Atomistic Mechanisms of Metal-Assisted Hydrogen Storage in Nanostructured Carbons

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Project ID
BES005

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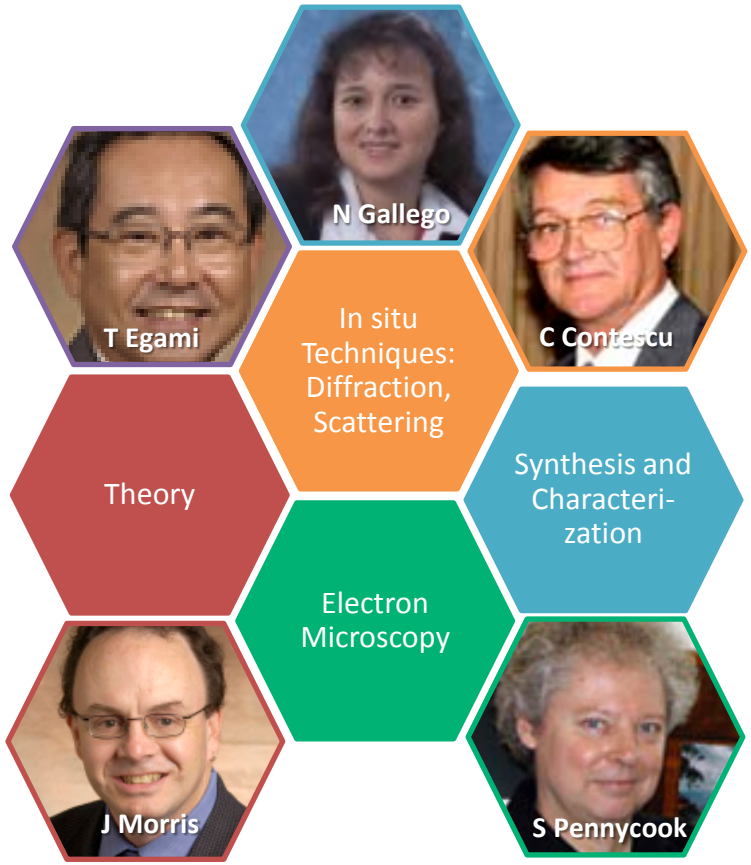
Goals

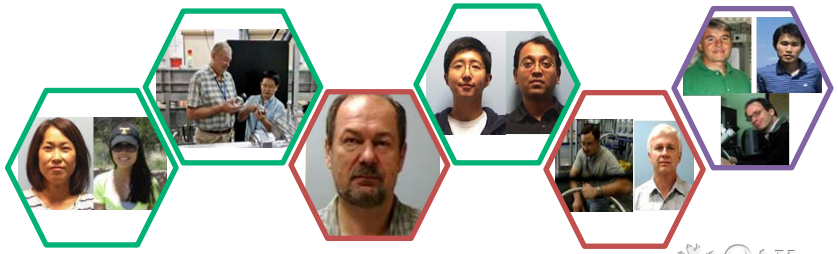
- Understanding the mechanisms of synergetic interaction in metal-doped nanostructured carbons that lead to enhanced hydrogen adsorption at near-room temperatures.
  - *Identification of local atomic structures in nanoporous carbons*
  - *Nature of hydrogen binding sites*
  - *Adsorption mechanisms, energetics and dynamics of adsorbed H_2*

- 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)



