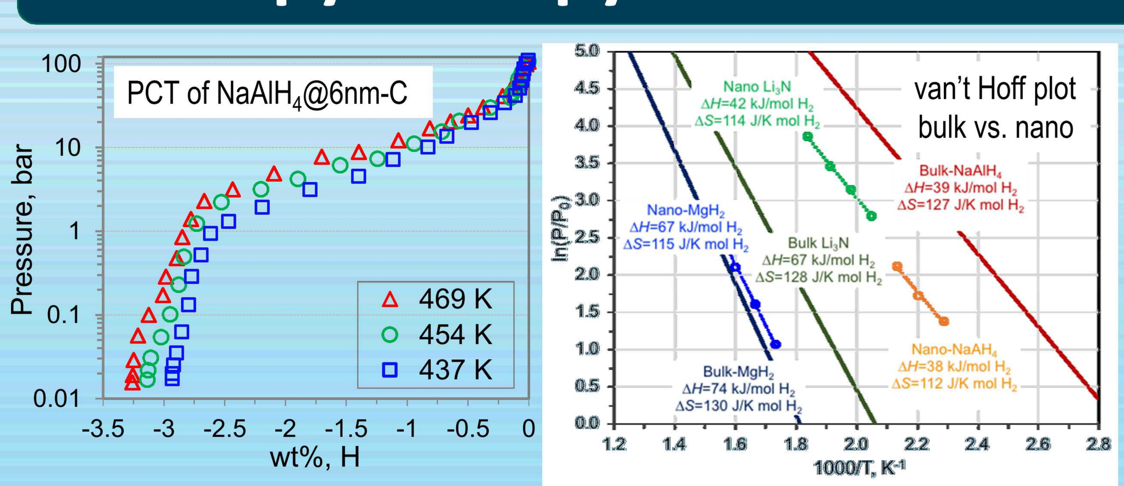
Synthesis of nanoscale metal hydrides

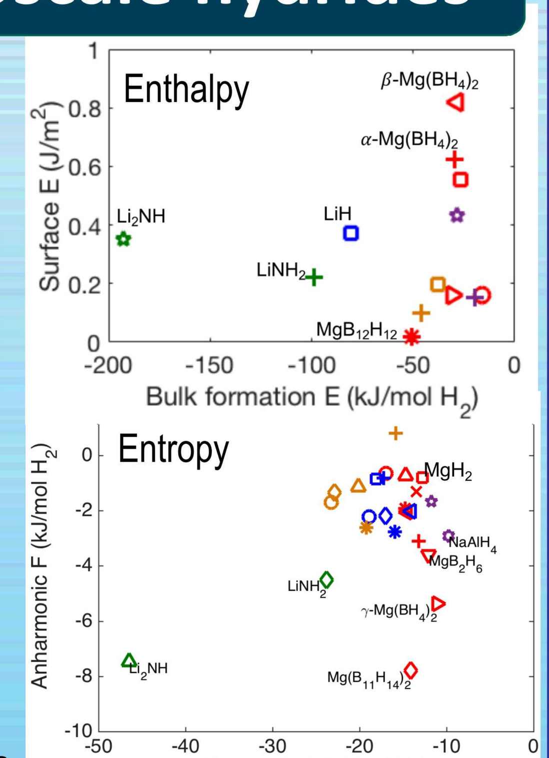




The HyMARC team exploring nanoconfinement as a general strategy to create nanoscale metal hydrides, either by confining nanoparticles inside a host (nanoscaffolding) or by encapsulation of a material with a rigid matrix (nanoencapsulation). The scaffold has pores into which the confined material is introduced, bound, and then restricted from movement. Nanoencapsulation includes incorporation of a nanoscale hydride inside a secondary material which is not necessarily porous, and involves a pre-formed nanostructure that acts as a barrier to particle/grain growth and agglomeration.

