

# Atomistic Mechanisms of Metal-Assisted Hydrogen Storage in Nanostructured Carbons

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May 16, 2012

Project ID  
BES005

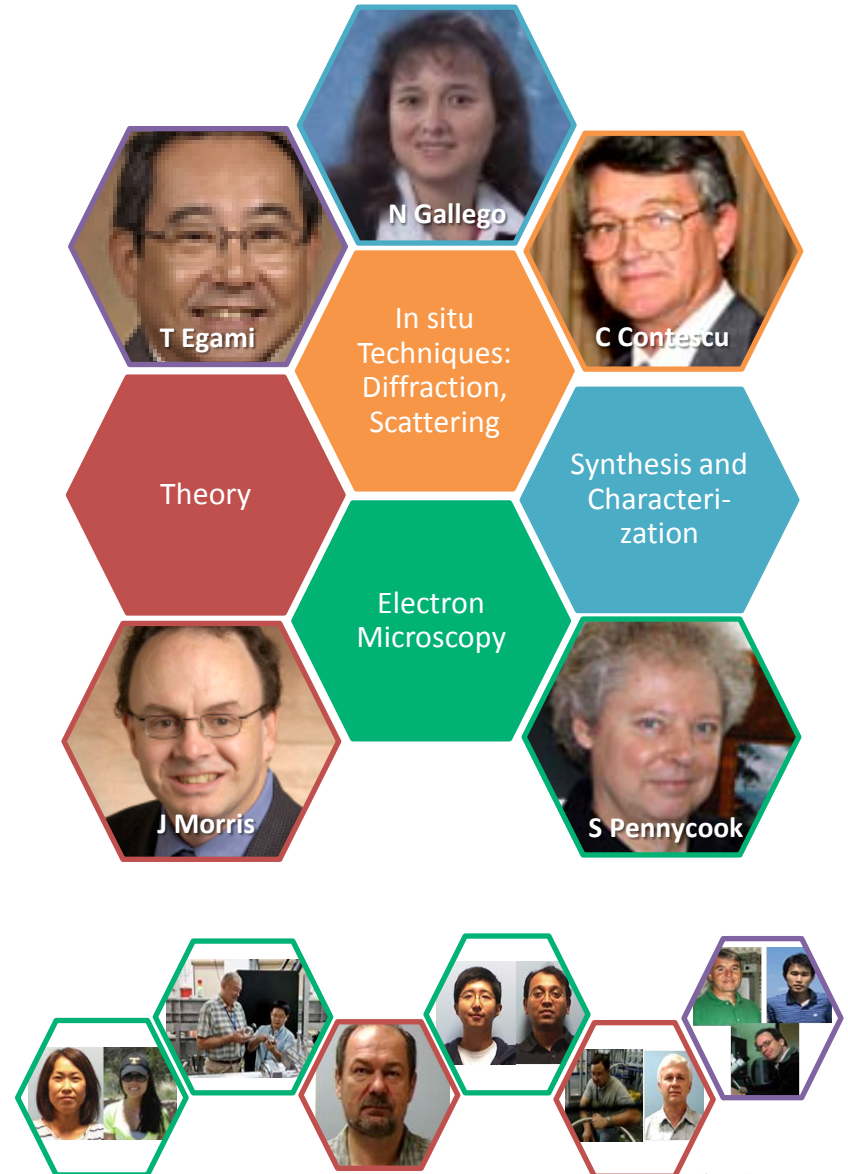
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# Goals

- Understanding the mechanisms of synergetic interaction in metal-doped nanostructured carbons that lead to enhanced hydrogen adsorption at near-room temperatures.
  - *Identification of local atomic structures in nanoporous carbons*
  - *Nature of hydrogen binding sites*
  - *Adsorption mechanisms, energetics and dynamics of adsorbed H<sub>2</sub>*
- Understanding the impact of local atomic order and topological defects in disordered nanostructured carbons on their specific properties related to gas adsorption
  - *Relationship between local atomic structures and large scale architecture of nanoporous carbons*
  - *Confinement effects on the properties of trapped molecular species*

# Our team: Cross-cutting expertise

- Simulation of carbon structures and modeling of adsorption
- Electron microscopy: from atomic scale to mesoscale
- In-situ characterization methods: phase behavior and dynamics of confined fluids
- Synthesis, surface modification and characterization of carbon materials: texture, atomic structure, local density, order and disorder
- Collaborations:
  - University of Tennessee
  - Spallation Neutron Source (SNS)
  - High Flux Isotope Reactor (HFIR)

