IV.I.18 A Synergistic Approach to the Development of New Hydrogen Storage Materials, Part II: Nanostructured Materials

A. Paul Alivisatos, Marvin L. Cohen,
Jeffrey R. Long (Primary Contact),
Steven G. Louie, Samuel S. Mao,
Jeffrey J. Urban, and Alex Zettl
Materials Science Division,
Lawrence Berkeley National Laboratory
Berkeley, CA 94720

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The Berkeley Hydrogen Storage project consists of a broad-based, multi-investigator effort for developing new types of hydrogen storage materials. In particular, materials with the potential for meeting the 2010 DOE target of a reversible uptake of 6% H_2 by mass are sought. Our approach is to explore numerous possibilities for new materials, and narrow our focus as the research progresses. The synergy of many scientists in one location working toward a common goal is expected to accelerate our progress and lead to new ideas via cross-fertilization. One half of the project (Part I, currently funded through EERE) involves development of microporous metal-organic frameworks and polymers, as well as destabilized metal hydrides. The other half of the project (Part II, detailed here) focuses on the development of new nanostructured materials of potential utility in hydrogen storage applications. Specific areas under investigation include: the synthesis of new nanostructured boron nitride materials, computational work leading to the prediction of carbon boron nitride-containing structures with a high affinity for H_2, synthesis and evaluation of hydrogen uptake in magnesium-intermetallic nanocrystalline networks, and the development and characterization of nanocrystal/metal-organic framework hybrid materials exhibiting room-temperature hydrogen uptake via a spillover mechanism. A hydrogen storage characterization facility containing one gravimetric and two volumetric high-pressure adsorption analyzers has been created in order to provide accurate and immediate feedback on the properties of the many new materials generated.

Nanostructured Boron Nitride

Experimental efforts to explore the use of nanostructured boron nitride are being undertaken to complement the extensive work underway on nanostructured carbon. Both chemical vapor deposition and induction furnace methods have been refined for the large-scale synthesis of pure boron nitride nanotubes. Conditions for varying the morphology of nanostructured boron nitride have been identified. Testing of hydrogen storage properties is in progress to compare the effects of different morphologies, as well as with carbon-based analogues. Chemical vapor deposition methods have also been developed for the generation of composites of boron nitride nanostructured materials and metal or metal oxide nanoparticles. These studies include the synthesis of both boron nitride nanotubes (BNNTs) and activated boron nitride nanostructured material, and also boron carbon nitride (BCN) nanotubes and related nanostructured BCN material. Computational efforts have demonstrated a higher hydrogen binding affinity for boron nitride nanotubes compared to carbon nanotubes. In addition, the role of defect structures in enhancing hydrogen binding has been explored. The results have led to an experimental effort in which carbon atoms are implanted within high-defect boron nitride nanotubes using a hydrocarbon plasma.

Methods have also been developed recently to extensively functionalize the surface of both carbon and boron nitride nanostructured materials allowing tunable interaction with a diverse range of materials for the preparation of hybrid and composite nanostructured materials. Specifically, the surfaces of boron nitride nanotubes have been functionalized with amine groups via ammonia plasma irradiation. The functionalized tubes were characterized by Fourier transform infrared spectroscopy and electron energy loss spectroscopy. The resulting amine-functionalized BNNTs were found to be highly dispersible in chloroform, and are predicted to form the basis of a new class of chemically reactive nanostructures.

