Elucidation of Hydrogen Interaction Mechanisms With Metal-Doped Carbon Nanostructures

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Program Scope

This research work is aimed at obtaining a better understanding of the nanoscale level of hydrogen sorption behavior of Metal-Doped Carbon Nanostructures. The experimental work is closely linked to relevant modeling studies of these materials. Advances hydrogen storage technology based on carbon nano-structures and particularly metal-doped carbon nanotube (MD-CNT) require the development of a basic understanding of their physicochemical properties and the manner in which these properties influence the hydrogen bonding. Our effort is focused on understanding of the hydrogen interaction mechanisms such as physisorption, weak covalent bonding, and chemisorption in these nano-carbon systems.

We hypothesize that hydrogen bonding in MD-CNTs is controlled by:

1. modification of the electronic structure in the MD-CNT from the back-donation of electrons from the metal to the carbon;
2. quantized electron energy states that are controlled by the size of the metal particle and its composition/speciation; and
3. the presence of defects in the CNT and lattice deformation resulting from coherency strain at metal-CNT interface.

Our effort is conducted along the following integrated and parallel activities:

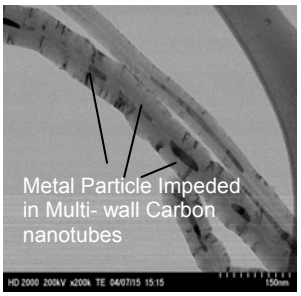
- Production, purification, and separation to develop MD-CNTs of highly controlled size and composition.
- Characterization of these materials and determination of hydrogen bonding pathway and equilibrium distribution of hydrogen bond types by analytical techniques (e.g., Raman spectroscopy, NMR, and neutron scattering and thermo-gravimetric and volumetric analyzers).
- Theoretical modeling is an essential part of our effort in order to confirm and guide the experimental work. The theory will guide the experiments toward

investigating stable and high hydrogen capacity structures. Theory will use experimental results to modify assumptions and reach realistic understanding of carbon nano-structures and MD-CNT systems.

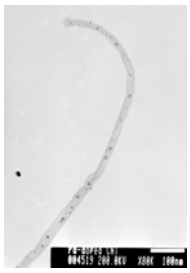
Recent Progress

(a)Production of controlled Size carbon nanotubes doped with different metals

Carbon nanotubes doped with different metals have been produced and the process is being optimized. The ultimate goal is to control the size and type as needed. Different diameter patches of carbon nano tubes were produced in order to investigate the effect of curvature on the hydrogen bond.



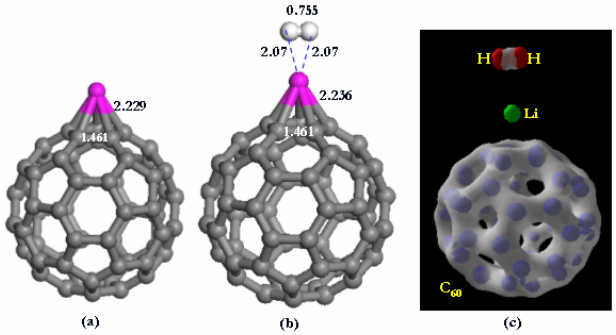
Synthesized Carbon Nanotubes doped with metals



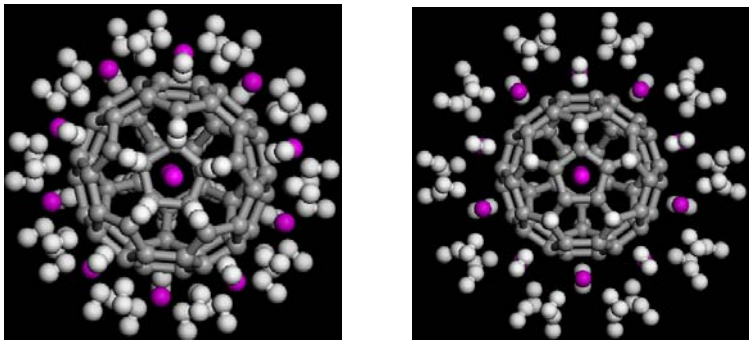
Comparable particles size of impeded metal

b) Density functional theory calculation identifies dihydrogen bond with carbon nanostructure

Recent studies illustrate that metallization of carbon nanotubes and fullerenes may enhance the strength of hydrogen bonding and lead to high gravimetric density. However, choosing the correct metal dopant is essential as they may cluster on the carbon frame and adversely affect the hydrogen gravimetric density. Using density functional theory we show that Li coated C_{60} fullerene may be a potential candidate for hydrogen storage. In particular, $Li_{12}C_{60}$ with the Li atoms located on the 12 pentagonal faces of the fullerene is able to store 120 hydrogen atoms in molecular form yielding a gravimetric density of 13 wt % and a volumetric density of 128 g/L.



DFT Calculation showing:
(a) Geometries of LiC_{60} and (b) $LiC_{60}H_2$. The valence charge density distribution (in white) in $LiC_{60}H_2$ is given in (c)



(a) (b)

(a) Initial and (b) optimized geometry of $Li_{12}C_{60}(H_2)_{60}$
Qiang Sun et al. *Alloys and Compounds,* submitted

Future Plans:

We plan to continue the production and characterization of different carbon nano structures and investigate their interaction with hydrogen. Experimental methods have been developed to try making the dihydrogen nanostructures predicated by theory in our program. For example, electrochemical cell has been constructed in order to electrochemically intercalate Li ions into graphite, fullerenes and carbon nanotubes. The preliminary results of intercalation technique were found to promising. Other techniques are being developed such as electro-crystallization of fullerene in chlorobenzene solution and lithium tetraphenylborate in THF. The electrolytic process will be tuned to control the amount of Li intercalated into the carbon structures. The goal is to achieve controlled nanostructures within a narrow distribution of possibilities.