CARBON NANOTUBES: PROPERTIES AND APPLICATIONS
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Introduction

Carbon nanotubes were discovered in 1991 as a minority byproduct of fullerene synthesis. Remarkable progress has been made in the ensuing years, including the discovery of two basic types of nanotubes (single-wall and multi-wall), great strides in synthesis and purification, elucidation of many fundamental physical properties, and important steps towards practical applications. Both the underlying science and technological potential of SWNT can profitably be studied at the scale of individual tubes and on macroscopic assemblies such as fibers. Experiments on single tubes directly reveal many of the predicted quantum confinement and mechanical properties.

Semiconductor nanowires have many features in common with nanotubes, and many of the same fundamental and practical issues are in play – quantum confinement and its effect on properties; possible device structures and circuit architectures; thermal management; optimal synthesis, defect morphology and control, etc. In 2000 we began a small effort in this direction, conducted entirely by undergraduates with minimal consumables support from this grant. With DOE-BES approval, this grew into a project in parallel with the carbon nanotube work, in which we studied of inorganic semiconductor nanowire growth, characterization and novel strategies for electronic and electromechanical device fabrication.

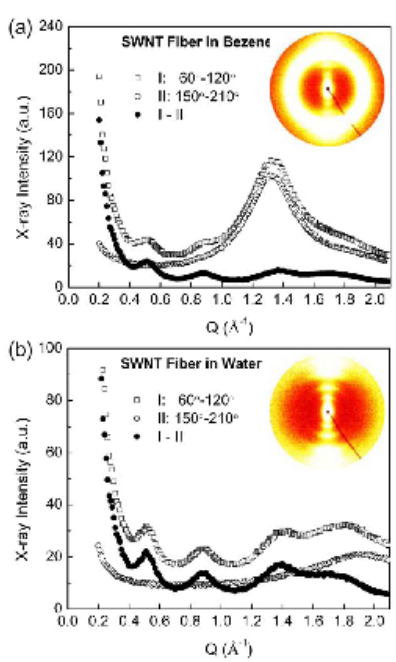
From the beginnings of research on carbon nanotubes, one of the major applications envisioned was hydrogen storage for fuel-cell powered cars and trucks. Subsequent theoretical models gave mixed results, the most pessimistic indicating that the fundamental H_2-SWNT interaction was similar to flat graphite (physisorption) with only modest binding energies implying cryogenic operation at best. New material families with encouraging measured properties have emerged, and materials modeling has gained enormously in predictive power, sophistication, and the ability to treat a realistically representative number of atoms. One of the new materials, highly porous carbide-derived carbons (CDC), is the subject of an add-on to this grant awarded to myself and Taner Yildirim (NIST). Results from the add-on led eventually to a new 3-year award DE-FG02-08ER46522 *"From Fundamental Understanding to Predicting New Nanomaterials for High Capacity Hydrogen Storage"*, $1000K, (05/31/2008 - 05/01/2011) with Taner Yildirim and myself as co-PI's.

Highlights 2004-2008

Single-walled carbon nanotubes suspended in superacids

Liquid anhydrous sulfuric acid forms a partly ordered structure in the presence of single-walled carbon nanotubes (SWNTs). X-ray scattering from aligned fibers immersed in acid shows the formation of molecular shells wrapped around SWNTs. Differential scanning calorimetry of SWNT-acid suspensions exhibits concentration-dependent supercooling/melting behavior, confirming that the partly ordered molecules are a new phase. We propose that charge transfer between nanotube π electrons and highly oxidizing superacid is responsible for the unique partly ordered structure.

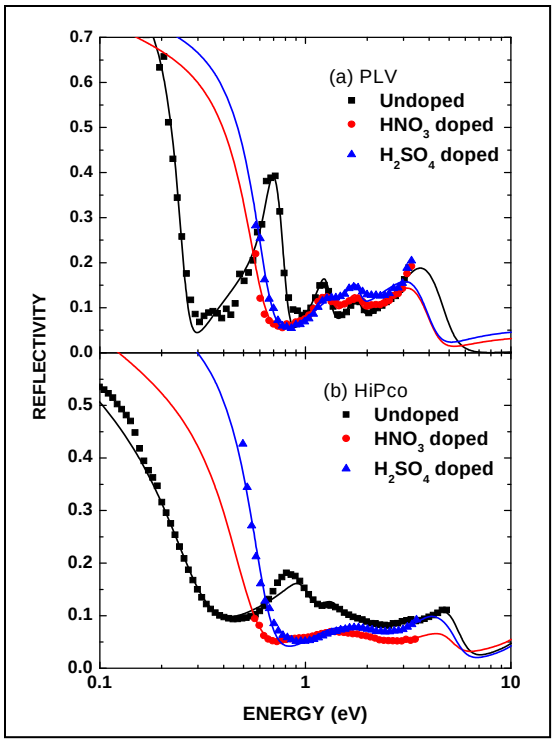
We used X-ray scattering from fibers of well-oriented SWNT to identify partly ordered solvent molecules surrounding a molecular scale solute in a hydrogen-bonded system. Acid molecules intercalate into ropes and form cylindrical shells wrapped around nanotubes and/or ropes. DSC confirms that the partly ordered acid associated with nanotubes is a different phase from bulk acid. Highly oriented solvent molecules have been previously observed in a rodlike polymer/polyphosphoric acid solution, as part of a study focusing on a crystal solvate phase[i]. Partly ordered structures should also exist for SWNT in other superacids (chlorosulfonic acid, triflic acid etc.). All of these can be thought of as super-ionic surfactants from the standpoint of separating and isolating SWNT and ropes. We find no evidence for ordered or aligned molecules once the superacids are exposed to water. Presumably this is due to the high affinity of H_2O for H_2SO_4 and the diminished oxidizing power of the diluted solvent. Partly ordered structures were not observed using ordinary solvents (H_2O, benzene etc.) which have no strong interaction with nanotubes. The mechanism of charge transfer as the driving force for partly ordered acid shells is also supported by the observation of strongly metallic behavior in acid-doped SWNT.



X-ray scattering data from SWNT fibers in benzene (a) or water (b). Insets are 2-D detector false-color images. Azimuthal integrations of the 2-D data 60° wide in χ centered at 90° (I, empty squares) and 180° (II, empty circles) are shown. The difference (I-II, solid circles), which would expose an ordered structure of solvent wrapped around SWNT, shows only Bragg peaks from SWNT ropes. The absence of excess solvent scattering proves the absence of ordered solvent phases associated with SWNT.

Charge transfer and Fermi level shift in p-doped single-walled carbon nanotubes

The electronic properties of p-doped single-walled carbon nanotube (SWNT) bulk samples were studied by temperature-dependent resistivity and thermopower, optical reflectivity and Raman spectroscopy. These all give consistent results for the Fermi level downshift (ΔE_F) induced by doping. We find $\Delta E_F \approx 0.35$ eV and 0.50 eV for concentrated nitric and sulfuric acid doping respectively. With these values, the evolution of Raman spectra can be explained by variations in the resonance condition as E_F moves down into the valence band. Furthermore, we find no evidence for diameter-selective doping, nor any distinction between doping responses of metallic and semiconducting tubes.



Reflectivity and Drude-Lorentz fits for undoped, HNO_3-doped and H_2SO_4-doped PLV (a) and HiPco (b) buckypapers. Two systematic effects are observed: a blueshift of the reflectivity minimum (increasing Drude plasma frequency) and decreased intensity of the peaks at higher energy (quenching interband transitions by shifting E_F).