Building on these capablilites, solution chemical routes to depositing a diverse range of metal and semiconductor nanocrystals, nanorods and quantum dots on the carbon and boron nitride nanotubes have been developed. The principle example of this strategy is the decoration of BNNTs with 4-nm gold nanocrystals (see Figure 1). Gold nanoparticles were self-assembled at the surface of both amine- and thiol-functionalized boron nitride nanotubes (BNNTs) in solution. The chemical functionalization of the surface of the BNNTs was achieved following ammonia plasma irradiation in order to generate amine functional groups at the surface of the BNNTs. The amine-functionalized BNNTs were then covalently modified by the coupling of short-
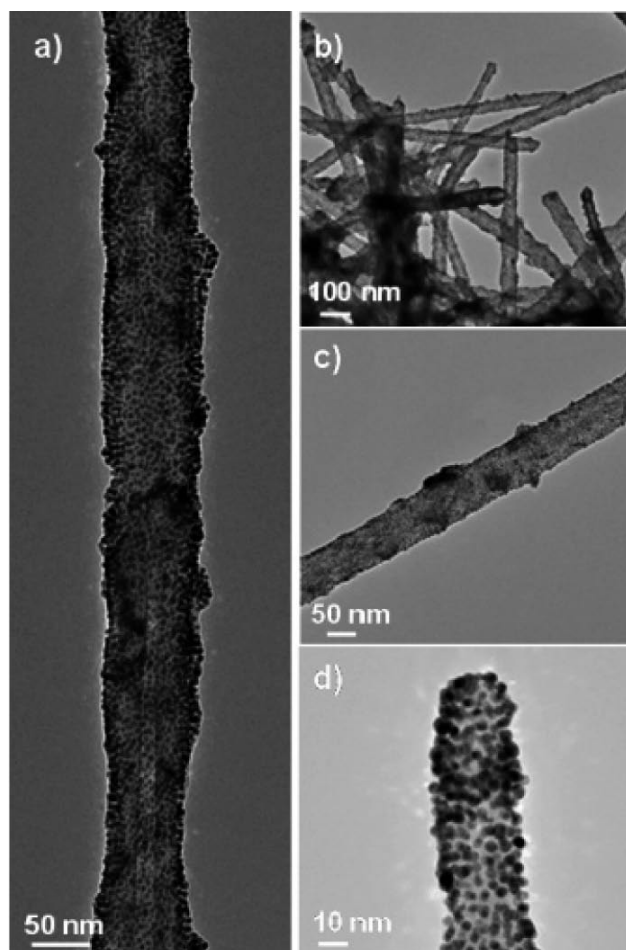
FIGURE 1. Typical low-resolution TEM images of DMAP-stabilized gold nanoparticles self-assembled at the surface of different amine-functionalized BNNTs, where the lengths of the BNNTs shown are approximately 750 nm (a), 1 μm (b), 600 nm (c), and 100 nm (d).

FIGURE 2. (a) Two Ca atoms individually attached on a (7,7) pristine CNT. (b) Two Ca atoms aggregated on a pristine (7,7) CNT. (c) Initial geometry of seven H_2 molecules on the two aggregated Ca atoms. (d) Geometry of the seven H_2 molecules on the two aggregated Ca obtained from energy minimization calculation. (e) Two Ca atoms individually attached on a B-doped (7,7) CNT. (f) Two Ca atoms aggregated on a B-doped (7,7) CNT. (g) Two Ti atoms individually attached on a B-doped (7,7) CNT. Black dots indicate the Ti atoms. (h) Two Ti atoms aggregated on a B-doped (7,7) CNT. The total energy of the lower energy structure between aggregated and unaggregated structure is set to zero.

chain thiol-terminated organic molecules to result in thiol-functionalized BNNTs. The functionalization of the BNNTs was characterized using XPS, FT-IR spectroscopy, and EDS, whereas the nanoparticle-nanotube assemblies were characterized using HR-TEM and EELS. This approach constitutes a basis for the preparation of highly functionalized BNNTs and their utilization as nanoscale templates for assembly and integration with other nanoscale materials. It is expected that analogous materials in which nickel or palladium nanocrystals are covalently attached to BNNTs will be of interest for the study of hydrogen storage via a spillover mechanism.

