# A Room Temperature Reversible Hydrogen Storage Material Studied by SANS

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A talk given at ihe first meeting of the "Union for Compact Accelerator-Driven Neutron Source (UCANS), Tsinghua University, Beijing, China, August 16-18, 2010.

# Motivation for Choice of Problems

- Problem addressed should be timely and satisfies a social need.

- Problem addressed should be tailored to a medium flux neutron source.

- Material chosen should be such that neutron scattering technique is most powerful.

# Climate Change and the Integrity of Science



The planet is warming due to increased concentrations of heat-trapping gases in our atmosphere. A snowy winter in Washington does not alter this fact.

Most of the increase in the concentration of these gases over the last century is due to human activities, especially the burning of fossil fuels and deforestation.

The good news is that smart and effective actions are possible. But delay must not be an option.

Science **328**, 689 (2010)

# FUEL OF THE FUTURE?



Hydrogen fuel-cell vehicles, largely forgotten as attention turned to biofuels and batteries, are staging a comeback. **Jeff Tollefson** investigates.

THE HYDROGEN CHALLENGE

The future of hydrogen fuel-cell vehicles depends on advances in four key areas: the hydrogen source, the distribution infrastructure, the on-board fuel tank and the on-board fuel cell.

**Fuel tank**
Fuel-cell vehicles must store enough hydrogen to go several hundred kilometres between refuelling stops. Liquid hydrogen requires insulated tanks at −253 °C. So most companies have chosen to compress the hydrogen inside high-strength carbon-fibre tanks.

**Infrastructure**
Once the hydrogen is made, it must be distributed via special pipelines and tankers to an extensive network of hydrogen refuelling stations. But who will buy the vehicles if the stations don't exist? And who will invest in the stations if the vehicles don't exist?

**Source**
Hydrogen must be derived from carbon-free renewable sources before fuel-cell vehicles can make a dent in the climate problem. One idea is to make the hydrogen by splitting water using electricity from wind farms, solar panels or nuclear plants.

**Fuel cell**
This device converts hydrogen to electric power. The challenge is to make it light, cheap, robust and durable — yet powerful enough to run the engine, lights and air conditioning.

1263
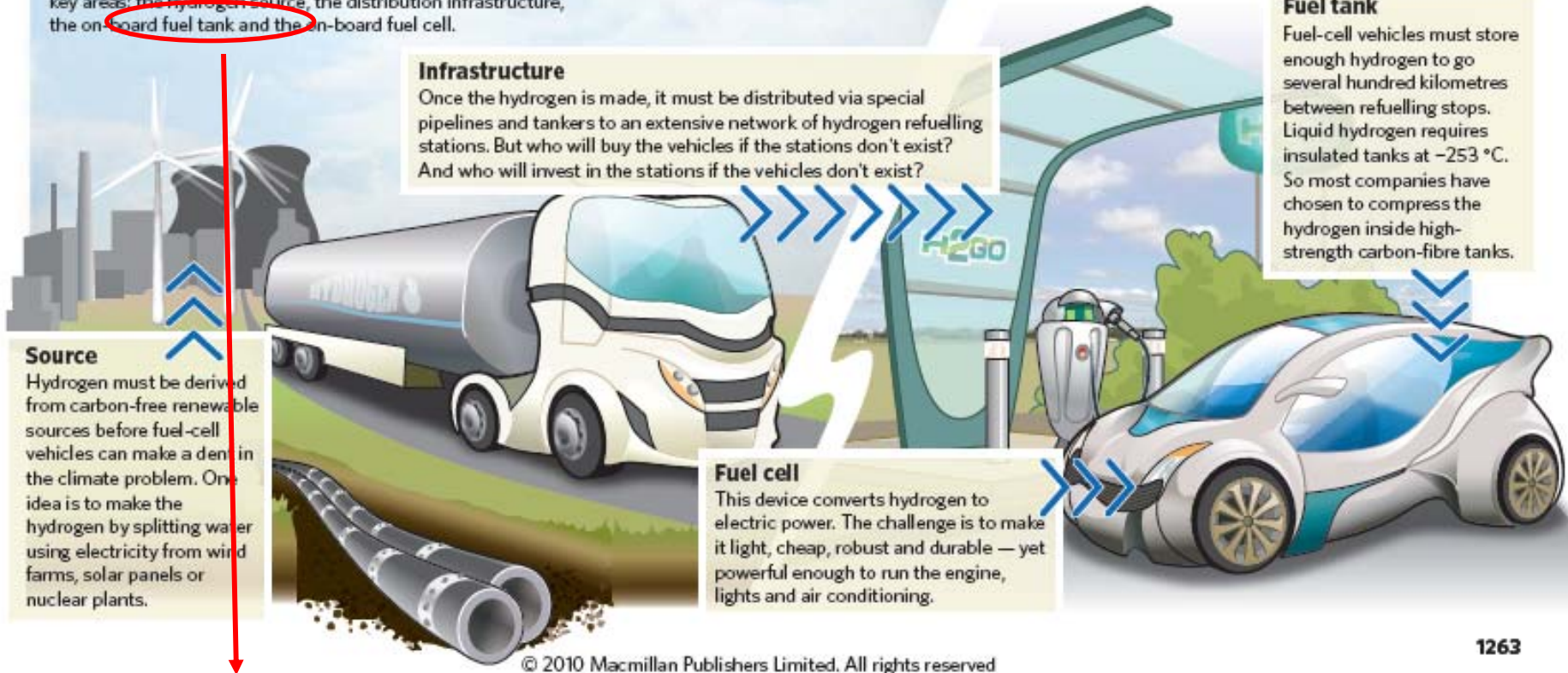
**On-board hydrogen storage**

None of the materials developed so far can satisfy the target criteria set by the U.S. Department of Energy.

i.e., **4.5 wt %** by 2010 , **5.5 wt%** by 2015; reversible at ambient temperature and at moderate pressures.

# H$_2$ storage – the Grand Challenge

US DOE targets for on board hydrogen storage materials

| Storage Parameter | Units | 2010 | 2015 | Ultimate |
|---|---|---|---|---|
| System Gravimetric Capacity | g H$_2$/kg | 45 (4.5 wt%) | 55 (5.5 wt%) | 75 (7.5 wt%) |
| System Volumetric Capacity | g H$_2$/L | 28 | 40 | 70 |

Solid H$_2$ density at 0 K and zero pressure is 86 g/L!

# Initial H-Prize Competition for Breakthrough Advances in Materials for Hydrogen Storage

February 15, 2010: Deadline for Registration and Eligibility Documentation.
.
November 15, 2010: Deadline for submittal of material samples for testing.
.
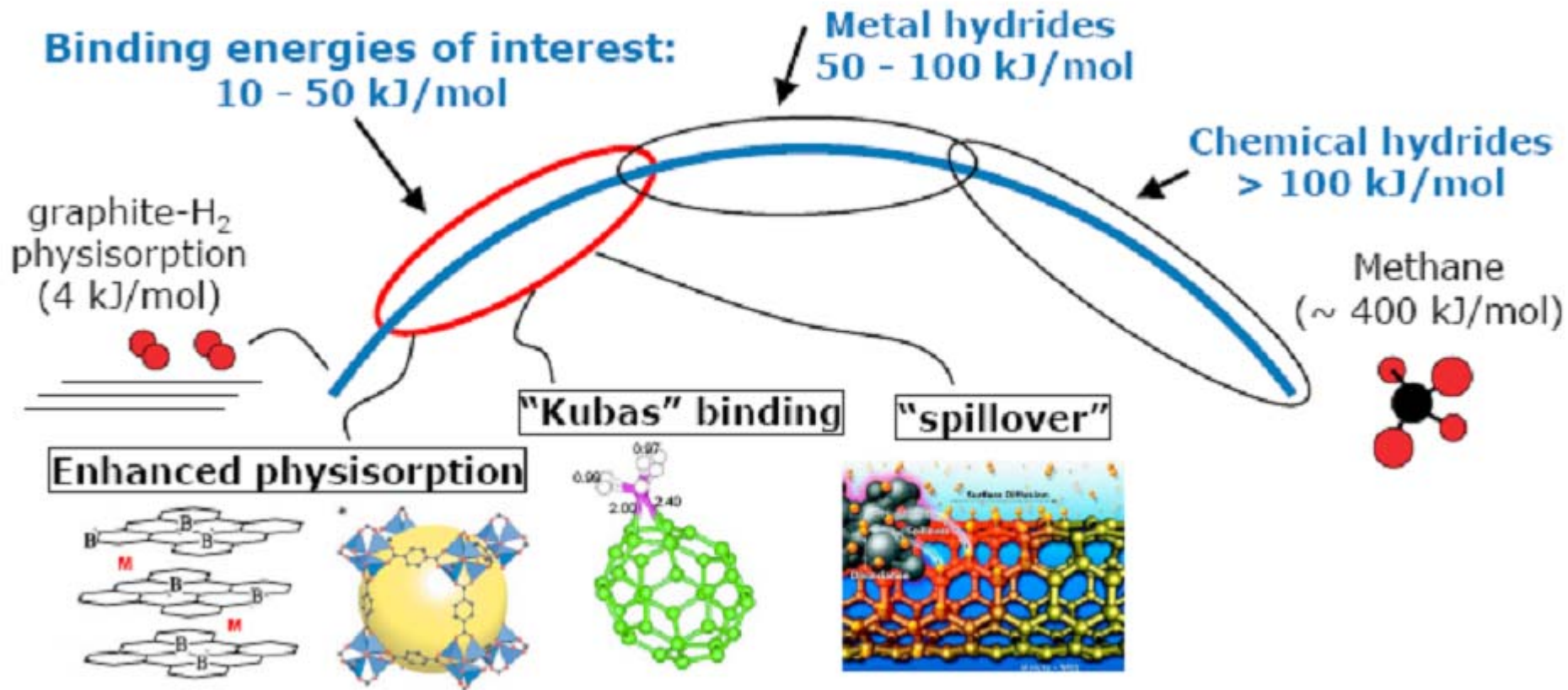Dec 2010/Jan 2011: Sample testing by an independent third party laboratory.
.
Dec 2010/Jan 2011: Panel of Judges reviews and evaluates the independent third party testing data.
.