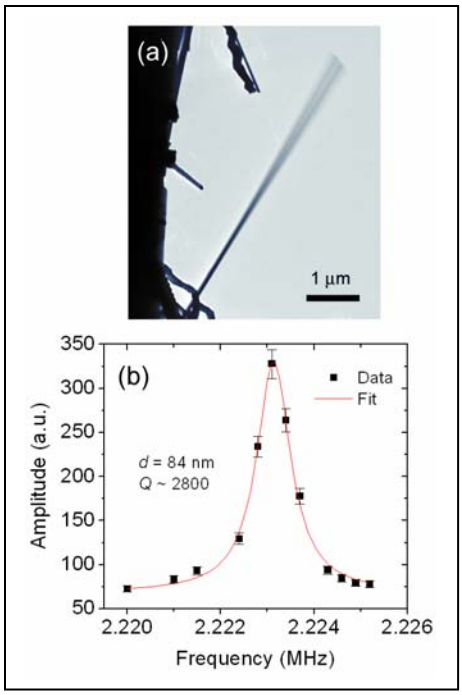
Synthesis and Post-growth Doping of Silicon Nanowires

High quality silicon nanowires (SiNWs) were synthesized via a thermal evaporation method without the use of catalysts. Scanning electron microscopy and transmission electron microscopy showed that SiNWs were long and straight crystalline silicon with an oxide sheath. Field effect transistors (FETs) were fabricated to investigate the electrical transport properties. Devices on as-grown material were p-channel with channel mobilities 1 - 10 $cm^2\ V^{-1}\ s^{-1}$. Post-growth vapor doping with bismuth converted these to n-channel behavior.

Diameter-dependent Electromechanical Properties of GaN Nanowires

Diameter-dependent Young's modulus *E* and quality factor *Q* of GaN nanowires were measured using electromechanical resonance analysis in a transmission electron

microscope. For a large diameter nanowire (d = 84 nm), E is close to the theoretical bulk value ~300 GPa but is significantly smaller for smaller diameters. At room temperature, Q is as high as 2800 for d = 84 nm and also appears to decrease with decreasing diameter. For all diameters, Q is significantly greater than is obtained from micromachined Si resonators of comparable surface-to-volume ratio, implying significant advantages of smooth-surfaced GaN nanowire resonators for nanoelectromechanical system (NEMS) applications. Two closely-spaced resonances are observed and attributed to the low symmetry triangular cross-section of the nanowires.



(a) Low magnification TEM image of a d = 84 nm diameter GaN nanowire in the fundamental resonance, 2.223 MHz. (b) Amplitude vs. frequency from CCD images, fit to a Lorentzian; the quality factor Q is 2800.

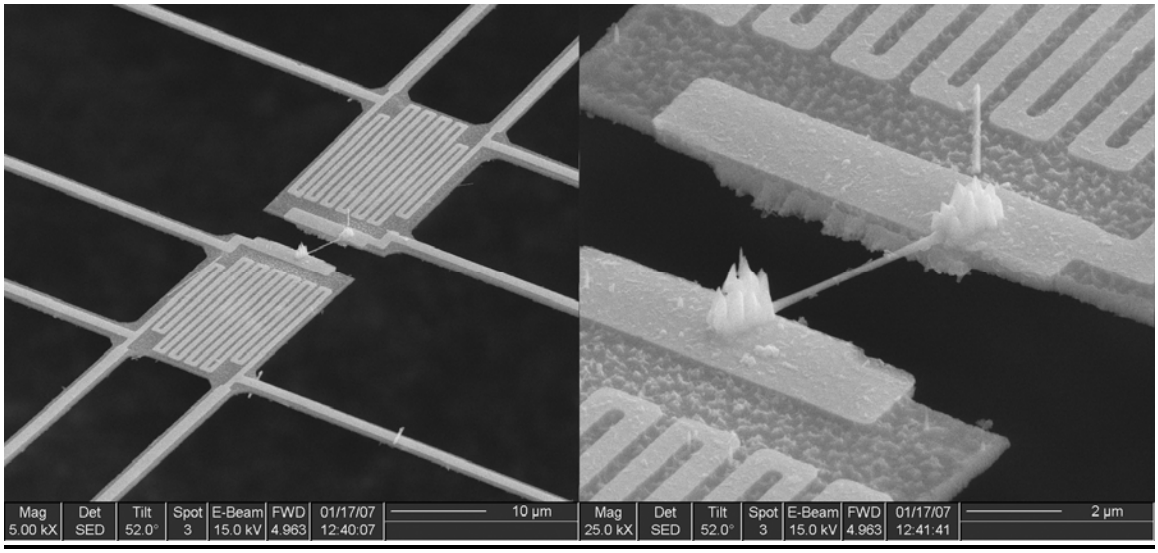
Disorder Effects in Focused Ion Beam Deposited Pt Contacts to GaN Nanowires

The current-bias (I-V) characteristics at various temperatures T of focused ion beam (FIB)-deposited Pt contacts on GaN nanowires evolves from low-resistance ohmic (linear I-V) to rectifying as the diameter increases, and both exhibit strongly non-metallic T dependence. The small-diameter (66 nm) T-dependent resistance is explained by 2-dimensional variable range hopping with a small characteristic energy, ensuring low resistance at 300 K. For large diameters (184 nm), back-to-back Schottky barriers explain the nonlinear I-V at all T, and permit an estimate of doping concentration from the bias-dependent barrier height. Both behaviors can be understood by accounting for the role of FIB-induced amorphization of GaN underneath the contact, as confirmed by cross-sectional transmission electron microscopy.

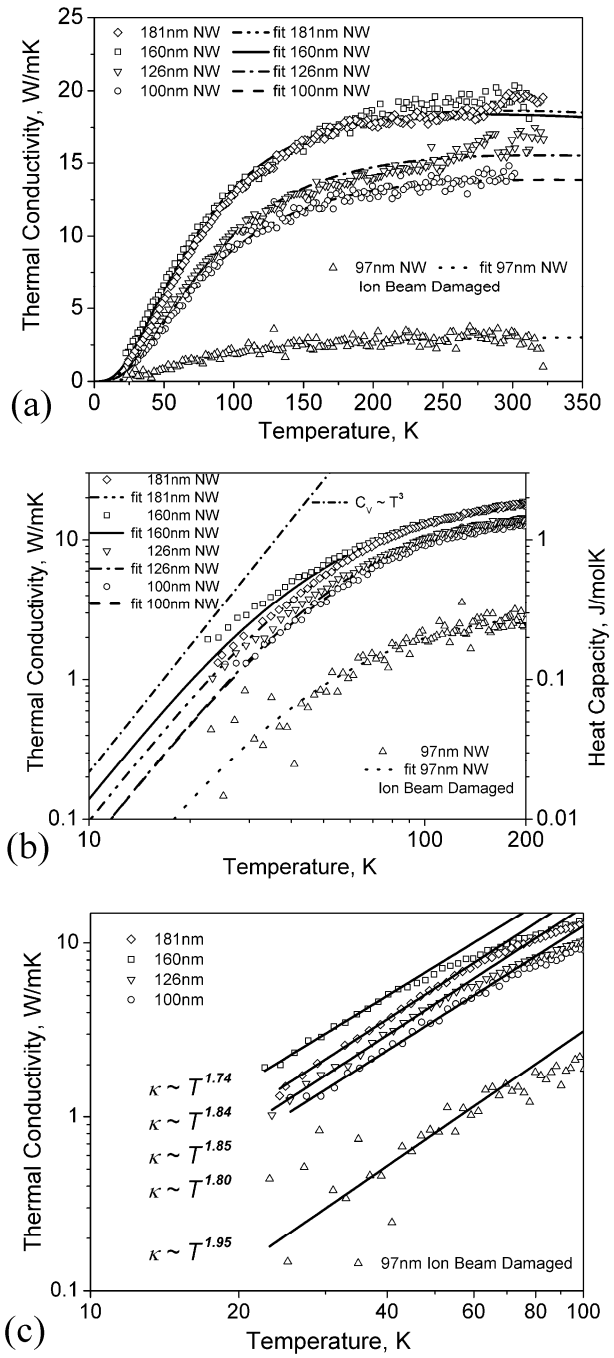
Unusually Low Thermal Conductivity of Gallium Nitride Nanowires