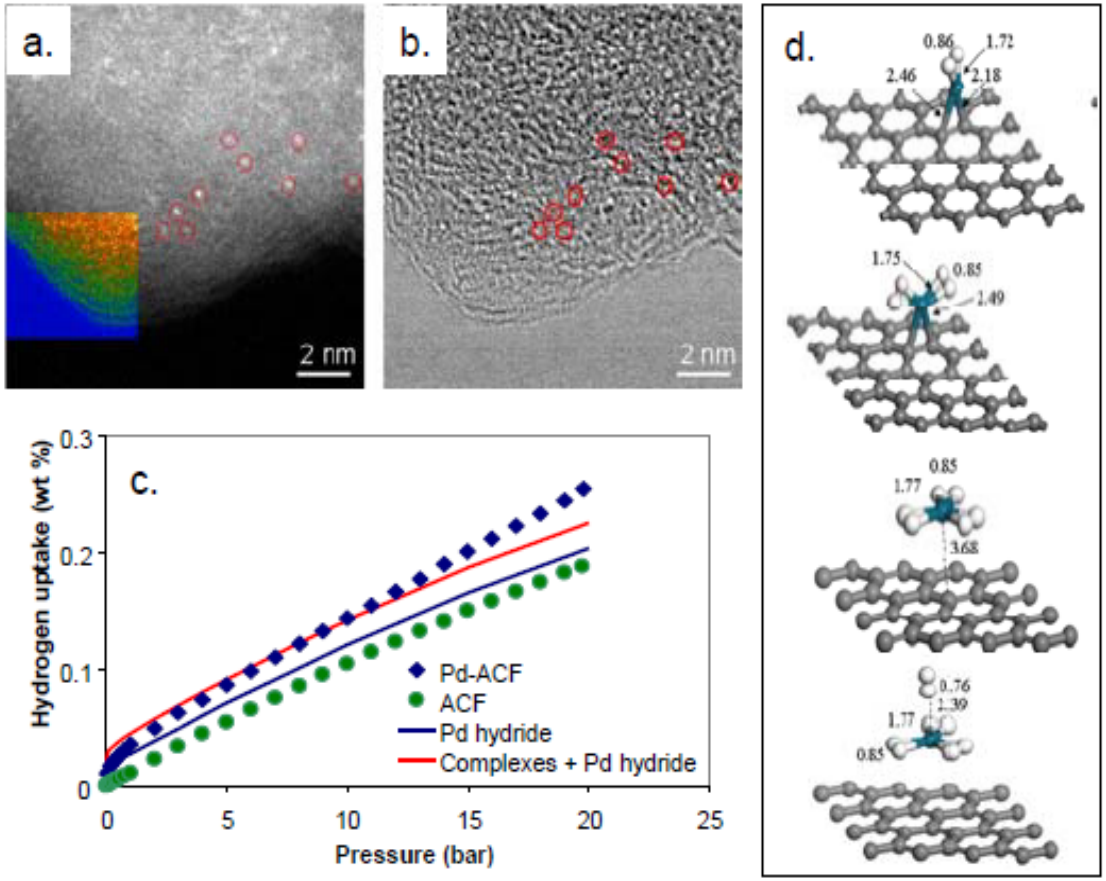


Approach

- 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 form X-ray and neutron scattering*
- Characterization of adsorbed H_2 using in-situ methods
  - *Phase behavior and densification of adsorbed H_2 (SANS)*
  - *Restricted dynamics of confined H_2 molecules (QENS)*
- Understanding atomistic mechanisms of H_2 adsorption
  - *Role of transition metals*
  - *Role of alkali atoms*

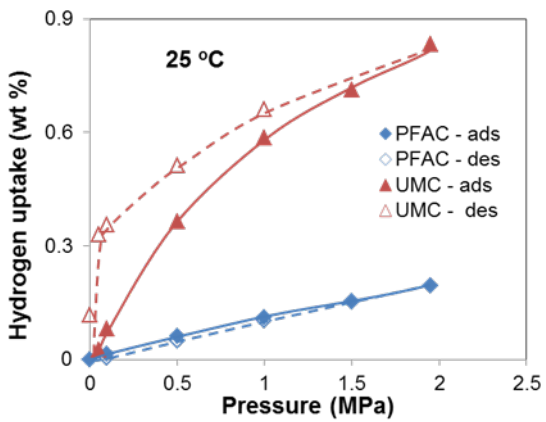
Role of transition metals doping

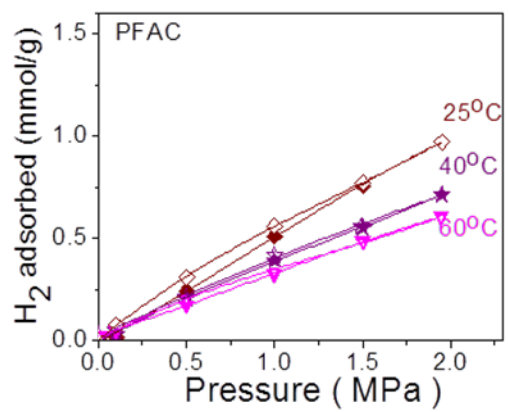
- ✓ Demonstrated the presence of single Pd atoms stabilized in carbon structure
- ✓ Together with earlier results, this leads to the possibility of multiple mechanisms for enhance H_2 uptake in Pd-doped activated carbon fibers:
  - ✓ Destabilization of Pd hydride and release of H atoms to carbon
  - ✓ Spillover of H atoms and bonding to dangling bonds of unsaturated C atoms
  - ✓ Kubas-type bonding of multiple H_2 molecules to single Pd atoms

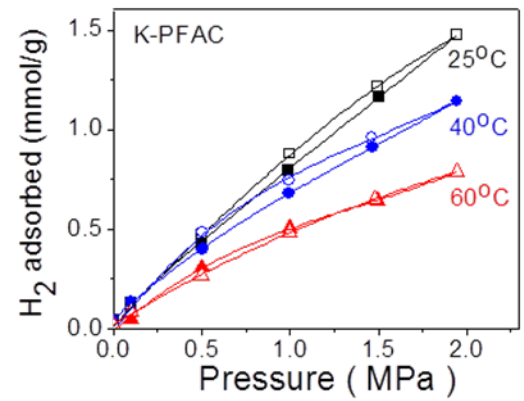


van Benthem et al. *Carbon* **49** (2011) 4059-4073
Contescu et al. *Carbon* **49** (2011) 4050-4058
Contescu et al, *J Phys Chem C* **113** (2009) 5886-5890
Bhat et al *Nanotechnology* **20** (2009) 204011 [10 p]