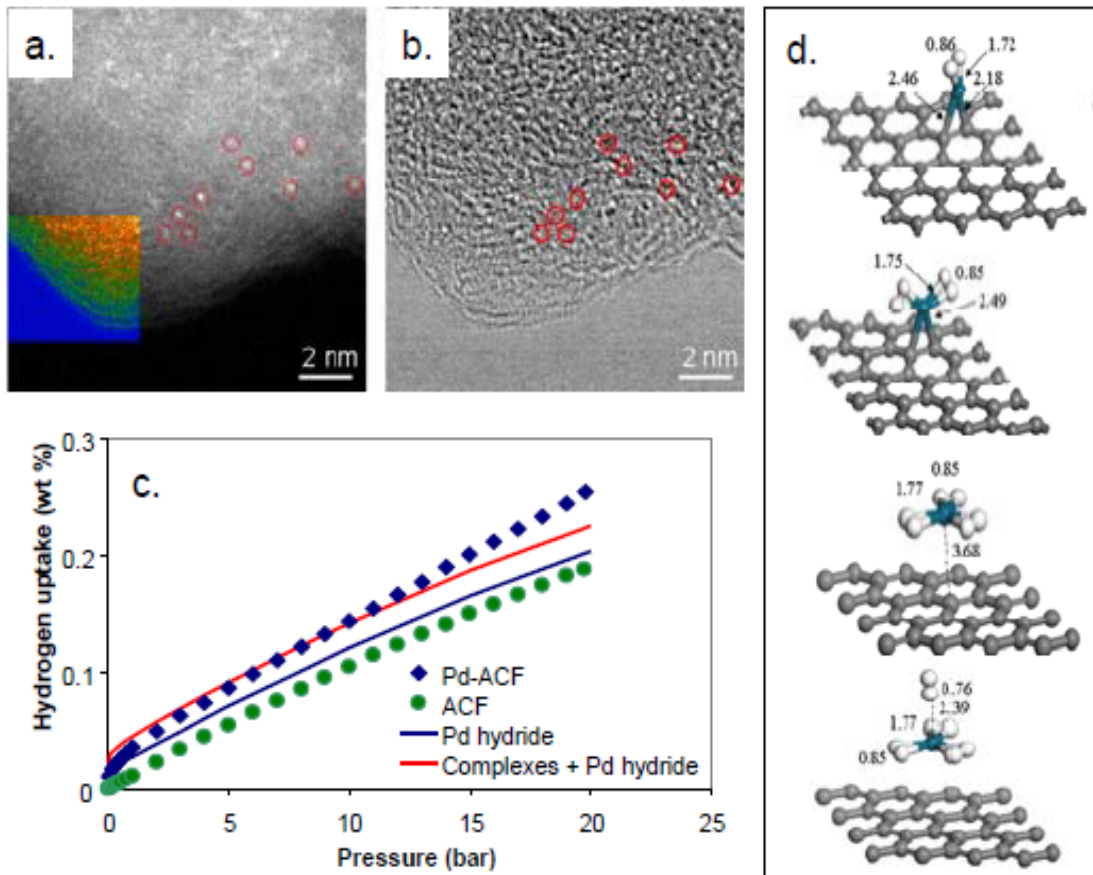


# Approach

- Developing realistic structural models for nanoporous carbons
  - *Tight-binding molecular dynamics simulations of nanoporous carbons*
  - *Structural information from X-ray and neutron scattering*
- Structure characterization of nanoporous carbons
  - *Atomic resolution electron microscopy*
  - *Order/disorder characterization from X-ray and neutron scattering*
- Characterization of adsorbed H<sub>2</sub> using in-situ methods
  - *Phase behavior and densification of adsorbed H<sub>2</sub> (SANS)*
  - *Restricted dynamics of confined H<sub>2</sub> molecules (QENS)*
- Understanding atomistic mechanisms of H<sub>2</sub> adsorption
  - *Role of transition metals*
  - *Role of alkali atoms*

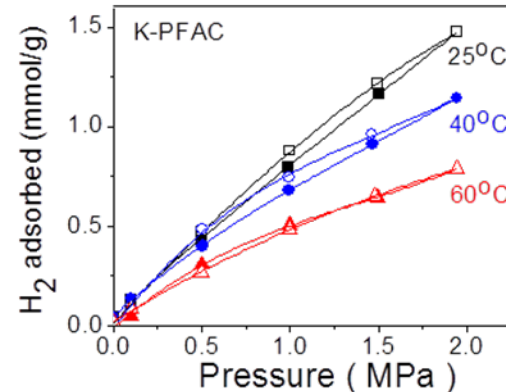
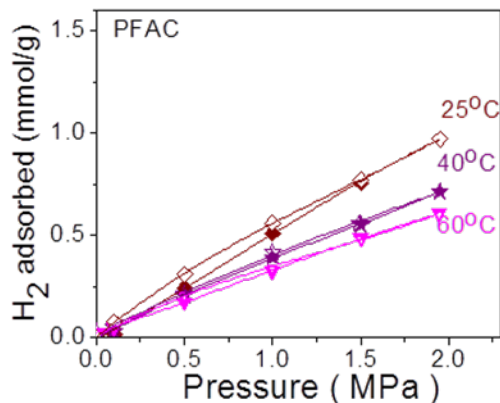
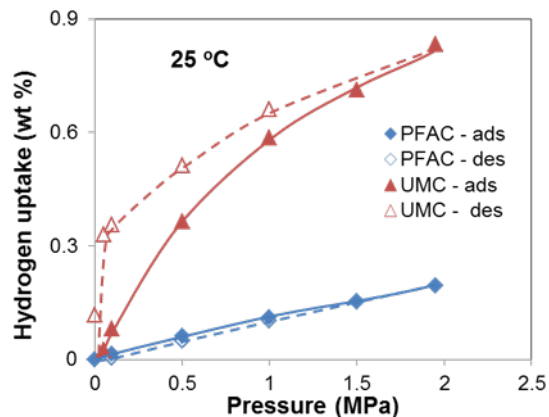
# Role of transition metals doping