Enthalpy-entropy effects in nanoscale hydrides

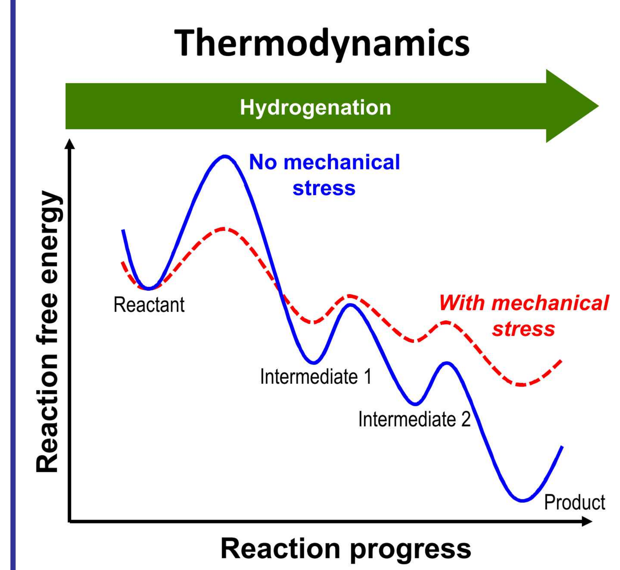


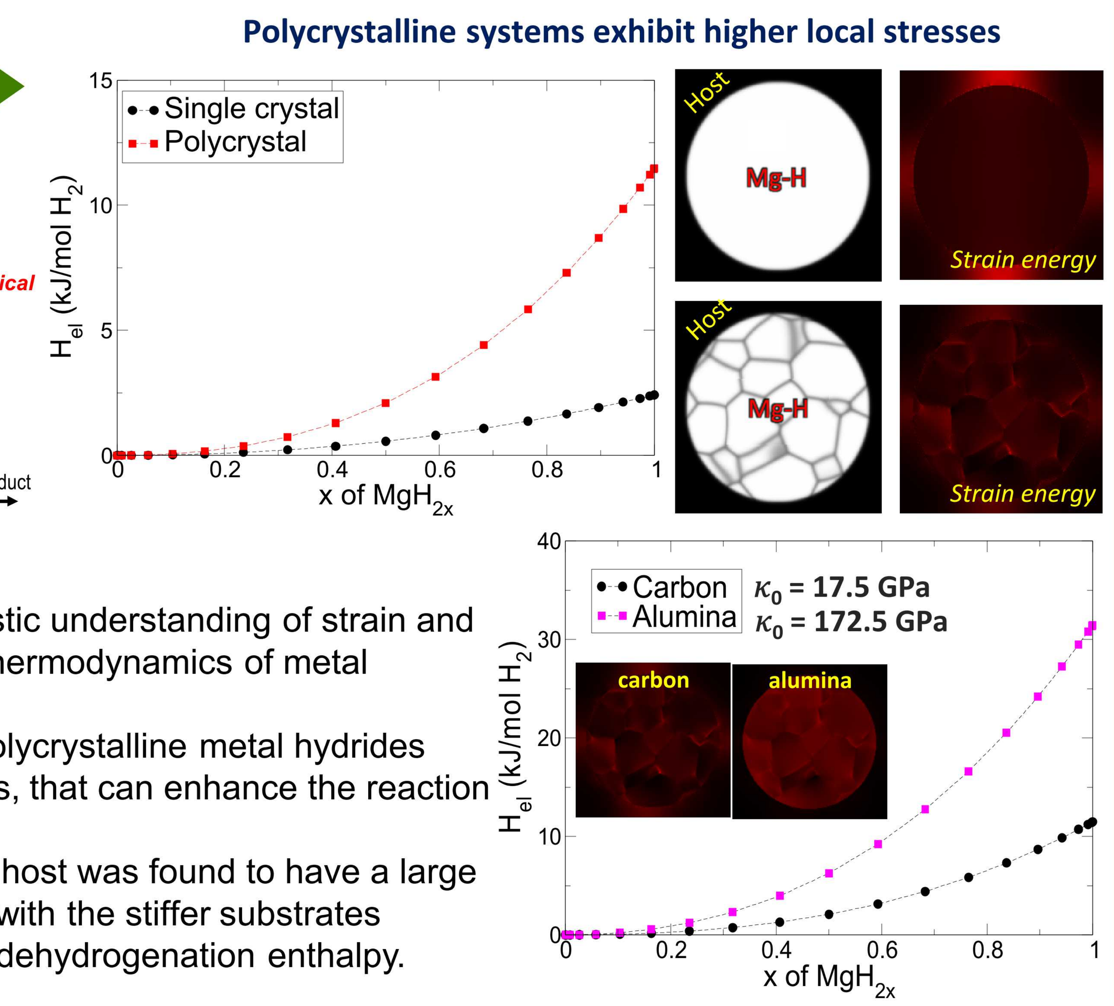


Nanoscale metal hydrides display Pressure-Composition-Temperature (PCT) isotherms that are substantially modified compared to bulk.