Role of alkali metals doping







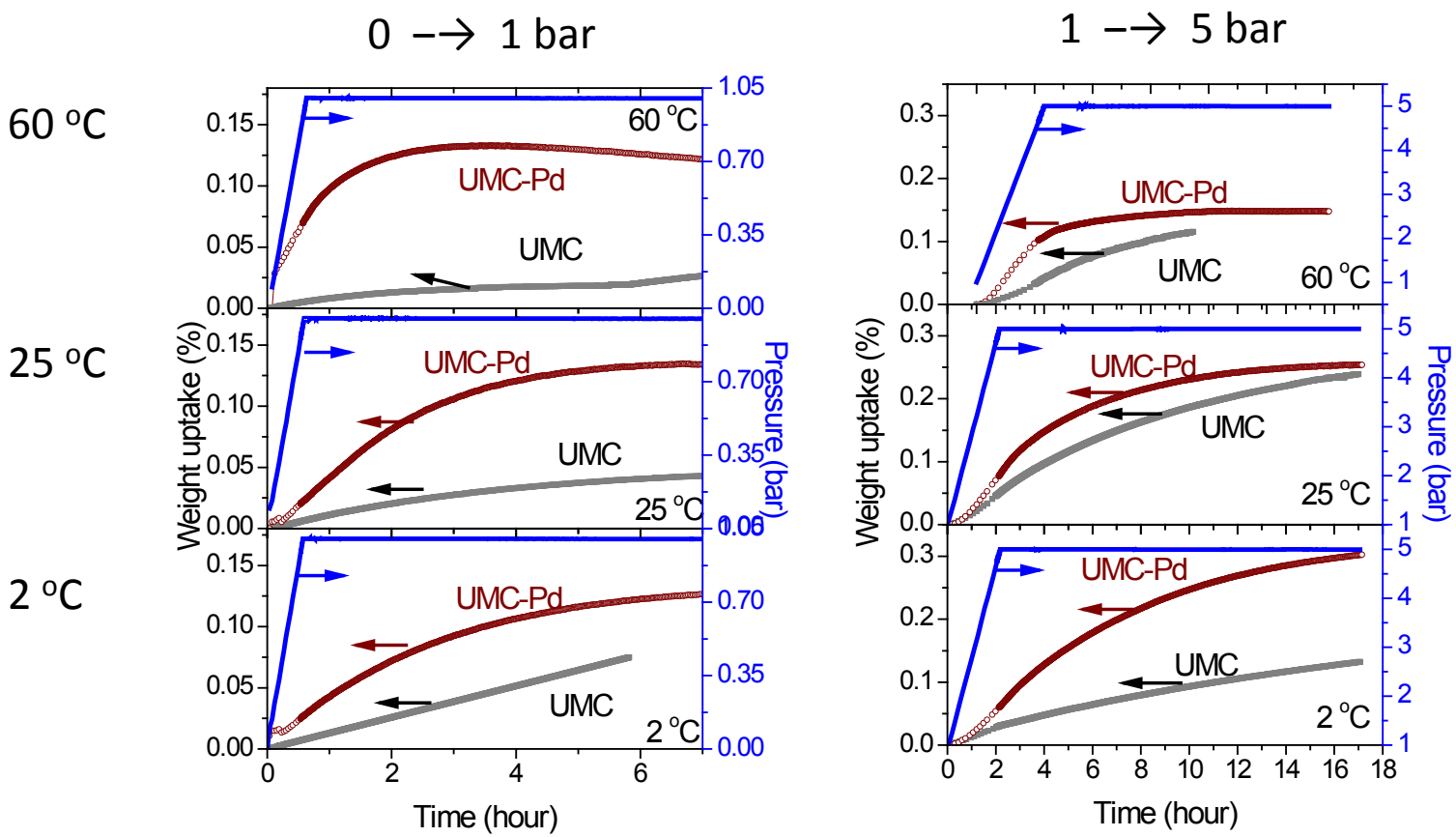
- ✓ Demonstrated higher H_2 uptake on ultramicroporous carbon (UMC) compared with other carbons in equal conditions.
  - ✓ Hypothesized that alkali metal traces cause enhanced uptake through polarization-induced physisorption.
  - ✓ Adsorption is slow and desorption shows hysteresis.
  - ✓ Physical mixing 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_2 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