- ✓ Demonstrated the presence of single Pd atoms stabilized in carbon structure
- ✓ Together with earlier results, this leads to the possibility of multiple mechanisms for enhance H<sub>2</sub> uptake in Pd-doped activated carbon fibers:
  - ✓ Destabilization of Pd hydride and release of H atoms to carbon
  - ✓ Spillover of H atoms and bonding to dangling bonds of unsaturated C atoms
  - ✓ Kubas-type bonding of multiple H<sub>2</sub> molecules to single Pd atoms



van Benthem et al. *Carbon* **49** (2011) 4059-4073  
Contescu et al. *Carbon* **49** (2011) 4050-4058  
Contescu et al, *J Phys Chem C* **113** (2009) 5886-5890  
Bhat et al *Nanotechnology* **20** (2009) 204011 [10 p]

# Role of alkali metals doping



- ✓ Demonstrated higher H<sub>2</sub> uptake on ultramicroporous carbon (UMC) compared with other carbons in equal conditions.
  - ✓ Hypothesized that alkali metal traces cause enhanced uptake through polarization-induced physisorption.
  - ✓ Adsorption is slow and desorption shows hysteresis.
  - ✓ Physical mixing with Pd black accelerates adsorption but has no effect on desorption.
- ✓ Enhanced uptake found on other alkali-doped (K, Li) carbons confirms the hypothesis of polarization-induced physisorption
  - ✓ Adsorption energy was higher on K-doped carbon (15 - 23 kJ/mol) compared with the same carbon with no K doping (14 - 16 kJ/mol).
  - ✓ Adsorption energy on K- and Li-doped carbons is in the range considered optimal for practical H<sub>2</sub> storage.

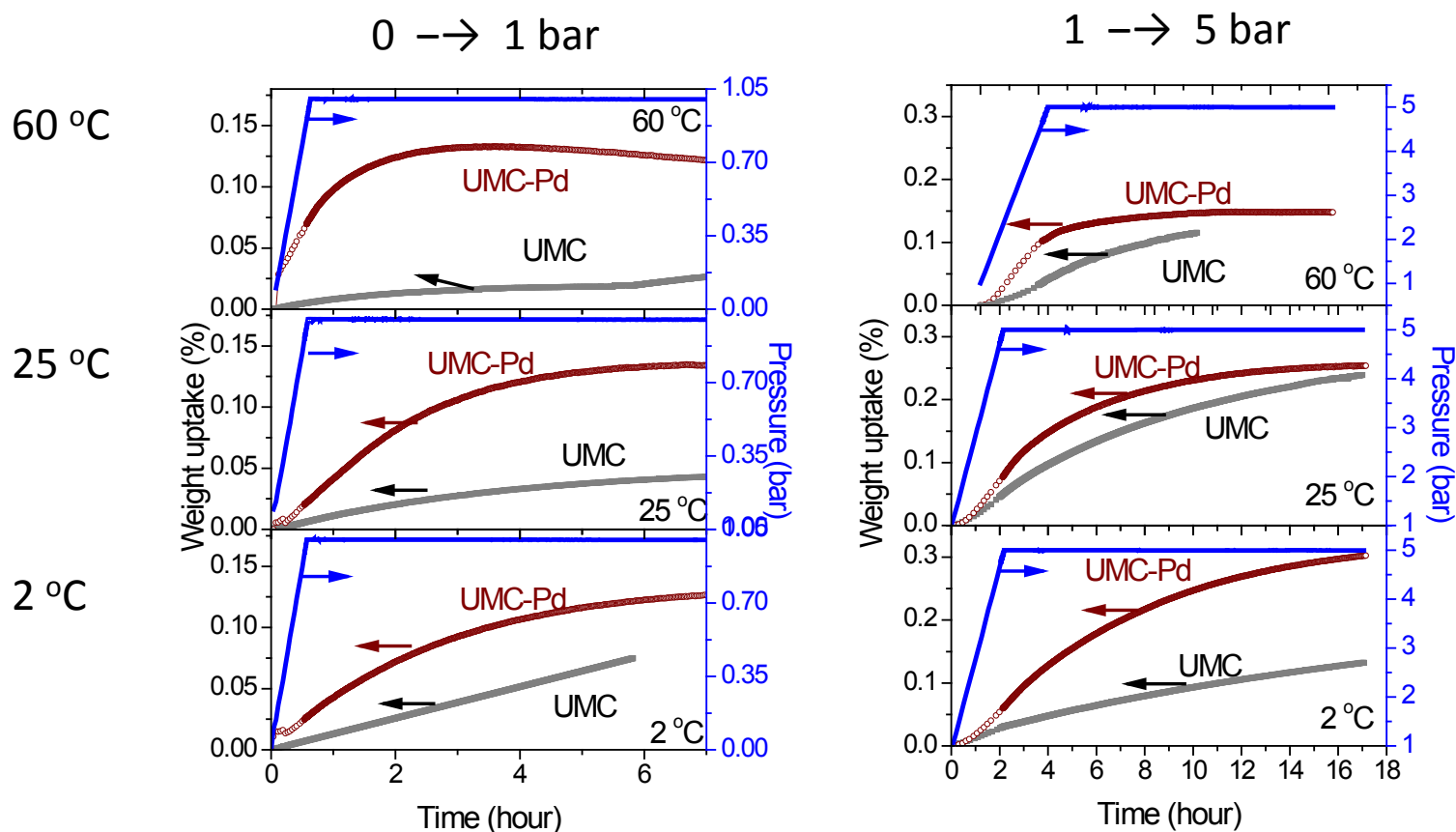
Bhat et al, *Carbon* **48** (2010) 1331-1340