We report measurements of thermal conductivity κ on individual gallium nitride nanowires (GaN NWs) with diameters ranging from 97 to 181 nm grown by thermal chemical vapor deposition (CVD). We observed unexpectedly small kappa values, in the

range 13-19 W/m-K at 300K, with very weak diameter dependence. We also observe unusual power law $\kappa \sim T^n$ behavior with n = 1.8 at low temperature. EELS measurements indicate Si and O concentrations in the range 0.1-1 at% and 0.01-0.1 at%, respectively. Based on extensive numerical calculations, we conclude that both the unexpectedly low κ and the $T^{1.8}$ dependence are caused by unusually large mass-difference scattering, primarily from Si impurities. Our analysis also suggests that mass-difference scattering rates are significantly enhanced by the reduced phonon group velocity in nanoscale systems. Planar defects running the length of the NW, previously characterized in detail, may also play a role in limiting the phonon mean free path.



SEM images of the suspended device showing the islands (15µm x 25µm), suspending beams (500nm x 3 µm x 250 µm), serpentine GRTs (30 nm thick) with connecting leads and GaN NW bridging the islands. A DC current I is applied to the heating GRTs. The generated Joule heat in the GRT and the two Au leads supplying the current raises the temperature of the heating island to T_h. The sample bridging the two islands conducts an amount of heat Q_2 from the heating island to the sensing one raising the temperature of the latter to T_s. Q_2 is further conducted to the environment at T_0 through the five beams suspending the sensing island. These five beams serve as a measure of the heat current Q_2 through the sample.

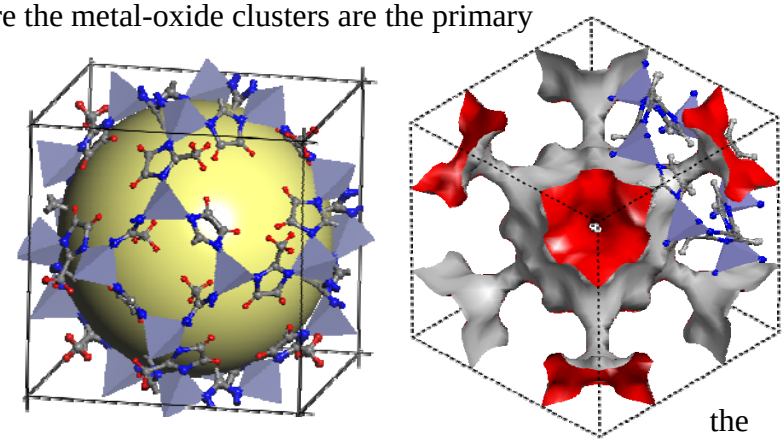


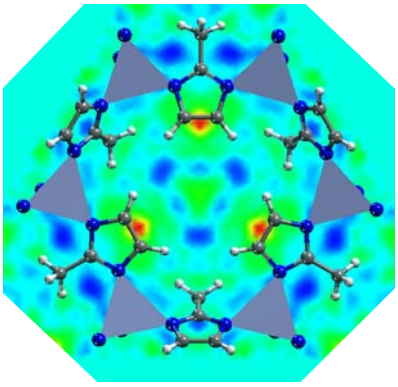
(a) Temperature dependence of the experimental κ·of GaN NWs in the range of 24-320 K and the best fits using the Callaway approach. All samples with apparent triangular cross-section (160 nm, 100 nm, 126 nm and 181 nm) have very similar room T κ values in the range of 13-19 W/m-K. The much lower κ of 97nm sample is due to FIB damage. (c) All samples exhibit an unusual $T^{1.8}$ low temperature κ dependence (note the log-log scale).

Hydrogen Storage in a Prototypical Zeolitic Imidazolate Framework-8

Using the difference-Fourier analysis of neutron powder diffraction data along with first-principles calculations, we reveal detailed structural information such as methyl group orientation, hydrogen absorption sites and binding energies within the nanopore structure of ZIF8 ($Zn(MeIM)_2$). Surprisingly, the two strongest adsorption sites that we identified are both directly associated with the organic linkers, instead of the ZnN_4 clusters, in strong contrast to MOFs, where the metal-oxide clusters are the primary adsorption sites.

These observations are important and hold the key to optimizing this new class of ZIF materials for practical hydrogen storage applications. Finally, at high concentration H_2-loadings, ZIF8 structure is capable of holding up to 28 H_2 molecules (i.e. 4.2 wt%) in the form of highly symmetric novel three-dimensional interlinked H_2-nanoclusters with relatively short H_2-H_2 distances compared to solid H_2. Hence, ZIF compounds with robust chemical stability can be also an ideal template host-material to generate molecular nanostructures with novel properties.

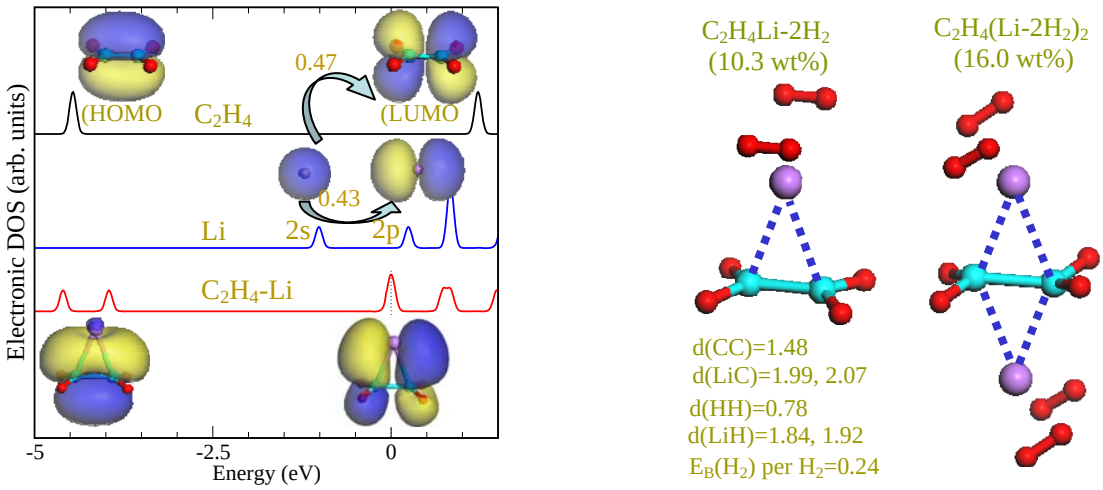




(a) Crystal structure of ZIF8, (b) Calculated available free volume in ZIF8, (c) Neutron Fourier difference data, showing the major H_2-binding sites in ZIF8 structure.