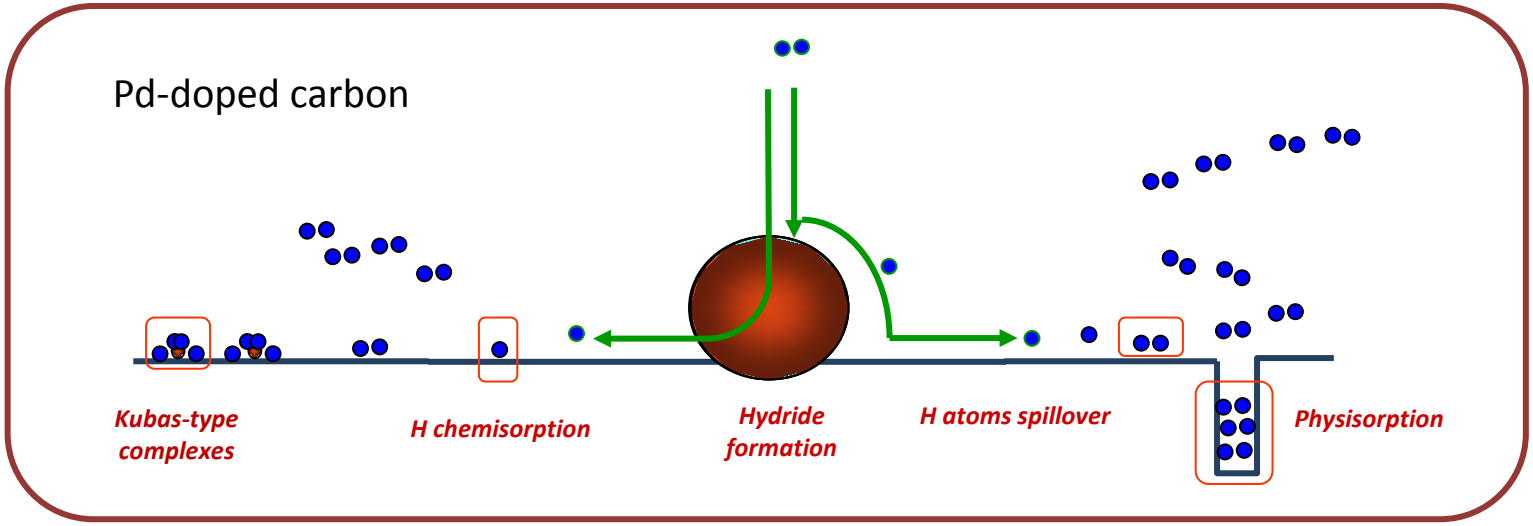
Effect of physically-mixing Pd

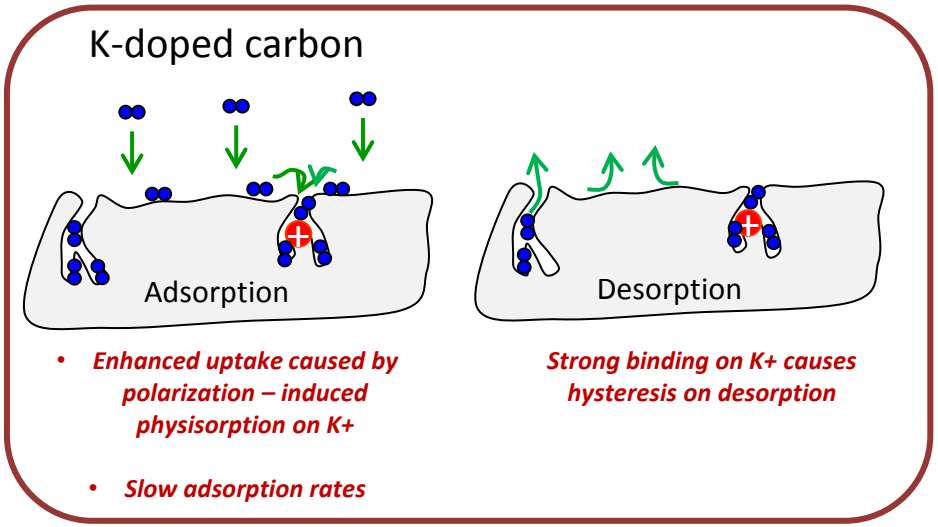
- ✓ Physically mixing with 10 wt % Pd black causes a small increase in H_2 uptake.
- ✓ Adsorption kinetics was much faster after addition of Pd.
- ✓ Desorption rates were not changed.