Bhat et al, *Carbon* **48** (2010) 2361-2364

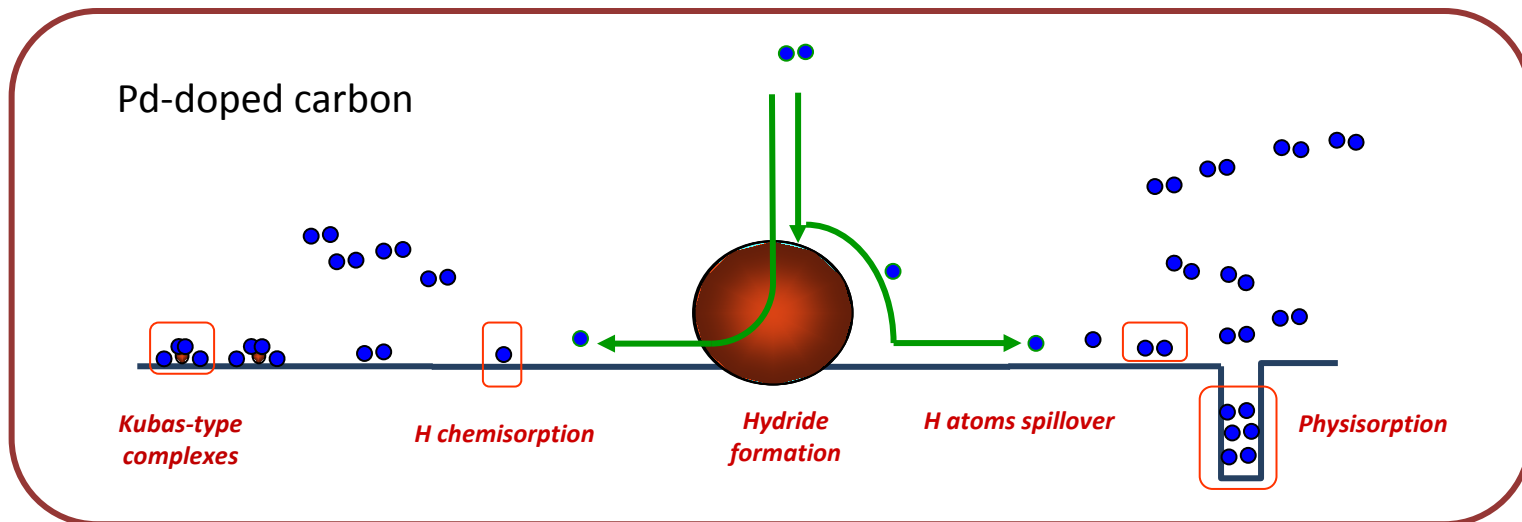
Saha et al, *Langmuir* (2012) dx.doi.org/10.102/la3002948

# Effect of physically-mixing Pd

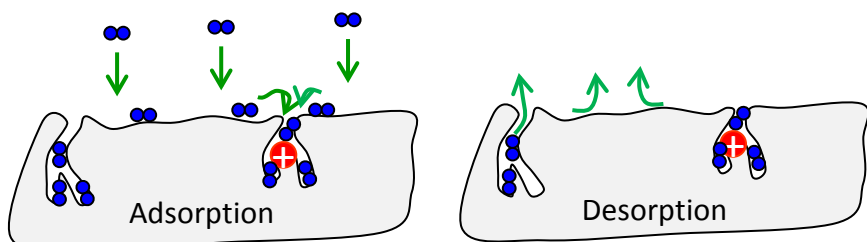
- ✓ Physically mixing with 10 wt % Pd black causes a **small increase in H<sub>2</sub> uptake**.
- ✓ **Adsorption kinetics was much faster** after addition of Pd.
- ✓ Desorption rates were not changed.



# Summary on the role of metals



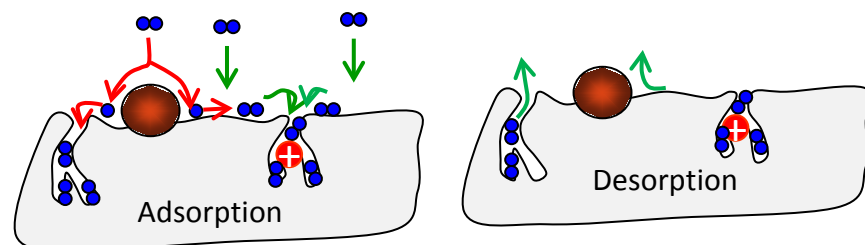
## K-doped carbon



- *Enhanced uptake caused by polarization – induced physisorption on K+*
- *Slow adsorption rates*

