DOE Hydrogen Program

Single-Walled Carbon Nanohorns

Novel Materials for Hydrogen Storage and Catalyst Supports

Background

Single-walled carbon nanohorns (SWNHs) are being synthesized and processed as economical media with tunable porosity and metal cluster catalyst supports for hydrogen storage and fuel cell applications. The morphology of the SWNHs including the shape, surface area and pore size are tuned during both (1) synthesis and (2) post-processing for optimal hydrogen storage in accordance with theory and modeling.

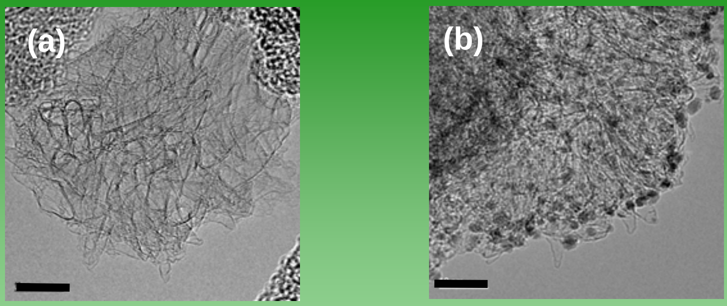

Figure 1. TEM images of (a) SWNHs and (b) Pt decorated SWNHs. (scale bar: 10 nm).

Technology

A high temperature, tunable pulse-width laser vaporization technique has been developed at ORNL to synthesize SWNHs with variable morphology at ~20 g/hour rates has been developed. In situ diagnostics including high-speed videography of the synthesis process, fast pyrometry of the graphite target, and differential mobility analysis monitoring of particle size distributions are applied to understand growth times and provide in situ process control of SWNH morphology. Post-processing treatments have been developed to tailor the pore size and surface area of the SWNHs, and also decorate them with metal catalyst clusters. High (1900 m2/g) surface area SWNH materials with variable pore sizes (Figure 1 (a)) and metal-decorated SWNHs (Figure 1 (b)) have been demonstrated with metals (Pt, Pd) resulting in catalyst-assisted hydrogen storage.

In collaboration with Hydrogen Sorption Center of Excellence partners, evidence for spillover mechanism in both Pt- and Pd-decorated SWNHs have been observed by neutron scattering monitoring of free H2 (Figure 2), where the temperature onset for catalytic storage was determined to be between 150K < T < 298K. Nuclear magnetic resonance measurements at Univ. of North Carolina showed possible spillover-related storage in Pt-decorated SWNHs at room-temperature. In addition, enhanced binding energies for Pt-decorated SWNHs have been measured by both TPD (36 ± 2 kJ/mol, NREL) and NMR (7.1 kJ/mol, UNC). Hydrogen storage capability measurements by CalTech, NIST, NREL and UNC demonstrated hydrogen uptake of SWNHs with 0.2-0.8 wt% at room temperature and 1-3.5% at 77K. Theory and simulation of effects of metal decoration on hydrogen binding energy and storage are being studied to predict enhanced binding energy vs. induced field strength.

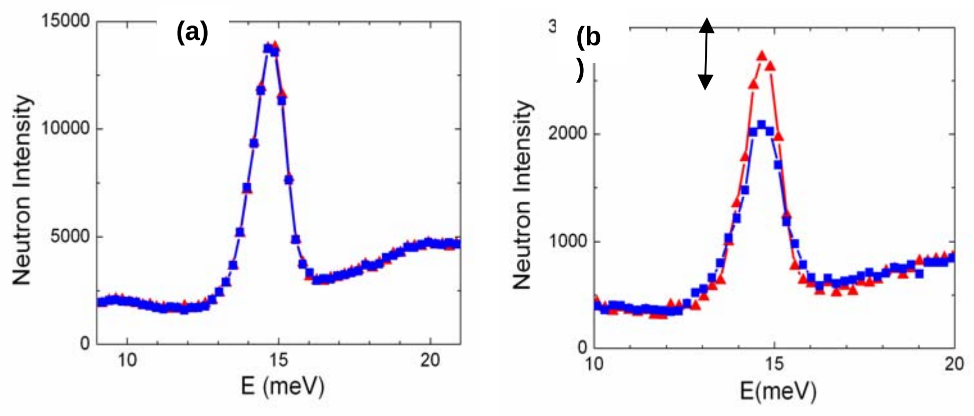

Figure 2 Neutron scattering measurements of rotational band of H_2 showing "spillover" losses of H_2 for Pt-decorated SWNHs after heating samples from 77K (red) to (a) 150K (blue), (b) 298K (blue). NIST (unpublished) data Y. Liu, C. Brown, and D. Neumann.

Benefits

- Single wall structures for maximal surface area, without bundling/dispersion problem.
- As synthesized, are excellent supports for metal nanoparticles.
- External and internal pore size can be adjusted and tuned by oxidation and pressing.
- Bottom-up approach (unlike CDC) with economical, pure material.
- Decorated by simple chemical procedures.
- Dense (1-1.5 g/cm3) bulk material composed of nanohorns with uniform distribution of metal nanoparticles can be prepared (high expected volumetric capacities)
- High volumeteric (70 g/L) storage densities measured in both internal and external pores at 77K/ 5MPa. [Murata, et al. (J. Phys. Chem. B, **106,** 11132 (2002)].

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