Computational Work on Nanostructured Carbon and Boron Nitride

Using first-principles calculations, we performed a search for high-capacity hydrogen storage media based on individually dispersed calcium atoms on doped or
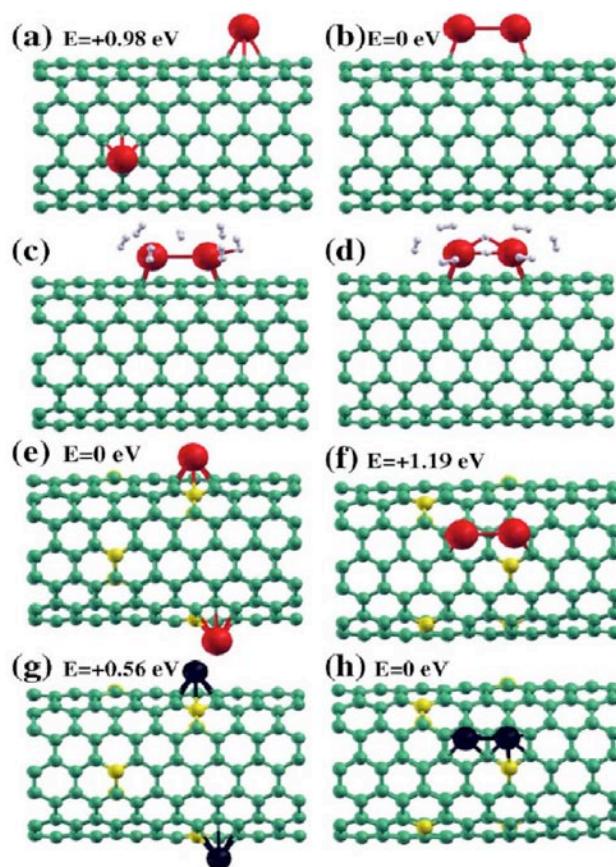
defective carbon nanotubes. We found that up to six H_2 molecules can bind to a Ca atom each with a desirable binding energy of ca. 0.2 eV/H_2. The hybridization of the empty Ca 3d orbitals with the H_2 σ orbitals contributes to the H_2 binding, and clustering of Ca atoms (a major problem in previous studies of using metal atoms for H_2 adsorption) is suppressed by preferential binding of Ca atoms to doped boron and defect sites dispersed on carbon nanotubes. We also found that individual Ca-decorated B-doped carbon nanotubes with a concentration of ~6 at% B doping can reach the gravimetric capacity of ca. 5 wt% hydrogen.

Figure 2 illustrates that, unlike transition metal atoms, Ca atom clustering is suppressed on B-doped carbon nanotubes by preferential binding of Ca atoms to B sites. Figure 3 shows the fully optimized
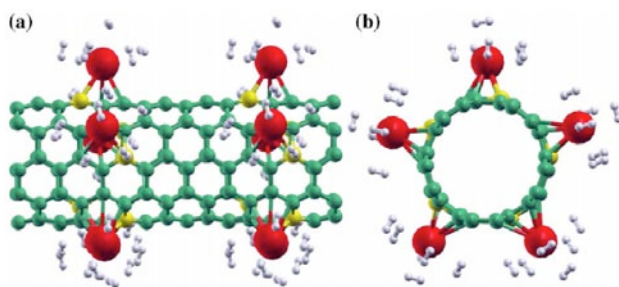
FIGURE 3. Side (a) and cross-sectional (b) views for the optimized atomic structure of maximal number of adsorbed H_2 molecules for a B-doped (5,5) CNT (6.25 at% of B), respectively.

structure for a maximum hydrogen-storage capacity in (5,5) carbon nanotubes with a concentration of 6.25 at% B, corresponding to 4.94 wt% uptake of H_2, where the molecular formula may be expressed as $(C_{75}B_5 \cdot 5Ca \cdot 30H_2)_n$ with n as an integer. Up to six H_2 molecules are adsorbed on a Ca atom with the binding energy of 0.20, 0.21, 0.20, 0.19, 0.18, and 0.17 eV/H_2 for 1, 2, 3, 4, 5, and 6 H_2 molecules, respectively, which corresponds to the desirable binding energy of H_2 molecules for room temperature hydrogen storage.