*Strong binding on K+ causes hysteresis on desorption*

## K-doped carbon physically mixed with Pd particles



- *Pd particles accelerates adsorption*
- *SPILLOVER*

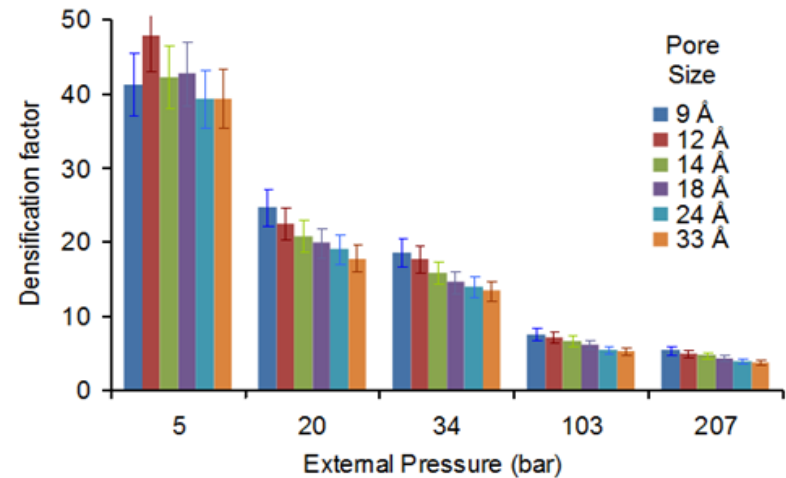
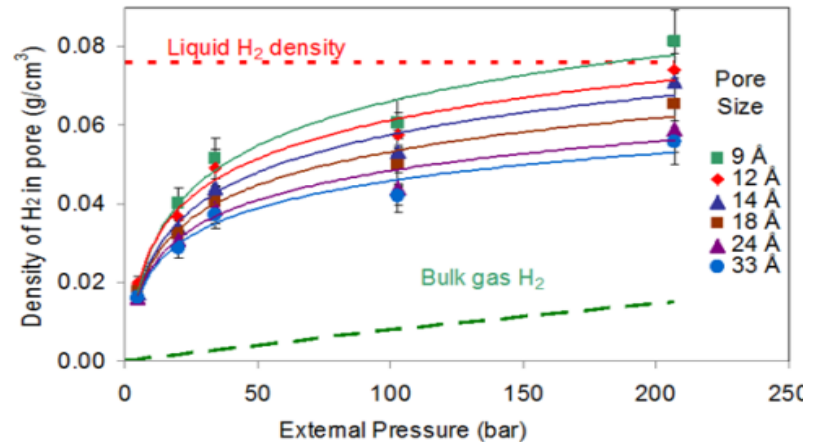
- *Pd particles have no effect on desorption*
- *NO REVERSE SPILLOVER*

**HYDROGEN CAPACITY DEPENDS CRITICALLY ON CARBON PROPERTIES**



# Superdensification of adsorbed H<sub>2</sub>

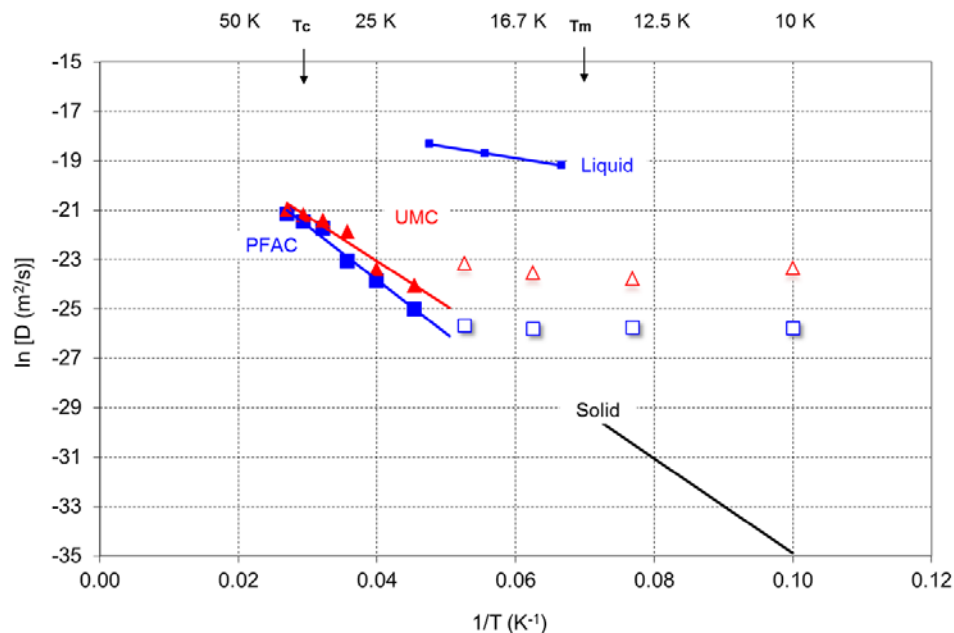
- ✓ Used high-pressure in-situ small angle neutron scattering (SANS) to estimate the density of H<sub>2</sub> trapped in nanopores as a function of pore size and external H<sub>2</sub> pressure.
- ✓ At room temperature and 200 bar H<sub>2</sub>, the hydrogen density in narrow pores (9 Å) approaches the density of liquid hydrogen.
- ✓ Densification factors are much higher at low pressures and gradually weaken at higher pressures.
- ✓ This demonstrates the advantage of adsorptive storage over compressed storage.