February 2011: Award of $1 million prize, if the Panel of Judges determines that there is a winning entry.

# Main Challenge: Right Binding Strength



*Challenges for physisorption methods:*
1.  *Binding strength is still too weak to adsorb hydrogen at ambient conditions.*
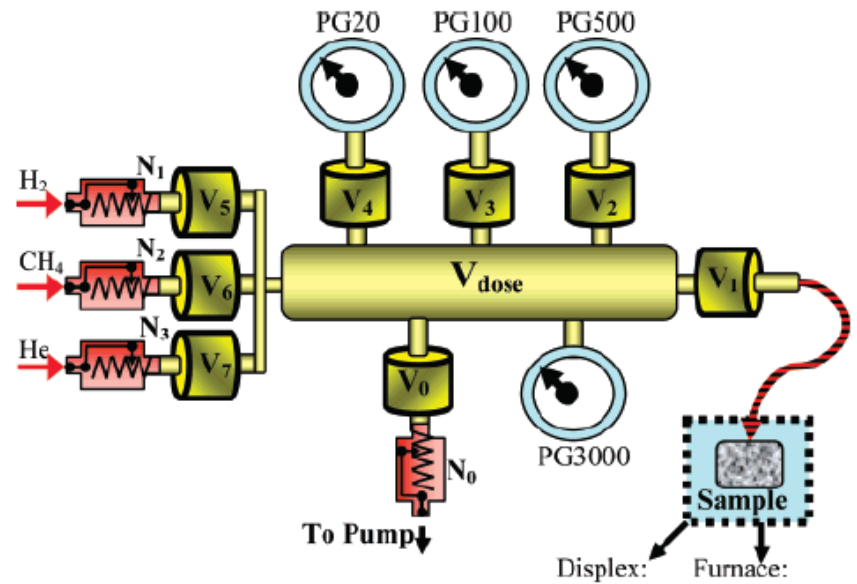2.  *The hydrogen density is still too low compared to that of metal hdyrides materials.*

# Traditional methods for isotherm measurements

Gravimetric method
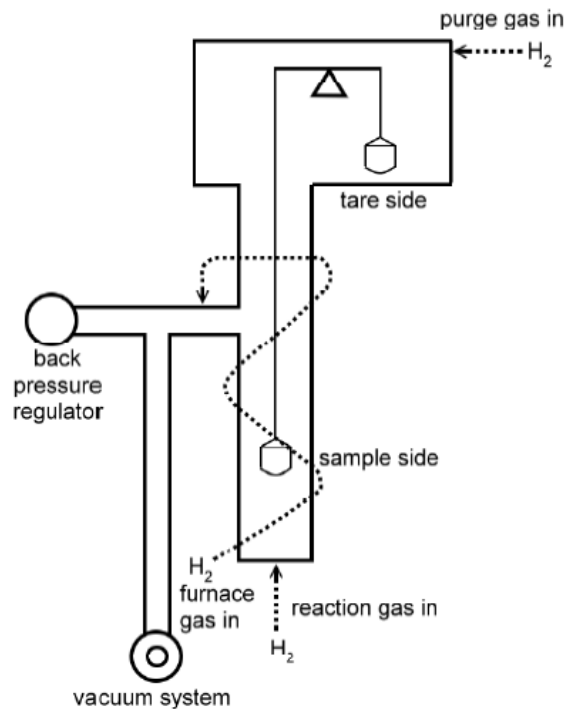


**HPTGA** measures the gravity change of a sample. Buoyancy correction is the key for a correct measurement.

Volumetric method



**SIEVERTS** type instrument measures the pressure change. Carefully calibrated volume for the measurement of a small sample is critical.

**New Material**: Pt-impregnated activated carbon (Pt/AC) developed by Institute of Nuclear Energy Research (INER)

Performance:  Reversible room-teperature hydrogen storage capacity at 1000 psi via the **spillover** effect - - - 5.6 wt%

$(143-128)/128=0.117 \approx 11.7$ wt%

AC grain
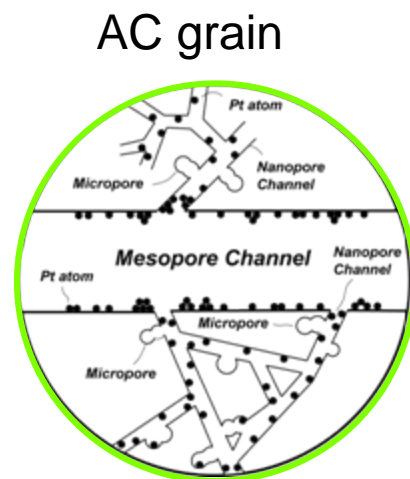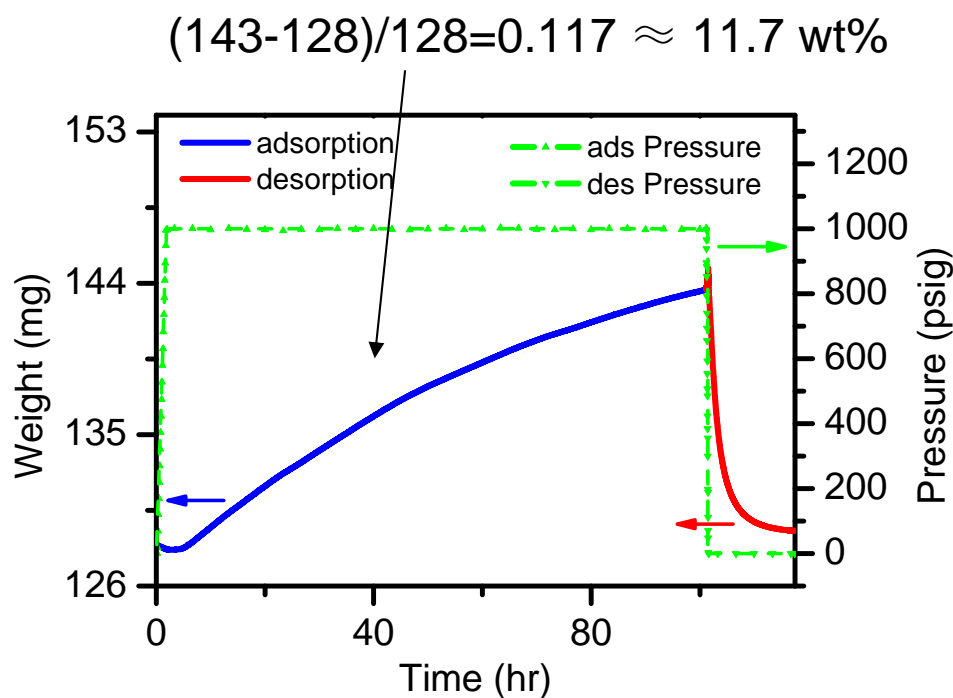
Schematic Pt/AC structure, SEM images
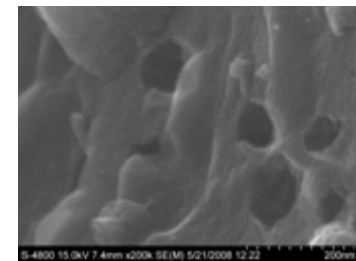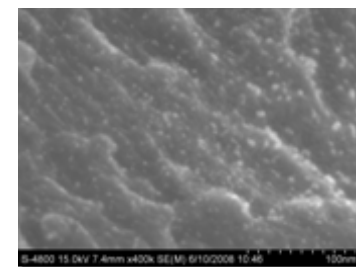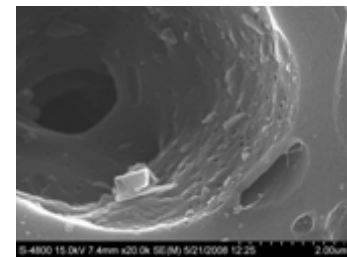
Tsao, C.-S. & Chen, S.-H. et al. "Effect of Catalyst Size on Hydrogen Storage Capacity of Pt-impregnated Active Carbon via Spillover", *Journal of Physical Chemistry Letters* (2010) **1**,1060-1063.