- Nanoconfinement of binary (MgH_2) and complex metal hydrides ($LiNH_2$/2LiH, $NaAlH_4$) is accompanied by a decrease in ΔH, which is often counterацted by a decrease in ΔS.
- Calculations reveal that the enthalpy-entropy compensation in nanoscale metal hydrides is due to anharmonic surface entropy effects.

Stress and strain effects

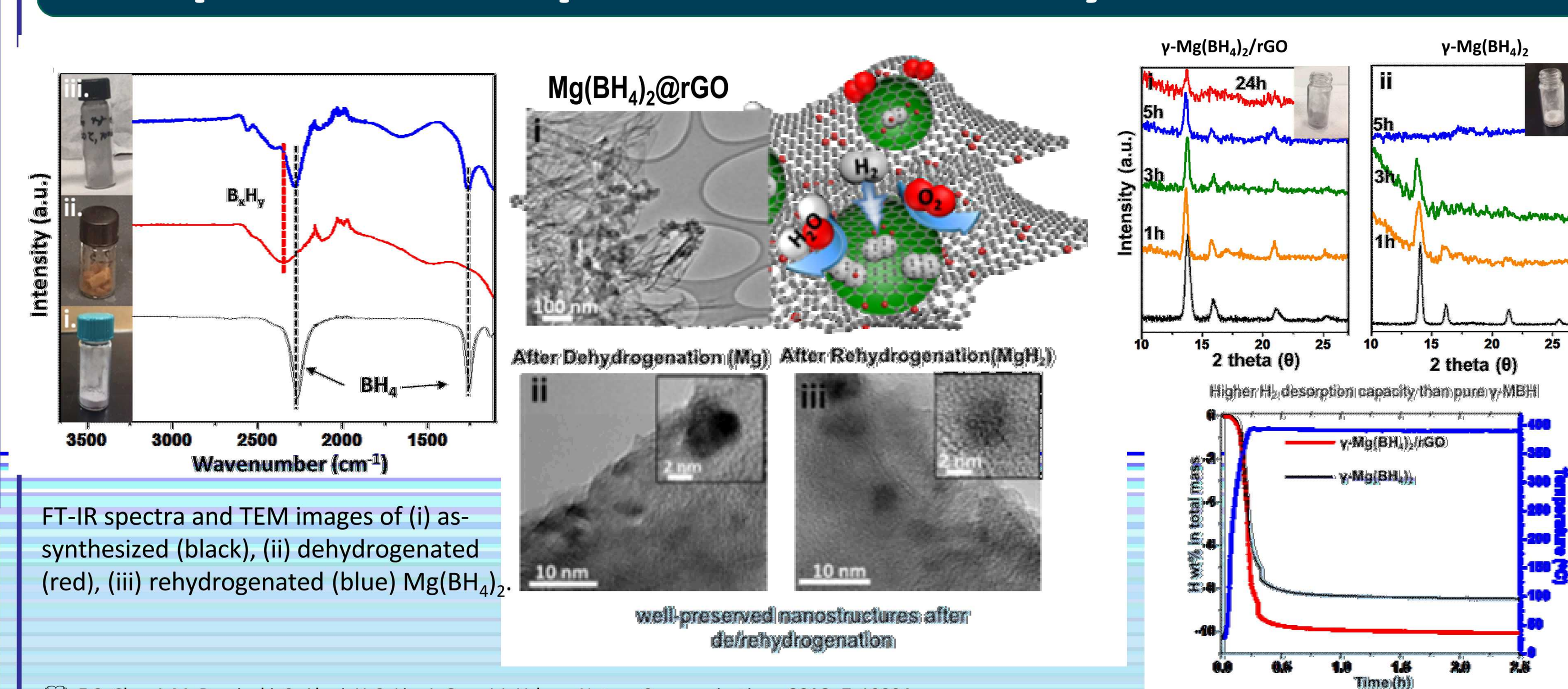




Our goal is to establish a mechanistic understanding of strain and stress effects on the kinetics and thermodynamics of metal hydrides.

