
IV.B.4I Chemical Hydrogen Storage using Ultra-High Surface Area Main Group Materials

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Contract Number: DE-FC36-05GO15055

Start Date: January 1, 2005
Projected End Date: January 1, 2010

Technical Targets

This project is conducting fundamental studies of light element nanoparticles and molecular compounds. Insights gained from these studies will be applied toward the design and synthesis of hydrogen storage materials that meet the following DOE 2010 hydrogen storage targets:

- Cost: \$4/kWh net
- Specific energy: 2 kWh/kg
- Energy density: 1.5 kWh/L

Accomplishments

- Low temperature synthetic route to amine terminated silicon nanoparticles. Preliminary measurements indicate generation of ammonia via thermolysis.
- Low temperature solution synthetic route to boron nanoparticles. Preliminary synthetic demonstration of hydrogen on the surface.
- Low temperature solution synthetic route for macroscopic amounts of silicon nanoparticles with hydrogen terminated surface. Preliminary measurements indicate H₂ generation via hydrolysis and thermolysis.

Objectives

- To identify light element nanomaterials and molecular compounds as storage materials with potential to meet DOE targets.
- To design and test simple routes to such materials and compounds using mild conditions.
- Optimize the synthesis and hydrogen capacity of these materials, while providing detailed physical characterization.
- Demonstrate the viability of the synthesized materials for commercial application by studying their weight and volume as well as the reversibility of hydrogen uptake.

Technical Barriers

This project addresses the following technical barriers from the Storage section (3.3.4.2) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (B) System Cost
- (A) System Weight and Volume
- (E) Charging/Discharging Rates

Introduction

This project is focused on the design and synthesis of light element compounds and nanomaterials that will reversibly produce molecular hydrogen for hydrogen storage materials. The large surface area of nanoparticles should facilitate a favorable weight to volume ratio, and low molecular weight elements such as boron, nitrogen and silicon exist in a variety of inexpensive and readily available precursors. Furthermore, the small nanoparticles are non-toxic and non-corrosive. Particular attention will be focused on silicon and other light element nanomaterials and also Group III-V containing compounds. During this time period, we concentrated primarily on the design and synthesis of light element hydrogen-capped and amine-capped nanoparticles. Insights gained from these studies will be applied toward the design and synthesis of hydrogen storage materials that meet the DOE 2010 hydrogen storage targets, especially cost, hydrogen capacity and reversibility.

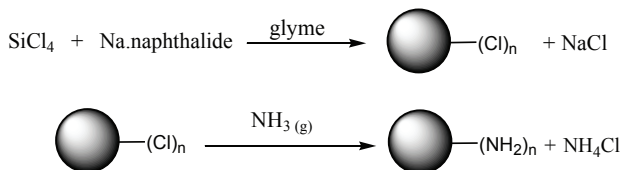
Approach

Two primary routes were explored for the production of nanoparticles smaller than 10 nm in diameter. The first was the reduction of the elemental halides to achieve nanomaterials with chloride surface termination that could subsequently be replaced with amine or hydrogen. The second was the reaction of metal main group intermetallics with ammonium halides to produce hydrogen-capped nanomaterials. These materials were characterized via x-ray powder diffraction, transmission electron microscopy (TEM), Fourier transform infrared (FTIR), thermogravimetric/differential scanning calorimetry, and nuclear magnetic resonance (NMR) spectroscopy.

Results

Amine-Capped Silicon Nanoparticles

The room temperature, solution synthesis of silicon nanoparticles below 10 nm (previously developed in the Kauzlarich group) has been applied to the synthesis of amine-capped silicon nanoparticles. The following synthetic route is successful in producing small nanoparticles:



Spectroscopic analysis by solid-state ^{29}Si NMR indicates the nano-structure of the material and compares well with ^{29}Si NMR published by this group. Characterization by powder x-ray diffraction shows the material to be amorphous and infrared analysis shows the existence of Si-N and N-H interactions that are assumed to be located on the surface. Infrared analysis of the material shows hydrolytic decomposition of the Si-(NH₂) interactions to form Si-O(H) bonds upon exposure to air. The gas that results from the hydrolysis was not analyzed and neither was the remaining solid product. Regeneration seems unlikely, but no efforts were made in that direction. The process of hydrolysis is seen to begin after less than a day but is not completely decomposed even after two weeks, which shows the material should be handled under inert conditions but is not so sensitive as to exclude it from application. This material showed significant weight loss at temperature above 100°C. The resulting gas was qualitatively analyzed with a pH indicator suggesting that the gas is basic and it is presumed to be ammonia.

