IV.C.1e Neutron Scattering Characterization of Carbon Based Hydrogen Storage Materials

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Partner Approach

NIST will provide important materials characterization for Center of Excellence (CoE) partners using neutron-scattering measurements to probe the amount, location, bonding states, dynamics, and morphological aspects of hydrogen in carbon-based materials such as polymers, metal organic frameworks (MOFs), and carbonaceous materials such as carbon nanohorns. NIST will work directly with CoE partners that produce novel hydrogen storage materials to analyze the most promising samples and to help determine the fundamental issues that need to be addressed.

Partner FY 2006 Results

Non-destructive elemental analysis of CoE materials. A crucial step in the initial stages of sample development is the thorough knowledge of sample compositions. We used prompt gamma activation measurements to elucidate detailed elemental compositions of CoE generated materials.

- Measured boron content in arc (0.6 atomic%, at%) and laser (1.2 at%) produced boron-substituted carbon nanotubes from NREL. Our boron content measurements agree well with their electron energy loss spectroscopy (EELS) measurements.
- Measured boron content and platinum loading levels in Oak Ridge National Laboratory (ORNL) produced carbon nanohorns.
- Measured less than 2 at% boron in carbon from preliminary doped samples provided by Chung at Penn State. Subsequent synthesis refinements produced samples with larger amounts of boron to carbon, on the order of 10 at%.

Rotational spectra of physisorbed hydrogen. We measured the neutron rotational spectra of physisorbed hydrogen on selected CoE materials as a function of coverage to ascertain differences in hydrogen binding sites. We list the materials here.

- ORNL produced (closed) nanohorns and platinum decorated nanohorns. Figure 1 shows the low temperature neutron spectra for the two types of nanohorns. The spectra are very similar and essentially there is very little difference between the hydrogen loading capacities and binding sites between the two.
- Boron doped nanotubes from both NREL and Penn State: At low hydrogen loadings commensurate with boron content, a split rotational peak (Figure 2) may be evidence of the predicted binding enhancement for hydrogen on a boron substituted carbon as predicted by Kim et al.[1].

Understanding hydrogen dynamics in metal-organic framework materials. A full understanding of the rotation/vibration neutron spectrum of hydrogen in MOF materials has so far been unaddressed in the literature. In principle, these spectra contain the underlying physics of the substrate-hydrogen interactions in these materials and this understanding could lead to an improved system design. We are making progress in understanding these interactions.

- Using an empirical atom-atom Van der Waals potential and a simple model to consider the electric quadrupole moment of H_2 within a perturbation approach, we calculated the splitting of the J=1 rotational state.
- The Coulomb interaction seems to be important to interpret the observed spectrum.

Other Achievements

- Hydrogen locations in a Prussian Blue analogue (in collaboration with J. R. Long, University of Berkeley). The adsorption of molecular hydrogen in the Prussian Blue analogue $Cu_3[Co(CN)_6]_2$ was investigated using high-resolution neutron powder diffraction and neutron vibrational spectroscopy. Hydrogen was absorbed at two sites within the