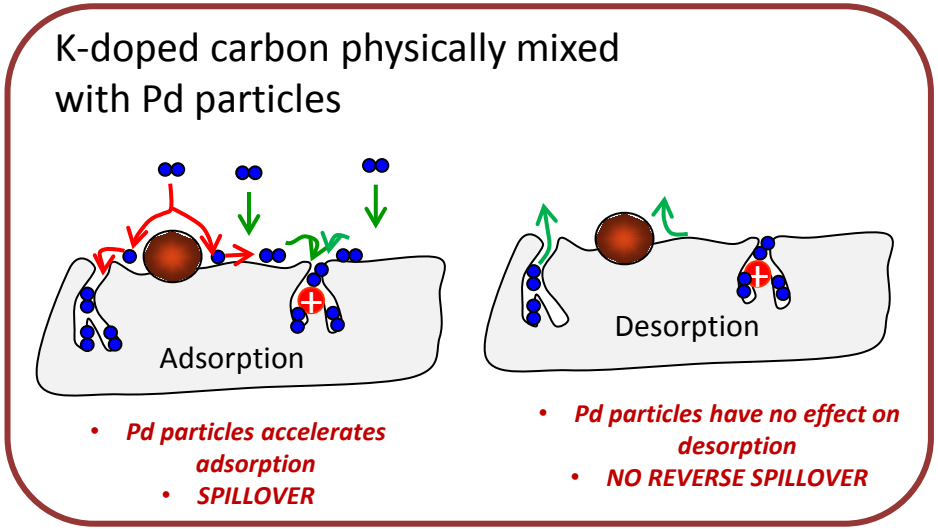


Bhat et al, *Carbon* **48** (2010) 2361-2364

Summary on the role of metals



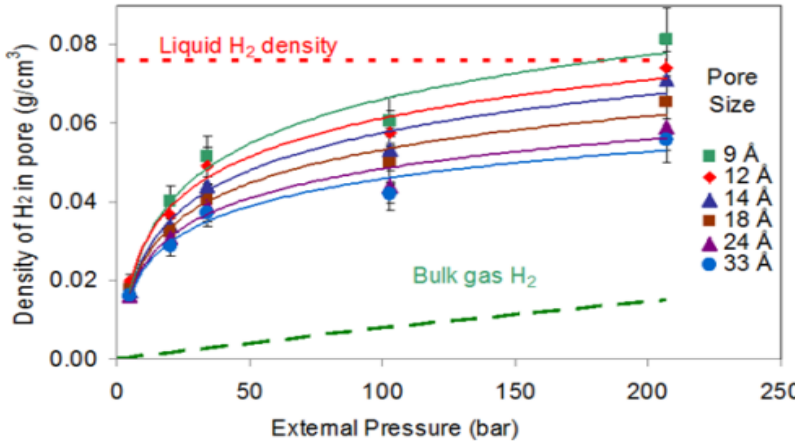


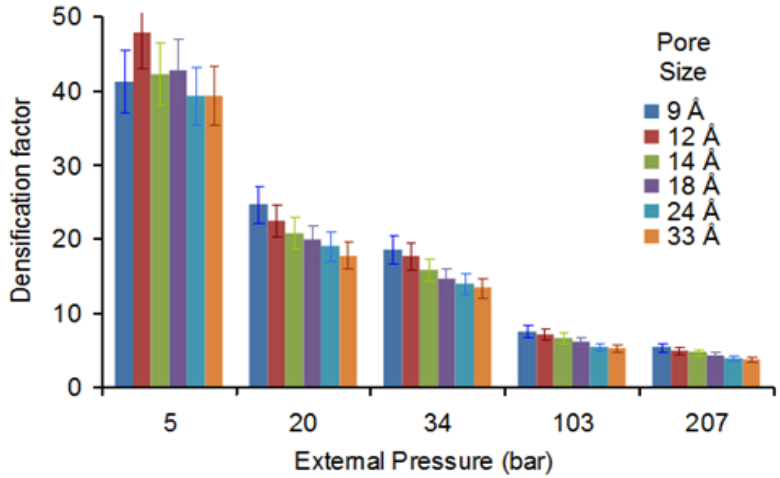


HYDROGEN CAPACITY DEPENDS CRITICALLY ON CARBON PROPERTIES

Superdensification of adsorbed H_2

- ✓ Used high-pressure in-situ small angle neutron scattering (SANS) to estimate the density of H_2 trapped in nanopores as a function of pore size and external H_2 pressure.
- ✓ At room temperature and 200 bar H_2, 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)

