

Nanomaterials Engineering for Hydrogen Storage

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Objective: The objective of this project is to develop optimized nanocomposite materials for high-density H₂ reversible storage applications. Specifically, carbon nanotube-catalyst nanoparticle composite materials with well-controlled nanotube size will be developed, that are optimized to satisfy the target fundamental characteristics for hydrogen storage. A systematic design and fabrication process will be followed that will permit not only controlled growth of carbon nanotubes but also incorporation of nanoparticles to decorate the nanotubes to catalyze H₂ adsorption and desorption processes.

Background: Nanomaterials have diverse tunable physical properties as a function of their size and shape due to strong quantum confinement effects and large surface/volume ratios. A single wall carbon nanotube (SWCNT) has the same structure as a roll of a single graphene sheet and has nanometer sized diameters ranging from 4 to over 100 Å. Due to their large surface areas with relatively small mass, SWCNTs have been considered as potential materials for high capacity hydrogen storage. Theoretically, they can store hydrogen up to 7.7 wt%, as every carbon atom in SWCNTs chemisorbs one hydrogen atom. In addition, the subsequent physisorption of hydrogen on the surfaces of hydrogenated SWCNTs can increase the capacity of hydrogen storage even further. In spite of the strong potential of SWCNTs, current experimental findings are not very promising mainly due to the lack of control in preparing SWCNTs as a hydrogen storage medium. It has recently been shown that the H-CNT interaction energy is a very sensitive function of the nanotube size, and a sample of a wide range of CNT sizes would have only a small fraction of the CNT surface suitable for hydrogen storage. There is currently much skepticism on carbon nanotube hydrogen storage due to early mistakes in experimental publications and therefore a rational basis for high capacity hydrogen storage materials is being developed through the systematic nano-materials research undertaken in this effort.

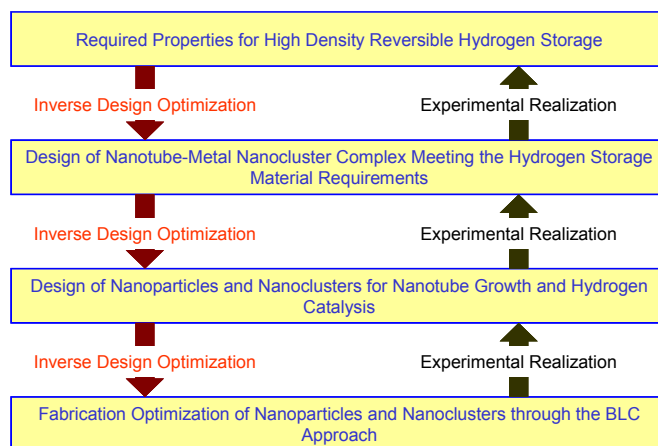


Figure 1: Flow diagram of the project

Approach: The framework of nanomaterial design, fabrication and characterization illustrated in Figure 1 will be used to optimize the catalyzed nanotube for hydrogen storage. A systematic search process in material parameter space (particle composition and size) will be applied. The materials design will be implemented by fabrication and characterization of the nanocomposite materials for their reversible hydrogen storage capacity. The four main thrusts of this approach are discussed below:

- *Computation:* Intelligent Computer Aided Materials Design (ICAMD) principles and simulation tools will be applied to the design of the desired nanocomposite materials based on the merging of evolutionary computing techniques such as the genetic algorithm (GA) approach with quantum ab-initio and tight-binding simulation methods for applications pathways. The simulation process involves: (a) design and construction of an appropriate “fitness function,” based on final application specifications, against which the overall design and application pathway is continually optimized; (b) generation of a population of structures and their associated physical and chemical characteristics; (c) GA based evolution of the population until a best fit with the fitness-function is achieved within a prescribed error bar; and (d) comparison and experimental feasibility testing of the best fit design by additional quantum simulation and comparison with experimental data.

- *Control of Chemical Reactivity:* One of the most critical requirements for hydrogen storage materials besides storage capacity is reversibility. The storage material should be able to both absorb and release hydrogen easily. The reversibility can be controlled by the hydrogenation energy of a SWCNT, which is enhanced as the curvature of the SWCNT increases. Different atomic scale catalysts will be designed which can remove most of the energy barrier of around 2 eV between H₂ gas and the chemisorbed H atoms, and SWCNTs with radii equal to or smaller than a (12, 0) SWCNT will be grown.

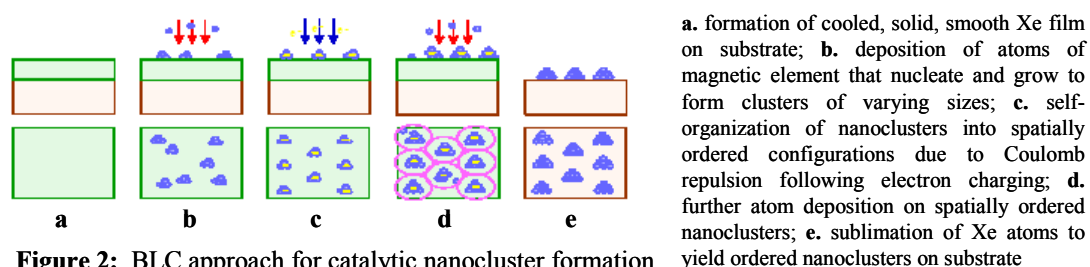


Figure 2: BLC approach for catalytic nanocluster formation

- *Fabrication:* Three conceptually different approaches will be applied to fabricate nanoclusters with the right size and spatial distributions that can serve as catalytic centers for growth of SWCNTs. These include (a) catalytic nanocluster formation using an inert gas buffer plus Coulomb charging (BLC) technique as depicted in Figure 2. First principles based simulation approaches will be used to map out the precise growth conditions for size selection and control for a variety of nanocluster-substrate combinations and the process may be modified to generate a hybrid nanocluster-nanotube system with both size and radius selectivity. (b) Size selection of catalytic nanoclusters induced by the steering effect of substrate superstructures. In this approach, these nanochemical features will be used to investigate the effect of spatially varying surface chemistry on thin film growth and nucleation. (c) Selection of magic sized nanoclusters due to quantum size effects. The confined motion of the conduction electrons in the

nanometer or smaller size regime in a metallic system may lead to the existence of highly preferred length scales (both horizontal and vertical)

- *Characterization:* The adsorption of hydrogen in carbon nanotubes will be followed using two different techniques: X-ray spectroscopy and Temperature Desorption Spectroscopy (TDS). The former will be used to study electronic structure rearrangements as a signature of hydrogenation of the carbon π -system, and the latter will measure the strength of adsorption (i.e. chemisorption, physisorption, and/or van der Waals interaction) and the amount of hydrogen that is released due to an increase in temperature via linear heating of the sample. The total amount of hydrogen can be calibrated against hydrogen monolayer coverage on metal surfaces.

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