Hydrogen absorption properties of metal-ethylene complexes

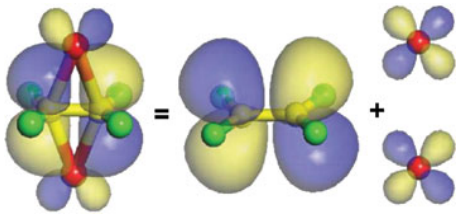
Summary: From first-principle calculations, we recently predicted [Phys. Rev. Lett. **97**, 226102 (2006); see below] that a single ethylene molecule can form stable complexes with light transition metals (TM) such as Ti and the resulting TM_n-ethylene complex can absorb up to ~12 and 14 wt % hydrogen for n=1 and 2, respectively. Thereafter, we extended the study to include a large number of other metals and different isomeric structures. We obtained interesting results for light metals such as Li. The ethylene molecule is able to complex with two Li atoms with a binding energy of 0.7 eV/Li which then binds up to two H_2 molecules per Li with a binding energy of 0.24 eV/H_2 and absorption capacity of 16 wt%, a record high value reported so far (See the figure). The stability of the proposed metal-ethylene complexes was tested by extensive calculations such as normal-mode analysis, finite temperature first-principles molecular dynamics simulations, and reaction path calculations. They are found to be stable up to 500 K. These results suggest that co-deposition of ethylene with a suitable precursor of TM or Li into nanopores of light-weight host materials may be a very promising route to discovering new materials with high-capacity hydrogen absorption properties.



LEFT: Electronic density of states of C_2H_4, Li atom, and C_2H_4+Li complex, along with the isosurfaces of relevant molecular orbitals. The binding of Li on the ethylene molecule is due to the hybridization of the Li-2p state and the LUMO of C_2H_4. RIGHT: Hydrogen absorption configurations on C_2H_4Li and $C_2H_4Li_2$ complexes. In both cases, each Li can bind two H_2, resulting in high absorption capacities. Large, medium and small balls represent Li, C and H atoms, respectively.

Transition-Metal-Ethylene Complexes as High-Capacity Hydrogen-Storage Media
(This work was chosen as cover page paper for PRL)

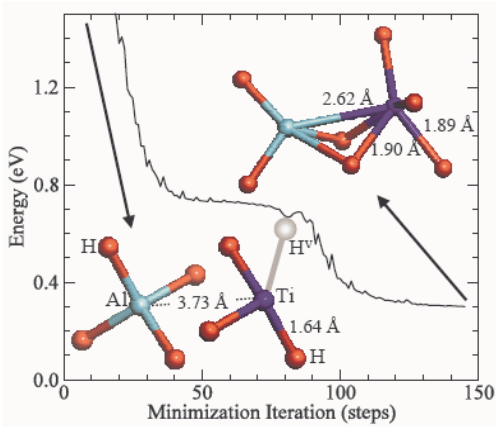
From first-principles calculations, we predict that a single ethylene molecule can form a stable complex with two transition metals (TM) such as Ti. The resulting TM-ethylene complex then absorbs up to ten hydrogen molecules, reaching to gravimetric storage capacity of 14-wt%. Dimerization, polymerizations, and incorporation of the TM-ethylene complexes in nanoporous carbon materials are also discussed. Our results are quite remarkable and open a new approach to high-capacity hydrogen-storage materials discovery.



Moleculer orbial of Ti_2-C_2H_4 complex, which is a superposition of -C_2H_4 -LUMO and Ti-d orbitals, suggesting Dewar coordination for Ti--C_2H_4 interaction.

Hydrogen-related catalytic effects of Ti and other light transition metals on NaAlH4 surfaces

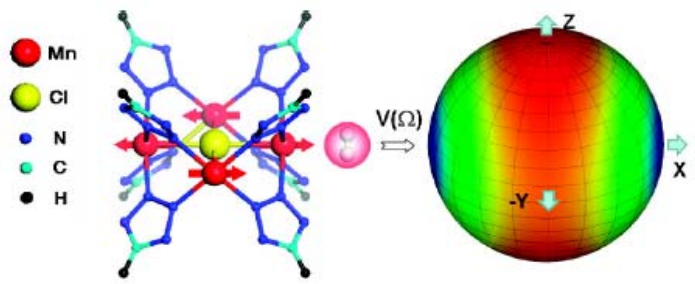
We report a first-principles study of the energetics of hydrogen absorption and desorption (i.e. H-vacancy formation) on pure and Ti-doped sodium alanate ($NaAlH_4$) surfaces. We find that the Ti atom facilitates the dissociation of H_2 molecules as well as the adsorption of H atoms. In addition, the dopant makes it energetically more favorable to creat H vacancies by saturating Al dangling bonds. Interestingly, our results show that the Ti dopant brings close in energy all the steps presumably involved in the absorption and desorption of hydrogen, thus facilitating both and enhancing the reaction kinetics of the alanates. We also discuss the possibility of using other light transition metals (Sc, V, and Cr) as dopants.



Nature and Tunability of Enhanced Hydrogen Binding in Metal-Organic Frameworks with Exposed Transition Metal Sites

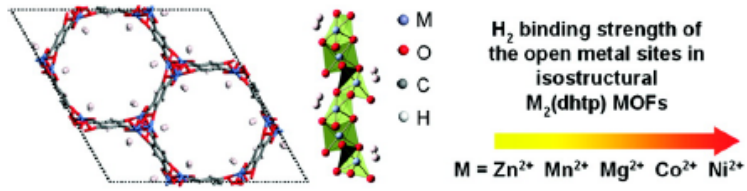
Metal-organic framework (MOF) compounds with exposed transition-metal (TM) sites were recently found to exhibit significantly larger experimental heats of adsorption of H2 than classical MOFs, thus attracting greater attention.

Here we show that the hydrogen binding in Mn4Cl-MOF is not of the expected Kubas type because there is (a) no significant charge transfer from TM to H2, (b) no evidence of any H2-σ* Mn-*d* orbital hybridization, (c) no significant H-H bond elongation, and (d) no significant shift in H-H stretching mode frequency. We make predictions for the magnetic superexchange interactions in Mn4Cl-MOF and determined low- and high-spin states of the Mn ion as local minima with very different hydrogen binding energies. We show that, by replacing Cl with F or Br, one can tune the H2 binding energy. We further reveal that the major contribution to the overall binding comes from the classical Coulomb interaction which is not screened due to the open-metal site and explains the relatively high binding energies and short H2-TM distances observed in MOFs with exposed metal sites compared to traditional ones. Finally, we show that the orientation of H2 has a surprisingly large effect on the binding potential, reducing the classical binding energy by almost 30%.



Contour plot of the orientation dependence of the binding energy of H2 on Mn4Cl-MOF cluster in (θ,ϕ) space. The red and blue regions represent strong and weak binding energy, respectively.

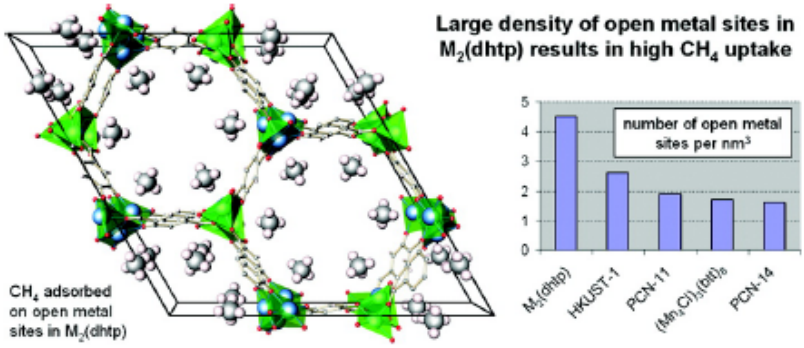
Enhanced H2 Adsorption in Isostructural Metal-Organic Frameworks with Open Metal Sites: Strong Dependence of the Binding Strength on Metal Ions



The c-axis view of the unit cell of MOF-74, showing the one-dimensional pore geometry.