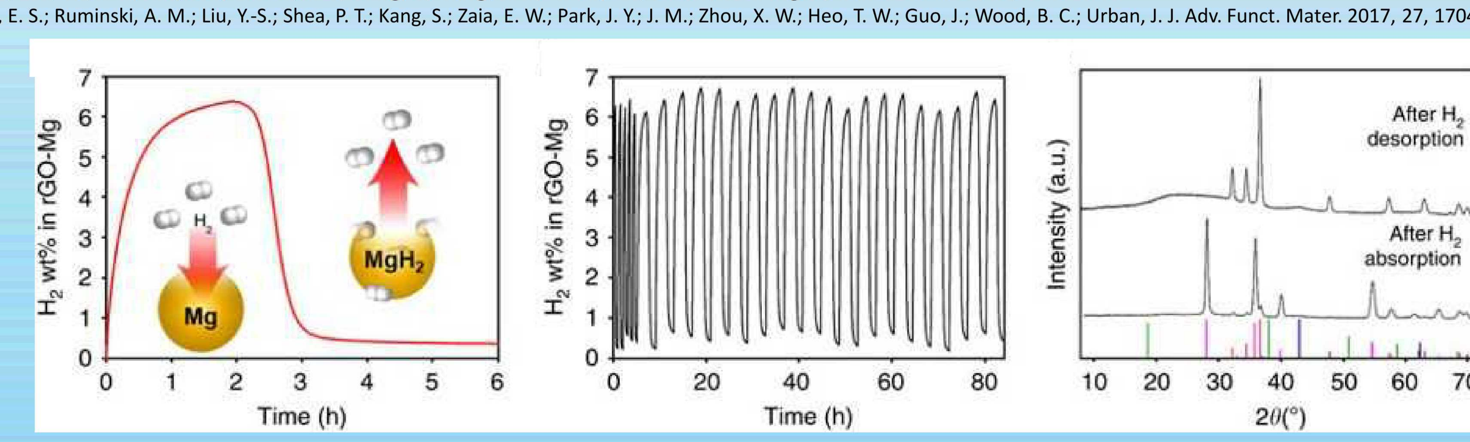
- Our calculations indicate that polycrystalline metal hydrides experience higher local stresses, that can enhance the reaction kinetics .
- The mechanical stiffness of the host was found to have a large effect on the reaction enthalpy, with the stiffer substrates resulting in larger decreases in dehydrogenation enthalpy.

Graphene-encapsulated metal hydrides



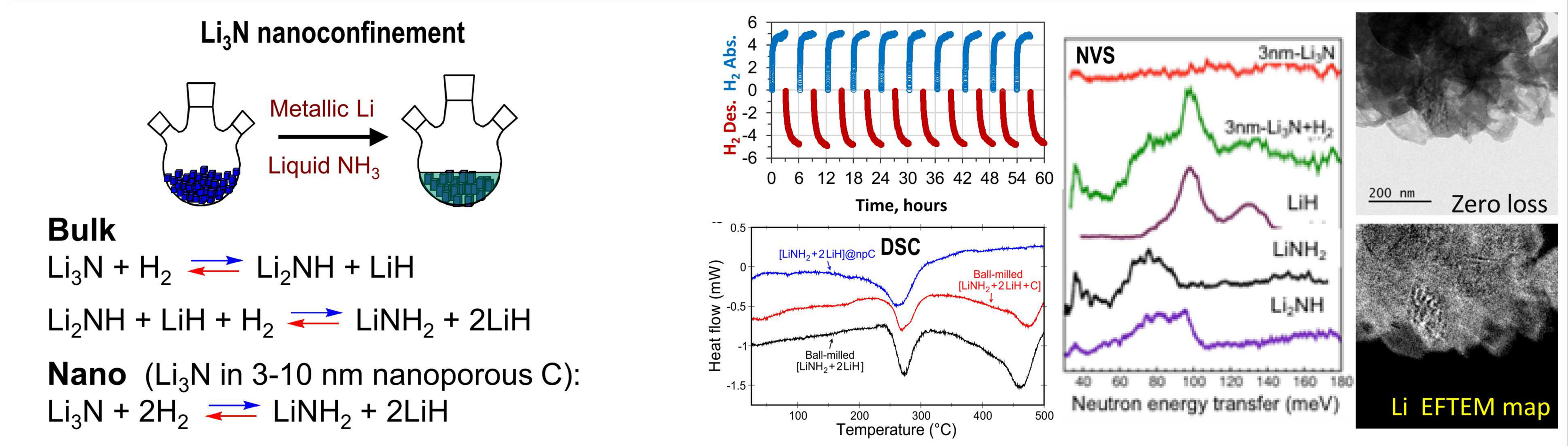
FT-IR spectra and TEM images of (i) as-synthesized (black), (ii) dehydrogenated (red), (iii) rehydrogenated (blue) $Mg(BH_4)_2$.