# Hydrogen storage is the main bottleneck of **Hydrogen Economy**

None of Materials developed so far satisfy the on-board target criteria of DOE for hydrogen storage: Reversible 4.5 wt% by 2010 at ambient temperature and a maximum applied pressure of 1200 psi.
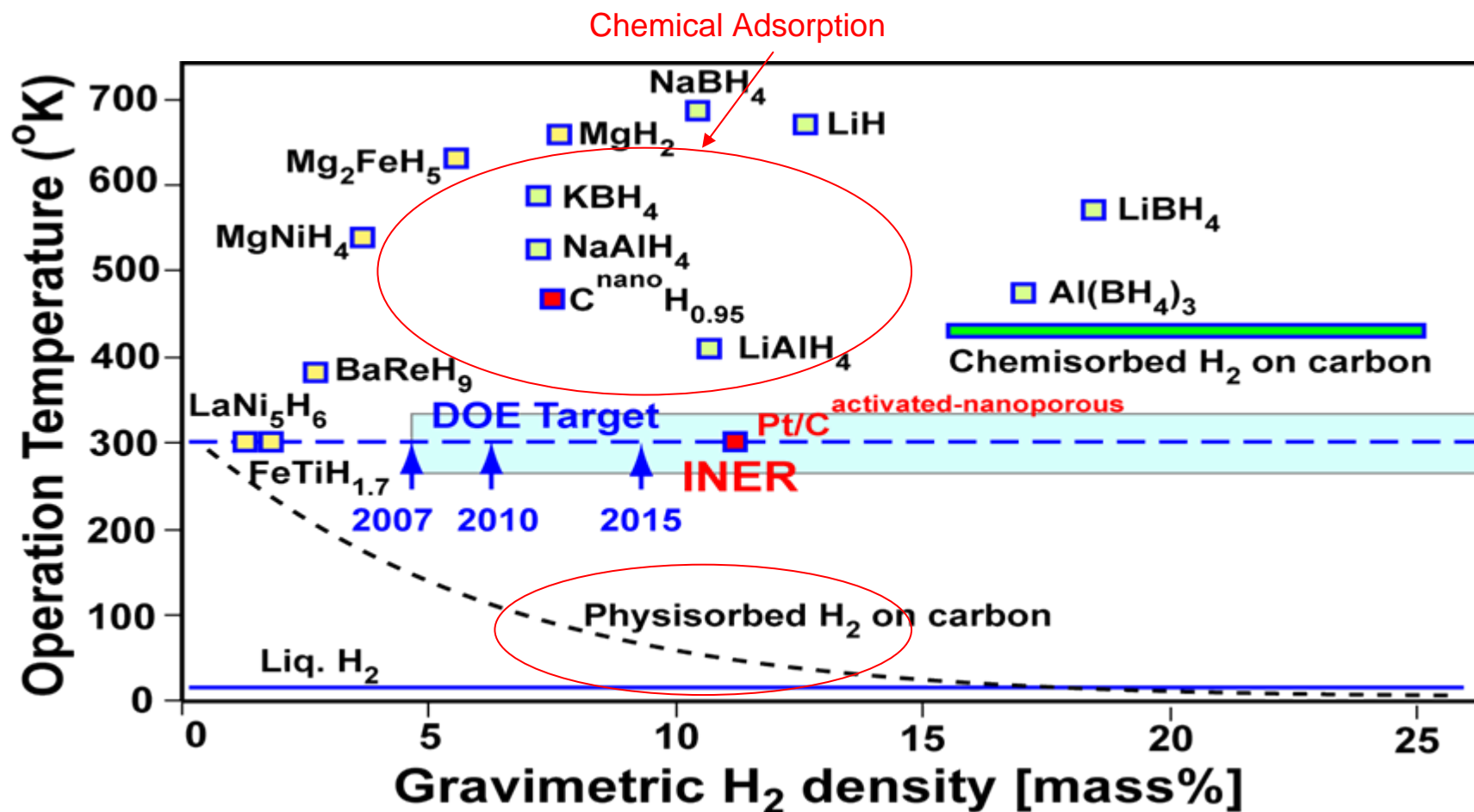
# Probing H$_2$ in Storage Materials Using Neutron Scattering
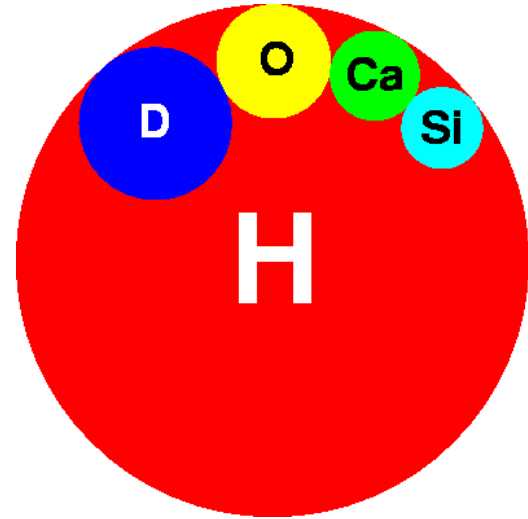


- •Unlike X-ray scattering, neutron scattering is
  VERY SENSITIVE to hydrogen.
- • Appropriate energy, capable of selectively probing the key motions
  of the hydrogen atoms bound in a substrate.
- • Good penetrating capability of metal pressure cell.
- • Possibility of the H to D Isotope labeling in diffraction experiments

Comparison of the coherent neutron scattering cross sections
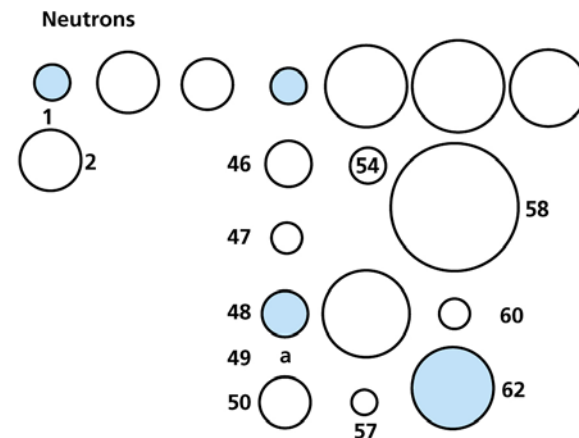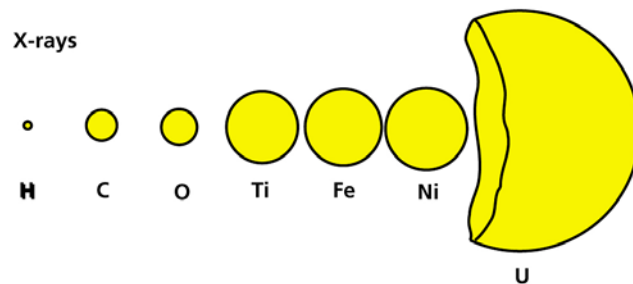
# Neutron Scattering Techniques Applied to Hydrogen-Storage Materials

A <u>unique and powerful tool</u> for solving the hydrogen-storage mechanism in **materials** to optimize the design of **Commercial** products and improve their performance

**(1) Incoherent Inelastic Neutron Scattering (INS): "QENS"**
To study the binding energies of atomic and molecular hydrogen with each adsorption site.

**(2) Small-Angle Neutron Scattering (SANS): "SAND"**
(a) To study the spatial distribution and local aggregation of hydrogen confined in the pore structure (b) Measure the RT hydrogen storage capacity on an atomic scale.

