From fundamental understanding to predicting new nanomaterials for high capacity hydrogen/methane storage and carbon capture

DOE-BES DE-FG02-08ER46522

Taner YILDIRIM[1,2]

[1]Department of Materials Science and Eng.,
University of Pennsylvania, Philadelphia, PA 19104

[2]NIST Center for Neutron Research, Gaithersburg, MD 20899

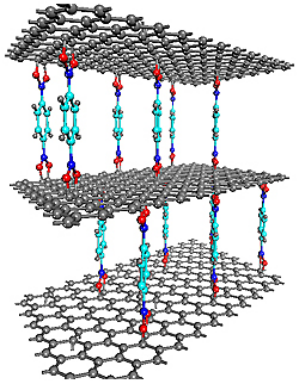
Program Manager: Dr. Thiyaga P. Thiyagarajan
Neutron Scattering
Office of Basic Energy Sciences
U.S. Department of Energy

Date: April 2, 2012
Project ID#: BES002

This presentation does not contain any proprietary, confidential, or otherwise restricted information

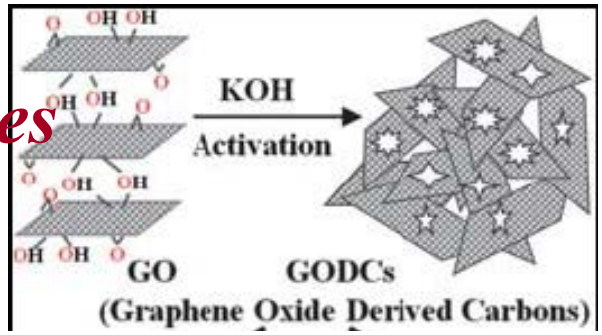
OUTLINE

- **Graphene-Oxide-Frameworks (GOFs) for Hydrogen Storage and Carbon Capture**



J. Burres,…, T. Yildirim, *Angewandte Chem. Int. Ed.* Vol. 49, 8902, 2010.
G. Srinivas,…,T. Yildirim, *J. Mater. Chem.* Vol.21, 11323, 2011.

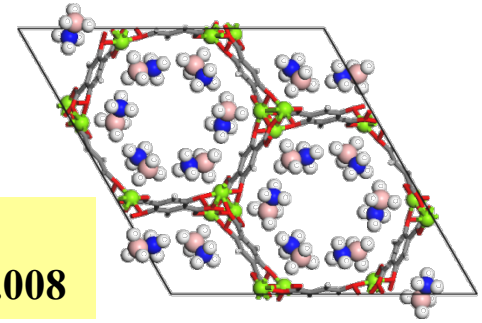
- **GO-Derived Carbons (GODCs):** ***Synthesis and Gas Adsorption Properties***



G. Srinivas , J. Burres, T. Yildirim, Energy Environ. Sci., 2012, DOI: 10.1039/C2EE21100A

Can we store H_2 at room T with *van der Waals* Interaction???

- Yes, store H_2-rich molecule such as AB instead of H_2! *Nanoconfined AB in MOFs…*



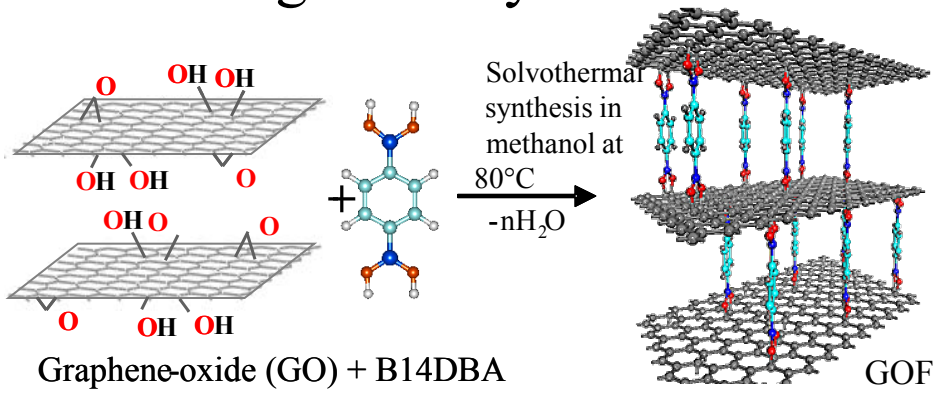
G. Srinivas,…,T. Yildirim, *Chem. Eur. J. 2011; 17, 6043*.
G. Srinivas,…,T. Yildirim, *Int. J. Hyd. Ener*. DOI:10.1016/j.ijhydene.2011.04.008

Nanoporous solid adsorbents are considered one of the key materials to solve many energy and environment related problems...

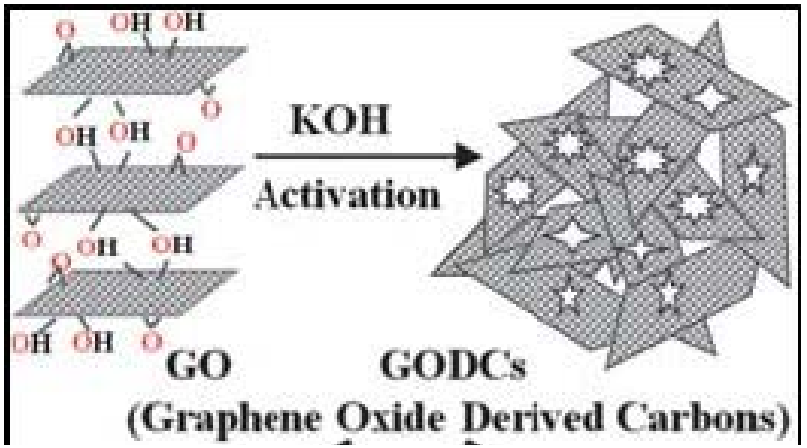
Graphene-Oxide Derived-Carbons (GODCs)

GO

Pillaring GO-Layers



Chemical Activation …

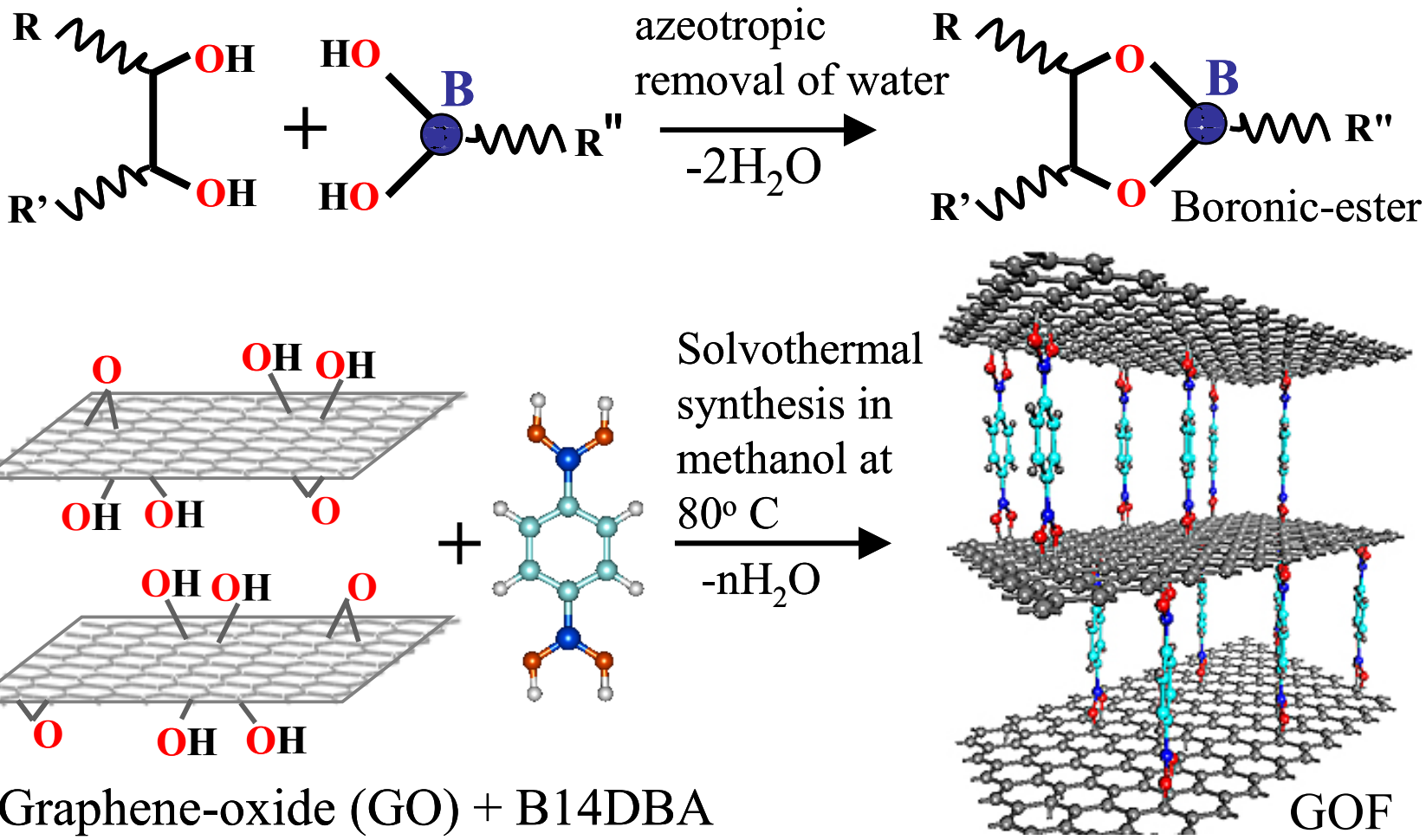


[1] J. Burres,…, T. Yildirim, *Angewandte Chem. Int. Ed.* Vol. 49, 8902, 2010.

[2] G. Srinivas,…,T. Yildirim, *J. Mater. Chem.* Vol.21, 11323, 2011.

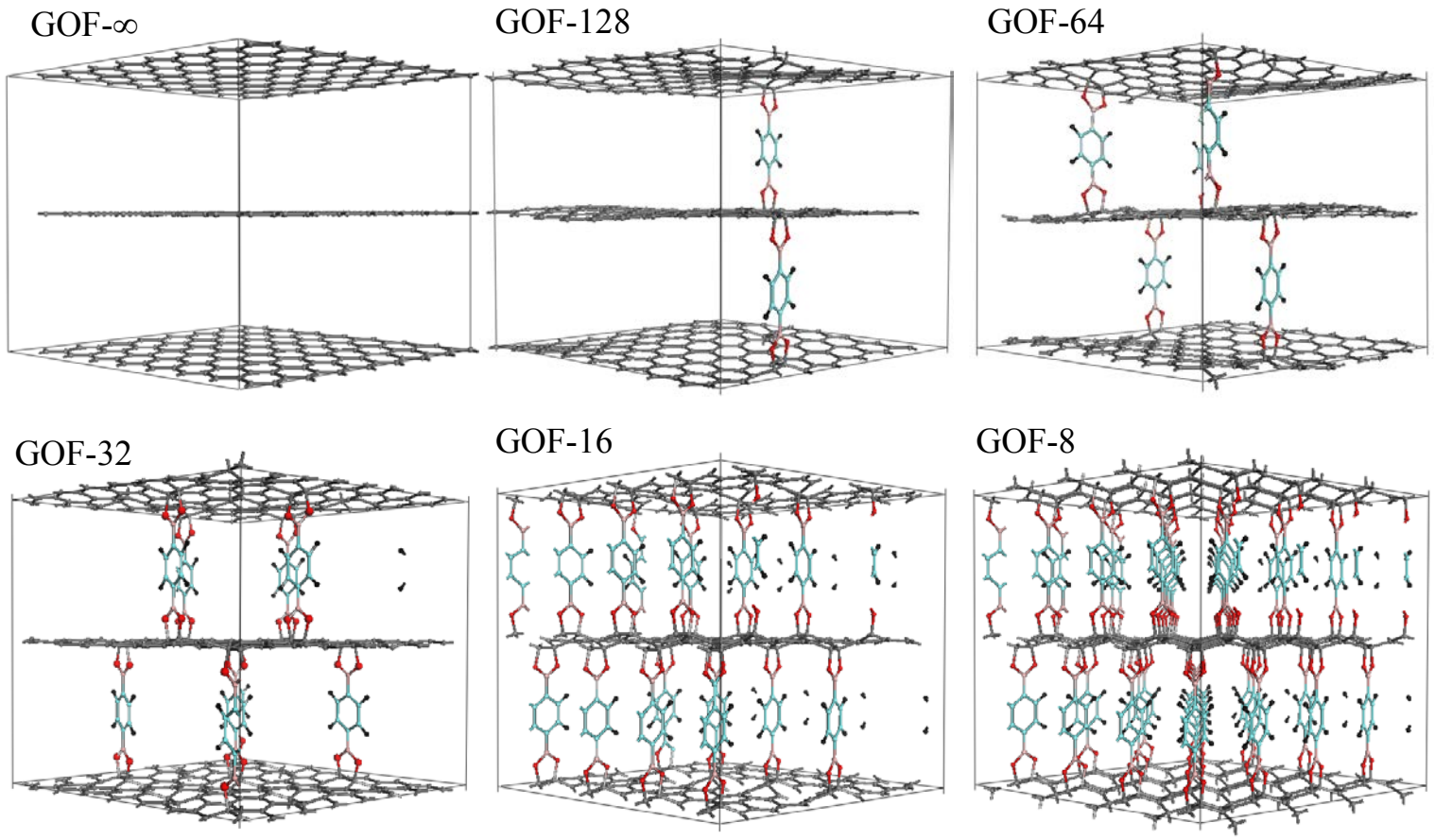
G. Srinivas, J. Burres, and T. Yildirim, *Energy Environ. Sci., 2012, DOI: 10.1039/C2EE21100A*

Graphine-Oxide Framework Materials (GOF)



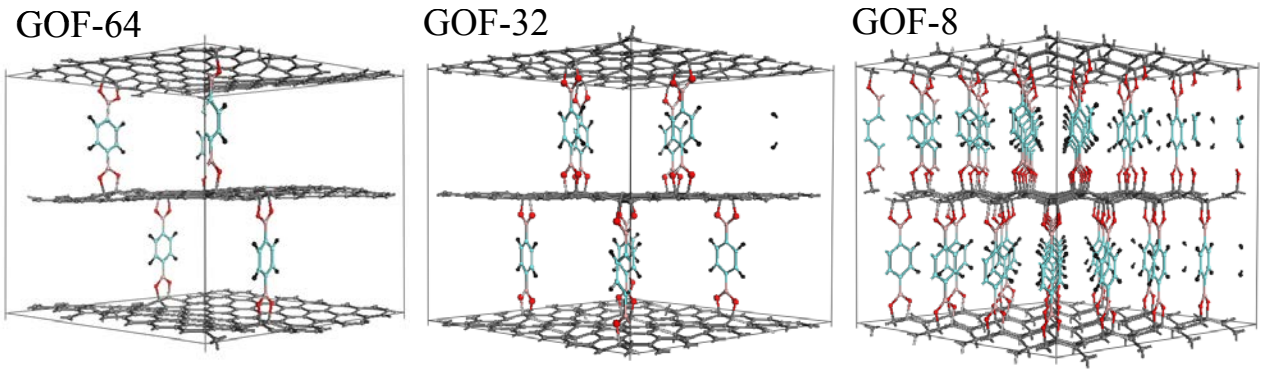
A schematic view of boronic-ester (top) and GOF formation (bottom). Idealized graphene-oxide framework (GOF) materials proposed in this study are formed of layers of graphene oxide connected by benzene-diboronic acid "pillars".