E.S. Cho, A.M. Ruminski, S. Aloni, Y.-S. Liu, J. Guo, J.J. Urban, *Nature Communications*, **2016**, *7*, 10804.
Wan, L. F.; Liu, Y.-S.; Cho, E. S.; Forster, J. D.; Jeong, S.; Wang, H.-T.; Urban, J. J.; Guo, J.; Prendergast, D., Nano Lett. 2017, 17, 5540-5545.
Cho, E. S.; Ruminski, A. M.; Liu, Y.-S.; Shea, P. T.; Kang, S.; Zaia, E. W.; Park, J. Y.; Ai, M.; Zhou, X. W.; Heo, T. W.; Guo, J.; Wood, B. C.; Urban, J. J., Adv. Funct. Mater. 2017, 27, 1704316.

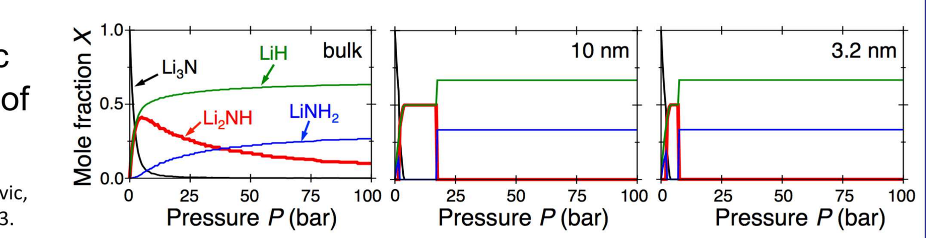


- Reduced graphene oxide (rGO) are versatile in encapsulation of MgH_2 and $Mg(BH_4)_2$ nanoparticles.
- The weight penalty is minimized by confining the hydride in atomically thin graphene sheets, with the added benefit of protecting the hydride from oxygen and moisture.
- In the case of MgH_2, the reversible capacity reaches 7.0% by weight, whereas in the case of $Mg(BH_4)_2$, the maximum hydrogen capacity exceeds 10%.