**(3) Powder Neutron Diffraction (PND): "GPPD", "SEPD"**
To locate the adsorption sites of hydrogen in porous materials.
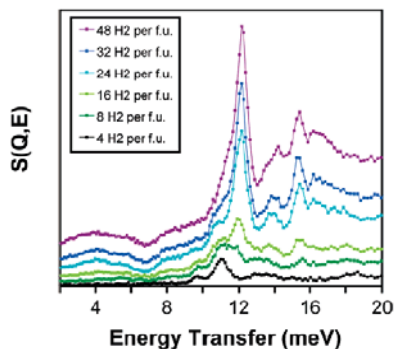


Figure 4. Inelastic neutron scattering spectra for MOF-177 at various loadings of H2.

J. Am. Chem. Soc. 2005, 127, 14904
J. Am. Chem. Soc. 2008, 130, 15896
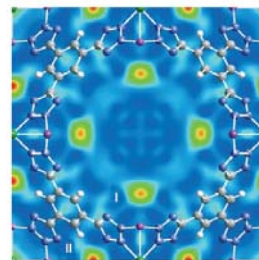Science 2003, 300, 1127



Figure 4. Difference Fourier map after loading 12 D$_2$ molecules per formula unit within **2d** at 4 K, calculated from powder neutron diffraction data. The view is down a fourfold rotational axis. Red maxima indicate the centroids of the adsorbed D$_2$ molecules; adsorption sites I and II are labeled.

Angew. Chem. Int. Ed. 2007, 46, 1719

Phys. Rev. Lett. 2005, 95, 215504

However, almost all past neutron scattering studies were focused on the physical adsorption at 77K

**Small-angle neutron scattering (SANS)** is a powerful tool **(**a) to study the spatial distribution and local aggregation of hydrogen confined in the pore structure from nanoscale to mesoscale, (b) to measure the RT hydrogen storage capacity on an absolute scale.

Motivation – I

To date, SANS study of the hydrogen storage at RT in a porous materials, using a Pt/AC powder sample with an aim to test the spillover effect, is very rare.

However, The RT hydrogen storage capacities of porous materials with the spillover effect measured from different laboratories was disputed because of the difficulties in obtaining the reproducible data. The discrepancy is mainly due to many potential sources of measurement errors and their experimental validations. Measurement of the relatively low uptake of hydrogen ($< 5$ wt%) in porous materials at RT and high pressures have resulted in many challenges to traditional volumetric and gravimetric methods.

## Motivation – II

Improving the technique or designing new method for hydrogen storage measurement is critically necessary to develop and test the promising materials.

The disadvantages of the volumetric method (Sieverts apparatus) are, for example, (1) the potential leakage at high pressure, (2) the temperature gradients on the measured pressure (1 degree temperature rise can cause an artifact of 2.6 wt% adsorption), and (3) the other uncertainties coming from instrumental calibrations. One limitation of the gravimetric method is to correct for the volume buoyancy effect, which is further amplified for low-density materials.

(1) Wang, L. and Yang, R. T. *Energy Environ. Sci.* **2008**, 1, 268-279.
(2) Wang, C. Y. and Tsao, C. S. et al. *J. Alloys Compd.* **2010**, 492, 88 - 94.
(3) Lupu, D.; Biris, A. R.; Misan, I.; Jianu, A.; Holzhüter, G.; Burkel, E. *Int. J. Hydr. Ener.* **2004**, 29, 97-102.
(4) Furukawa, H.; Miller, M. A.; Yaghi, O. M. *J. Mater. Chem.* **2007**, 17, 3197 – 3204.
(5) Lachawiec, A. J.; DiRaimondo, J. T. R.; Yang, R. T. *Rev. Sci. Instrum.* **2008**, 79, 063906.

# Neutron Scattering Methodology for Absolute Measurement of Room temperature Hydrogen Storage Capacity and Evidence for Spillover Effect in a Pt-doped Activated Carbon

Cheng-Si Tsao, Yun Liu, Mingda Li, Yang Zhang, Juscelino Leao, Hua-Wen Chang, Ming-Sheng Yu and Sow-Hsin Chen,* **J. Phys. Chem. Lett. (2010), 1,** 1569-1573.
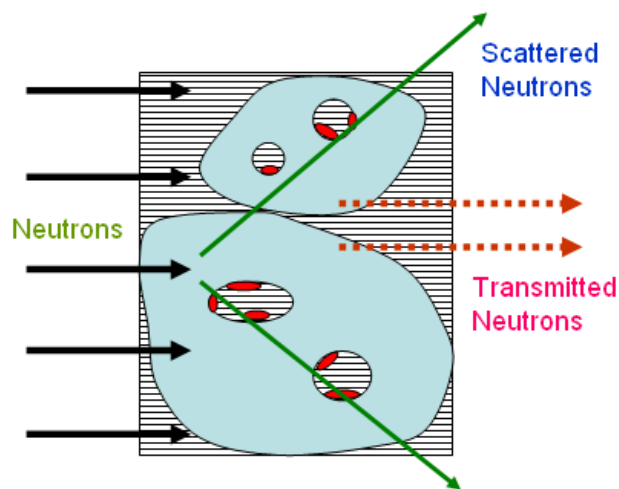
## Neutron scattering methodology:

(1) Transmission measurement: simultaneously determine the total hydrogen adsorption, the excess hydrogen adsorption, hydrogen gas confined in the porous sample and bulk density of the sample.

(2) Combined with in-situ small-angle neutron scattering: determine the corresponding distribution of the excess hydrogen adsorbed due to the spillover effect.

Our method is simple and capable of directly measuring the hydrogen storage capacity accurately with small amount of sample without need for laborious calibrations such as empty volume or buoyancy corrections that are crucial for traditionally used thermodynamic methods. It is not likely to be affected by the instrumental factors from the traditional gravimetric and volumetric methods.



Pressure-dependent hydrogen gas

Excess hydrogen adsorbed

Pores in the grain

Voids between carbon grains
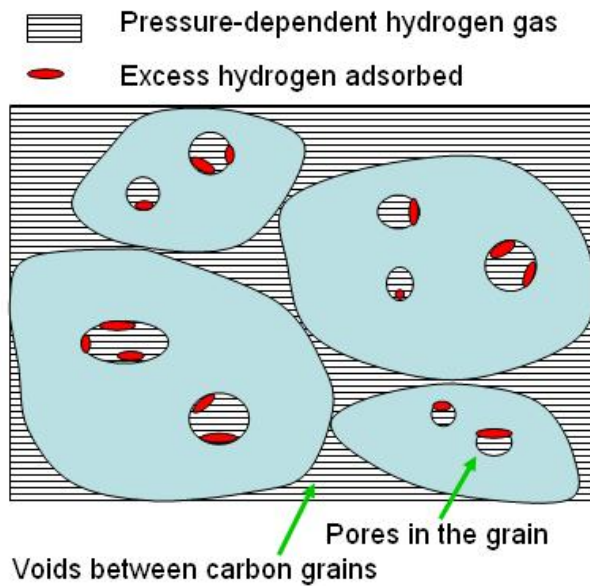
void volume: $V_{void}$ ,
carbon volume: $V_c$ ,
pore volume: $V_{pore}$ ,
total volume irradiated by neutron beam: $V_{tot}$ ($V_{tot} = V_{void} + V_c + V_{pore}$),
carbon mass: $W_c$ ,
mass of total hydrogen adsorption: $W_H$ ,
mass of excess hydrogen adsorption: $W_{H1}$ ,
mass of hydrogen gas confined in the sample (voids and pores): $W_{H2}$ ,
bulk density of carbon sample (considering the grain packing and internal pores): $d_{bulk}$ ($d_{bulk} = W_c / V_{tot}$),
skeletal (solid state) density of carbon: $d_s$ ($d_s = W_c / V_c$)
hydrogen gas density as a function of pressure: $\rho_{gas}$ ,.

**A two-step measurement:** is conducted for measuring the adsorption capacity at a given hydrogen pressure $P_0$: **(1)** Measure the neutron transmission factor (i.e., the sigma-carbon value) of the carbon sample at P=0 (vacuum), and **(2)** Measure the transmission factor (i.e., the sigma-carbon+hydrogen value) of the carbon sample with the adsorbed hydrogen at pressure $P_0$.