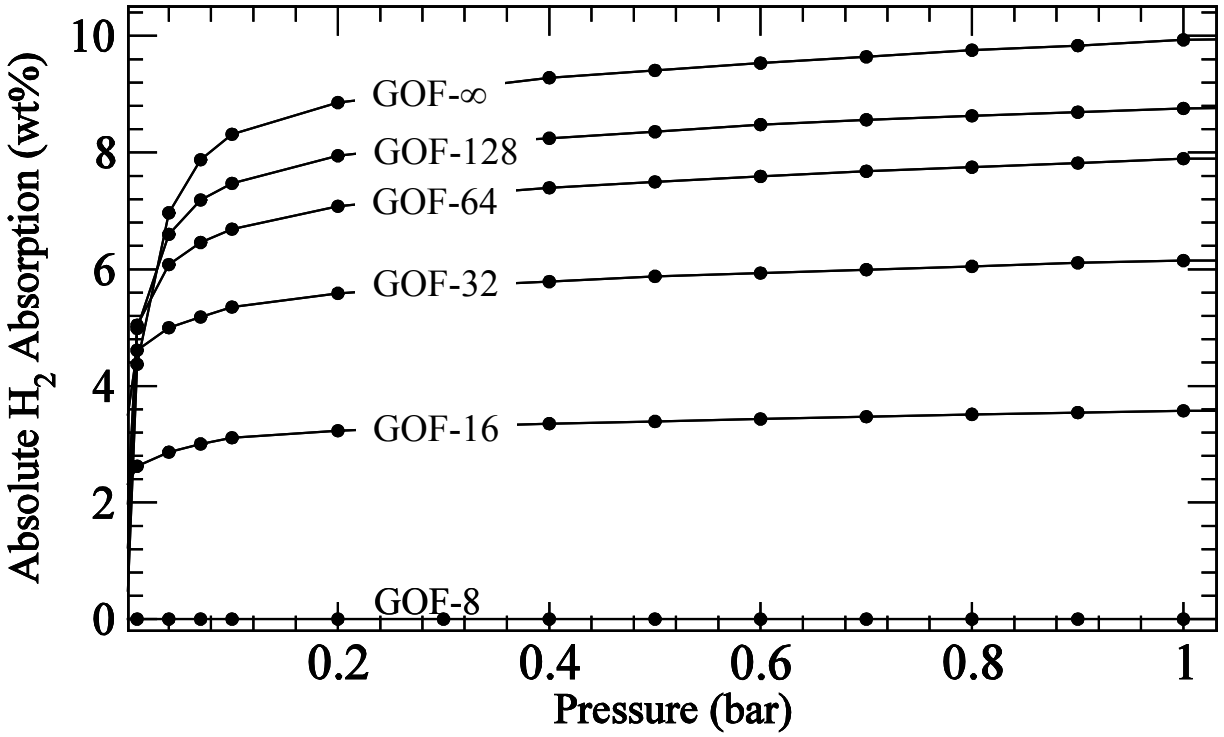
Theoretical modeling and GCMC simulations on GOFs



Model systems of GOFs were built based on graphene oxide layers and rigid diboronic acid linkers. We label these structure by GOF-n where n is the number of GO carbon per linker. Various n=carbon:linker ratios (n=∞, 128, 64, 32, 16, and 8) were adopted and uniform linker distribution was assumed, leading to a series of structures with different pore size, pore volume and surface areas as shown below.

Theoretical modeling and GCMC simulations on GOFs

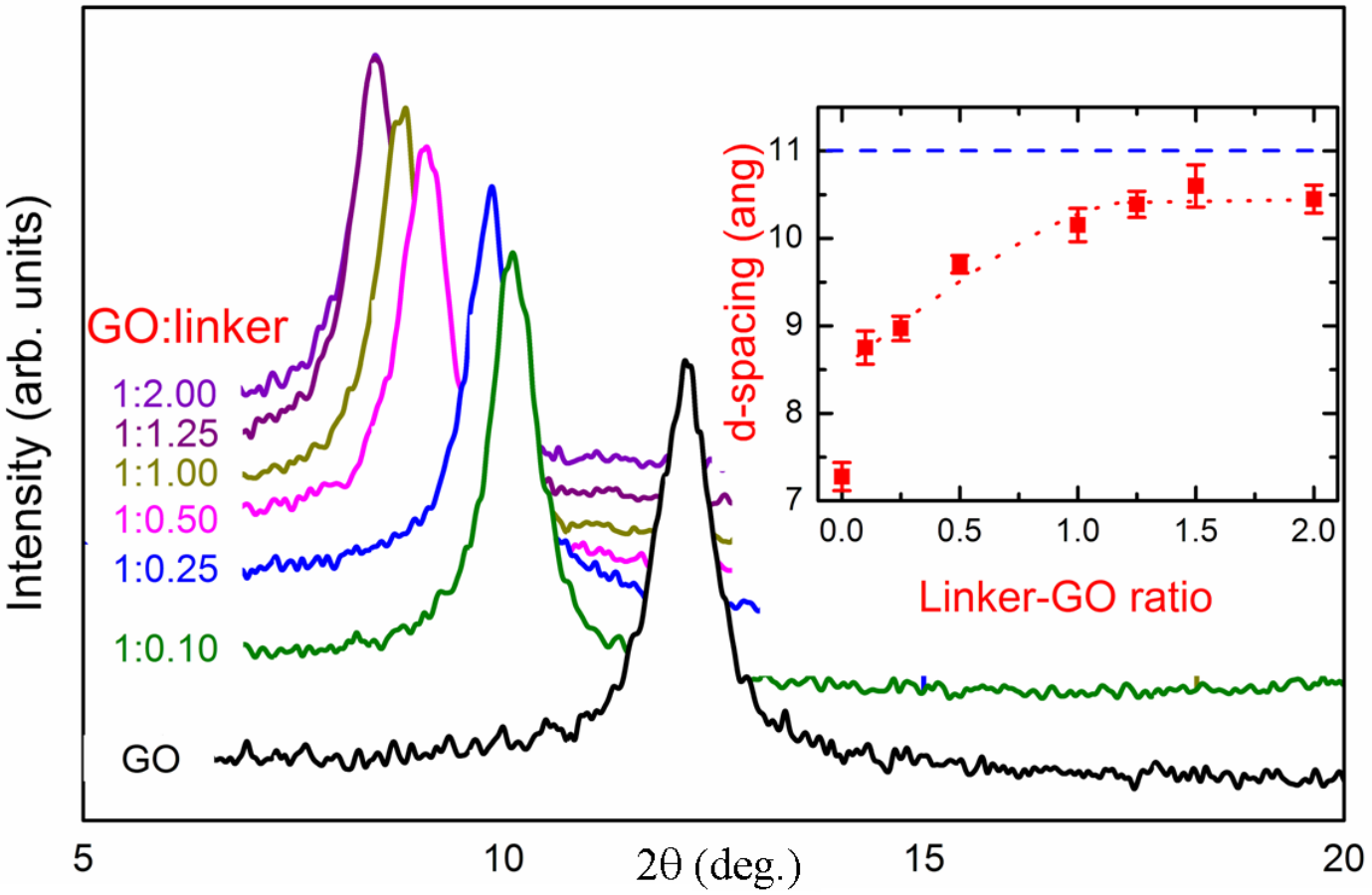




The GCMC simulations for ideal GOF-n structures with n-graphene carbons per linker. ***Similar calculations for H_2 uptake in MOF-5 gives 1.67 wt%, reasonably close to the experimental value ~1.3 wt%, giving confidence for the accuracy of GCMC simulations for GOF.***

Graphene Oxide Framework Materials

Methanol solvothermal synthesis:

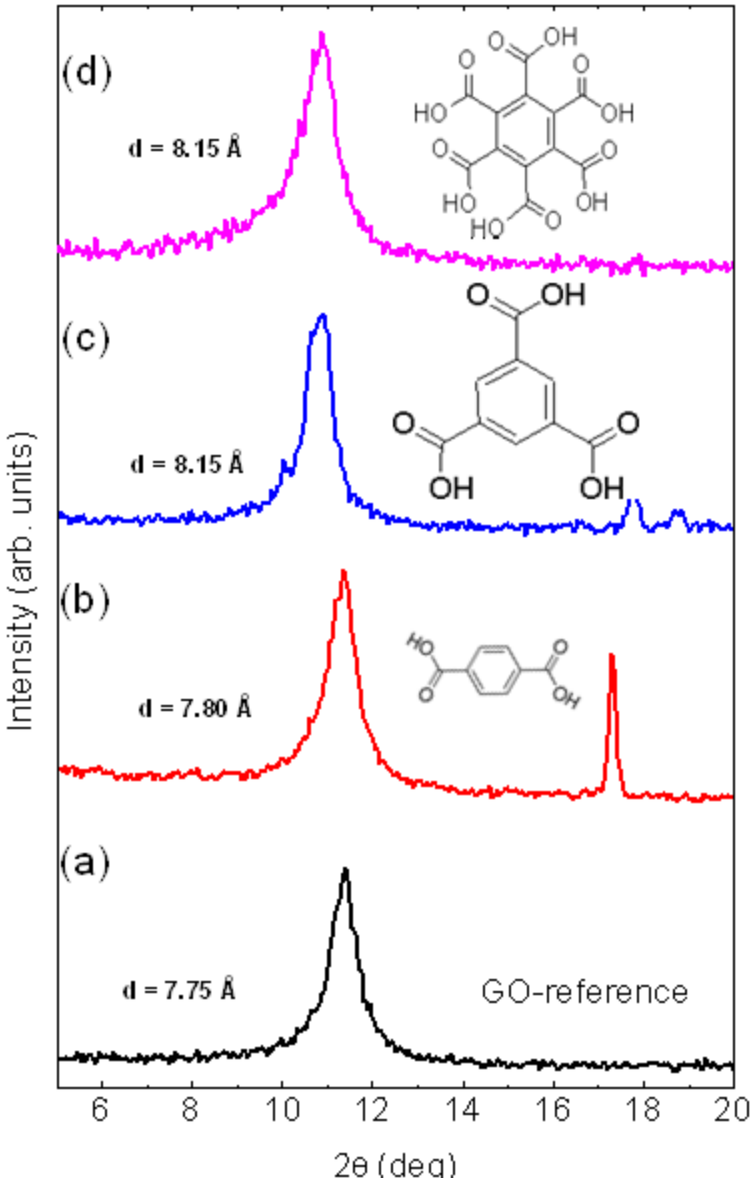


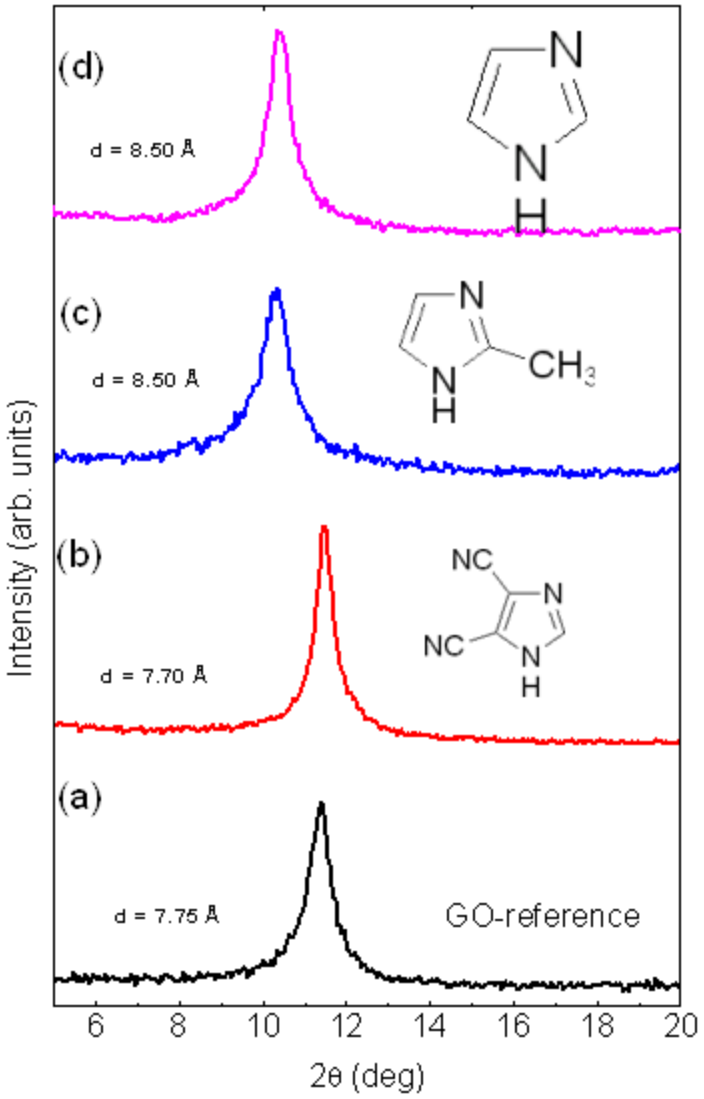
We synthesized samples containing varying amounts of linker and characterized them with PXRD. As shown above, we observed a controllable, monotonic increase in the interlayer spacing in the GOF samples, from 0.75 nm to 1.05 nm.