Role of internal nanointerfaces

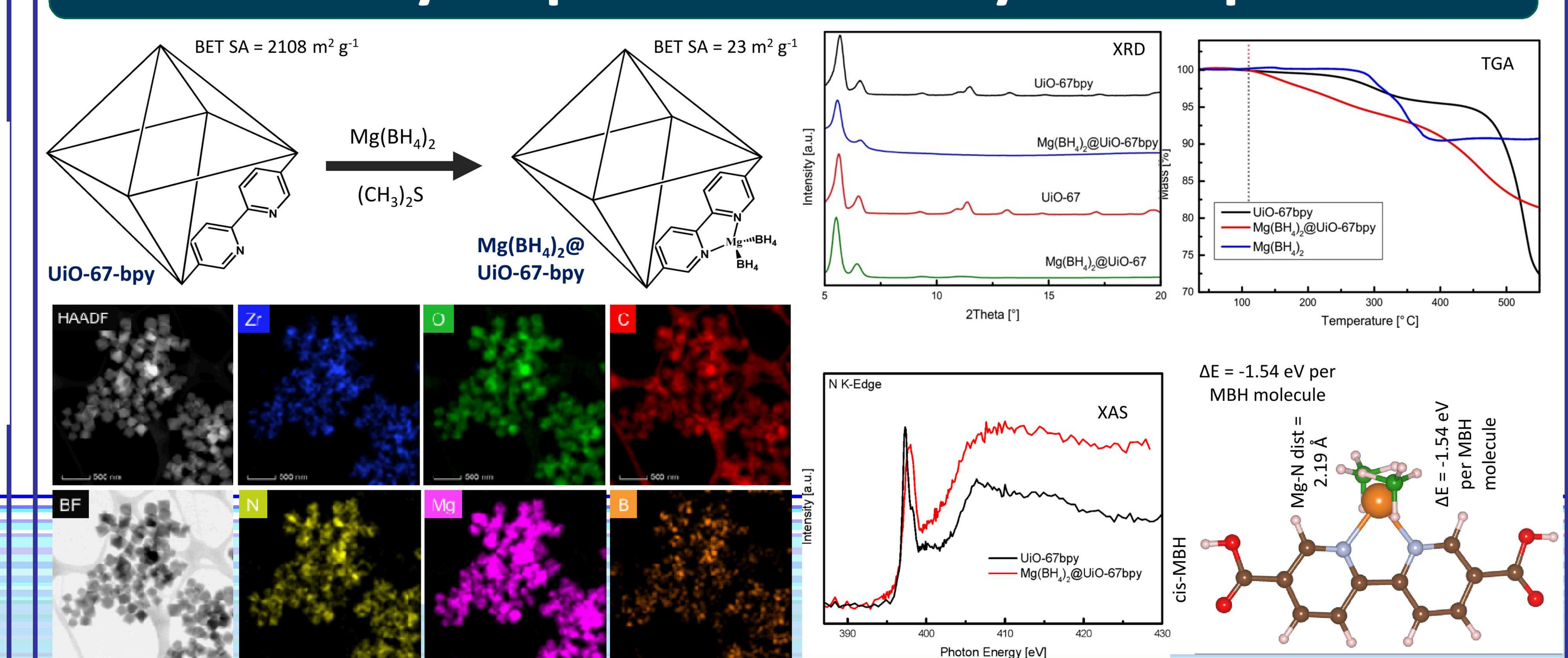


- The Li_3N@C nanocomposite displays one of the highest reversibly H_2 capacity among nanoconfined metal hydrides (5.2 wt% H_2).
- The full cycling capacity in the Li_3N/[$LiNH_2$ + 2LiH] system occurs 180°C lower than bulk.
- DFT and phase-field modeling results show that internal nanointerfaces and the core-shell microstructure are responsible for the dramatic improvements in hydrogen storage properties of the nanoconfined Li_3N/[$LiNH_2$+2LiH].



B.C. Wood, V. Stavila, N. Poonyayant, T.-W. Heo, K. Ray, L.E. Klebanoff, T.J. Udovic, J.R.I. Lee, N. J.D. Sugar, P. Pakawatpanurut. *Adv. Mater. Interfaces* **2017**, *4*, 1600803.

Molecularly dispersed metal hydride species



- A new form of hydride nanoconfinement is demonstrated by creating molecular $Mg(BH_4)_2$ species coordinated to bipyridine nitrogen atoms inside pores of UiO-67bpy.
- TEM/EDS measurements reveal that Mg and B are homogeneously distributed within UiO-67-bpy.
- Nitrogen and magnesium edge XAS data confirm bidentate coordination of Mg(II) by N-chelate groups.
- Sieverts measurements unveil that the hydrogen desorption kinetics are faster than for bulk $Mg(BH_4)_2$, with the onset of hydrogen desorption lower compared to bulk.

Summary and Conclusions

⇒ Nanoscaffolding in carbons and nanoencapsulation in graphene-based materials leads to significant improvements in both the kinetics and thermodynamics of hydrogen storage reactions.

⇒ PCT and direct van't Hoff measurements indicate that the entropy of hydrogen desorption is reduced at nanoscale. DFT data show that this is due to anharmonic surface entropy effects.

⇒ Experiments and theory suggests that strain, stress, and nanointerfaces can govern the hydrogen uptake and release in MgH_2, $NaAlH_4$, $LiNH_2$/2LiH, and high-capacity metal borohydrides.

Acknowledgements

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