The following equation system can be established from the first principle:

$$\Sigma_C = \sigma_C N_C = \sigma_C \frac{W_C}{M_C V_{tot}} N_0 \qquad \text{(at P=0)} \qquad (1)$$

$$\Sigma_{C+H} = \sigma_C N_C + \sigma_H N_H = \sigma_C \frac{W_C}{M_C V_{tot}} N_0 + \sigma_H \frac{W_H}{M_H V_{tot}} N_0 \qquad \text{(at P= P}_0) \qquad (2)$$

Based on Eq. (1) and the measured sigma-carbon value, the value of $d_{bulk}$ can be determined as:

$$d_{bulk} = \frac{W_C}{V_{tot}} = \Sigma_C \times \frac{M_C}{\sigma_C N_0} \qquad (3)$$

Subtracting Eq.(1) from Eq.(2), we directly obtain the total adsorption capacity $W_H/V_{tot}$ (volumetric form) as given by

$$\frac{W_H}{V_{tot}} = (\Sigma_{C+H} - \Sigma_C) \times \frac{M_H}{\sigma_H N_o} \qquad (4)$$

The total adsorption capacity is the sum of excess hydrogen adsorption and hydrogen gas confined in the sample as given by

$$\frac{W_H}{V_{tot}} = \frac{W_{H1}}{V_{tot}} + \frac{W_{H2}}{V_{tot}} \qquad (5)$$

The amount of pressure-dependent hydrogen gas confined in the sample can be expressed as

$$\frac{W_{H2}}{V_{tot}} = \frac{V_{pore}\rho_{gas} + V_{void}\rho_{gas}}{V_{tot}} = \rho_{gas} \times \left( \frac{V_{pore} + V_{void}}{V_{tot}} \right) = \rho_{gas} \times \left( \frac{V_{tot} - V_C}{V_{tot}} \right) \qquad (6)$$

Combining with $\quad V_{tot} : V_C = d_{bulk}^{-1} : d_s^{-1}$

and the skeletal density $d_s$ determined from the helium density method,
the amount of hydrogen gas confined in the sample (volumetric form) $W_{H2}/V_{tot}$ can be obtained.
Finally, according to Eq. (5) and the deduced amounts, the excess hydrogen adsorption $W_{H1}/V_{tot}$ can be determined in turn.
By dividing by the determined value of $d_{bulk}$ (= $W_c / V_{tot}$), all calculated values for (1) total hydrogen adsorption, (2) excess hydrogen adsorption and (3) hydrogen gas confined in the sample could be transformed into the gravimetric form (in unit of wt%) from the volumetric form.
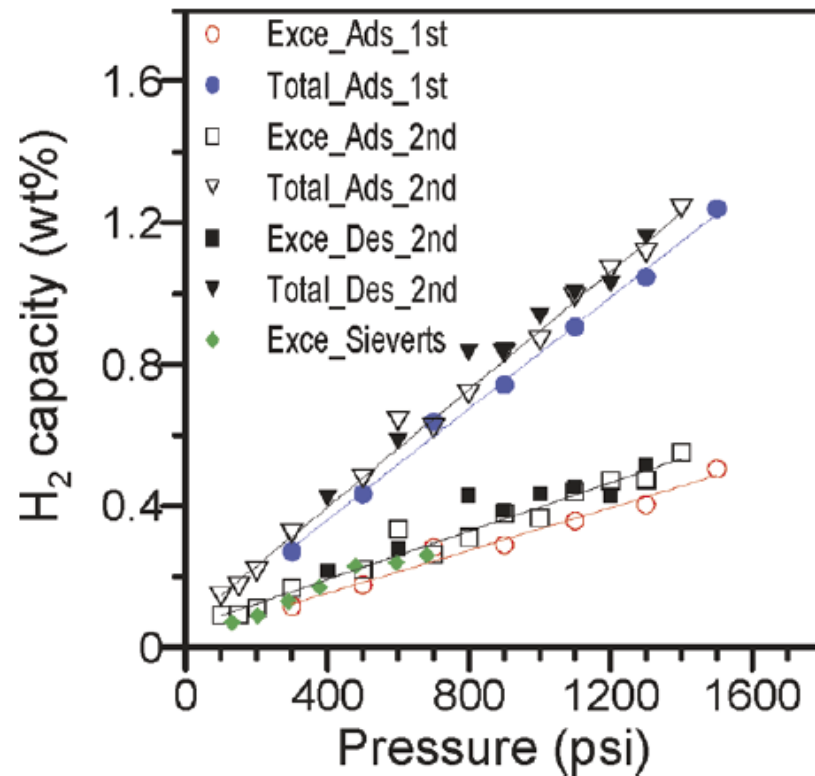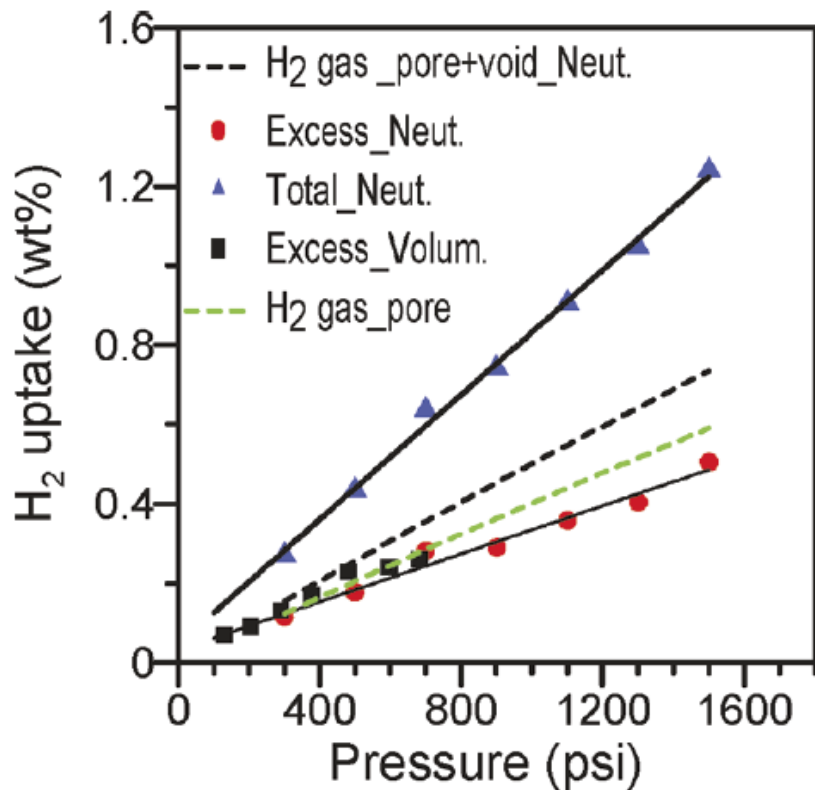
Measurement of RT hydrogen storage capacity as a function of hydrogen gas pressure (in terms of total adsorption, excess adsorption and hydrogen gas confined in the sample) for Pt/AC sample determined by neutron transmission method, in comparison with the excess adsorption obtained by Sieverts (volumetric) method.