Graphene Oxide Framework Materials

Other non-boronic acid linkers???:

Other Linkers do not WORK, suggesting that boronic acid is the key for GOF!





Graphene Oxide Framework Materials

Prompt Gamma Activation Analysis and XPS

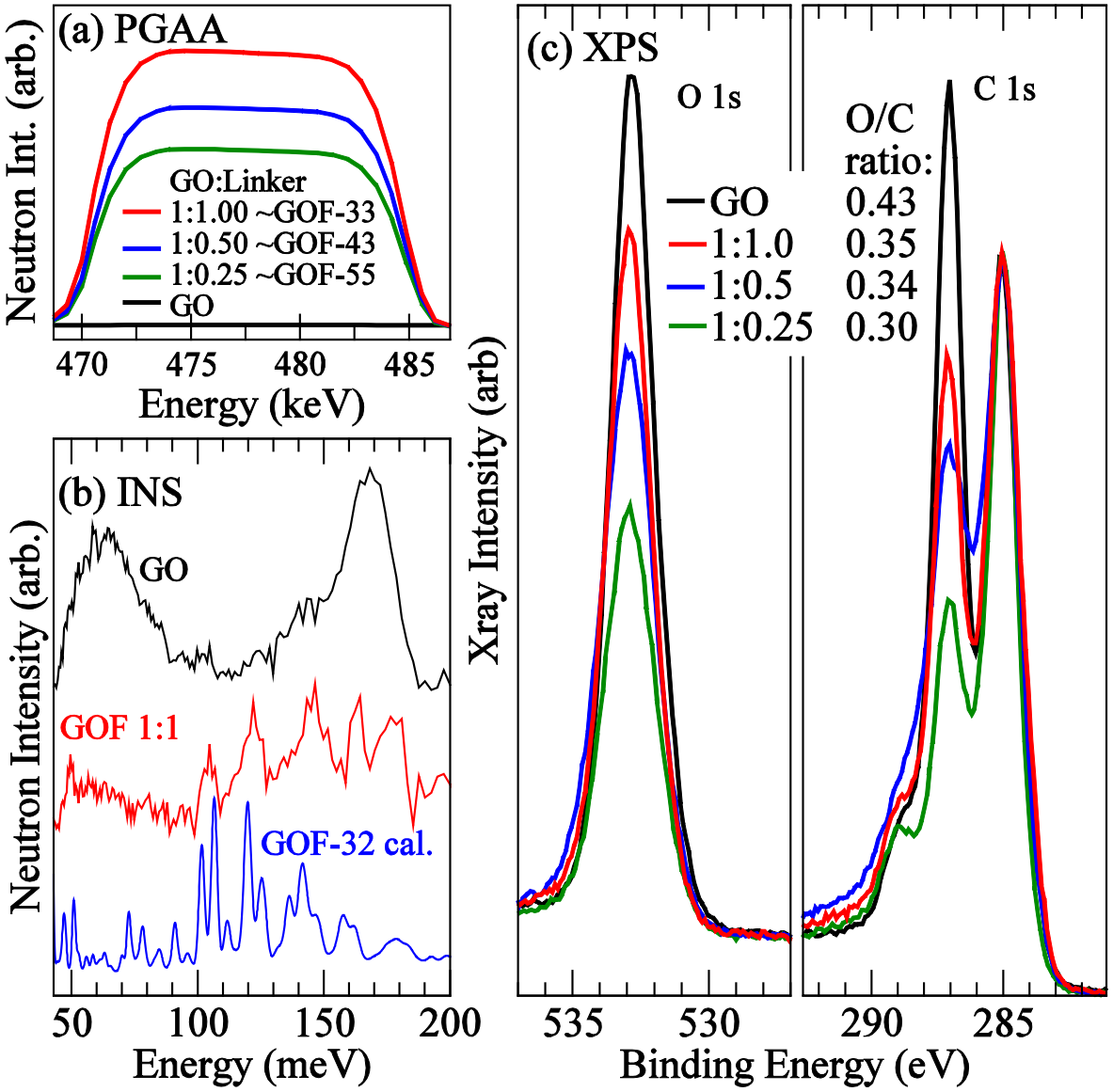
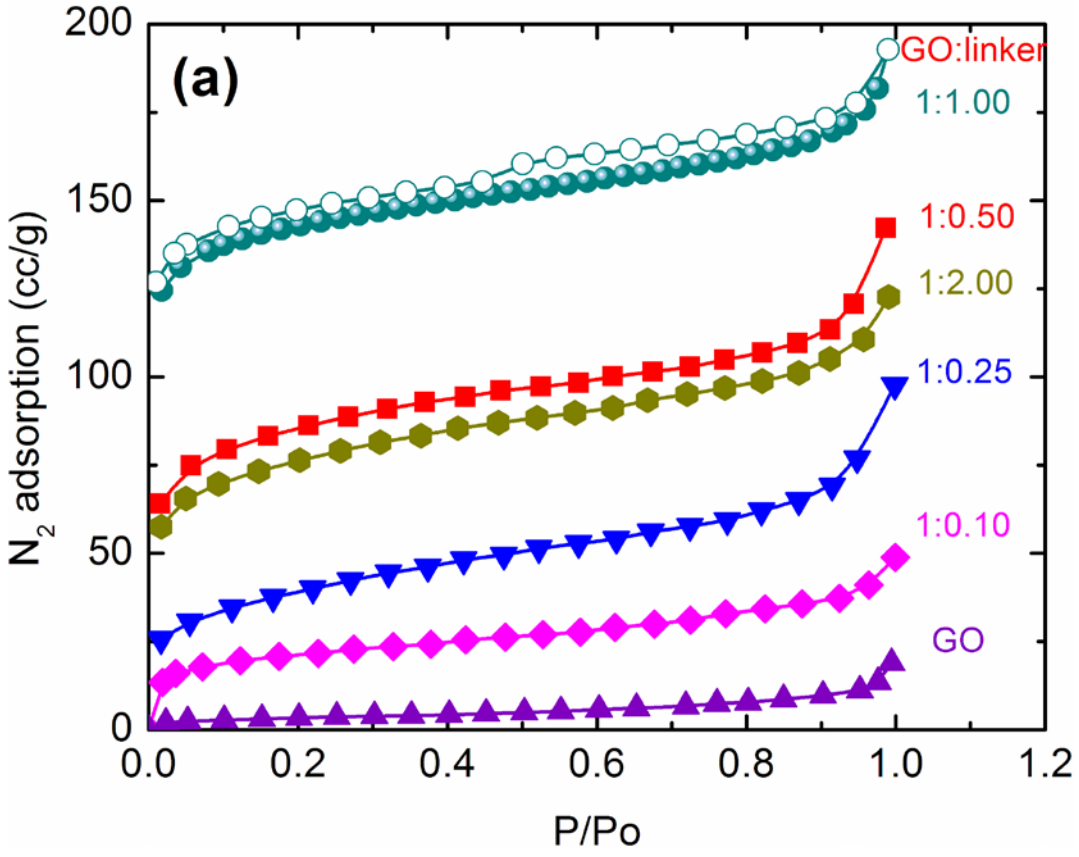


Figure (a) The major boron peaks normalized to carbon peak in PGAA spectra, indicating the approximate relations between GO:Linker samples and the ideal GOF-n structures. (b) INS spectra of GO and GOF 1:1 sample and a model calculation based on GOF-32 structure. (c) XPS O 1s and C 1s core level spectra for GO and three different GOFs.

Graphene Oxide Framework Materials

BET Surface Area

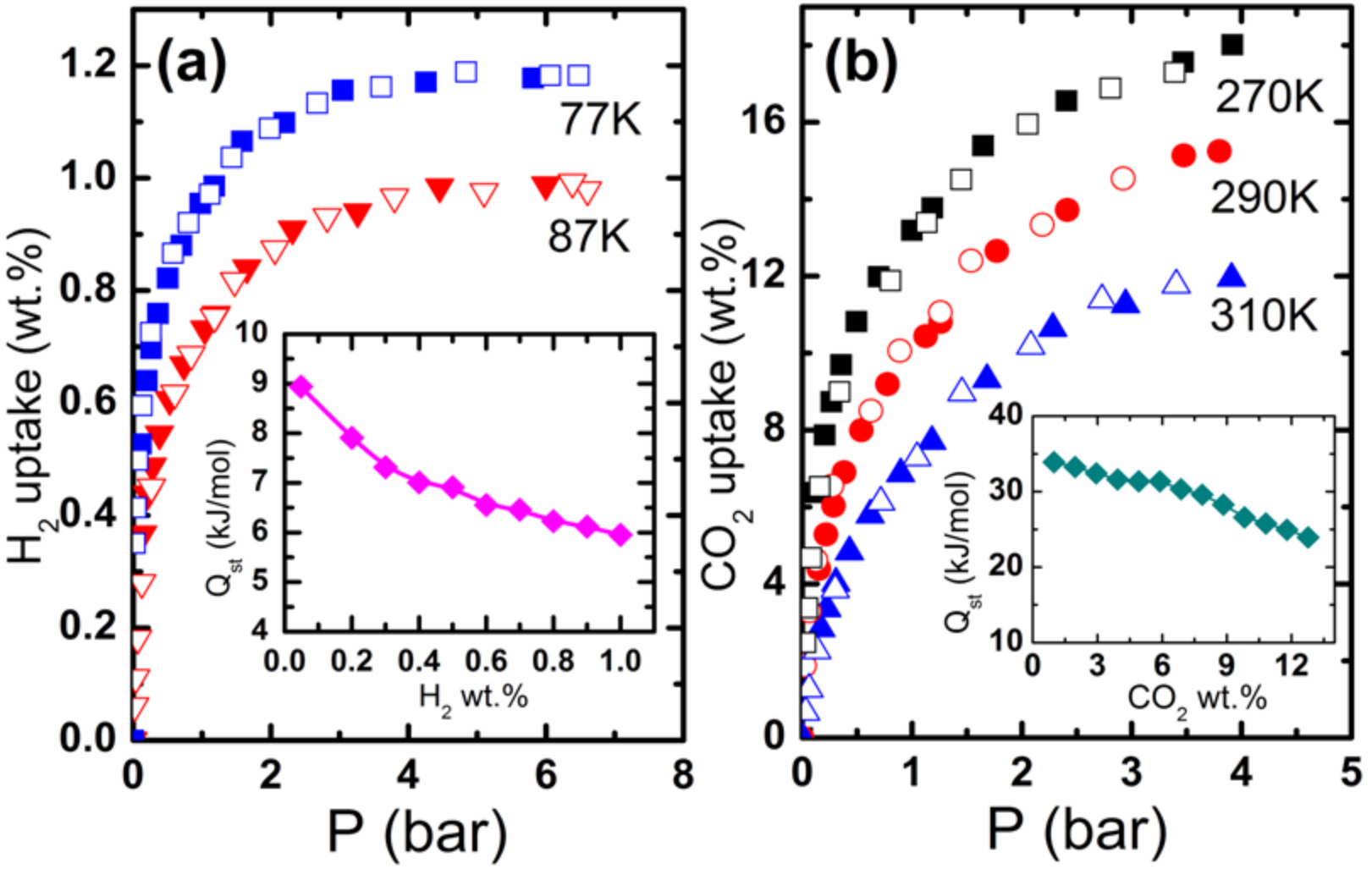


Nitrogen sorption isotherms of GO precursor with a BET specific surface area (SSA) of 16 m^2/g and GOFs which have BET SSA's of 74 m^2/g, 138 m^2/g, 280 m^2/g, 470 m^2/g and 275 m^2/g for the initial GO to linker weight ratios of 1:0.1, 1:0.25, 1:0.5, 1:1, and 1:2, respectively.

Given that the GO alone has almost no usable surface area (< 20 m^2/g), there is essentially no H_2 adsorption, however, it is clear that the addition of the diboronic acid linker progressively increases the accessible surface area and thereby increases the H_2 uptake. Eventually, increased linker concentrations reduce the accessible surface area due to the filling up of the inter-layer space, which also reduces the H_2 uptake. The BET of nearly 500 m^2/g obtained for the 1:1 initial mass loading is considerably higher from the graphene oxide sheets.

Graphene Oxide Framework Materials

Hydrogen and CO_2 Uptake



Excess H_2 and CO_2 isotherms at various temperatures, indicating GOF exhibits a considerably large isosteric heat of adsorption for both H_2 and CO_2, as compared to other nanoporous materials.

Graphene Oxide Framework Materials

Conclusions:

1.We have successfully shown that graphene oxide layers can be used as building blocks for new nanoporous materials by interlinking them with diboronic acids.

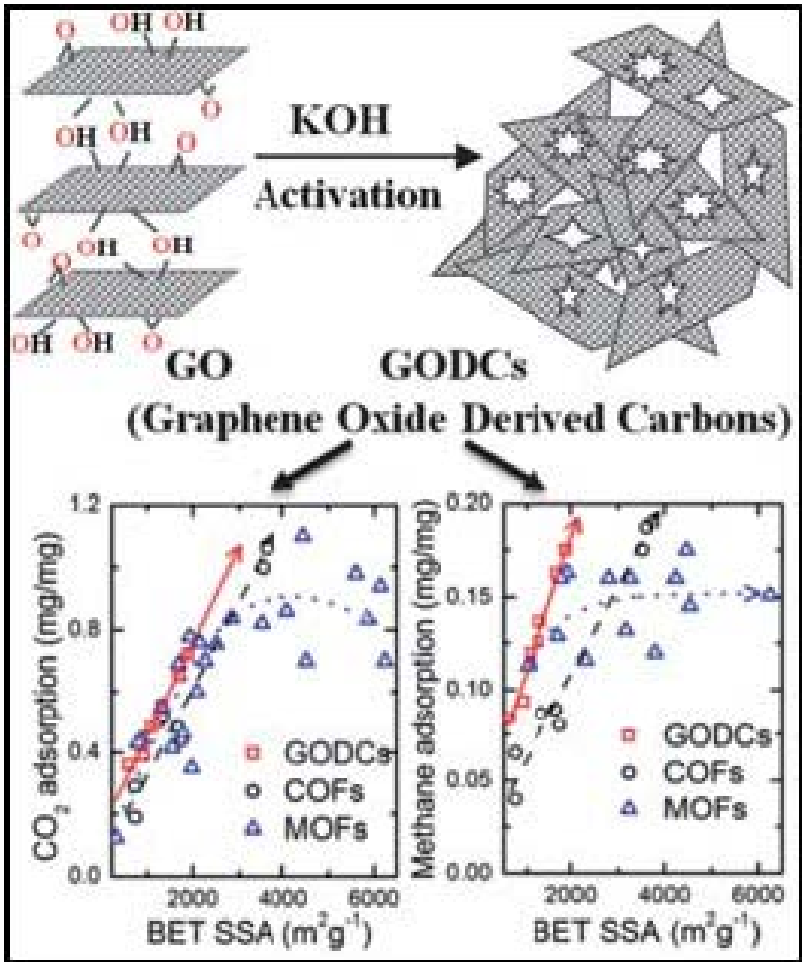
2.Considering the rich boron chemistry and large number of different types of boronic acids, it is quite possible that there are other linkers that will perform better than B14DBA used in this study.