Boron Nanoparticles

The synthesis of amorphous, surface-functionalised boron nanoparticles has been achieved *via* the reduction of boron tribromide with sodium naphthalene and subsequent reaction with octanol. This is the subject of a submitted communication and the reader should contact the PI for further information. Solution ^1H NMR (CDCl_3) indicates the presence of the octyloxy-capping groups on the surface of the nanoparticles, which is further supported by FTIR analysis with absorbances corresponding to alkyl C-H groups between 2,800 and 3,000 cm^{-1} and B-OR groups at ca. 800 cm^{-1} . The solution ^{11}B NMR (CDCl_3) spectrum shows a resonance at 18.5 ppm with respect to $\text{BF}_3\cdot\text{OEt}$ (0 ppm), which is consistent with results obtained for molecular B-OR compounds and provides further evidence of B-O bonding on the surface of the particles. Figure 1 shows TEM micrographs of a number of the octyloxy-capped boron nanoparticles. The size distribution of the particles was determined by measuring 937 nanoparticles

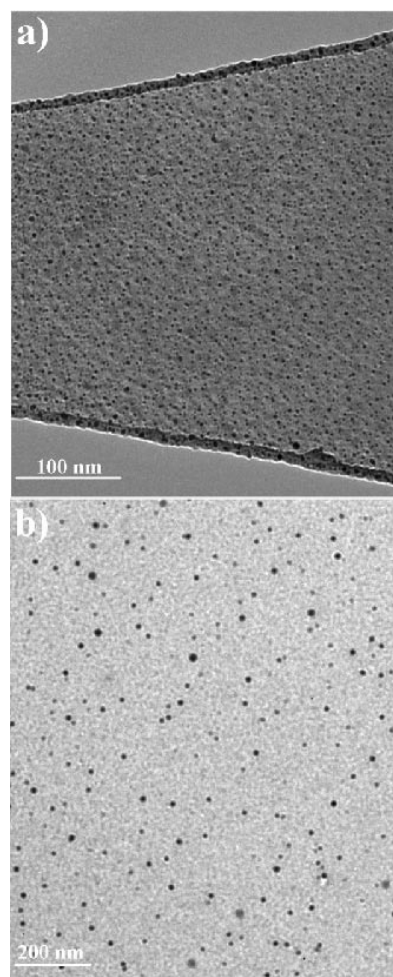


FIGURE 1. Low magnification, bright field TEM images showing examples of a) 2-4 nm boron particles and b) 18-20 nm boron particles.

from different regions of the grid. Analysis of the particle size distribution indicates that the particles lie in the range 1 to 45 nm (with 1.8% lying in the range 30 to 45 nm). The majority of particles are 1-3 nm (54%), with the remaining particles quite evenly distributed between 4 to 20 nm.

Elemental analysis via electron dispersive x-ray spectroscopy (EDS) is not possible on elements lighter than carbon, so a combination of scanning