RT Hydrogen Isotherms measured by neutron transmission method for a Pt/AC sample under first and second cycles, together with the excess adsorption obtained by Sieverts method.
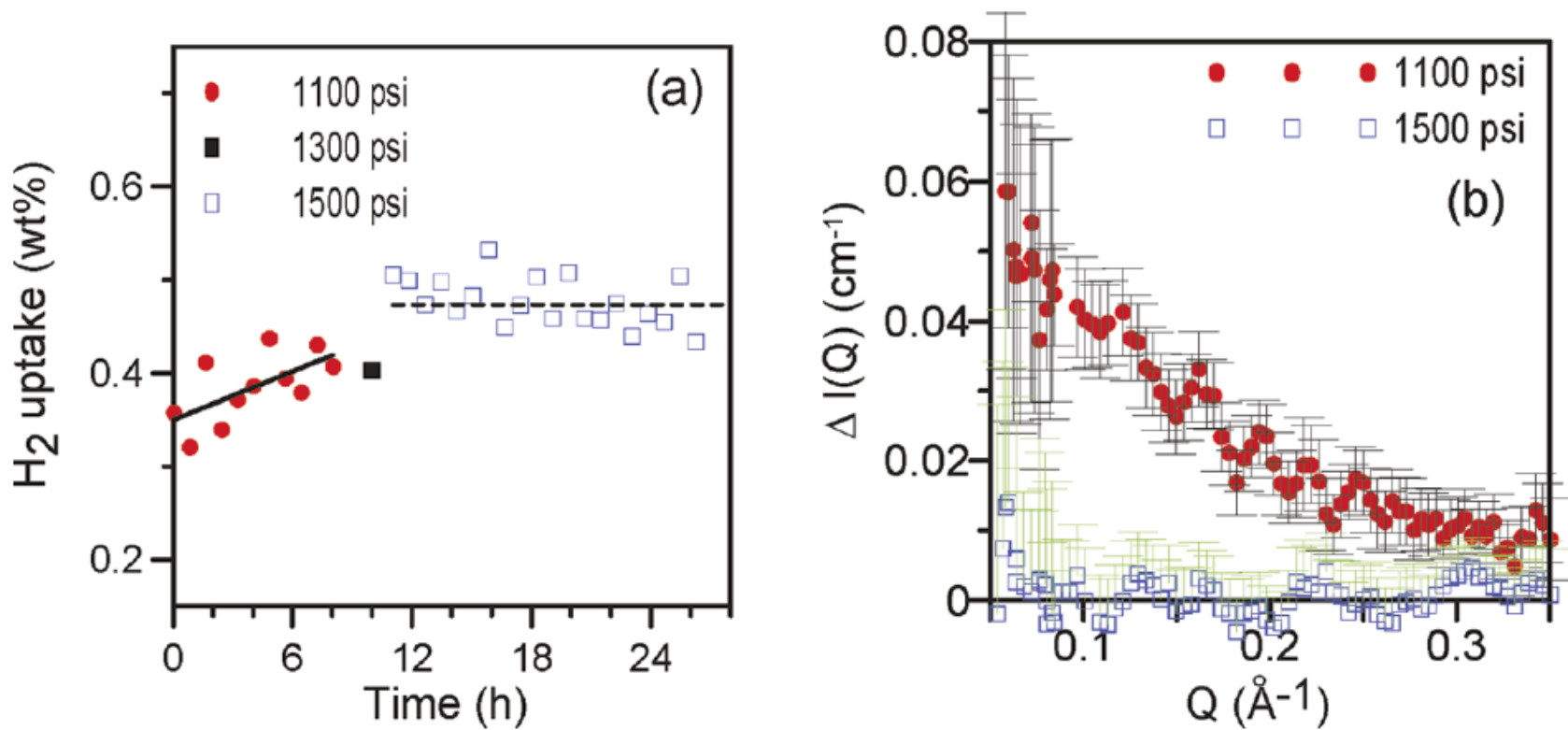
(a) Kinetic (excess) adsorption measurement of Pt/AC sample at 1100 and 1500 psi, respectively, using the neutron transmission method. The single point at 1300 psi is taken between 1100 and 1500 psi. (b) Difference of SANS intensity profiles between the initial and final states in the kinetic adsorptions corresponding to Figure 4(a).

# Probing the Room-temperature Spatial Distribution of Hydrogen in Nanoporous Carbon by use of Small-angle Neutron Scattering

Cheng-Si Tsao, Yun Liu, Mingda Li, Yang Zhang, Juscelino Leao, Wei-Shan Chiang, Tsui-Yun Chung, Yi-Ren Tzeng, Ming-Sheng Yu and Sow-Hsin Chen,*   **(to appear in J. Phys. Chem. C, 2010)**
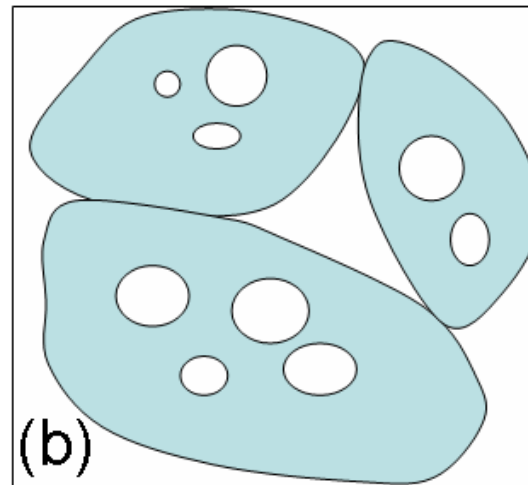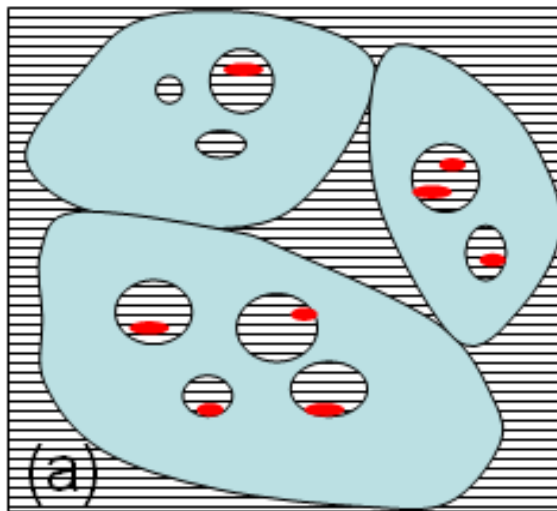
**Neutron scattering contrast maps:**
**(a) carbon powder system (under the hydrogen pressure)** comprised of the carbon grains (light blue), the excess adsorbed hydrogen (red) and the hydrogen gas (lines) confined in the pores (inside the carbon grain) and the voids (between the carbon grains), **(b) the carbon powder system under vacuum**.

(c) is the subtraction of (a) from (b)
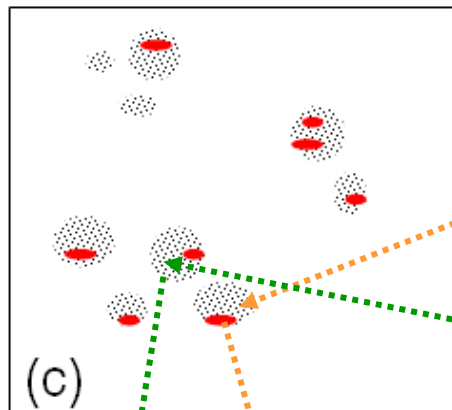
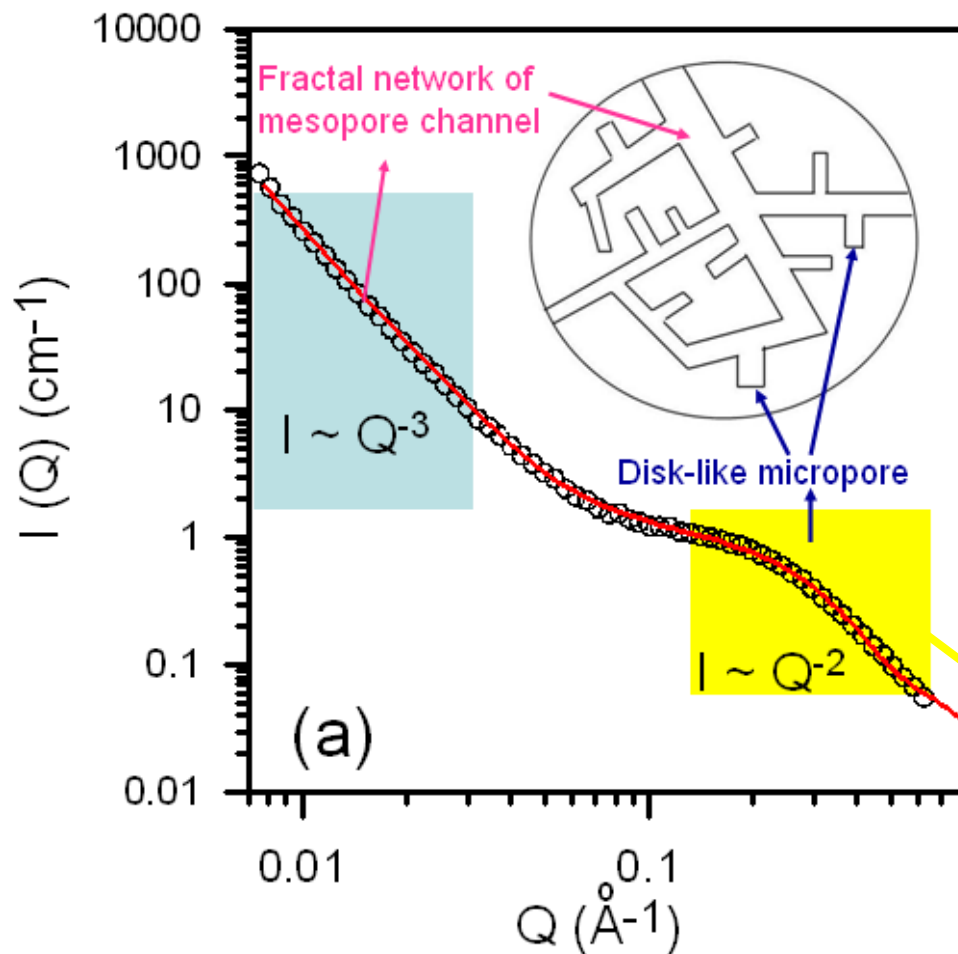(1) strong scattering from excess adsorption