MOFs with open metal sites exhibit much stronger H_2 binding strength than classical MOFs. Yet, how the binding strength varies with different open metal species was previously unknown. We conducted a systematic study of the H_2 adsorption on a series of isostructural MOFs, M_2(dhtp) (M=Mg, Mn, Co, Ni, Zn). The experimental Q_{st} for H_2 of these MOFs range from 8.5 to 12.9 KJ/mol, with increasing Q_{st} in the following order: Zn, Mn, Mg, Co, and Ni. The H_2 binding energies derived from DFT calculations follow the same trend. We also found a strong correlation between the metal ion radius, the M-H_2 distance and the H_2 binding strength, which provides a viable, empirical method to predict the relative H_2 binding strength of different open metals.

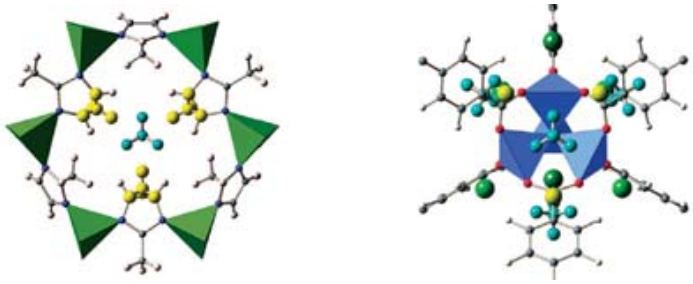
High-Capacity Methane Storage in Metal-Organic Frameworks M2(dhtp): The Important Role of Open Metal Sites



Methane absorbed in MOF-74 as obtained from neutron diffraction.

We found that metal-organic framework (MOF) compounds M_2(dhtp) (open metal M=Mg, Mn,Co, Ni, Zn) possess exceptionally large densities of open metal sites.
By adsorbing one CH4 molecule per open metal, these sites alone can generate very large methane storage capacities, 160-174 cm^3(STP)/cm3, approaching the DOE target of 180 cm3(STP)/cm3 for material-based methane storage at room temperature. Our adsorption isotherm measurements at 298 K and 35 bar for the five M2(dhtp) compounds yield excess methane adsorption capacities ranging from 149 to 190 cm3(STP)/cm3 (derived using their crystal densities), indeed roughly equal to the predicted, maximal adsorption capacities of the open metals (within (10%) in these MOFs. Among the five isostructural MOFs studied, Ni2(dhtp) exhibits the highest methane storage capacity, □200 cm3(STP)/cm3 in terms of absolute adsorption, potentially surpassing the DOE target by □10%. Our neutron diffraction experiments clearly reveal that the primary CH4 adsorption occurs directly on the open metal sites. Initial first-principles calculations show that the binding energies of CH4 on the open metal sites are significantly higher than those on typical adsorption sites in classical MOFs, consistent with the measured large heats of methane adsorption for these materials. We attribute the enhancement of the binding strength to the unscreened electrostatic interaction between CH4 and the coordinatively unsaturated metal ions.

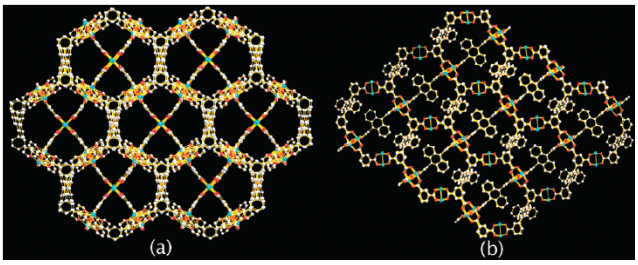
Methane Sorption in Nanoporous Metal-Organic Frameworks and First-Order Phase Transition of Confined Methane



Methane adsorption sites in ZIF-8 and MOF-5 as revealed by neutron diffraction.

Using neutron powder diffraction, we have directly determined the methane sorption sites in two prototypical MOF materials: ZIF-8 and MOF-5. The primary methane adsorption sites are associated with the organic linkers in ZIF-8 and the metal oxide clusters in MOF-5. Methane molecules on these primary sites possess well-defined orientations, implying relatively strong binding with the framework. With higher methane loading, extra methane molecules populate the secondary sites and are confined in the framework. The confined methanes are orientationally disordered and stabilized by the intermolecular interactions. An unusual reversible methane-induced structural phase transition in MOF host lattice is observed at ~60 K in both ZIF-8 and MOF-5 due to strong intermolecular interaction between confined methane molecules in the pores of the host lattice.

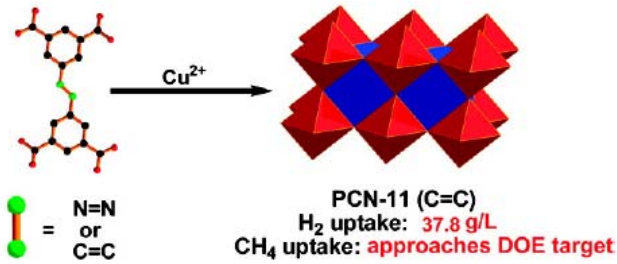
Metal-Organic Framework from an Anthracene Derivative Containing Nanoscopic Cages Exhibiting High MethaneUptake



Different views of PCN-14, which exhibits record high methane absorption at room temperature.

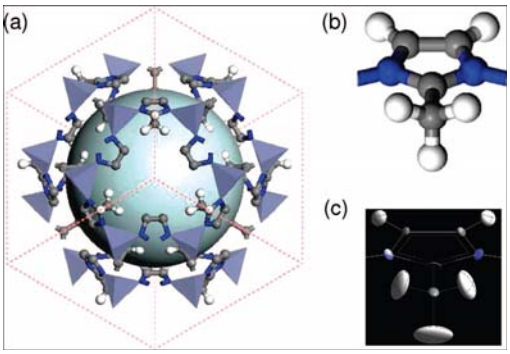
A microporous metal-organic framework, PCN-14, based on an anthracene derivative, 5,5-(9,10-anthracenediyl)di-isophthalate (H4adip), was synthesized under solvothermal reaction conditions. X-ray single crystal analysis revealed that PCN-14 consists of nanoscopic cages suitable for gas storage.
N2-adsorption studies of PCN-14 at 77 K reveal a Langmuir surface area of 2176 m2/g and a pore volume of 0.87 cm3/g. Methane adsorption studies at 290 K and 35 bar show that PCN-14 exhibits an absolute methane-adsorption capacity of 230 v/v, 28% higher than the DOE target (180 v/v) for methane storage.

Metal-Organic Frameworks Based on Double-Bond-Coupled Di-Isophthalate Linkers with High Hydrogen and Methane Uptakes



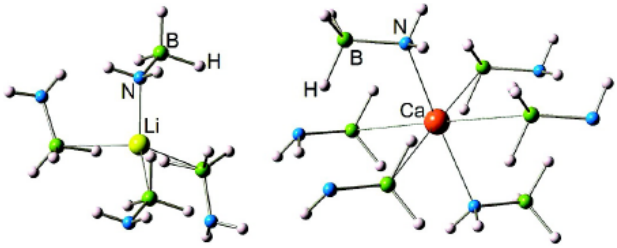
Utilization of double-bond-coupled di-isophthalate ligands,
H4aobtc and H4sbtc, in reactions with Cu(NO3)2 yielded two isostructural microporous MOFs, PCN-10 and PCN-11, respectively. Upon guest removal, both MOFs contain two types of pores, open metal sites, and retain enduring porosity.
In particular, both contain nanoscopic cages that are particularly suitable for gas storage. At 760 Torr, 77 K, the excess hydrogen uptake of PCN-10 is 2.34 wt % (18.0 g/L) and that of PCN-11 is as high as 2.55 wt % (19.1 g/L). Gasadsorption experiments suggest that MOFs containing CdC double bonds are more favorable than those with NdN double bond in retaining enduring porosity after thermal activation, although the NdN double bond has slightly higher H2 affinity. When the pressure is increased, the excess adsorption at 77 K saturates around 20 atm and reaches values of 4.33% (33.2 g/L) and 5.05% (37.8 g/L) for PCN-10 and PCN-11, respectively. In addition, PCN-11 exhibits an excess methane uptake of 171 cm3(STP)/cm3 at 298 K and 35 bar, approaching the DOE target of 180 v(STP)/v for methane storage at ambient temperatures. Thus, PCN- 11 represents one of the few materials that are applicable to both hydrogen and methane storage applications.