3.Furthermore, different activation procedures other than heat treatment could improve the adsorption capacity of GOFs. In particular, chemical reduction to remove unreacted functional groups could improve the pore size and surface area significantly.

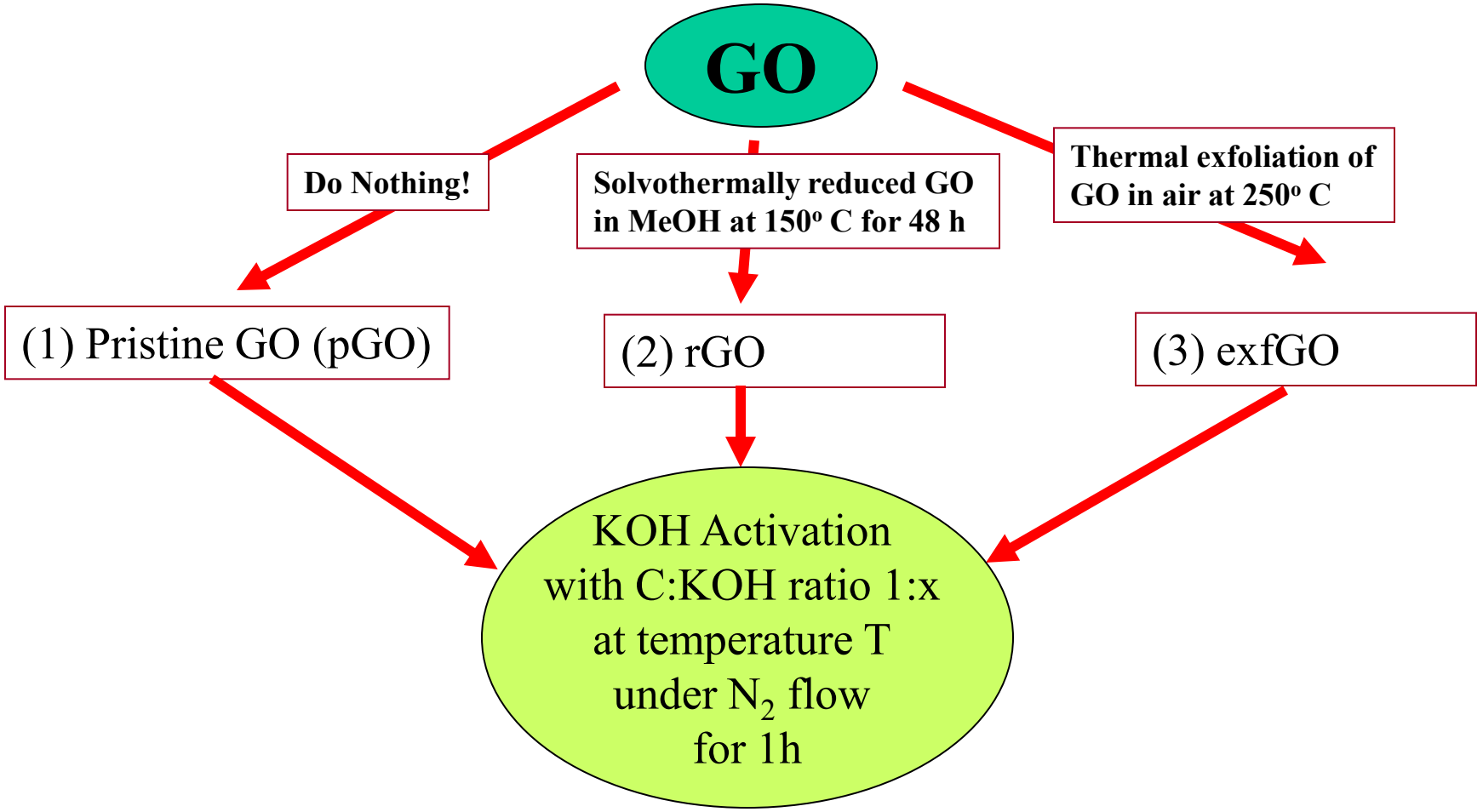
We are currently carrying out more detailed research along these lines. *We hope that our theoretical predictions and the first experimental results reported here will start a new research direction based on cheap and environmentally friendly GO as a building block for new nanoporous materials with better gas adsorption properties.*

Graphene oxide derived carbons (GODCs): synthesis and gas adsorption properties

G. Srinivas, J. Burres, and T. Yildirim,
Ener. and Environ. Sci., Feb. 2012, DOI: 10.1039/c2ee21100a



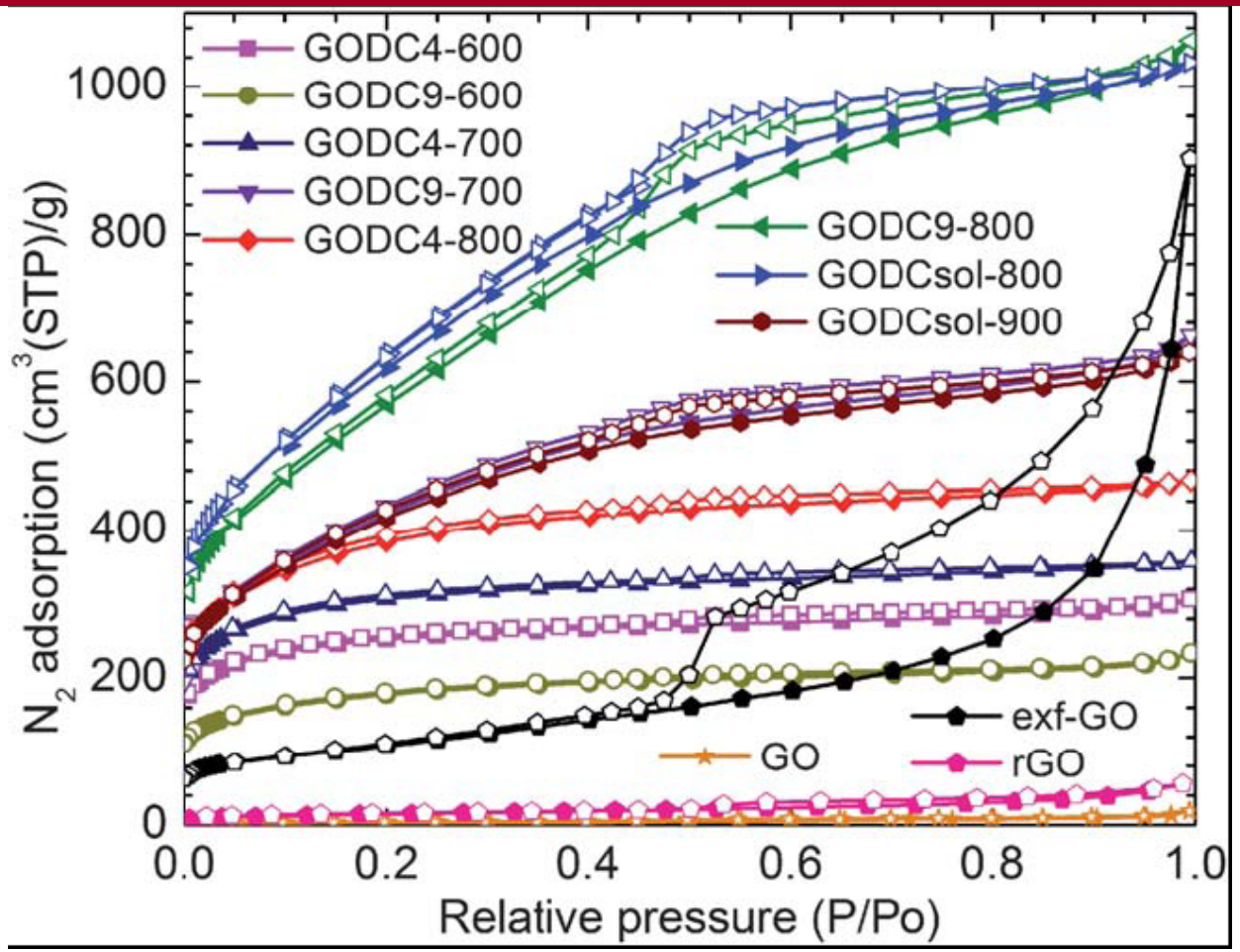
Synthesis of GODCs…



pGOGC6-800 ⟶ Pristine GO, with 1:6 ratio of C:KOH and 800 C activation

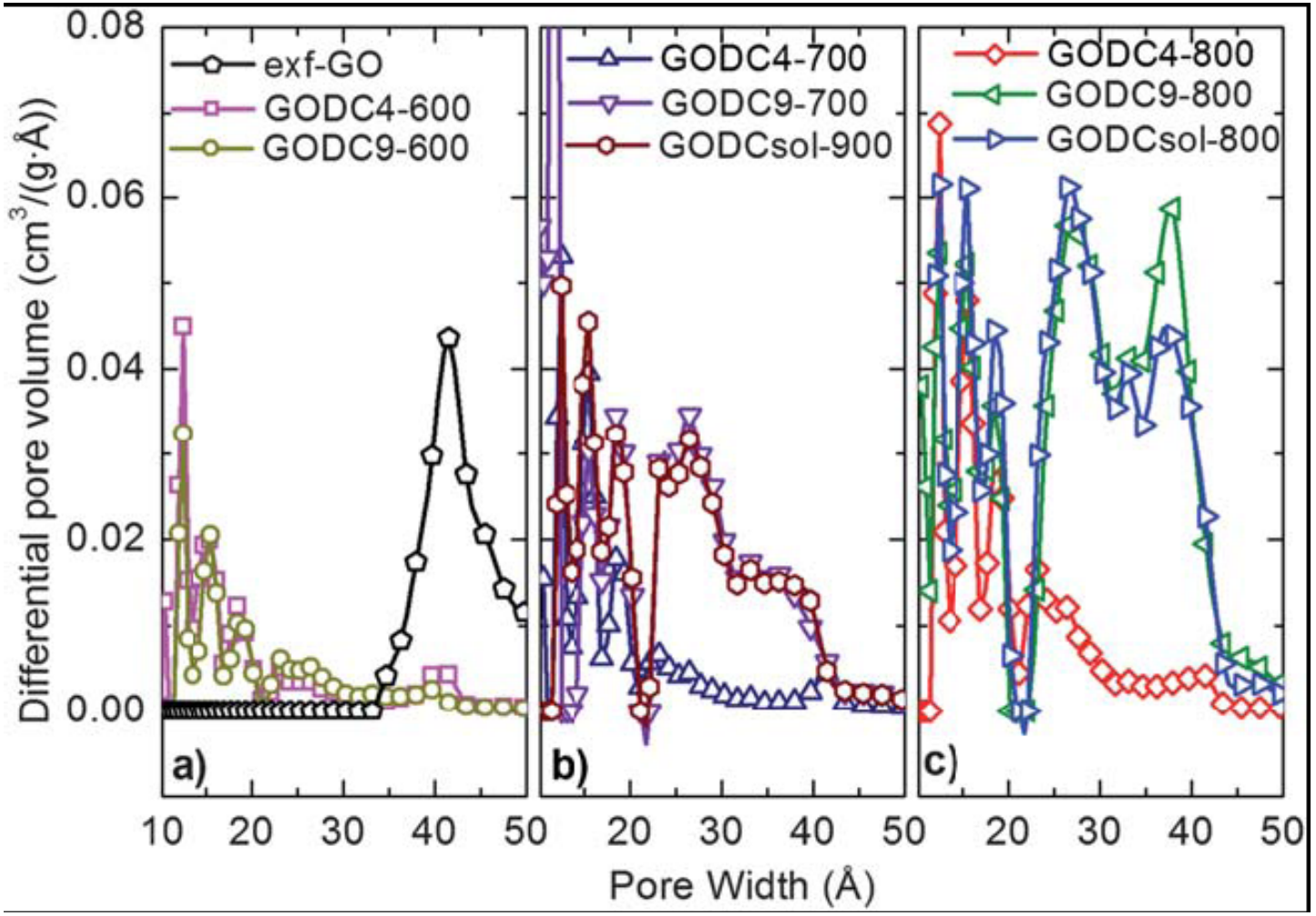
exfGOGC4-900 ⟶ Thermal. exfoliated GO, with 1:4 ratio of C:KOH and 900 C

GODCs: Surface Area (1000-1900 m^2/g)



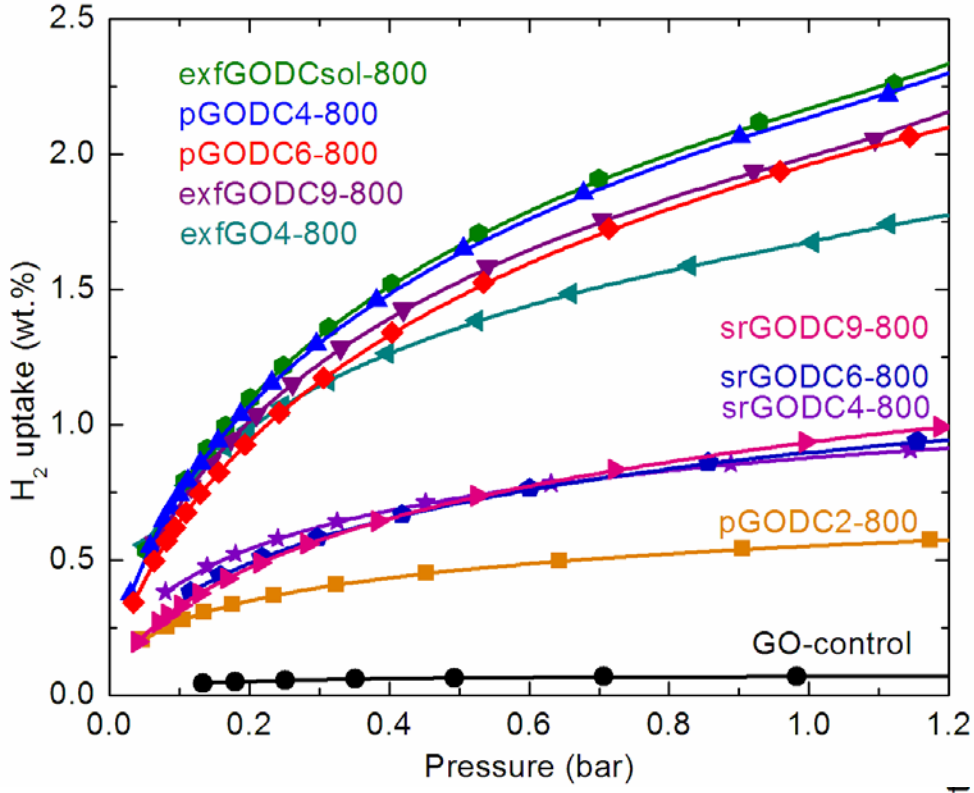
N_2 adsorption–desorption isotherms of GO, rGO, exf-GO and GODCs produced under different activation conditions, measured at 77 K. The solid and open data points represent adsorption and desorption isotherms respectively.