Gallego et al *J Amer Chem Soc* **133** (2011)

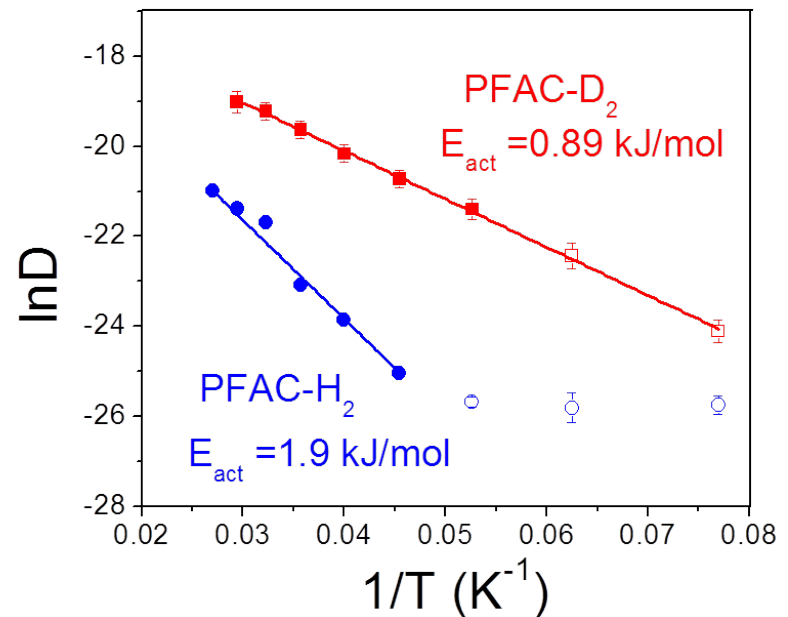
# Restricted mobility of confined H<sub>2</sub>

- ✓ Used quasi-elastic neutron scattering (QENS) to probe the dynamics of H<sub>2</sub> confined in carbon nanopores.
- ✓ Hydrogen became mobile at temperatures some 8-11 K above the melting point of bulk H<sub>2</sub> (13 K).
- ✓ After becoming mobile, diffusion occurs by the solid-like mechanism with activation energies close to those of solid H<sub>2</sub>



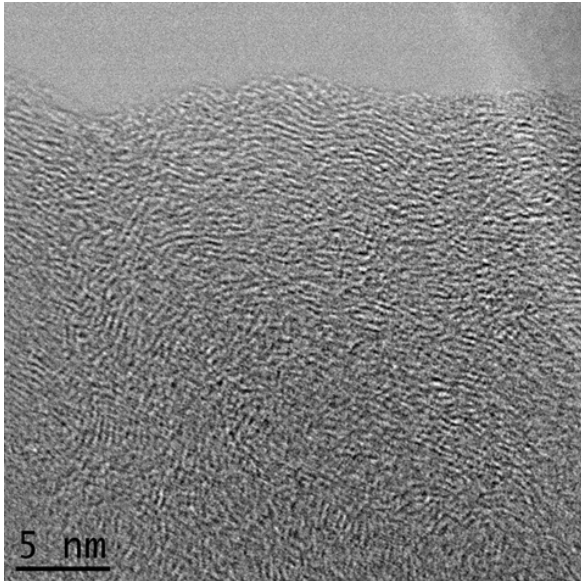
# Role of quantum confinement in diffusion

- ✓ Usual isotope effect would suggest that  $D_{D_2} < D_{H_2}$  due to doubled mass of molecule.
- ✓ Quantum de Broglie wavelength of  $D_2$  is significantly smaller than that of  $H_2$  because  $D_2$  is heavier.
- ✓ Under the same conditions,  $D_2$  shows higher mobility.
- ✓ The restricted mobility of  $H_2$  is caused by extreme confinement and strong quantum effects at low temperatures.