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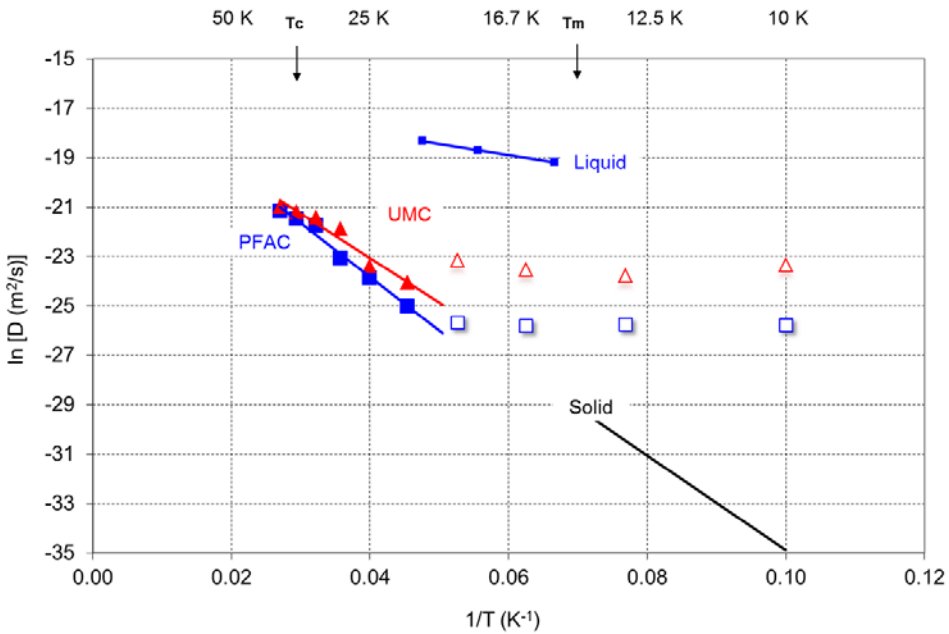
Restricted mobility of confined H_2

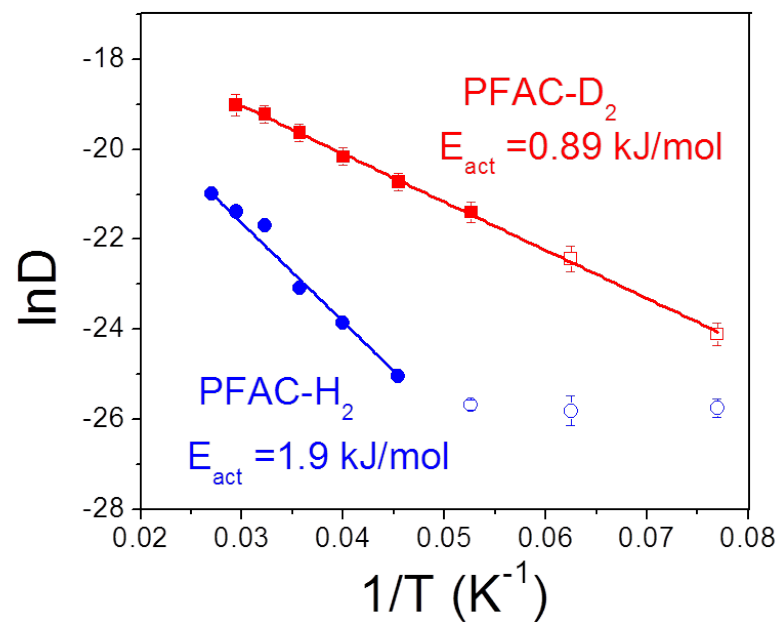
- ✓ Used quasi-elastic neutron scattering (QENS) to probe the dynamics of H_2 confined in carbon nanopores.
- ✓ Hydrogen became mobile at temperatures some 8-11 K above the melting point of bulk H_2 (13 K).
- ✓ After becoming mobile, diffusion occurs by the solid-like mechanism with activation energies close to those of solid H_2



Contescu et al, *Carbon* **50** (2012) 1071-1082

Role of quantum confinement in diffusion

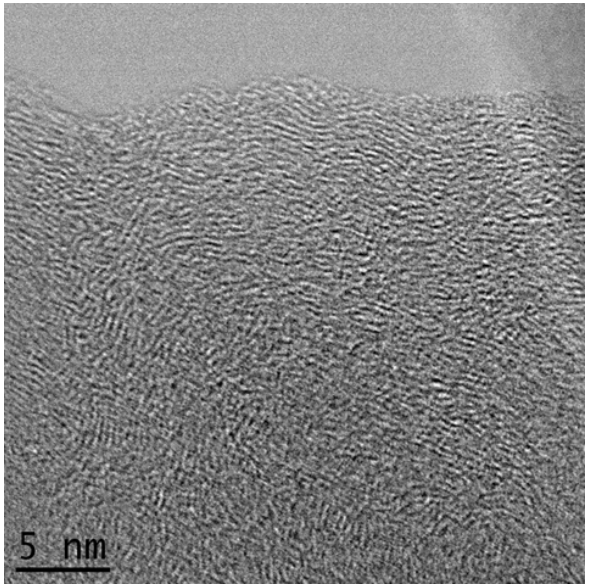
- ✓ Usual isotope effect would suggest that $D_{D2}<D_{H2}$ due to doubled mass of molecule.
- ✓ Quantum de Broglie wavelength of D_2 is significantly smaller than that of H_2 because D_2 is heavier.
- ✓ Under the same conditions, D_2 shows higher mobility.
- ✓ The restricted mobility of H_2 is caused by extreme confinement and strong quantum effects at low temperatures.