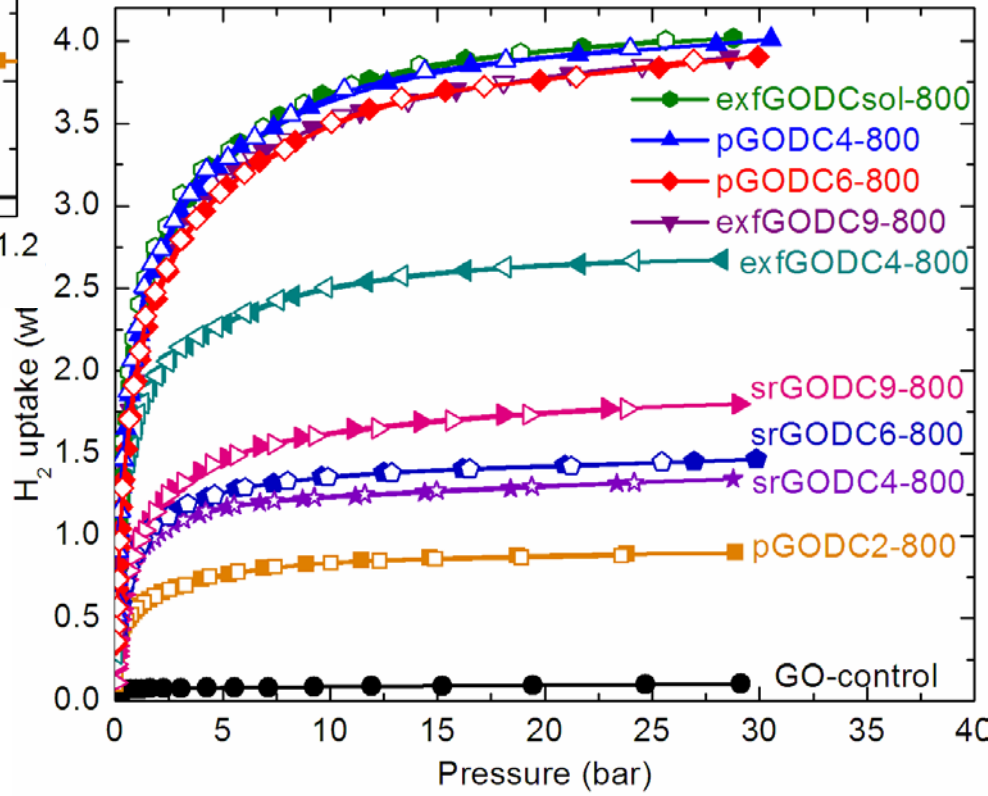
GODCs: Pore Size Distribution…



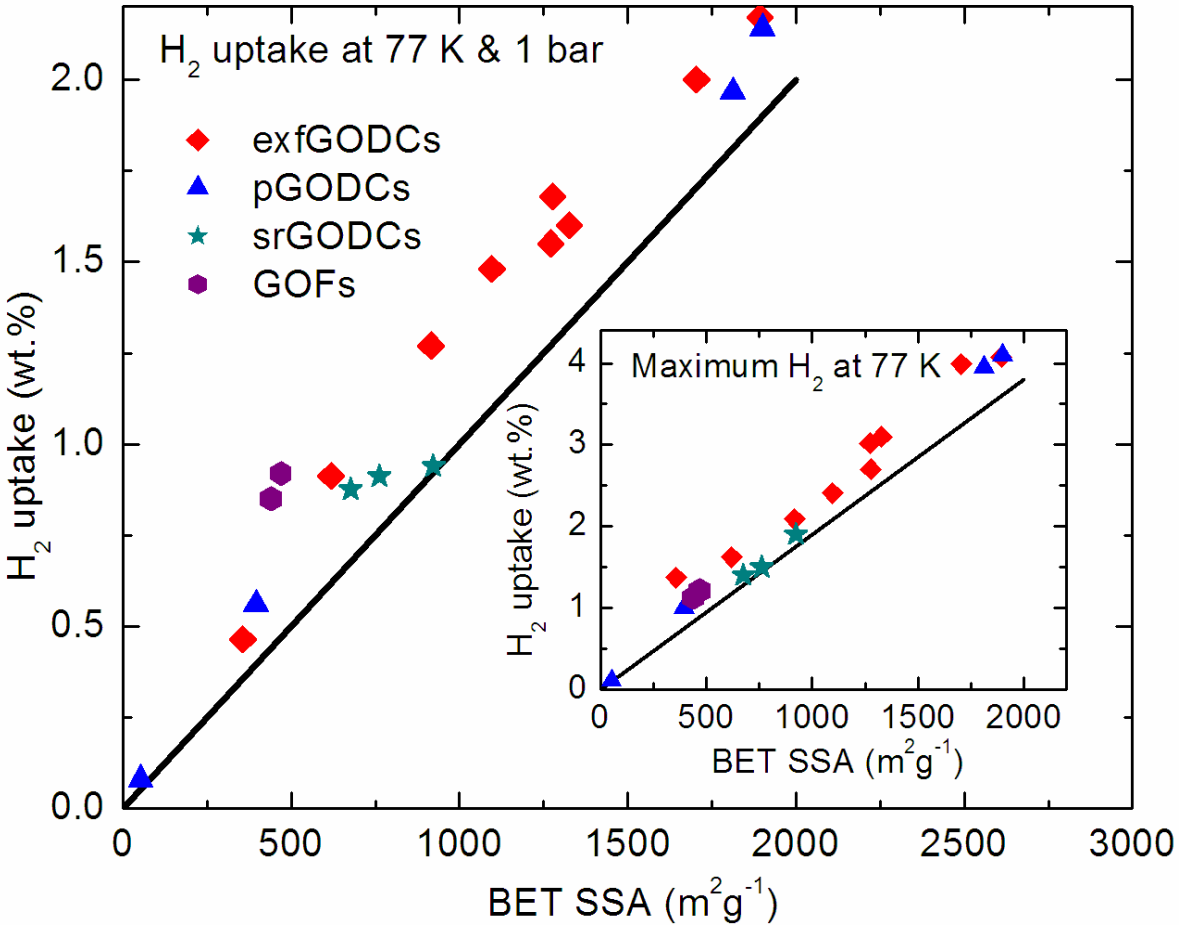
Pore size distribution of exf-GO and GODCs produced under different activation conditions. The data are derived from the N_2 adsorption isotherms...

GODCs: Hydrogen Absorption Properties



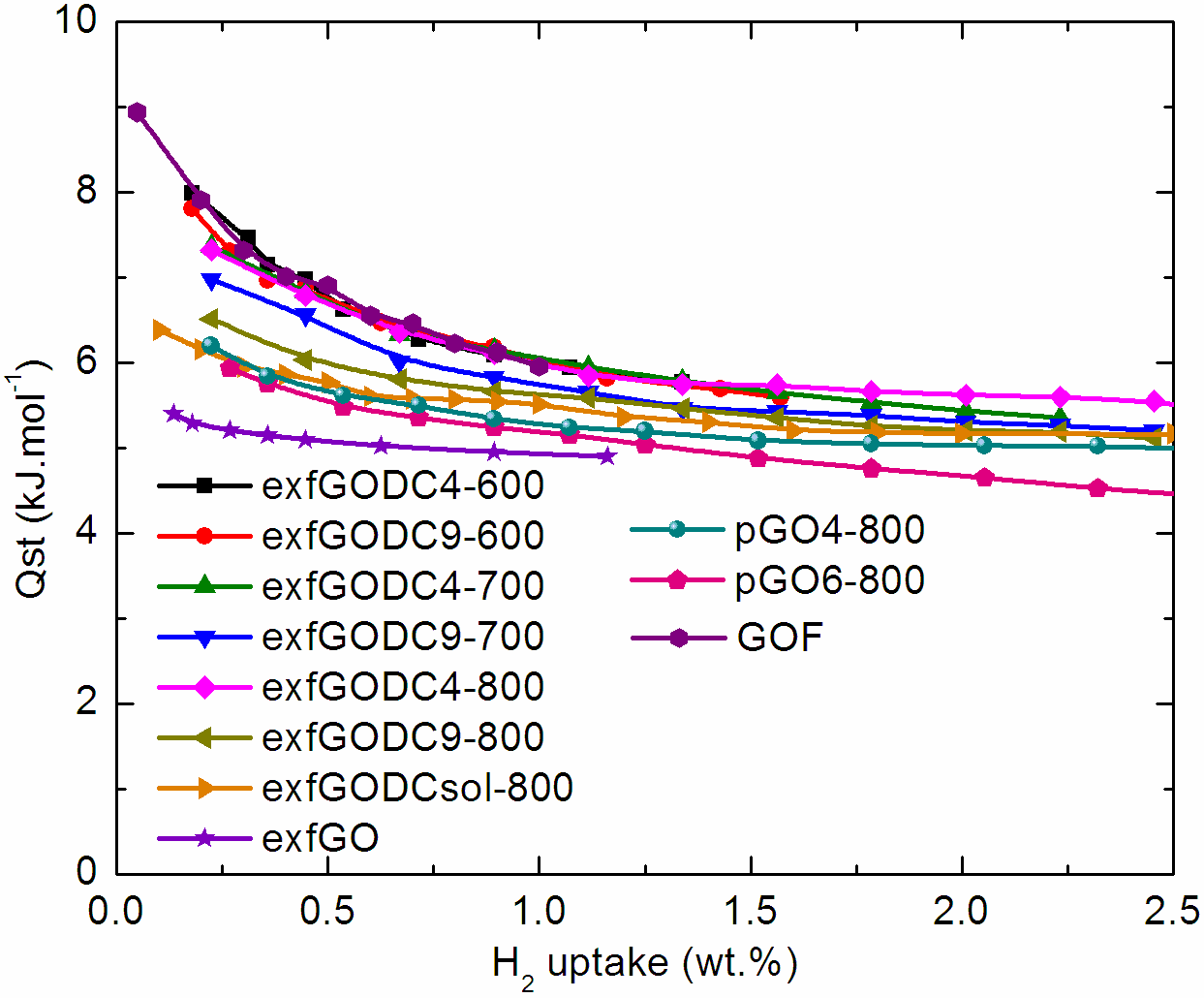


GODCs: Hydrogen Absorption Properties



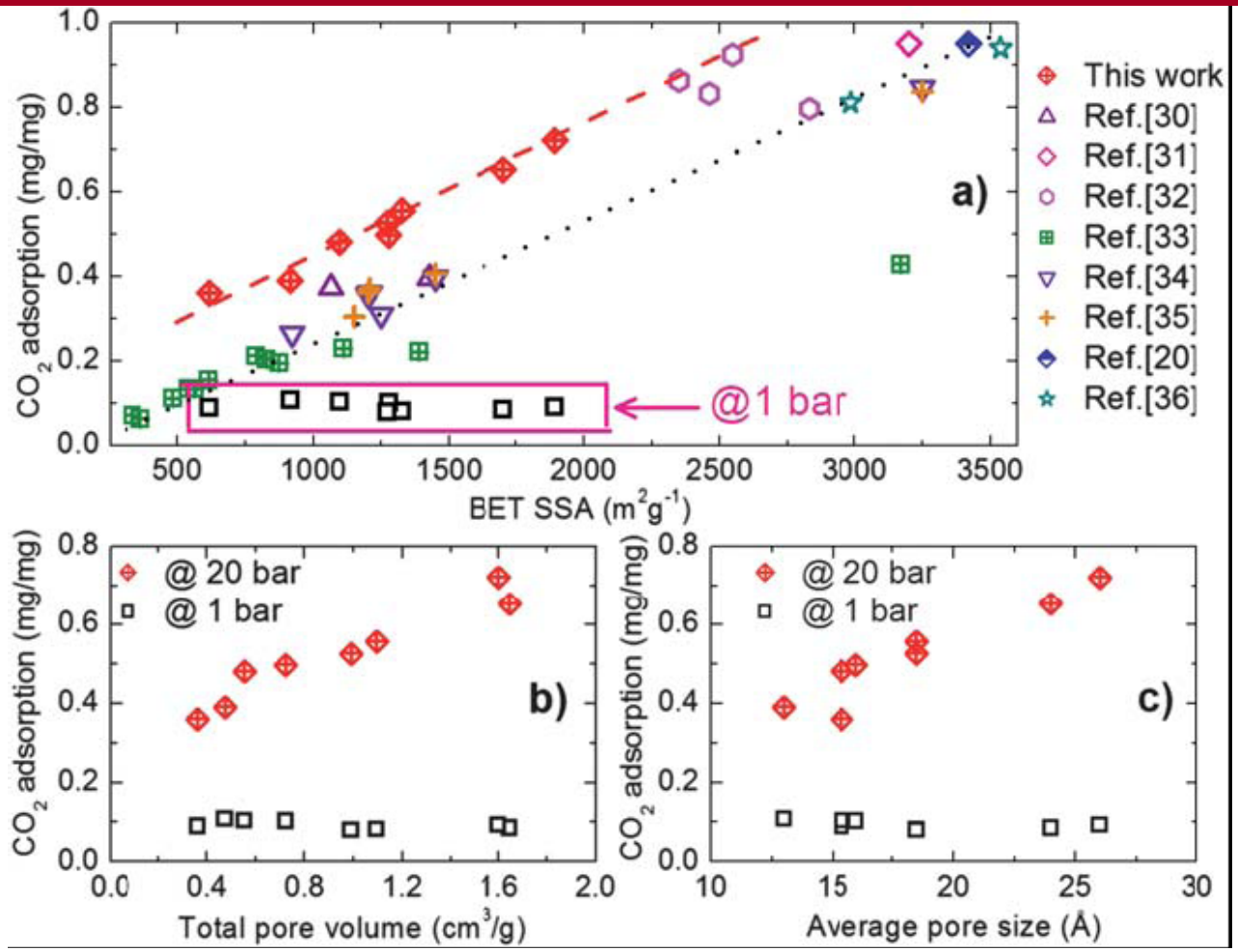
BET vs H_2 uptake (at 77 K) of pillared GOs (GOFs) and different types of GODCs. The solid represents the generalized behavior for range of porous carbons.