Quasi-Free Methyl Rotation in Zeolitic Imidazolate Framework-8



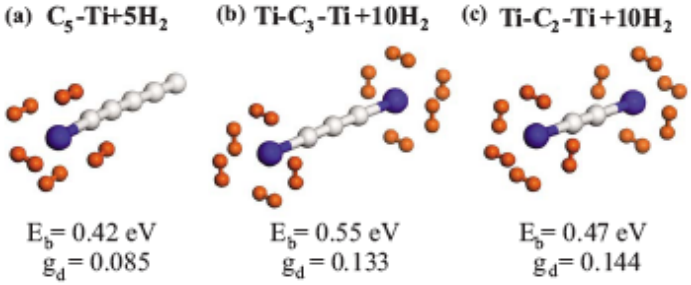
The reorientational motion of the methyl group is an intriguing physics phenomenon. It can be well described by classical random jumps at high temperature, whereas at low temperature it is dominated by quantum-mechanical rotational tunneling. Using neutron inelastic scattering and diffraction, we have studied the quantum methyl rotation in ZIF-8. The rotational potential for the CH_3 groups in ZIF-8 is shown to be primarily 3-fold in character. The ground-state tunneling transitions at 1.4 K of 334 ± 1 μeV for CH_3 groups in hydrogenated ZIF-8 and 33 ± 1 ueV for CD_3 groups in deuterated ZIF-8 indicate that the barrier to internal rotation is small compared to almost all methylated compounds in the solid state and that methyl-methyl coupling is negligible.

Alkali and Alkaline-Earth Metal Amidoboranes: Structure, Crystal Chemistry, and Hydrogen Storage Properties



Alkali- and alkaline-earth metal amidoboranes, a new class of compounds with rarely observed $[NH_2BH_3]^-$ units, have been recently reported to significantly improve the dehydrogenation properties of ammonia borane. We successfully prepared solvent-free lithium amidoborane $LiNH_2BH_3$ and calcium amidoborane $Ca(NH_2BH_3)_2$, and for the first time determined their structures, using a combined x-ray diffraction and first-principles molecular dynamics simulated annealing method. Through detailed structural analysis and first-principles electronic structure calculations, the improved dehydrogenation properties are attributed to the different bonding nature and reactivity of the metal amidoboranes compared to NH_3BH_3.

Functionalization of carbon-based nanostructures with light transition-metal atoms for hydrogen storage



The present paper extends this study further to investigate the hydrogen uptake by light transition-metal atoms decorating various carbon-based nanostructures in different types of geometry and dimensionality, such as carbon linear chain, graphene, and nanotubes. Using first-principles plane-wave method we show that not only outer but also inner surface of a large carbon nanotube can be utilized to bind more transition-metal atoms and hence to increase the storage capacity. We also found that scandium and vanadium atoms adsorbed on a carbon nanotube can bind up to five hydrogen molecules. Similarly, light transition-metal atoms can be adsorbed on both sides of graphene and each adsorbate can hold up to four hydrogen molecules yielding again a high-storage capacity. Interestingly, our results suggest that graphene can be considered as a potential high-capacity H2 storage medium. We also performed transition state analysis on the possible dimerization of Ti atoms adsorbed on the graphene and single-wall carbon nanotube.

Thesis students 2004-2008

1. Marc Llaguno, PhD Physics (2004), "Thermal Transport in Single Wall Carbon Nanotubes"
2. Juraj Vavro, PhD MSE (2004), "Transport Properties of Single Wall Carbon Nanotubes".
3. Wei Zhou, PhD MSE (2005), "Structural Characterization of Macroscopic Single-walled Carbon Nanotube Materials"
4. Kumhyo Byon, PhD MSE (2006), "The Synthesis and Properties of Silicon Nanowire Devices".
5. Csaba Guthy, PhD MSE (2007), "Thermal Transport in Individual GaN Nanowires"
6. Chang-Yong Nam, PhD MSE (2007), "Gallium Nitride Nanowires: Synthesis, Resonant Electromechanical Properties, Ion Beam Disorder effects on Contact Conduction, and Heterojunction Fabrication".
7. Michelle Chen, PhD MSE (2007), "Functionalized Carbon Nanotube Field Effect Transistor for Chemical and Biological Sensing".
8. Jinyong Kim, PhD MSE (2009), "Electrical properties and chemical sensing application of Ga_2O_3 and GaN nanowires"
9. Douglas Weng Wah Tham, MS MSE (2007), "Defects, Structure and Properties of GaN Nanowires and FIB-Pt/GaN Nanowire Contacts: A Transmission Electron Microscopy Study"

Publications 2004-2008 (DOE-supported students underlined)

1. "Small angle neutron scattering from single wall carbon nanotube suspensions: evidence of isolated rigid rods and rod networks", W. Zhou, M. F. Islam, H. Wang, D. Ho, A. G. Yodh, K. I. Winey and J. E. Fischer, *Chem. Phys. Letters* **384,** 185 (2004).
2. "Observation of thermopower oscillations in the coulomb blockade regime in a semiconducting carbon nanotube", M.C. Llaguno, J.E. Fischer, A.T. Johnson, Jr., *Nano Letters* **4**, 45 (2004).
3. "Single wall carbon nanotube fibers extruded from super-acid suspensions: Preferred orientation, electrical and thermal transport", W. Zhou, J. Vavro, C. Guthy, K. I. Winey, J. E. Fischer, L. M. Ericson, S. Ramesh, R. Saini, V. A. Davis, C. Kittrell, M. Pasquali, R. H. Hauge and R. E. Smalley, *J. Appl. Physics* **95,** 649 (2004).
4. "Out-of-plane preferred orientation of single wall carbon nanotube films", W. Zhou, K. I. Winey, J. E. Fischer, S. Kumar and H. Kataura, *Appl. Phys. Letters* **84,** 2172 (2004).
5. "Effect of the polar surface on GaN nanostructure growth and morphology", C. Y. Nam, D. Tham and J. E. Fischer, *Applied Physics Letters* **85,** 5676 (2004).