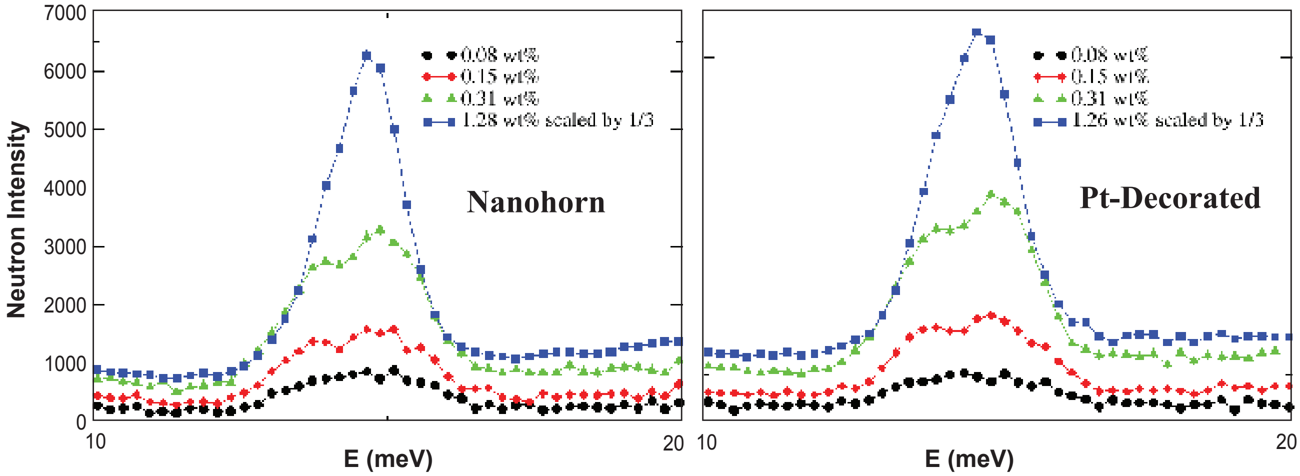

FIGURE 1. Neutron spectroscopy was used to characterize the binding sites of unopened Pt-decorated nanohorns. Left and right panels show the hydrogen rotational peak as a function of hydrogen content for undecorated and Pt-decorated nanohorns, respectively.

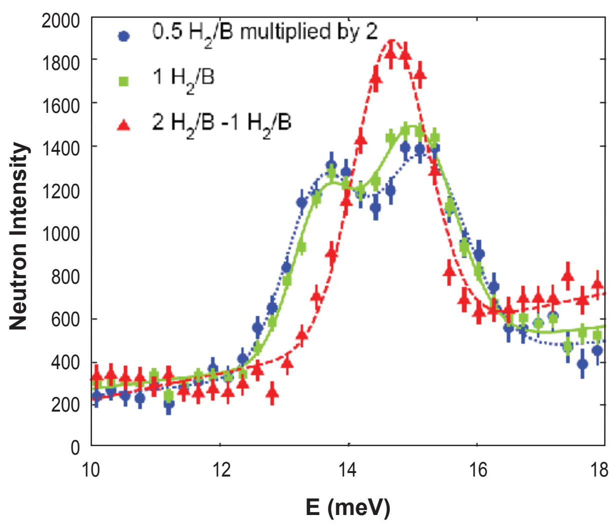

FIGURE 2. Low temperature splitting of the quantum rotational transition of hydrogen at low H_2 loadings. Upon further H_2 loading, there is transition to a single peak that resembles H_2 in as-prepared nanotubes [2].

structure. The most prominent adsorption site, located at the (1/4, 1/4, 1/4) crystallographic site, was an interstitial location within the structure. The second adsorption site was associated with exposed Cu^{2+} ion coordination sites that result from the presence of $[Co(CN)_6]^{3-}$ vacancies within the structure of the material. Neutron vibrational spectroscopy showed a range of local binding potentials for the adsorbed hydrogen.

- Designed and built a suitable gas loading system and sample cell that can apply 100 atmospheres of hydrogen gas at variable temperature for *in situ* neutron measurements.
- Performed multiple high-pressure, variable temperature hydrogen isotherm measurements.

Partner FY 2007 Plans

We have made significant progress in understanding and characterizing the hydrogen-substrate interactions of interest to the CoE. Outstanding work to complete includes confirming the boron substitution effect in nanotubes.

For the upcoming year we will continue high pressure isothermal gas loading, inelastic neutron scattering, neutron powder diffraction, and prompt gamma elemental composition measurements on samples of interest to the CoE and directed by the CoE Steering Committee. Work is in progress with Mike Heben at NREL, Peter Eklund and Mike Chung at Penn State, David Geohegan at ORNL and Ralph Yang at the University of Michigan. These further detailed neutron studies will be performed to evaluate the effects of controlled synthesis on materials such as MOFs and metal-decorated nanotubes with particular emphasis on the possible enhanced hydrogen adsorption capacities reported utilizing the 'spillover' phenomenon.