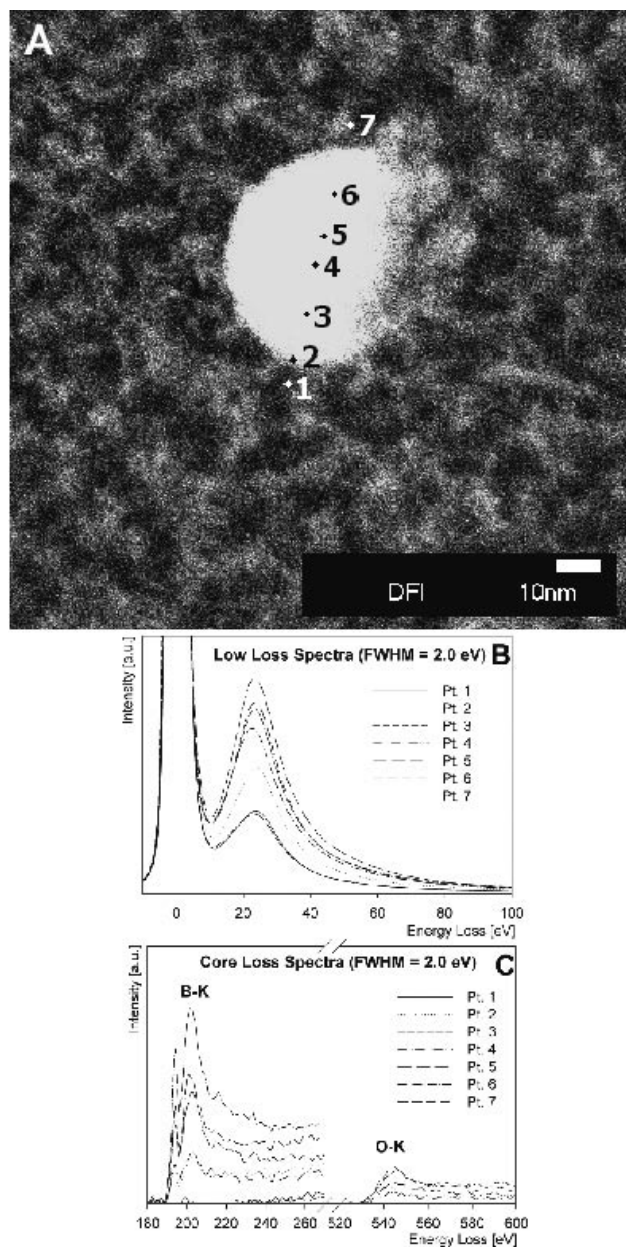


FIGURE 2. A) High-resolution Z-contrast image in STEM mode of an octyloxy-capped amorphous boron nanoparticle showing the position and the actual probe size (1 nm) of the EELS line scan across the particle, B) low loss and C) core loss spectra of the different positions (Point 1-7). All core loss spectra are background subtracted and Fourier-log deconvoluted.

transmission electron microscopy (STEM) and electron energy loss spectroscopy (EELS) has been used to confirm the presence of boron in the particles. Figure 2a shows a STEM dark field image of the octyloxy-capped amorphous boron nanoparticle, with a diameter of approximately 37 nm. Measurements were also performed on particles of each size range (20 and 3 nm), and concluded the presence of boron in each. The low loss spectra in Figure 2b are normalized to the height of the zero loss peak and trace the increased intensity of the plasmon peak (~ 24 eV) on the particle (points 3-6). The low loss region in EELS provides a quantitative measure of the specimen thickness. In the case of the measured boron nanoparticle the specimen thickness varies from 0.09 (points 1 + 7; on the carbon foil) to a maximum thickness of $0.20 t/\lambda$ inelastic (point 5). The core loss spectra (Figure 2c) were background subtracted using a power law fit and corrected for multiple scattering using a Fourier-log deconvolution algorithm. As expected, the intensity of the boron K edge increased to a larger extent towards the centre of the particle with respect to the oxygen K edge.

Hydrogen-Capped Silicon Nanoparticles

A simple low temperature route to hydrogen-capped silicon nanoparticles has been demonstrated. X-ray powder diffraction along with TEM images show discrete nanoparticles consistent with diamond structure silicon. Hydrogen termination is demonstrated with solid state NMR.

Conclusions and Future Directions

Amine-terminated nanoparticles can be prepared via a simple, straightforward solution route. The material reacts with water to produce a gas that has yet to be analyzed. A gas can also be formed via thermolysis and appears to be ammonia. However, problems with final purification have thwarted efforts to better characterize this material. Boron nanoparticles can also be prepared via this route. The current method capped the nanoparticles with an alkyloxy group for purification purposes. Macroscopic amounts of hydrogen-capped silicon nanoparticles have been prepared in a simple low cost solution method.

The amine-terminated silicon nanoparticles will not be pursued. Hydrogen- and amine-capped boron nanoparticles will be further investigated. Hydrogen-capped silicon nanoparticles will be further characterized for hydrogen generation and regeneration, in collaboration with PNNL. Hydrogen-capped silicon-boron and silicon-carbon alloy nanomaterials will be prepared. The scope of this project will be enlarged to include new investigations of the molecular chemistry of boron-halogen, boron-nitrogen, boron-phosphorus and boron hydrogen compounds and their interconversion

under mild conditions. The use of metal hydride species that can be regenerated in a facile manner from readily available and inexpensive routes will also be a major focus of this work. A variety of spectroscopic techniques will be used for the characterization of the new species including IR spectroscopy which will play a key role in the identification of hydride derivatives.

FY 2006 Publications/Presentations

1. *Nanocrystalline Silicon for Hydrogen Storage* D. Neiner, C. N. Chervin, H. W. Chiu, M. J. Blessent, S. M. Kauzlarich, 2006 MRS Spring Meeting, San Francisco, CA, April 17-21, 2006, EE3.19.

2. *Room Temperature Synthesis of Surface-Functionalised Boron Nanoparticles* A. L. Pickering, C. J. Mitterbauer, N. D. Browning, S. M. Kauzlarich, P. P. Power, 2006, *submitted*.

3. *A low temperature, solution route to macroscopic amounts of hydrogen terminated silicon nanoparticles*, D. Neiner, H. W. Chiu, and S. M. Kauzlarich, 2006, *submitted*.