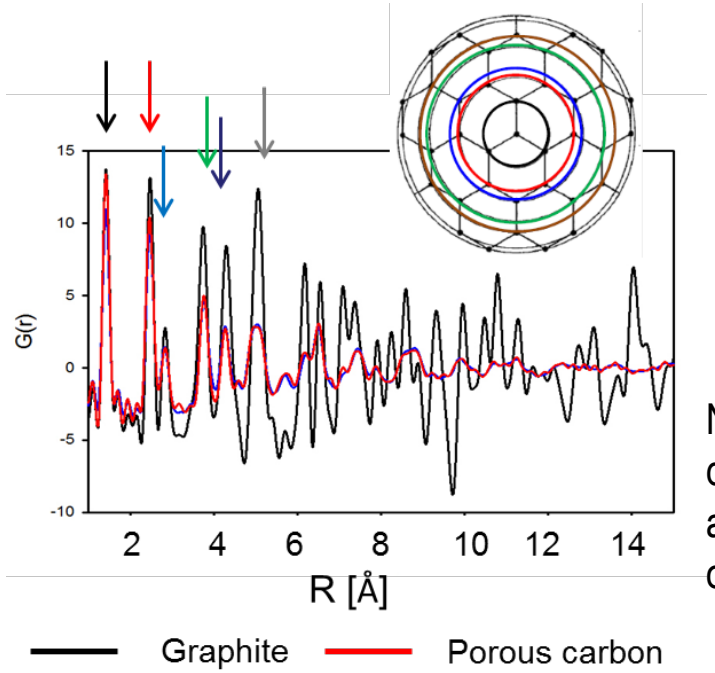
De Broglie wave-length $\lambda_T = \hbar / \sqrt{\mu k_B T}$

Preliminary results (2012)

Order vs. disorder in carbons



Electron microscopy: short graphene layers with random orientation

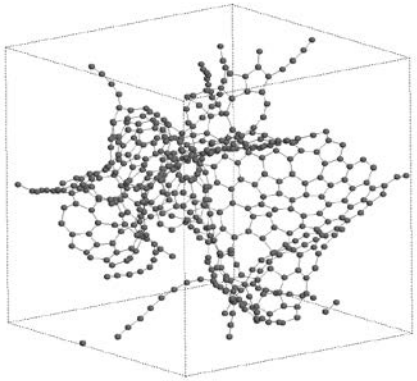


Neutron scattering and pair distribution function (PDF) analysis: short range 2D order

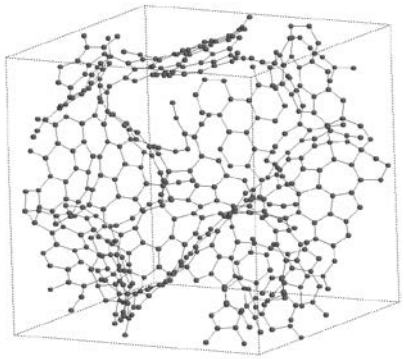
- ✓ Nanoporous carbons have 2D structures with short range order.
- ✓ Local folds and cusps limit lateral coherence to only 8-10 Å.
- ✓ Graphene layers are stacked closely but with minimal interlayer atomic correlation.
- ✓ Local atomic density is only 20 % lower than in graphite.