(2) weak scattering from pressure-dependent hydrogen gas confined in the pores
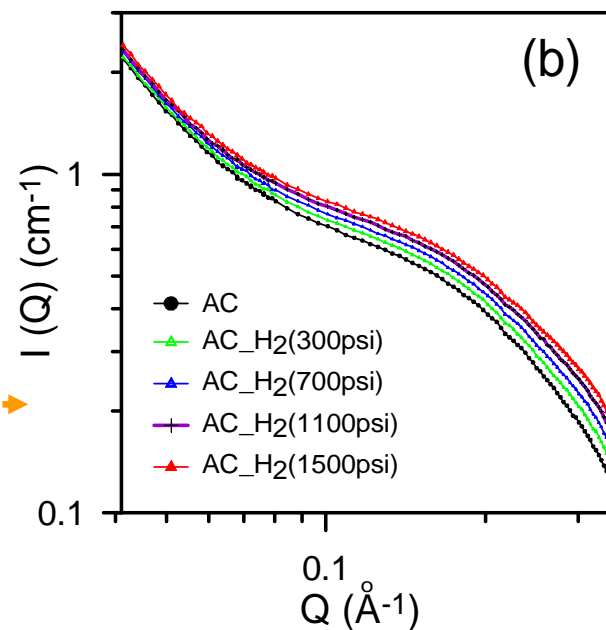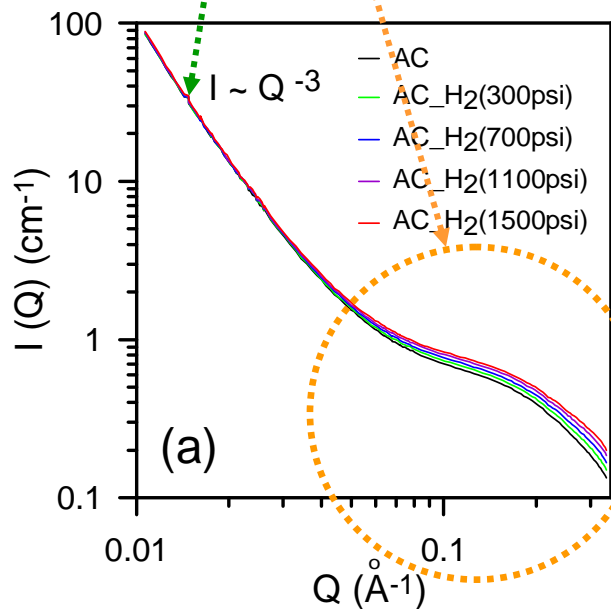
Selected pressure-dependent SANS profiles for the AC sample under increasing hydrogen pressure, staring from the vacuum case.

Detailed variation of SANS profiles (of (a)) with hydrogen pressure in the high Q region (0.04 ~ 0.33 Å-1).
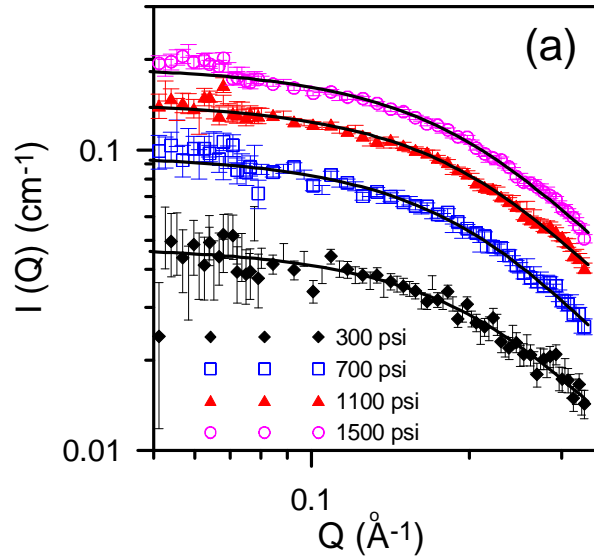
the fractal dimension, D, and channel width, w, of mesopore network are D = 3.0 and w = 2.1 nm, respectively.

The micropore is of disk-like geometry with an average thickness of t = 0.8 nm.
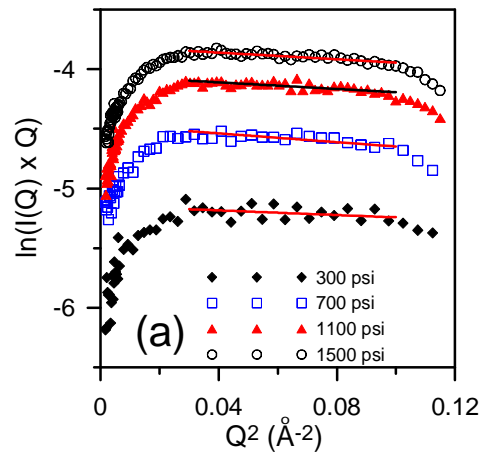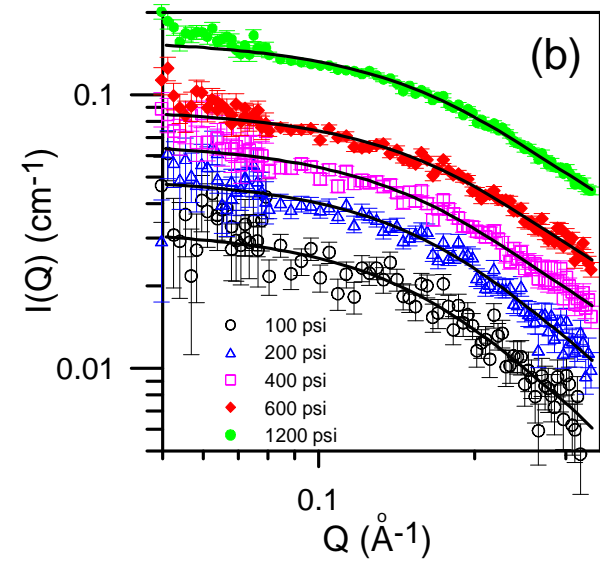
Comparison of the measured SANS profile (empty circle) of the AC sample under vacuum with the fitted intensity (red lines) using the model of the fractal network of mesopore channel and disk-like micropore.
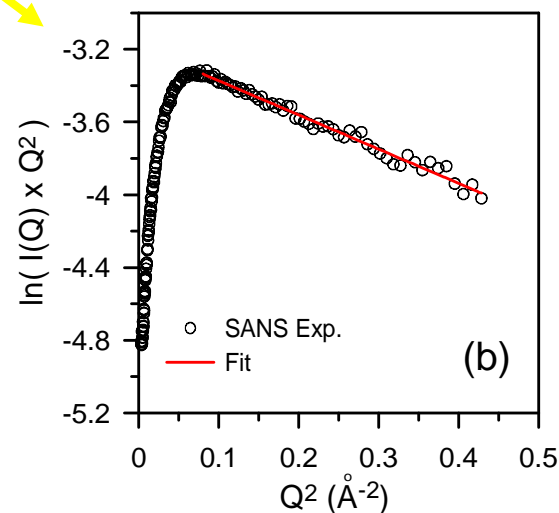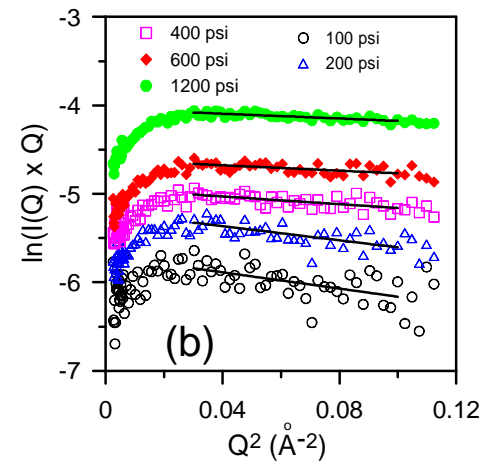
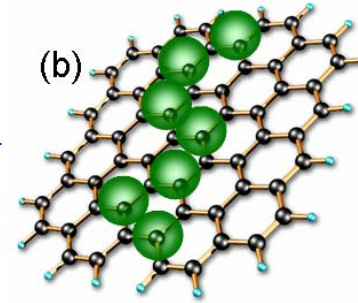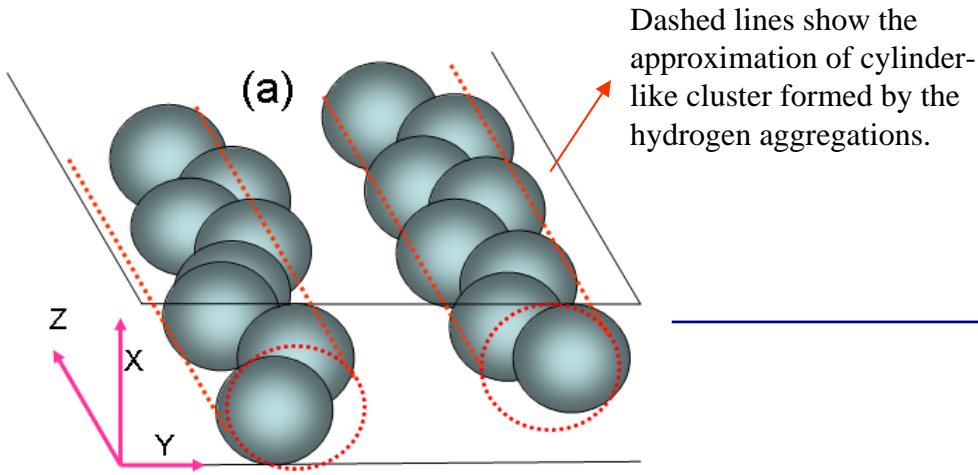# The cylinder-like clusters are formed by hydrogen aggregations (excess adsorption).