NIST FY 2006 Publications/Presentations

1. T. Yildirim and M.R. Hartman, "Direct Observation of Hydrogen Adsorption Sites and Nano-cage Formation in Metal-Organic Frameworks (MOF)", Phys. Rev. Lett., 95, 215504 (2005).

2. D.A. Neumann, "Neutron Scattering and Hydrogenous Materials", Materials Today, 9 (1-2), 34 (2006).

3. M. R. Hartman, V. K. Peterson, Y. Liu, S. S. Kaye and J. R. Long, "Neutron Diffraction and Neutron Vibrational

Spectroscopy Studies of Hydrogen Adsorption in the Prussian Blue Analogue $Cu_3[Co(CN)_6]_2$", Chem. Mater. ASAP (Web Release Date: 13-Jun-2006).

4. M.R. Hartman, T. Yildirim, T.J. Udovic, and C.M. Brown, "Hydrogen Adsorption and Dynamics in Metal-Organic Framework (MOF) Materials," presented at the Materials Research Society Fall 2005 Meeting, Boston, MA (2005) (#A9.51).

5. D.G. Narehood, Y. Liu, C.M. Brown, D.A. Neumann, and P.C. Eklund, "Inelastic Neutron Scattering of H_2 Adsorbed on Boron Doped (≤1%) Single Walled Carbon Nanotubes", March meeting of the American Physical Society (2006).

6. D.A. Neumann, "Neutron Metrologies for the hydrogen economy", ACS Fall meeting, Washington, DC, August 2005.

7. D.A. Neumann, "Neutron Metrologies for the Hydrogen Economy", MRS Fall Meeting, Boston, MA, November 2005.

8. Y. Liu, T. Yildirim, "Quantum Dynamics of H_2 in Metal-Organics Frameworks MOF-5", presented at the Materials Research Society Spring 2006 Meeting, San Francisco, CA (2006) (#EE6.9).

9. P. Eklund, D.G. Narehood, U. Kim, X. Liu, Y. Liu, C.M. Brown, D.A. Neumann and H. Gutierrez, "Boron-doped Single-walled Carbon Nanotubes for Enhanced Hydrogen-tube Interaction", 209th Meeting of The Electrochemical Society, Colorado, May, (2006).

10. C.M. Brown et. al, "Hydrogen Rotation in Carbon Materials", American Conference on Neutron Scattering, June 2006.

11. M. R. Hartman, V. K. Peterson and Y. Liu, "An Investigation of the Hydrogen Storage Properties of a Copper Prussian Blue Analogue using Neutron Powder Diffraction and Neutron Vibrational Spectroscopy", presented at the American Conference on Neutron Scattering, 2006, (Poster #WP29).

12. Y. Liu, C. M. Brown, M. R. Hartman, V. K. Peterson, D. A. Neumann, T. Udovic, D. Narehood , P. Eklund, S. S. Kaye, J. R. Long, "Investigating Structural and Dynamical Information of H_2 Inside Materials", Annual Sigma-Xi Postdoctoral Poster Presentation, 2006 (Poster #62).

13. T. Yildirim and M. R. Hartman, "Direct Observation of Adsorption Sites and Hydrogen Nano-Cage Formation in Metal-Organic Frameworks," presented at the Materials Research Society Fall 2005 Meeting, Boston, MA (2005) (Poster #A9.40).

References

1. Y.-H Kim,.Y. Zhao, A. Williamson, M. J. Heben, S. B. Zhang, Phys. Rev. Lett. 2006, 96, 016102.

2. C. M. Brown, T. Yildirim, D. A. Neumann, M. J. Heben, T. Gennett, A. C. Dillon, J. L. Alleman, J. E. Fischer, Chem. Phys. Lett., 329 (3-4), (2000), 311-316.