GODCs: Hydrogen Absorption Properties



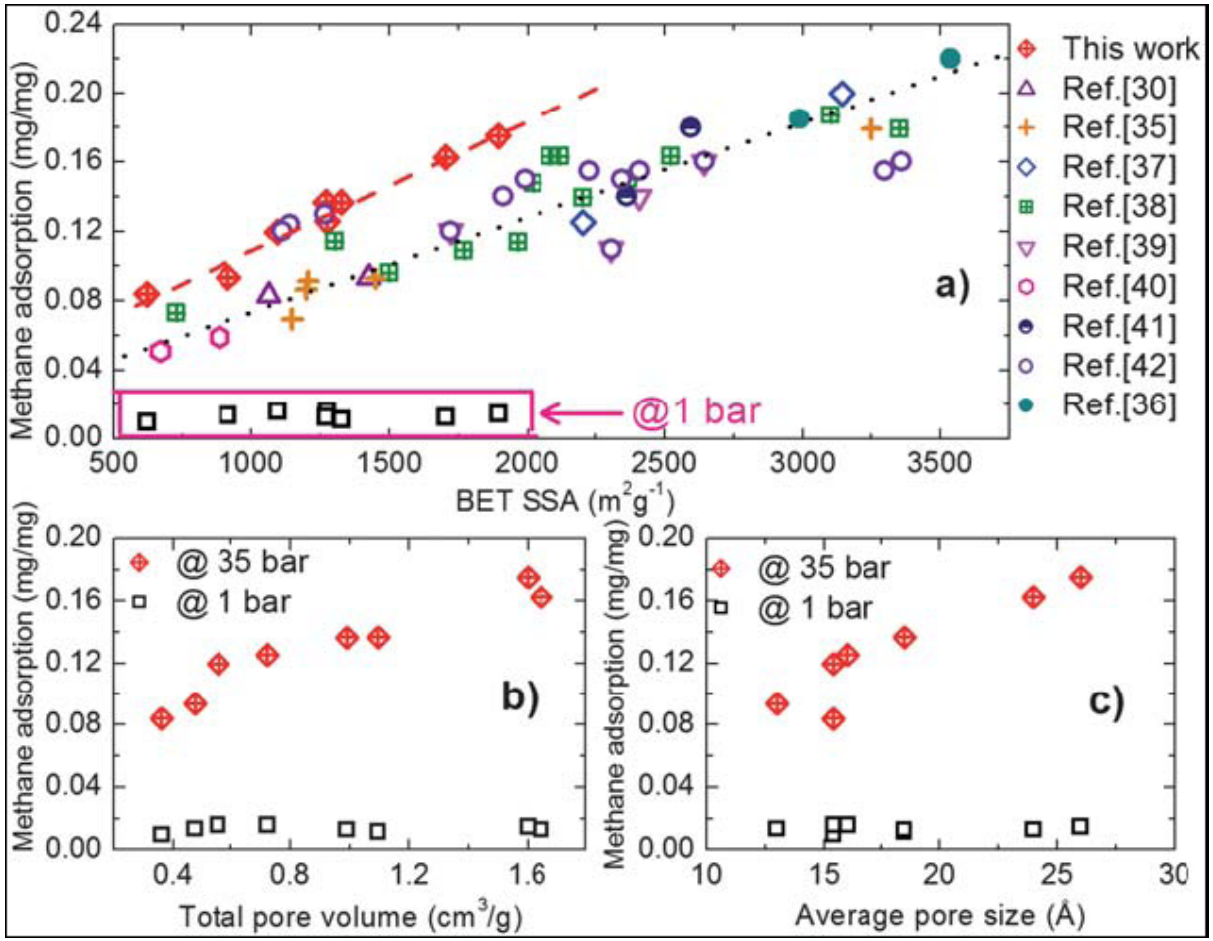
Q_{st} vs H_2 uptake (at 77 K) of pillared GO (GOF) and different types of GODCs.

GODCs: CO_2 Absorption Properties



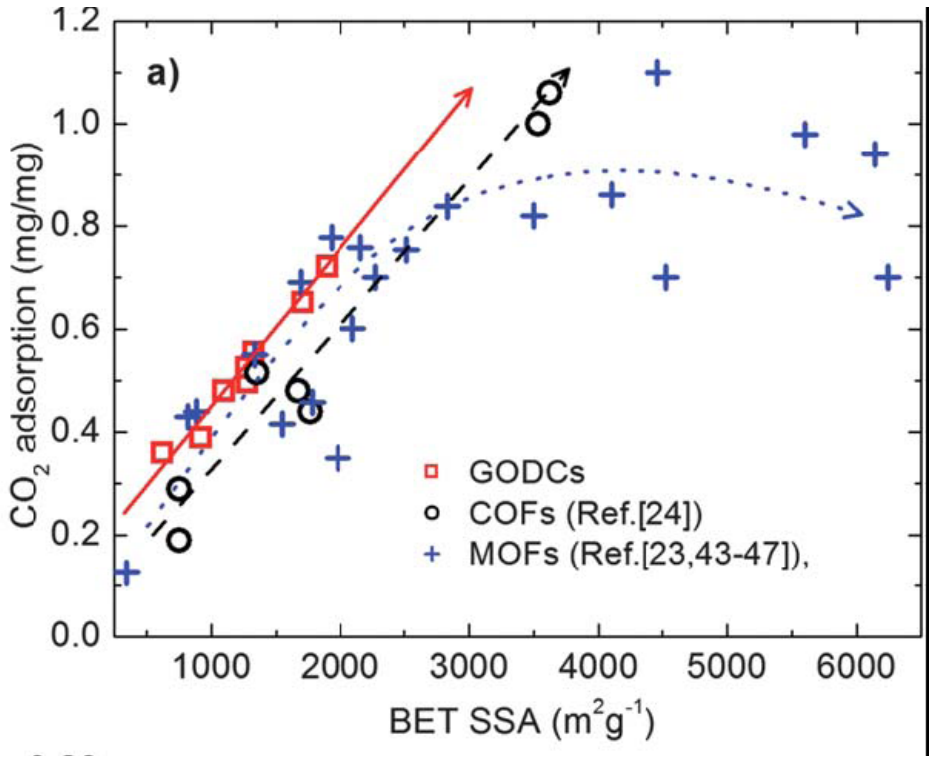
The low pressure (1 bar) and high pressure (20 bar) CO_2 adsorption capacities at 300 K with respect to the BET surface area (a), total pore volume (b) and average pore size (c). Around room temperature (298–300 K) the CO_2 adsorption capacities at 20 bar of our GODCs and a range of other porous carbons are compared with respect to the most important porosity parameter, BET surface area, that defines the adsorption capacities of most of the porous

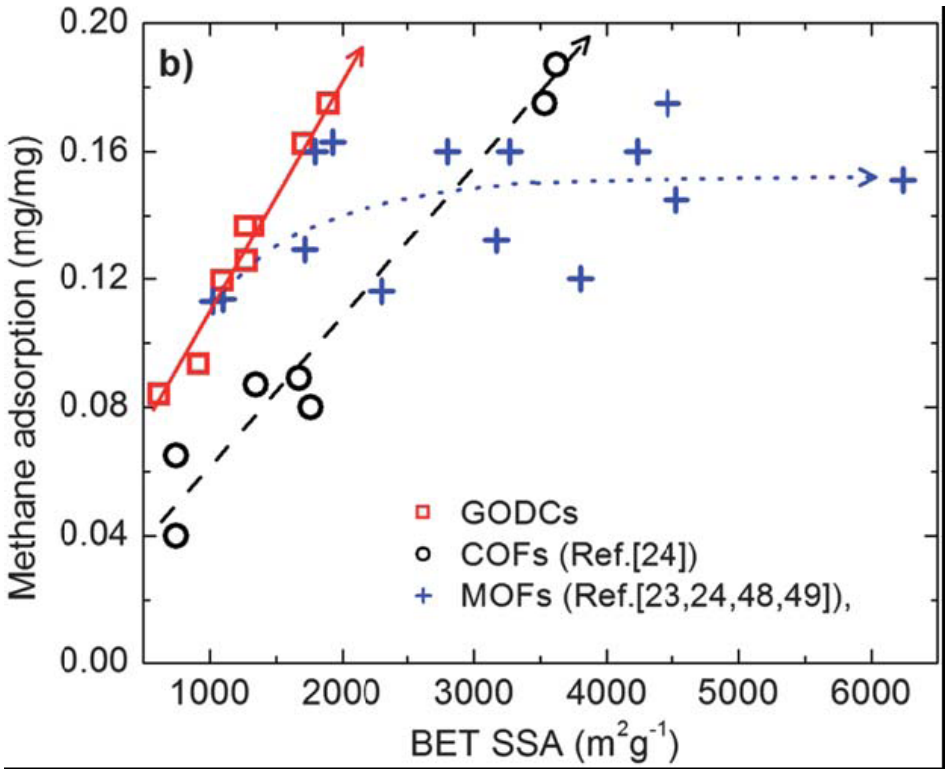
GODCs: CH_4 Absorption Properties



The low pressure (1 bar) and high pressure (35 bar) methane adsorption capacities at 300 K with respect to the BET surface area (a), total pore volume (b) and average pore size (c). Around room temperature (298–300 K) the methane adsorption capacities at 35 bar of our GODCs and a range of other porous carbons are compared with respect to the BET surface area (a) (ref. 35). "+" represents the commercial activated carbons.

GODCs versus MOFs/COFs…





The room temperature (298–300 K) and high pressure CO_2 (a) and methane (b) adsorption capacities at 20 bar and 35 bar, respectively, of our GODCs and a range of other porous organic frameworks compared with respect to the BET surface area.

GODCs: CONCLUSIONS..

- We report the synthesis of a range of high surface area graphene oxide derived carbons (GODCs) and their applications toward carbon capture and methane storage.

- We obtain largely increased surface areas up to nearly 1900 m^2/g for GODC samples from 10 m^2/g of precursor graphene oxide (GO).

- Our GODCs reveal favourable gas adsorption capacities compared to other high surface area carbons.

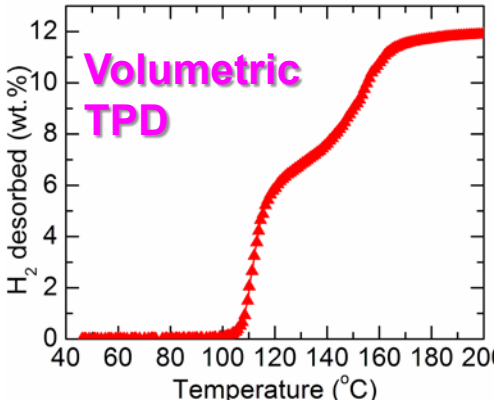
- We show that producing high surface area carbons from GO precursor is a viable method, and the porosity parameters are easily tunable for their potential gas adsorption applications.

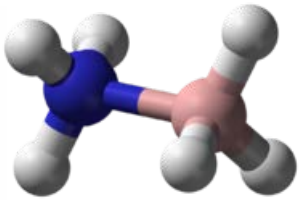
What about room temperature hydrogen storage?

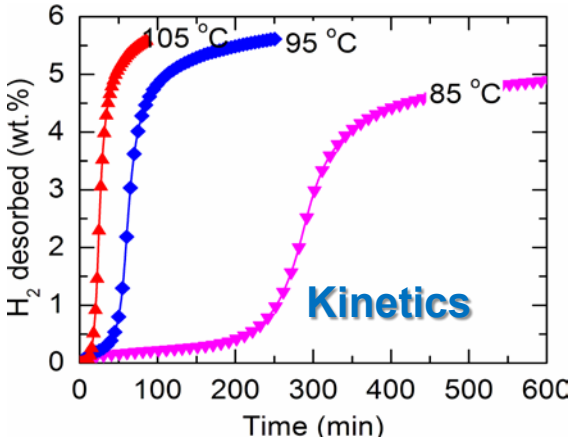
- Can we store hydrogen at room temperature in a van-der Waals host-material???
- We think YES:
- The key is not to try to store hydrogen molecule but rather hydrogen-rich molecules in nanoporous materials!
- Ammonia-Borane (AB) is such a promising hydrogen rich molecule!!!!