6. "Dispersing single-wall carbon nanotubes with surfactants: A neutron scattering study", H. Wang, W. Zhou, D. L. Ho, K. I. Winey, J. E. Fischer, C. J. Glinka and E. K. Hobbie, *Nano Letters* **4,** 1789 (2004).
7. "Macroscopic neat single-walled carbon nanotube fibers", L. M. Ericson, H. Fan, H. Peng, V. A. Davis, J. Sulpizio, Y. Wang, R. Booker, W. Zhou, J. Vavro, C. Guthy, S. Ramesh, C. Kittrell, G. Lavin, H. Schmidt, W. W. Adams, M. Pasquali, W.-F. Hwang, R. H. Hauge, J. E. Fischer and R. E. Smalley, *Science* **305,** 1447 (2004).
8. "Nanotube networks in polymer nanocomposites: rheology and electrical conductivity", F. Du, R. C. Scogna, W. Zhou, S. Brand, J. E. Fischer and K. I. Winey, *Macromolecules* **37,** 9048 (2004).
9. "Correlation of properties with preferred orientation in extruded and stretch-aligned single wall carbon nanotubes", Stéphane Badaire, Cécile Zakri, Philippe Poulin, Vincent Pichot, Pascale Launois, Juraj Vavro, Michelle Chen and John Fischer, *J. Applied Physics* **96,** 7509 (2004).
10. "Single-walled carbon nanotube-templated crystallization of H_2SO_4: direct evidence for protonation", W. Zhou, P. A. Heiney, H. Fan, R. E. Smalley and J. E. Fischer, *J. Am. Chem. Soc. J. Am. Chem. Soc.* **127,** 1640 (2005).
11. "Metal-insulator transition in doped single-wall carbon nanotubes", J. Vavro, J. M. Kikkawa and J. E. Fischer, *Phys. Rev.* B **71,** 155410 (2005).
12. "Focused ion beam platinum deposition for GaN nanowires: patterned growth and ohmic contacts", C. Y. Nam, J. Y. Kim, D. Tham and J. E. Fischer, *Applied Physics Letters* **86,** 193112 (2005).
13. "Charge transfer and Fermi level shift in p-doped single-walled carbon nanotubes", W. Zhou, J. Vavro, N. M. Nemes, J. E. Fischer, F. Borondics and K. Kamaràs, *Phys. Rev. B* **71**, 205423 (2005).
14. "Single-walled carbon nanotubes in superacid: x-ray and calorimetric evidence for partly ordered H_2SO_4", W. Zhou, J. E. Fischer, P. A. Heiney, H. Fan, V. A. Davis, M. Pasquali and R. E. Smalley, *Phys. Rev. B* **72,** 045440 (2005).
15. "Disorder effects in focused ion beam deposited Pt contacts to GaN nanowires", C. Y. Nam, D. Tham and J. E. Fischer, *Nano Letters* **5**, 2029 (2005).
16. "Synthesis and post-growth doping of silicon nanowires", K. Byon, D. Tham, A. T. Johnson and J. E. Fischer, *Appl. Phys. Letters* **87,** 193104 (2005).
17. "Lattice dynamics of metal-organic frameworks: Neutron inelastic scattering and first-principles calculations", W. Zhou and T. Yildirim, *Phys. Rev.* **B74**, 180301 (2006)
18. "Microstructure and composition of focused ion beam-deposited Pt contacts to GaN nanowires", D. Tham, C. Y. Nam and J. E. Fischer, *Advanced Materials* **18,** 290-294 (2006).
19. "Diameter-dependent electromechanical properties of GaN nanowires", C. Y. Nam, P. Jaroenapibal, D. Tham, D. E Luzzi, S. Evoy and J. E. Fischer, *Nano Letters* **6,** 153 -158 (2006).
20. "Defects in GaN nanowires", D. Tham, C. Y. Nam and J. E. Fischer, *Advanced Functional Materials* **16,** 1197 (2006).
21. "An infiltration method for preparing single wall nanotube/epoxy composite with improved thermal conductivity", F. Du, C. Guthy, T. Kashiwagi, J. E. Fischer and K. I. Winey, *J. Poly. Sci. B: Poly. Phys.* **44**, 1513-1519 (2006).

22. "Transition-Metal-Ethylene Complexes as High-Capacity Hydrogen-Storage Media", E. Durgun, S. Ciraci, W. Zhou, and T. Yildirim, Phys. Rev. Lett. 97, 226102 (2006).
23. "Applications of electron microscopy to the characterization of semiconductor nanowires", Douglas Tham, Chang-Yong Nam, Kumhyo Byon, Jinyong Kim and John E. Fischer, *Appl. Phys. A* **85,** 227 (2006).
24. "Li4Si2H(D) and Li4Ge2H(D): Electronic structure and lattice dynamics", H. Wu, W. Zhou, T. J. Udovic, J. J. Rush, T. Yildirim, M. R. Hartman, R. C. Bowman, and J. J. Vajo, *Phys. Rev*. B **76,** 224301 (2007).
25. "Hydrogen and Methane Adsorption in Metal-Organic Frameworks: a High-Pressure Volumetric Study", Wei Zhou, Hui Wu, M. R. Hartman, Taner Yildirim, *J. Chem. Phys.* C, **111**, 16131 (2007).
26. "Hydrogen absorption properties of metal-ethylene complexes", W. Zhou, T. Yildirim, E. Durgun, S. Ciraci, *Phy. Rev. B* **76,** 085434 (2007).
27. "Improved performance of silicon nanowire transistors: A systematic study of contact annealing", K. Byon, A. T. Johnson and J. E. Fischer, *Appl. Phys. Letters* **90**, 143513 (2007).
28. "Single wall carbon nanotube / polyethylene nanocomposites: Thermal and electrical conductivity", Reto Haggenmueller, Csaba Guthy, Jennifer R. Lukes, John E. Fischer and Karen I. Winey, *Macromolecule*s **40**, 2417-2421 (2007).
29. "Thermal conductivity of single-walled carbon nanotube/PMMA nanocomposites", Csaba Guthy, Fangming Du, Stijn Brand, Karen I. Winey and John E. Fischer, *J. Heat Transfer*. **129**, 1096 (2007).
30. "Thermal transport in MWNT ribbons and yarns", Ali E. Aliev, Csaba Guthy, Mei Zhang, Shaoli Fang, Anvar A. Zakhidov, John E. Fischer and Ray H. Baughman, *Carbon* **5**, 2880 (2007).
31. "Unusually low thermal conductivity of gallium nitride nanowires", Csaba Guthy, Chang-Yong Nam and John E. Fischer, *J. Applied Physics* **103,** 064319 (2008).
32. "Enhanced H2 Adsorption in Isostructural Metal-Organic-Frameworks with Open Metal Sites: Strong Dependence of the Binding Strength on Metal Ions", W. Zhou, H. Wu, and T. Yildirim, *J. Am. Chem. Soc*. **130**, 15268 (2008).
33. "Alkali and Alkaline-Earth Metal Amidoboranes: Structure, Crystal Chemistry, and Hydrogen Storage Properties", H. Wu, W. Zhou, and T. Yildirim, *J. Am. Chem. Soc*. 130, 14834 (2008).
34. "Origin of the exceptional negative thermal expansion in metal-organic frameworks-5 Zn4O(1,4-benzenedicarboxylate)(3), W. Zhou, H. Wu, T. Yildirim, *Phys. Rev. **B*** **78,** 054114 (2008).
35. "Quasi-Free Methyl Rotation in Zeolitic Imidazolate Framework-8", W. Zhou, H. Wu, T. J. Udovic, J. J. Rush, and T. Yildirim, *J. Phys. Chem*. **A 112,** 12602 (2008).
36. "Nature and tunability of enhanced hydrogen binding in metal-organic frameworks with exposed transition metal sites", W. Zhou and T. Yildirim, *J. Phys. Chem.* C **112**, 8132 (2008).
37. "Metal-organic frameworks based on double-bond-coupled di-isophthalate linkers with high hydrogen and methane uptakes", X. S. Wang, S. Q. Ma, K. Rauch, J. M.

Simmons, D. Q. Yuan, X. P. Wang, T. Yildirim, W. C. Cole, J. J. Lopez, A. de Meijere, H. C. Zhou, *Chem. Mater.* **20,** 3145 (2008).