Magnesium-Based Nanocrystals

Our objectives in this portion of the project are to: (i) develop novel composite materials with high storage density and improved cycling kinetics by using a platform of nanoscale inorganic earth metals with lowered enthalpic barriers and small gas diffusion lengths relative to bulk crystals and ball-milled powders, and (ii) develop gas-selective support matrices to improve retention of sorption properties over large numbers of cycling events.

We have discovered a chemical route for generating size-controlled MgO nanocrystals. These magnesium oxide crystals are pure, single-phase crystals for which the size (2-5 nm) and surface chemistry have been carefully elucidated (see Figure 4). Detailed spectroscopic and vibrational studies have shown that we can chemically functionalize the surface with desired molecular species by solution-phase chemical exchange. We envision using these nanocrystals as precursors to size-controlled nanoscale Mg crystals for detailed H_2 sorption studies. This proposed reduction of MgO to Mg is appealing as no size-controlled route to pure Mg nanoscale crystals exists at present.

We have also worked toward development of direct chemical routes to single-phase Mg nanocrystals. Recently, our lab has successfully prepared nanocrystals of Mg nanocrystals based upon a napthalide reduction of $MgCl_2$. Excitingly, the resultant Mg-metal product
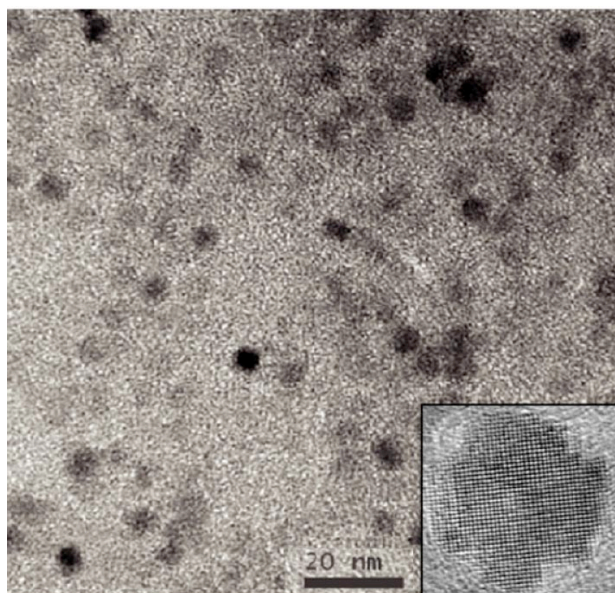

FIGURE 4. Low (panel) and high (inset) resolution transmission electron micrograph images of MgO nanocrystals 2 nm in diameter.
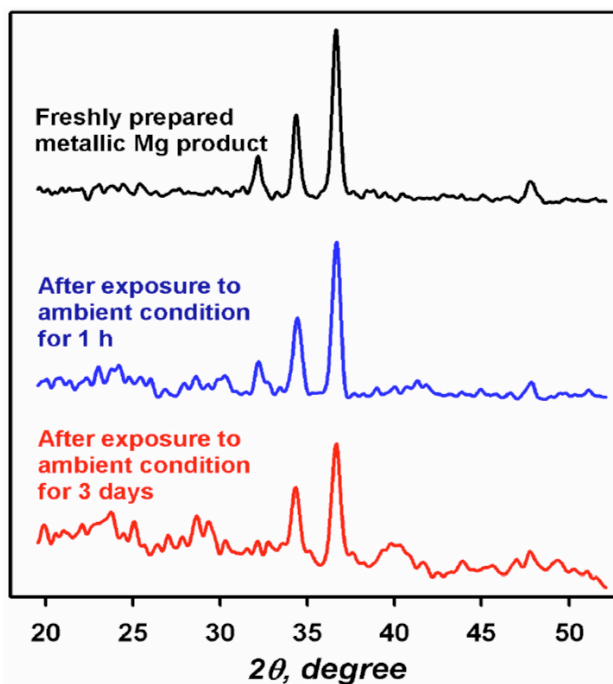

FIGURE 5. X-ray powder diffraction patterns of as-prepared metallic Mg products measured as exposure time increased.

was unexpectedly stable in atmosphere and resistant to oxidation or other chemical degradation (see Figure 5).