Ammonia Borane (NH3BH3, AB)

- Light weight, stable in the solid state at ambient temperatures
- High capacity 19.6 wt.% H_2 (1/3 at ~120°C, 2/3 at ~200°C & complete at >1000°C)





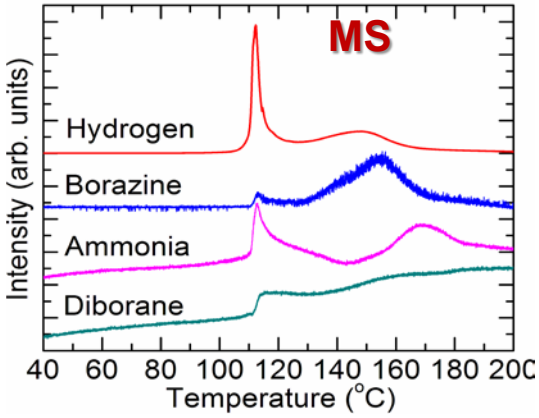


Practical application:

- very slow H_2 release <100°C
- poisonous byproducts
  - ammonia, borazine, diborane
- sample foaming
- irreversibility

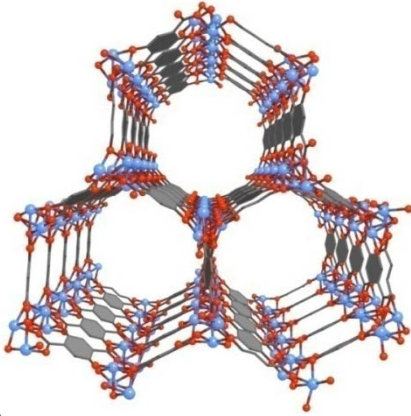
Metal-catalyst & porous support:

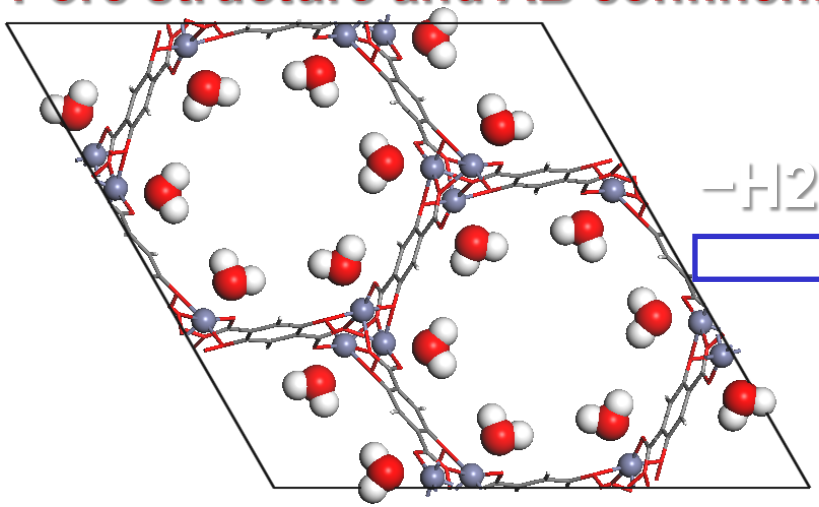
- ✓greater extents of H_2 release rate
- ✓much lowered temperatures
  - preventing byproducts
  - controllability in dehydrogenation
  - total system weight
  - reversibility



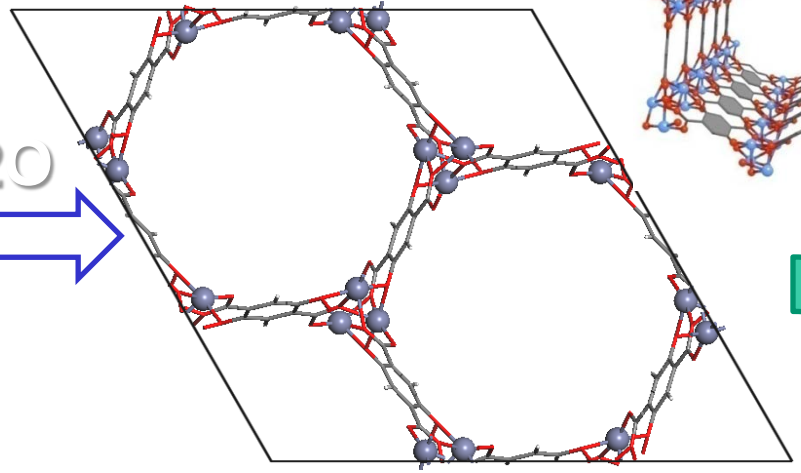
MOF-74

Pore structure and AB confinement





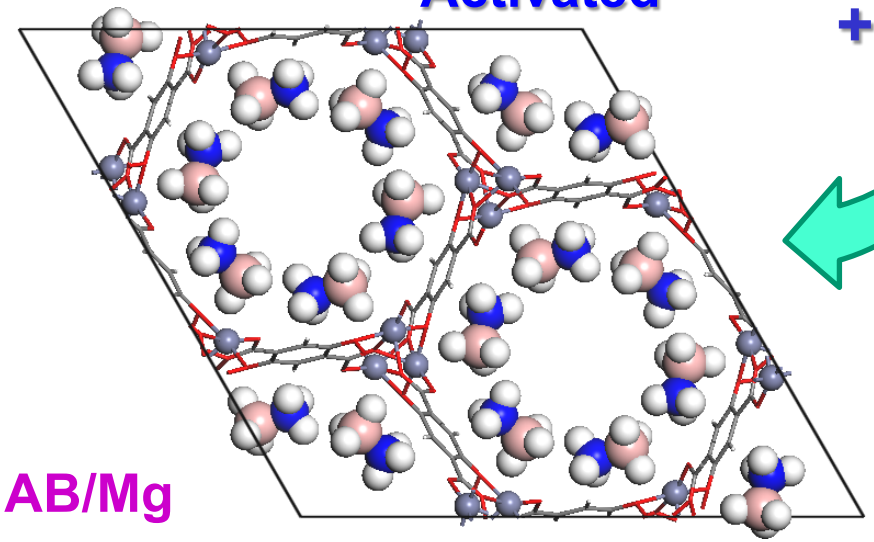
−H2O



As synthesized

Activated

+ AB



AB incorporated

Hexagonal one-dimensional
~12 Å pore channels

Unsaturated Mg-metal
centers at edges of the pores

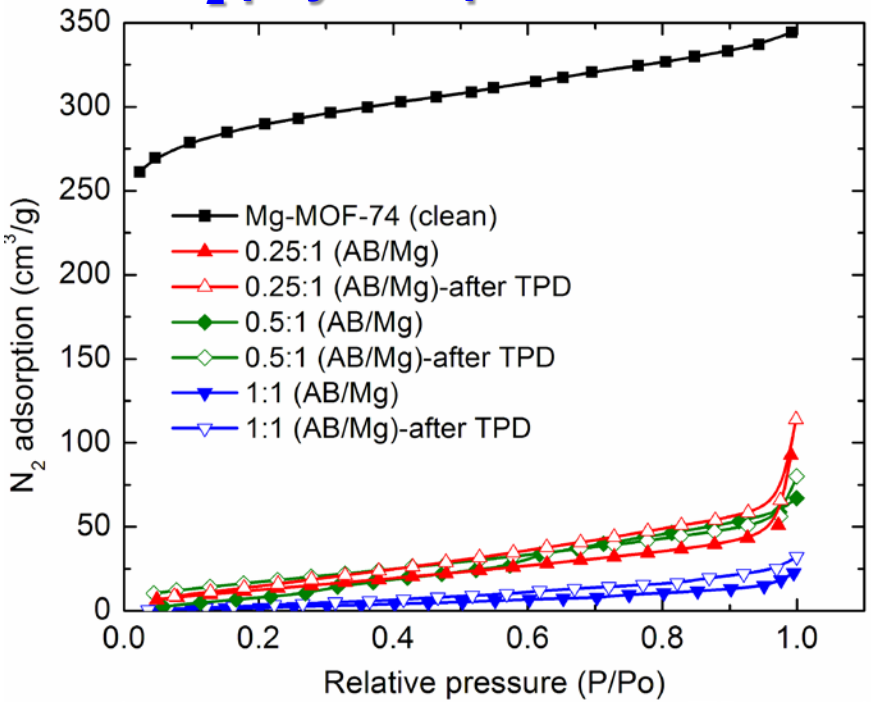
Stable pore structure

Easy loading of 1:1 mole ratio of AB/Mg
(~26 wt% of AB loading in MOF)

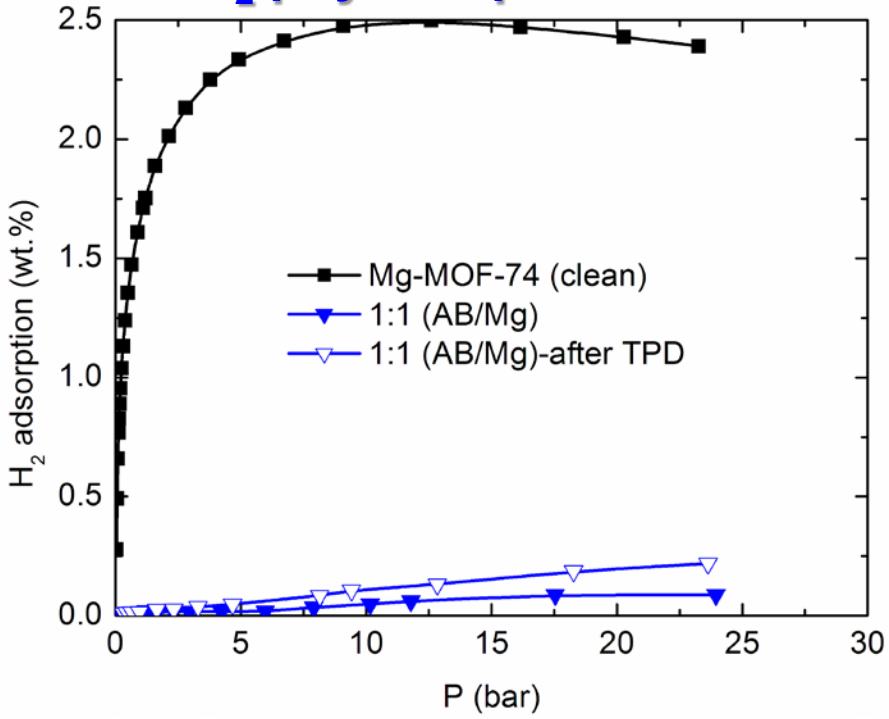
AB confinement & pore filling

AB impregnation within the MOF pores

N_2 physisorption at 77 K



H_2 physisorption at 77 K



Activated MOF-74:

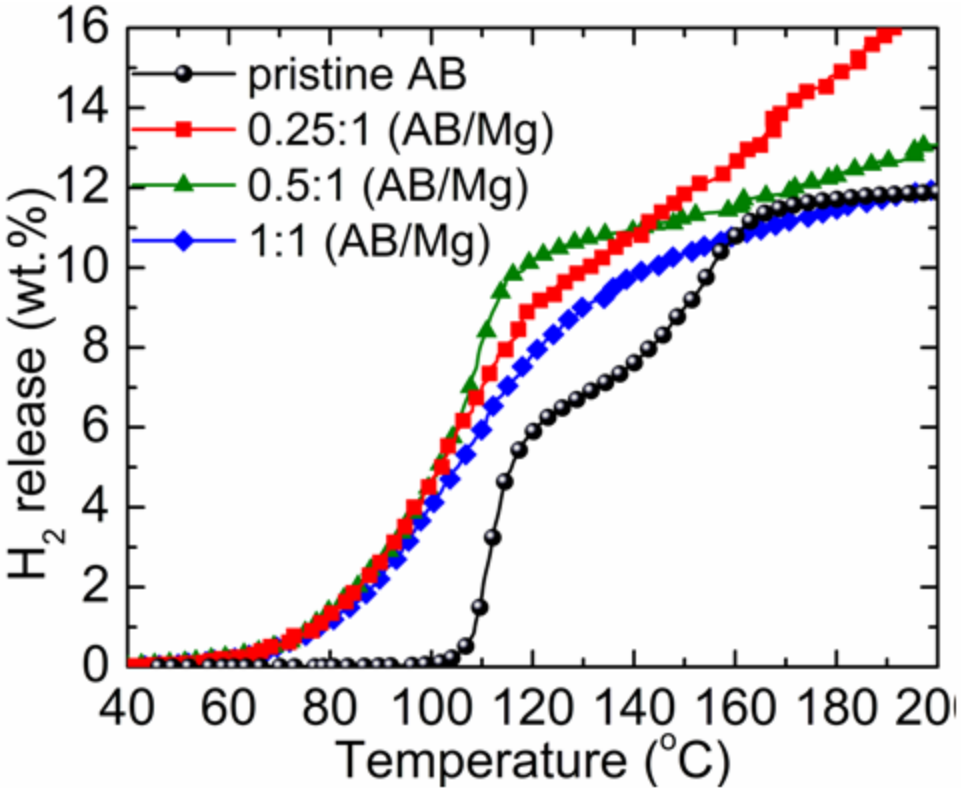
- open pores with BET surface area of ~1000 m^2/g

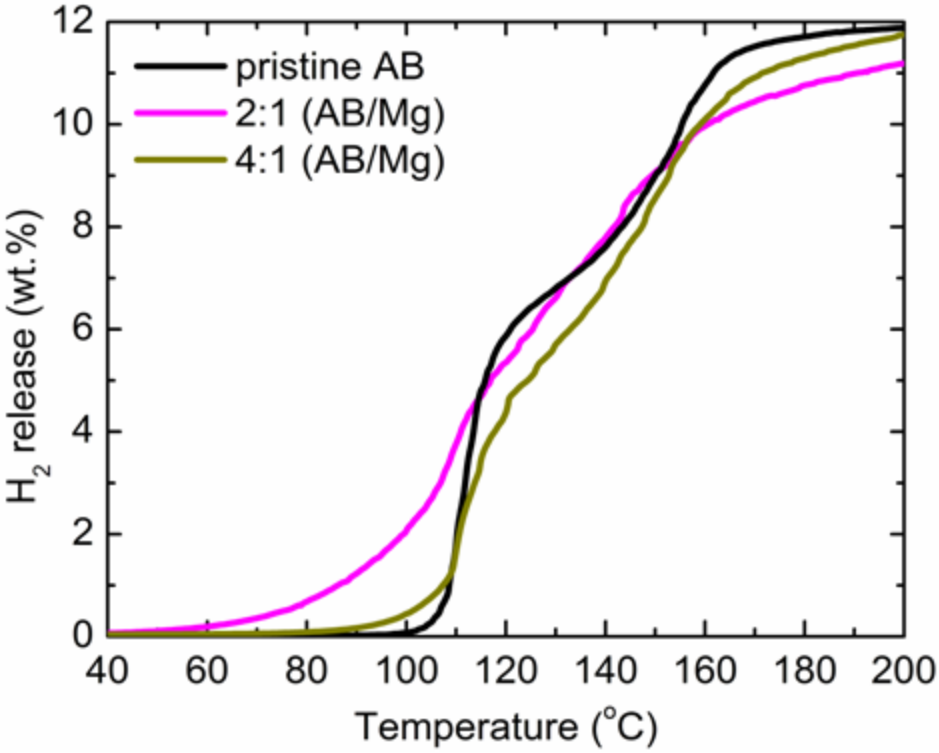
AB loaded MOF :