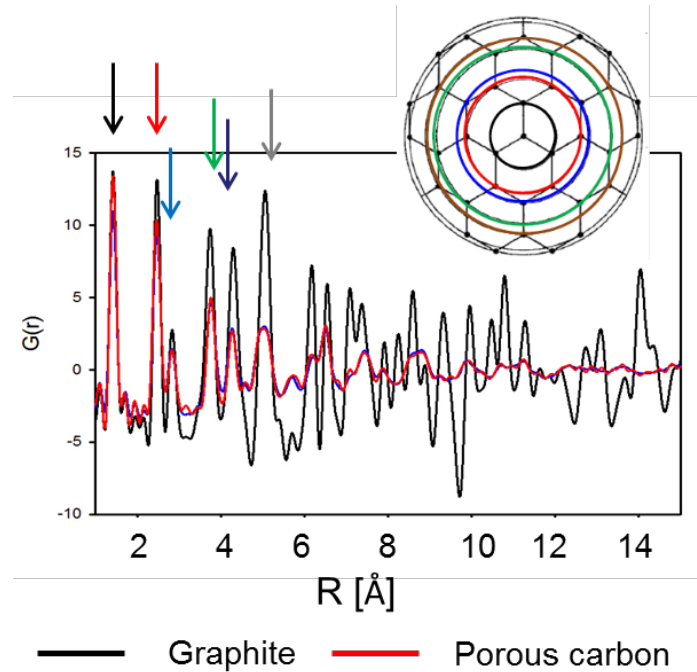


De Broglie wave-length  $\lambda_T = \hbar / \sqrt{\mu k_B T}$

# Order vs. disorder in carbons



Electron microscopy: short graphene layers with random orientation



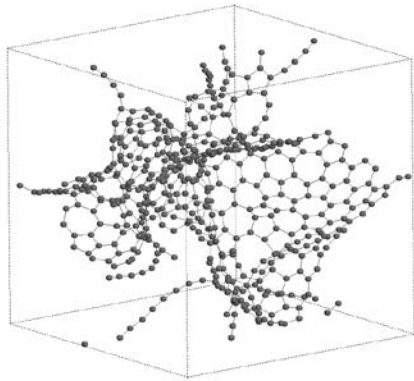
- ✓ Nanoporous carbons have 2D structures with short range order.
- ✓ Local folds and cusps limit lateral coherence to only 8-10 Å.
- ✓ Graphene layers are stacked closely but with minimal interlayer atomic correlation.
- ✓ Local atomic density is only 20 % lower than in graphite.

Bhat et al. *Carbon* **48** (2010) 1331-1340

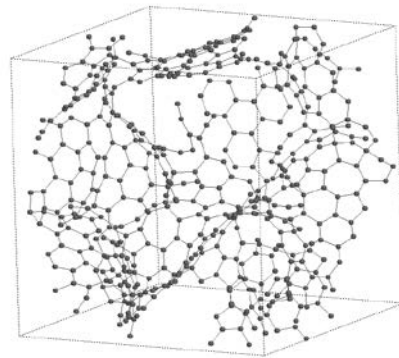
Jagiello, Contescu et al. *Adsorption Sci Technol.* **29** (2011) 769-780