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

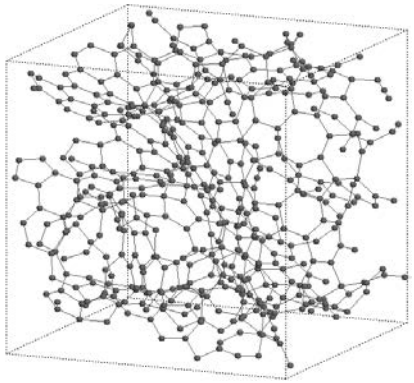
Effect of carbon density



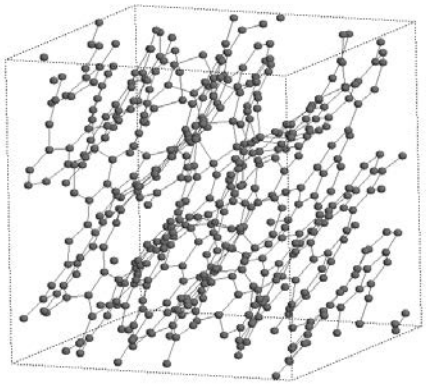
0.6 g/cm^3



1.0 g/cm^3

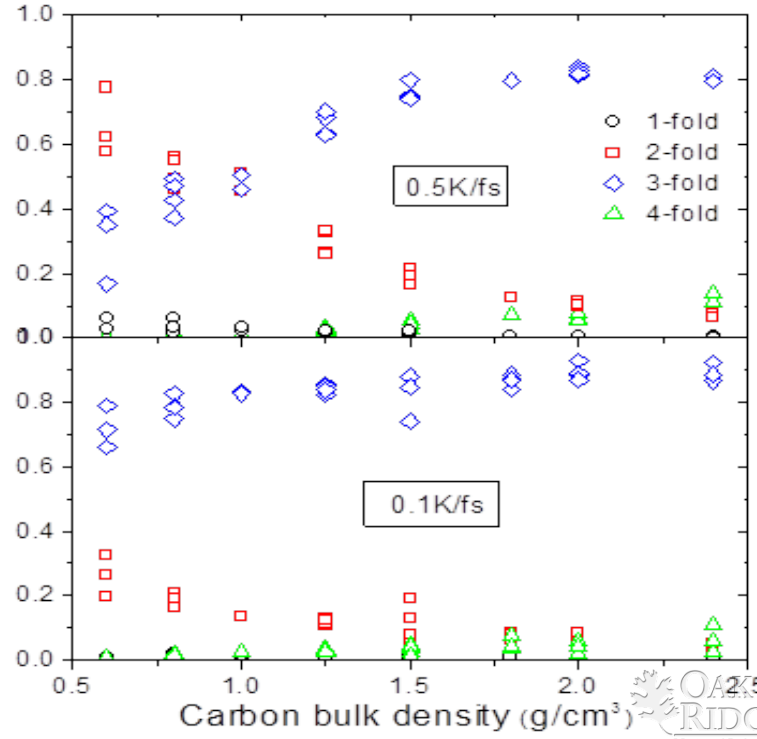


1.8 g/cm^3



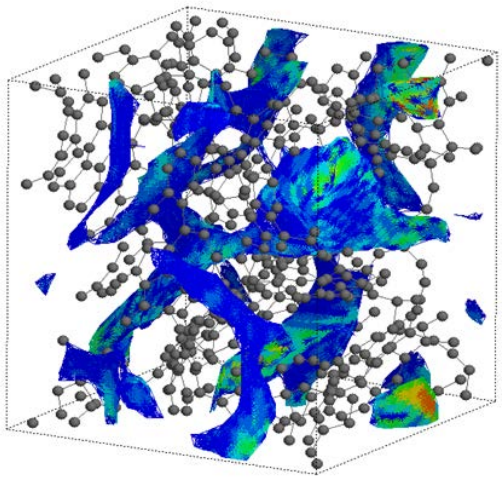
2.4 g/cm^3

- ✓ 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^3

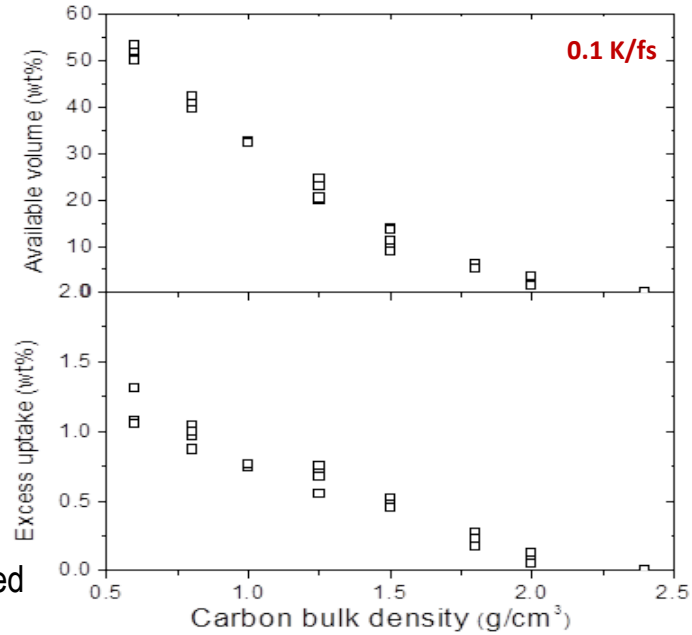


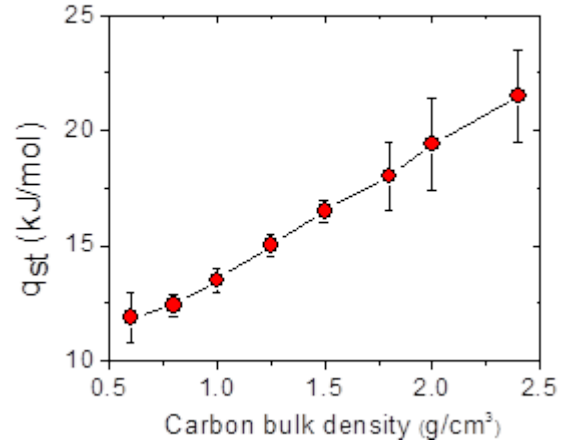
Peng, Morris, *Carbon* **50** (2012) 1394-1406

Adsorption calculations



Regions with E_{ads}< -10 kJ/mol in simulated carbon structure with density 1.25 g/cm^3





- ✓ 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.

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

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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 ?