- no open pore, no open metal-sites & BET surface area of ~4 m^2/g

Dehydrogenation

Volumetric thermal desorption





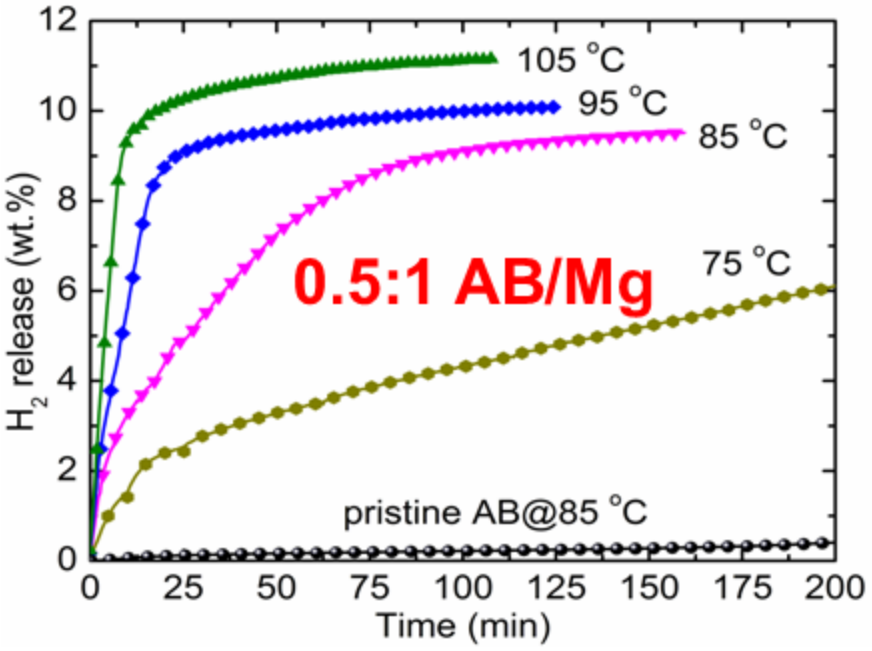
- Dehydrogenation temperature reduced down to ~65 °C compared to >100 °C of bulk AB

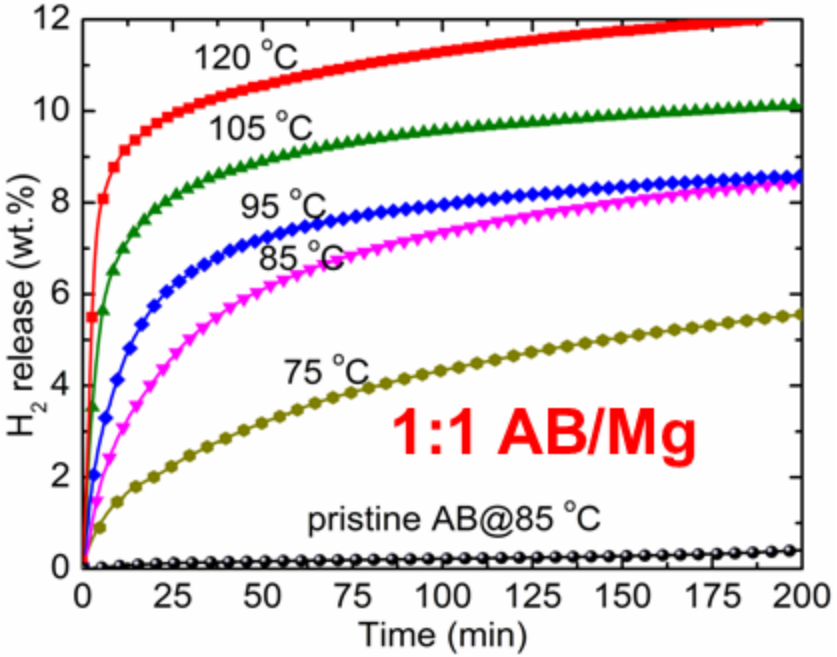
Heavy loading behaves like pristine AB

Heating rate of 2 °C/min

Dehydrogenation

Isothermal dehydrogenation kinetics



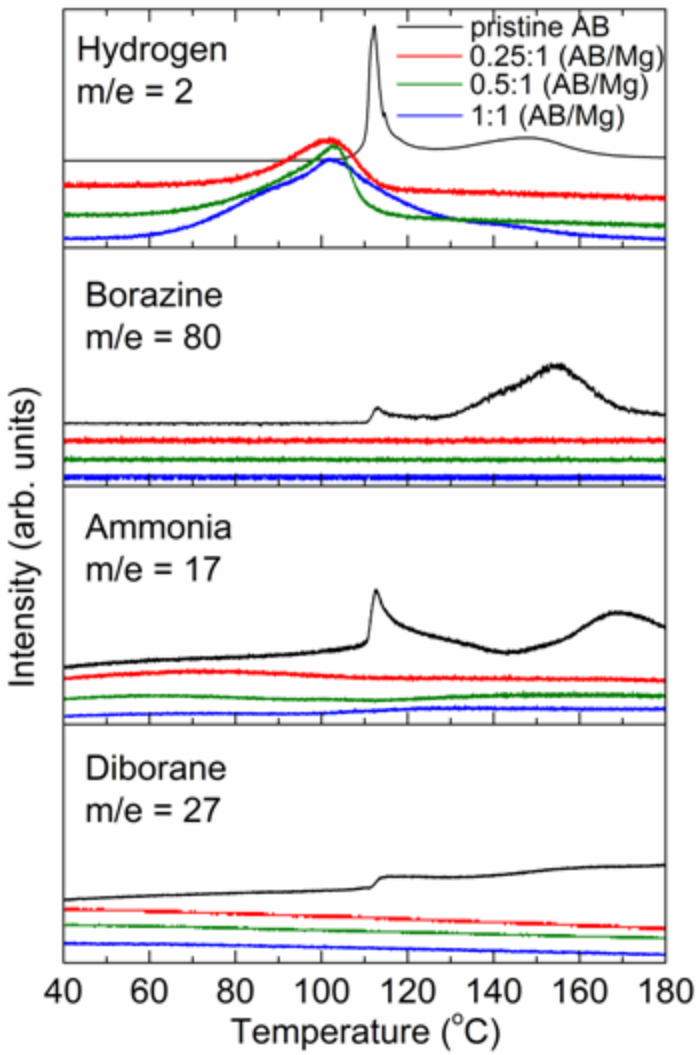


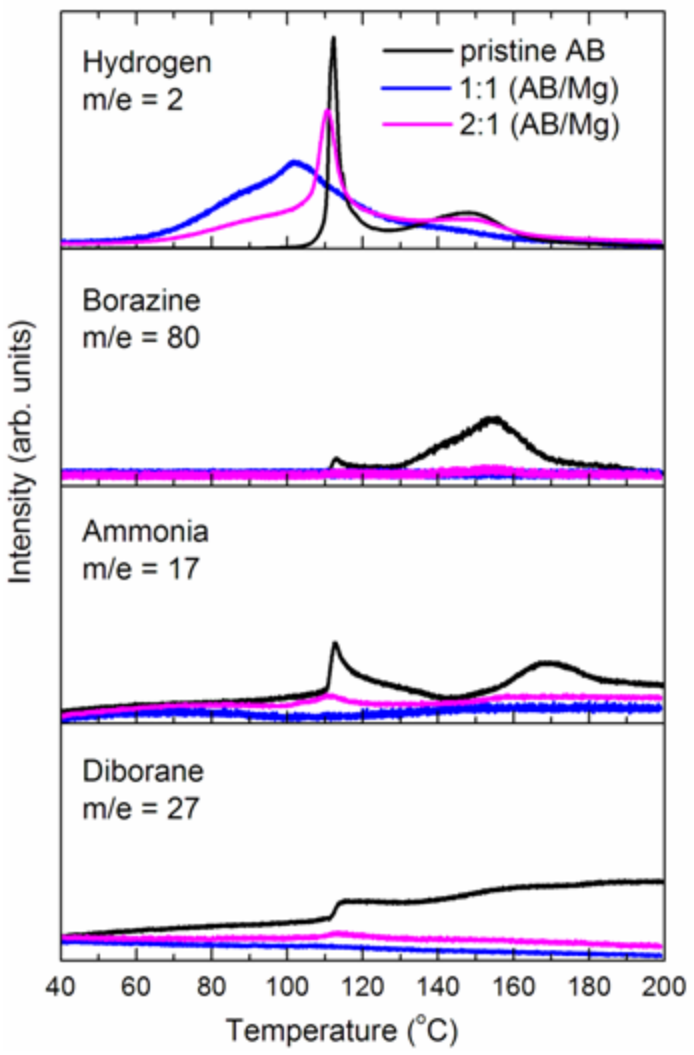
In conclusion, confining AB in one-dimensional nanopores of MgMOF74 improves the hydrogen release kinetics significantly.

What about the byproducts? Do we still get diborane, ammonia, borazine, etc???

Dehydrogenation

Mass spectroscopy



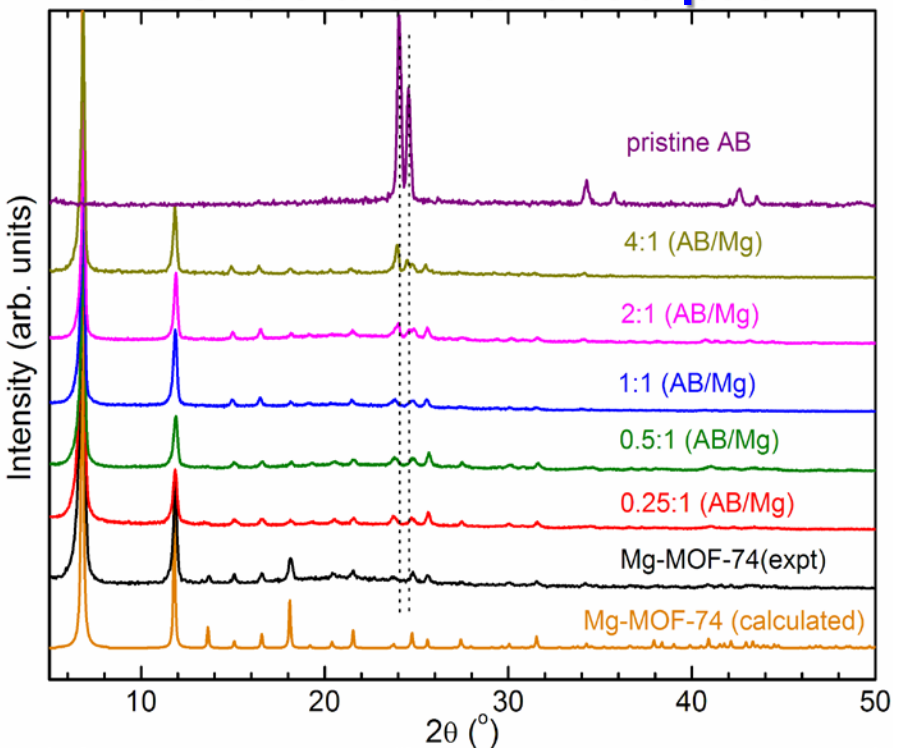


Heating rate of 2 °C/min

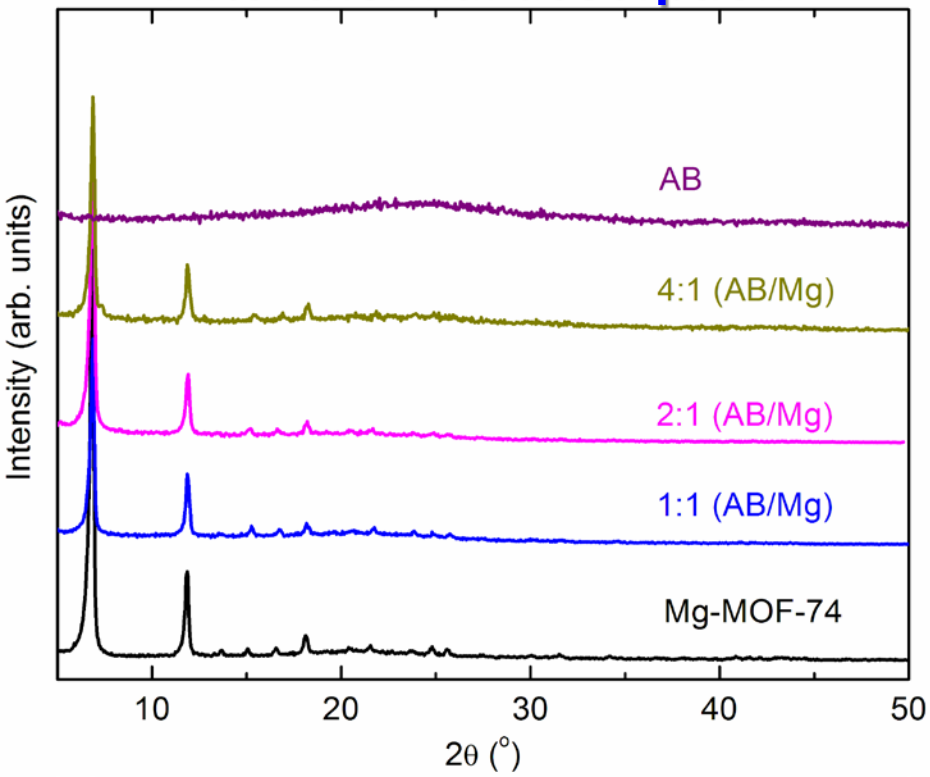
Powder X-ray diffraction

AB impregnation and structural stability of the MOF

Before thermal desorption



After thermal desorption



MOF-74 retains its framework structure

- upon AB loading
- after thermal dehydrogenation

Conclusion and out look

Our system demonstrates

- ✓ Highly enhanced kinetics at markedly reduced temperatures compared to the pristine AB
- ✓ Complete suppression of all the byproducts; Ammonia, borazine and diborane
- ✓ Offers controllable and efficient way of clean hydrogen generation
- ✓ For total system, include AB and MOF, H_2 delivery is ~3 wt.% (1:1 AB/Mg) and up to 6 wt.% for 2:1 AB/Mg, if we tolerate with release of little amount of byproducts

- ❖ Given the flexibility to design MOFs with varying pore sizes from required metal centers as well as organic ligand, it is possible that the efficiency in desorbed hydrogen increased.
- ❖ Our findings open new directions to optimize the conditions for clean and efficient way of hydrogen desorption from ammonia borane that can be suitable for operation conditions of polymer electrolyte fuel cells.

THANKS

NIST
National Institute of
Standards and Technology
U.S. Department of Commerce

Penn
University of Pennsylvania