Dmowski et al, *J Phys Chem C* **116** (2012) 2946-2951

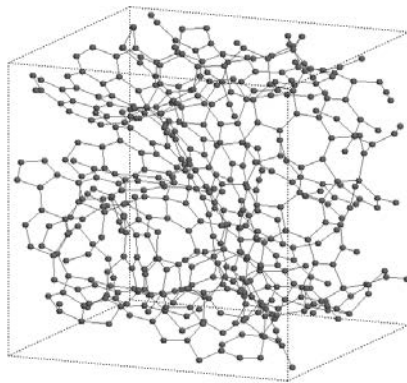
# Effect of carbon density



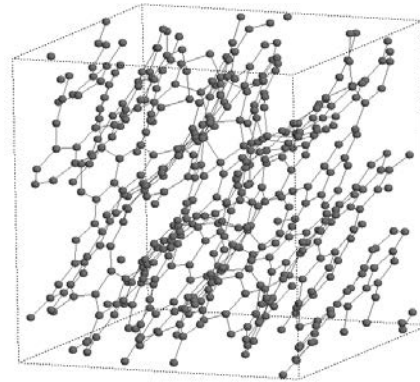
0.6 g/cm<sup>3</sup>



1.0 g/cm<sup>3</sup>

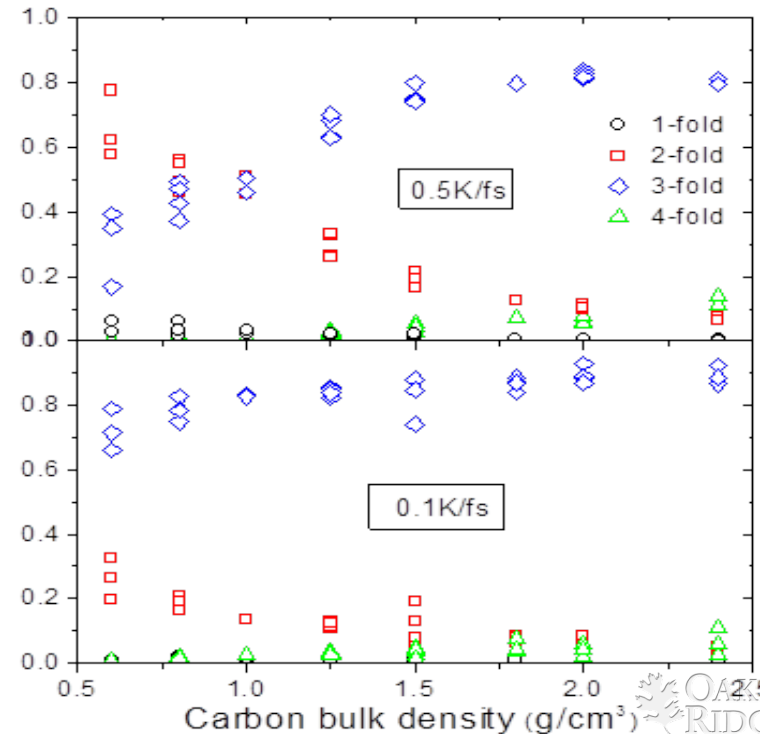


1.8 g/cm<sup>3</sup>



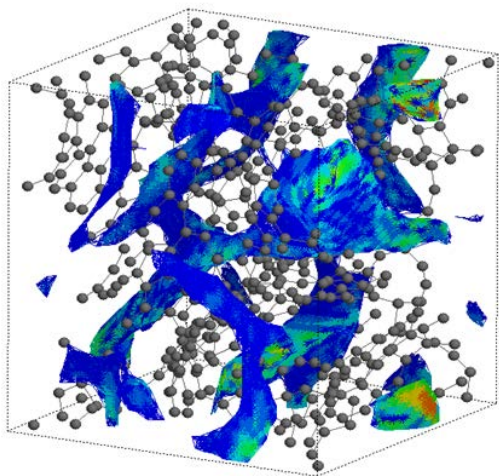
2.4 g/cm<sup>3</sup>

- ✓ Tight-binding simulations give realistic local structures
- ✓ Carbon structures depend on both density and quenching rate.
- ✓ Structures are primarily 3-fold bonded.
- ✓ Pore volumes increase rapidly for densities less than 1.7 g/cm<sup>3</sup>

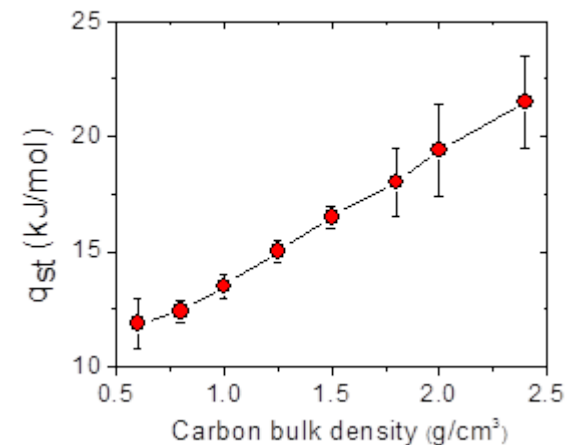
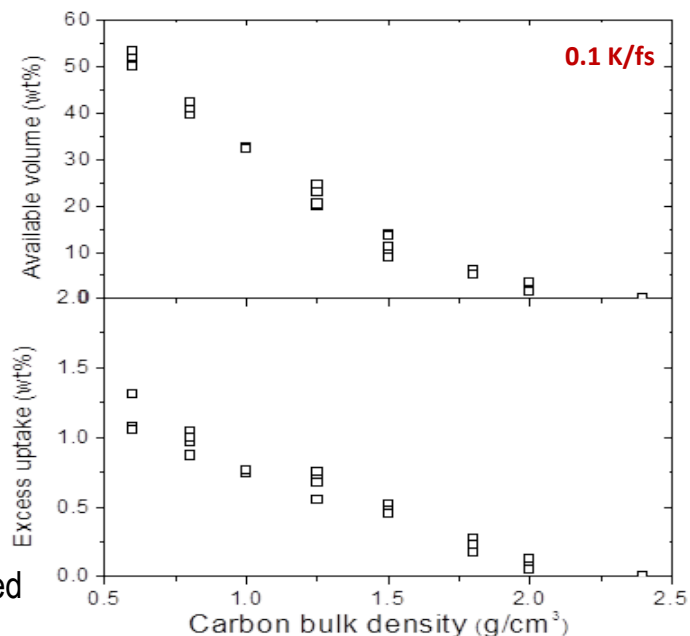


Peng, Morris, *Carbon* **50** (2012) 1394-1406

# Adsorption calculations



Regions with  $E_{\text{ads}} < -10$  kJ/mol in simulated carbon structure with density  $1.25$  g/cm<sup>3</sup>



- ✓ New computational approach allows rapid adsorption calculations for given carbon structures.
- ✓ First systematic
- ✓ Uptake rises with *decreasing* carbon density
- ✓ Opposite of trend for heat of adsorption (ranging from 12-23 kJ/mol).
- ✓ Small pores absorb strongly, but there are few such pores in dense materials.

# Conclusion

- ✓ The main contribution to hydrogen uptake capacity of metal-modified carbons is physisorption on the porous carbon support, which is strongly dependent on the properties of the porous carbon support
- ✓ Metal additions enhance the uptake through different mechanisms (spillover, Kubas binding, chemisorption, polarization) but their effect is secondary to physisorption on the carbon support.
- ✓ Narrow pores in carbon have favorable heat of adsorption (12-22 kJ/mol) and induce extreme densification of adsorbed hydrogen, approaching the density of liquid hydrogen at room temperature.
- ✓ Increasing the heat of adsorption by increasing carbon density does not necessarily increase the hydrogen uptake.
- ✓ The volume available for adsorption in narrow pores is as important as the heat of adsorption for hydrogen storage in nanoporous carbons.

# Future plans

We will focus on understanding the impact of local atomic order and topological defects in disordered nanoporous carbons on their specific properties determined by the presence of a large fraction of atoms exposed at interfaces.

- ✓ How do local atomic structures at the nanoscale relate to the mesoscale architecture in carbons of various origins, and how do they determine measurable texture properties (pore distribution, surface area) ?
- ✓ How do local structures affect interactions with gases and how does confinement change the phase behavior and properties of trapped molecular species ?