In addition, we are working toward the preparation of Mg-nanocrystal/polymer composites with gas-selective properties. We have recently initiated studies into incorporating our Mg nanocrystals into

polymer supports to both enhance stability and provide preferential diffusion of H_2 over O_2 and H_2O, a strategy to enhance material performance over many cycles of gas uptake and release.

Nanocrystal/Metal-Organic Framework Hybrid Materials

Metal-organic frameworks (MOFs) show great potential for hydrogen storage. For example, MOF-177 stores up to 7.0 wt% H_2 at 77 K and 70 bar. While this is attributed to the microporous structure of MOFs and their associated large surface area, room temperature hydrogen storage with pristine MOFs that meets DoE requirements has not been realized. However, mixtures of MOFs with commercially available platinum on activated carbon have shown up to 4 wt% storage of H_2 at 298 K and 100 bar. The goal of this work is to investigate this phenomenon of spillover by combining MOFs and Pt nanocrystals in a controlled manner.

Firstly, we have mixed colloidally-synthesized, faceted, 10-nm Pt nanocrystals with MOF-5, MOF-177 and HKUST-1. Since these Pt nanocrystals have a polyvinyl pyrolidone (PVP) coating, they are soluble in common organic solvents. Composites consisting of 3 wt% PVP/Pt- MOF mixtures were formed by stirring the nanocrystals with MOFs in dry dichloromethane. These composites were then degassed according to literature procedures and the surface area and hydrogen uptake were measured at 77 K. The materials exhibited a surface area slightly lower than that reported, but comparable or slightly higher hydrogen uptake at 77 K. The PVP/Pt-MOF-5 composite, however, showed hydrogen adsorption of just 0.3 wt% at 30 bar at 298 K. We plan to investigate the dependence of hydrogen storage on nanocrystal size, shape and loading.

Secondly, we have reduced Pt within a variety of metal-organic frameworks. By heating a mixture of $H_2PtCl_6 \cdot 6H_2O$ and the solid MOF in dry methanol, small Pt nanocrystals (<1 nm in diameter) can be inserted into the pores. While MOFs such as MOF-5 decompose under these conditions, HKUST-1 showed an uncompromised surface area and a slight increase in hydrogen adsorption at 77 and 87 K. We now plan to try different loadings of Pt and also use MIL-101 for this, since MIL-101 is stable in boiling water.

Publications

1. "Optimization of Metal Dispersion and Hydrogen Adsorption Strength in Doped Graphitic Materials for Hydrogen Storage" Kim, G.; Jhi, S.-H.; Park, N.; Louie, S.G.; Cohen, M.L. *Phys. Rev. B* **2008**, 78, 085408.

2. "The Two-Dimensional Phase of Boron Nitride: Few-Atomic-Layer Sheets and Suspended Membranes" Pacile, D.; Meyer, J. C.; Girit, C. O.; Zettl, A. *Appl. Phys. Lett.* **2008**, 92, 133107.

3. "Calcium-Decorated Carbon Nanotubes for High-Capacity Hydrogen Storage" Lee, H.; Ihm, J.; Cohen, M.L.; Louie, S.G., submitted.

4. "Size-Controlled Synthesis and Optical Properties of Monodisperse Colloidal Magnesium Oxide Nanocrystals" Moon, H.R.; Urban, J.J.; Milliron, D.J. *Angew. Chem., Int. Ed.*, submitted.

Personnel Supported

Dr. Hye Jin Choi, Postdoctoral Fellow (100%)
Dr. Hoonkyung Lee, Postdoctoral Fellow (100%)
Dr. Hoi Ri Moon, Postdoctoral Fellow (100%)
Dr. Ming Lee Tang, Postdoctoral Fellow (100%)