SANS profiles &
Model fittings

Model-independent:
Kractky-Porod plots

(a)

Dashed lines show the approximation of cylinder-like cluster formed by the hydrogen aggregations.

(b)

3D distribution of physisorbed hydrogen in the disk-like micropore (monolayer of the excess adsorbed hydrogen).

Schematic representation of hydrogen molecules (green balls) adsorbed on the hexagonally packed graphene sheet (black balls represent carbon atoms).



(c)
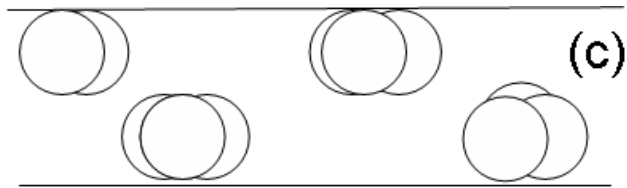
Side view (x-y plane) of 3D distribution of two-layers of hydrogen confined in the micropore.

(1)This form of cluster can be regarded as a basic unit for the spatial distribution of hydrogen.

(2)Its structure is related to the 3D structure of micropores confining the hydrogen.

(3)The volume fraction of the clusters increases linearly with increasing hydrogen pressure up to 1500 psi (or the hydrogen storage capacity up to 0.46 wt%).

# Studying H$_2$ dynamics using inelastic neutron scattering

Monitoring the amount of hydrogen molecules using inelastic neutron scattering.
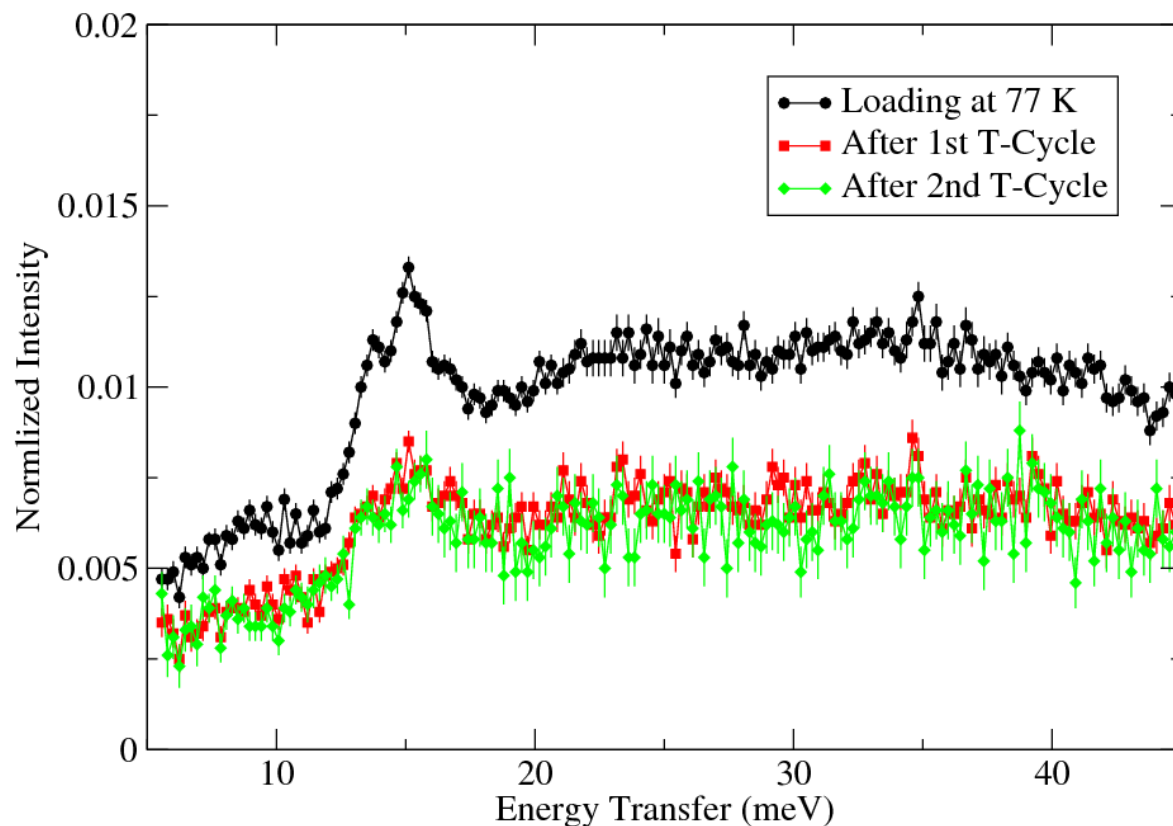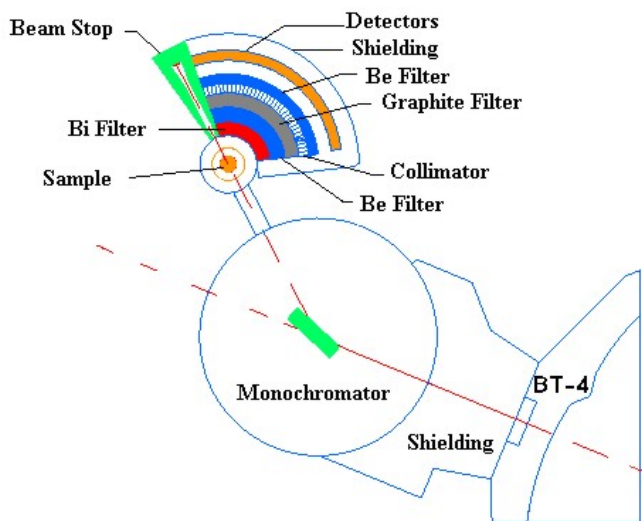


FANS (Filter-Analyzer Neutron Spectrometer) at NCNR, NIST

Loss of hydrogen molecules by conversion to atomic hydrogen, called the spill-over effect, is observed during our experiments.

# *Evidence of Enhanced Hydrogen Storage in Pt-Impregnated Activated Carbon by the Spillover Effect by C.S. Tsao et al*
## *(ACNS Conference, Ottawa, June 26-29, 2010 – Highlight)*

High hydrogen storage levels are critical for future mobile fuel cell vehicles. While various porous materials are under consideration for hydrogen storage, none of them yet satisfy the targets set, in particular by the U.S. Department of Energy. One potential option is using the "spillover" effect to enhance room temperature hydrogen storage capacity. In the spillover effect, in the case of Pt-doped activated carbon, atomic hydrogen is first generated by dissociation of hydrogen molecules on Pt particles, for instance. The atomic hydrogen then migrates onto the carbon by surface diffusion and is then adsorbed. The spillover effect is still rather poorly understood. Yang Zhang speaking on behalf of Cheng-Si Tao of MIT described the use of small angle neutron scattering (SANS) to study the spillover effect on Pt-impregnated activated carbon. The methodology involved transmission measurement combined with SANS. Inelastic neutron scattering was also used to study the state of the hydrogen and its interaction with the carbon adsorbent and carbon-supported metal particles. The results provided some evidence though not entirely conclusive for the spillover effect. However, the methodology used appears to be very useful for further studies to investigate the spillover effect.