38. "Metal-Organic Framework from an Anthracene Derivative Containing Nanoscopic Cages Exhibiting High MethaneUptake", Shengqian Ma, Daofeng Sun, Jason M. Simmons, Christopher D. Collier, Daqiang Yuan, and Hong-Cai Zhou, *J. Am. Chem. Soc.* **130,** 1012 (2008).
39. "Structures and Crystal Chemistry of Li2BNH6 and Li4BN3H10", Hui Wu, Wei Zhou, Terrence J. Udovic, John J. Rush, and Taner Yildirim, *Chem. Mater*. **20**, 1245 (2008).
40. "Crystal Chemistry of Perovskite-Type Hydride NaMgH3: Implications for Hydrogen Storage", Hui Wu, Wei Zhou, T. J. Udovic, J. J.Rush, and Taner Yildirim, *Chem. Mater*. **20**, 2335 (2008).
41. "Functionalization of carbon-based nanostructures with light transition-metal atoms for hydrogen storage", E. Durgun, S. Ciraci, and T. Yildirim, *Phys. Rev*. **B 77**, 085405 (2008).

Invited lectures 2004-2008

1. "Transport properties in carbon nanotube materials", J. E. Fischer, seminar at Centre de Recherche Paul Pascale, CNRS Bordeaux (May 24, 2004).
2. "Correlation of properties with preferred orientation in extruded and stretch-aligned single wall carbon nanotube fibers", J. E. Fischer, E-MRS Symposium on *Advanced Multifunctional Nanocarbon Materials and Nanosystems*, Strasbourg France (May 27, 2004).
3. "Nanoporous carbide-derived carbons with tuneable pore size", J. E. FischerE-MRS Symposium on *Advanced Multifunctional Nanocarbon Materials and Nanosystems*, Strasbourg France (May 28, 2004).
4. "Nanoporous carbide-derived carbons with tuneable pore size", J. E. Fischer, *Annual Conference of the American Carbon Society*, Providence RI (July 16, 2004).
5. "Single-wall carbon nanotubes in oleum: partly ordered solvent shells, templated crystallization and fiber spinning", J. E. Fischer, invited talk at *International Winterschool on New Materials*, Kirchberg, Austria (March 14-19, 2005). *Cancelled due to injury*.
6. "SWNT-oleum: partly ordered solvent shells, templated crystallization and fiber spinning", J. E. Fischer, *Sixth International Conference on the Science of Nanotubes (NT'05)*, Goteborg Sweden (6/26-7/1 2005).
7. "Nanoporous carbide derived carbon with tunable pore size: synthesis and energy related applications", J. E. Fischer, keynote lecture at the conference *Carbon for Energy Storage and Environment Protection - CESEP'05*, Orleans, France (October 2-6, 2005).
8. "Percolated networks in SWNT-polymer composites: polymer dynamics and electrical transport controlled by loading and alignment", J. E. Fischer, Euroconference GDR-E *"Science and applications of nanotubes"*, Houffalize, Belgium (October 10-14, 2005).

9. “Carbide-derived carbons with tailored porosity optimized for hydrogen storage”, J. E. Fischer, *WE-Heraeus-Seminar on Hydrogen Storage with Novel Nanomaterials*, Bad Honnef, Germany (October 23-27, 2005).
10. “High hydrogen storage in porous carbide-derived carbons”, J. E. Fischer, *Materials Research Society Fall Meeting Symposium A*, Boston (December 2, 2005).
11. “Hydrogen storage in porous carbons”, J. E. Fischer, *LRSM Series for High School Teachers*, Jan. 19, 2006.
12. “Gallium nitride nanowires”, J. E. Fischer, R. Agarwal, G. Piazza and R. J. Composto, *DARPA Workshop on Nanowires and Nanotubes for Defense Applications* Napa, CA; March 1-2, 2006.
13. “From fundamental understanding to predicting new nanomaterials for high capacity hydrogen storage technologies”**,** T. Yildirim, APS March Meeting, Baltimore (March 2006).
14. “Effect of nanotube alignment on percolation conductivity in SWNT/polymer composites”, Fangming Du, John E. Fischer and Karen I. Winey, *International Winterschool on New Materials*, Kirchberg Austria (March 5-11, 2006).
15. **“**Combined Neutron Scatterig and First-Principles Study of Novel Hydrogen Storage Materials”, T. Yildirim, MRS Spring Meeting, San Francisco (April 2006).
16. “Carbon nanotubes: structure, suspensions and networks”, J. E. Fischer, seminar at National Institute for Standards and Technology Polymer Division, Gaithersburg MD (April 25, 2006).
17. "Gallium nitride nanowires: synthesis, contacts, electron transport, resonators and defects, defects, defects.....", J. E. Fischer, MSE Department Seminar, Penn (April 27, 2006).
18. “Gallium nitride nanowires: synthesis, contacts, electron transport, mechanical resonators, and defects”, J. E. Fischer, seminar at National Institute for Standards and Technology Reactor Division, Gaithersburg MD (May 23, 2006).
19. “Electrical and thermal transport in carbon nanotubes”, J. E. Fischer, invited tutuorial at the *Seventh International Conference on the Science of Nanotubes (NT’06)*, Nagano Japan (May 29 – June 2, 2006).
20. “Neutron Scattering and First-Principles Characterization of Novel Hydrogen Storage Materials”, T. Yildirim, American Conference on Neutron Scattering St. Charles, IL, (June 18-22, 2006).
21. “Thermal properties of carbon nanotubes”, J. E. Fischer, tutorial lectures at *International Summerschool on Nanotubes*, Institut d’Ètudes Scientifiques de Cargèse, Corsica France (July 8-14, 2006).
22. “Magic Role of Ti in Novel Hydrogen Storage Materials”, T. Yildirim, the XV International Materials Research Congress (IMRC), Cancún, (Aug. 20 -24, 2006).
23. “Structural studies of buckyball and buckytube materials: solids, salts and suspensions”, J. E. Fischer, *American Chemical Society Memorial Symposium for Rick Smalley*, San Francisco (September 10-14, 2006).
24. Tailored nanoscale porosity in carbide-derived carbons: optimization for high capacity hydrogen storage”, J. E. Fischer, *MH2006* (Metal-Hydrogen interactions), Maui (October 1-4, 2006).

25. “Engineered Nano Materials for High-Capacity Hydrogen Storage”**,** T. Yildirim, Oak Ridge National Laboratory (Feb. 2007).
26. “Gallium nitride nanowires: Effective dimensionality and size-dependent roperties”, International Winterschool on New Materials, Kirchberg Austria (March 10-17, 2007).
27. “Nano Guest-Host Concept for High-Capacity Hydrogen Storage”**,** T. Yildirim, University of Virginia, Physics Seminer Series (April 2007).
28. “Gallium nitride nanowires: Impurity and disorder effects on thermal conductivity”, J. E. Fischer, invited lecture at the *International Winterschool onElectronic Properties of Novel Materials: Molecular Nanostructures*, Kirchberg Austria (March 1-8, 2008).
29. “The role of network formation in carbon nanotube-based solid and nanofluid composites”, J. E. Fischer, invited talk at Symposium O *Carbon Nanotubes and Related Low-dimensional Materials*, MRS Spring Meeting, San Francisco (March 24-28, 2008).
30. “Gallium Nitride Nanowires: Synthesis, Morphology, Defects and Properties”, J. E. Fischer, invited lecture at *Symposium on Nanotechnology: Materials Synthesis, Characterization, and Devices*, University of Puerto Rico, Humacao (May 2, 2008).
31. “Porous Carbons for Hydrogen Storage: Physics, Chemistry and Prospects”, J. E. Fischer, joint Physics and Chemistry colloquium at Georgetown University (Oct. 9, 2008).