

PROCEEDINGS OF THE 1999 DOE/NREL HYDROGEN PROGRAM REVIEW

MAY 4-6, 1999

CARBON NANOTUBE MATERIALS FOR HYDROGEN STORAGE

A.C. Dillon, T. Gennett, J. L. Alleman, K.M. Jones, P.A. Parilla,
and M.J. Heben

National Renewable Energy Laboratory
Golden, CO 80401-3393

Abstract

Carbon single-wall nanotubes (SWNTs) are essentially elongated pores of molecular dimensions and are capable of adsorbing hydrogen at relatively high temperatures and low pressures. This behavior is unique to these materials and indicates that SWNTs are the ideal building block for constructing safe, efficient, and high energy density adsorbents for hydrogen storage applications. In past work we developed methods for preparing and opening SWNTs, discovered the unique adsorption properties of these new materials, confirmed that hydrogen is stabilized by physical rather than chemical interactions, measured the strength of interaction to be ~ 5 times higher than for adsorption on planar graphite, and performed infrared absorption spectroscopy to determine the chemical nature of the surface terminations before, during, and after oxidation. We also made significant advances in the synthesis of SWNT materials by turning to a laser-vaporization method rather than the arc-generation method employed previously. In addition, we began to develop methods to purify nanotubes and cut nanotubes into shorter segments. This year we have made further advances in the development of our laser synthesis technique, and we now generate crude material containing 20-30 wt% SWNTs at a rate of ~150 mg / hr or ~ 1.5 g / day. In addition we have perfected a very simple 3-step purification process which results in material that is > 98 wt% pure which is the purest reported to date. In conjunction with the purification method we pioneered a thermal gravimetric analysis (TGA) technique which enables accurate determination of SWNT wt% contents in carbon soot. Finally, we have simplified our previous nanotube cutting technique and have developed a process that allows for highly reproducible cutting of our purified laser-generated materials. The new cutting method enables the opening of laser-produced tubes which were unreactive to the oxidation methods that successfully opened our previously synthesized arc-generated tubes, and offers a path towards organizing nanotube segments to enable high volumetric hydrogen storage densities. Most importantly, this year we have demonstrated that purified cut SWNTs adsorb between 3.5 – 4.5 wt% hydrogen under ambient conditions in several minutes and that the adsorbed hydrogen is effectively “capped” by CO₂ making it stable for weeks in atmospheric conditions.

Statement of the Problem / Relevance of the Work

Background

With the 1990 Clean Air Act and the 1992 Energy Policy Act, the United States recognized the need for a long-term transition strategy to cleaner transportation fuels ⁽¹⁾. This realization comes while the U.S. continues to increase petroleum imports beyond 50% of total oil consumption, with nearly 50% of the total oil consumed being used in the transportation sector ⁽²⁾. Because of the potential for tremendous adverse environmental, economic, and national security impacts, fossil fuels must be replaced with pollution-free fuels derived from renewable resources. Hydrogen is an ideal candidate as it is available from domestic renewable resources, and usable without pollution. It could therefore provide the long-term solution to the problems created by the Nation's dependence on fossil fuel.

Interest in hydrogen as a fuel has grown dramatically since 1990, and many advances in hydrogen production and utilization technologies have been made. However, hydrogen storage technology must be significantly advanced in performance and cost effectiveness if the U.S. is to establish a hydrogen based transportation system. As described in the U.S. DOE Hydrogen Program Plan for FY 1993 - FY 1997, compact and lightweight hydrogen storage systems for transportation do not presently exist.

Hydrogen provides more energy than either gasoline or natural gas on a weight basis. It is only when the weight, volume, and round-trip energy costs of the entire fuel storage system and charging/discharging cycle is considered that hydrogen's drawbacks become apparent. New approaches enabling more compact, lightweight, and energy efficient hydrogen storage are required in order for the wide-spread use of hydrogen powered vehicles to become a reality.

Research and development geared towards implementation of a national hydrogen energy economy has many indirect economic benefits. With almost 600 million vehicles in the world in 1992 - double the number in 1973 - the conflict between energy requirements, power generation, and environmental concerns is felt on a worldwide basis ⁽³⁾. Thus, in addition to providing domestic energy alternatives, investment in hydrogen energy research will result in opportunities for U.S. technologies in over-seas markets.

Currently Available Hydrogen Storage Technologies

Hydrogen can be made available on-board vehicles in containers of compressed or liquefied H₂, in metal hydrides, or by gas-on-solid adsorption. Hydrogen can also be generated on-board by reaction or decomposition of a hydrogen containing molecular species ⁽⁴⁾. Although each method possesses desirable characteristics, no approach satisfies all of the efficiency, size, weight, cost and safety requirements for transportation or utility use. The D.O.E. energy density goals for vehicular hydrogen storage call for systems with 6.5 wt % H₂ and 62 kg H₂/m³ to provide a 350 mile range in a fuel cell powered vehicle. This requirement amounts to the storage of ~2.9 kg of H₂ in the weight and volume occupied by a conventional gasoline tank. These storage density goals will only be met with significant advances in the capabilities of hydrogen storage technologies.

Gas-on-solid adsorption is an inherently safe and potentially high energy density hydrogen storage method that should be more energy efficient than either chemical or metal hydrides, and compressed gas storage. Consequently, the hydrogen storage properties of high surface area "activated" carbons have been extensively studied ^(5, 6, 7). However, activated carbons are

ineffective in hydrogen storage systems because only a small fraction of the pores in the typically wide pore-size distribution are small enough to interact strongly with gas phase hydrogen molecules.

Technical Approach and Summary of Past Work

The gas adsorption performance of a porous solid is maximized when all pores are not larger than a few molecular diameters⁽⁸⁾. Under these conditions the potential fields from the walls of the so-called micropores overlap to produce a stronger interaction than would be possible for adsorption on a semi-infinite plane. At sufficiently low temperatures, where the escaping tendency of the gas is much less than the adsorption potential, the entire micropore may be filled with a condensed adsorbate phase. For the case of hydrogen, with a van der Waals diameter of 2.89 Å⁽⁹⁾ pores would be required to be smaller than ~40 Å to access this nanocapillary filling regime. Sufficiently small pores would exhibit an adsorption potential strong enough to localize H₂ at relatively high temperatures. Ideally, the entire porous volume of an adsorbent would be of the microporous variety, and the volume and mass of the adsorbent skeleton would be the minimum necessary to develop the adsorption potential and provide sufficient thermal conductivity for management of heat fluxes associated with adsorption and desorption.

We have been working on the idea that aligned and self-assembled single wall carbon nanotubes could serve as ideal hydrogen adsorbents since 1993. The concept was motivated by theoretical calculations⁽¹⁰⁾ which suggested that adsorption forces for polarizable molecules within SWNTs would be stronger than for adsorption on ordinary graphite. Thus, high H₂ storage capacities could be achieved at relatively high temperatures and low pressures as compared to adsorption on activated carbons.

In the Proceedings of the 1994 Hydrogen Program Review, we presented microbalance data which demonstrated gravimetric hydrogen storage densities of up to 8.4 wt% at 82 K and 570 torr on samples containing carbon nanotubes. This substantial uptake at low hydrogen pressures demonstrated the strong interaction between hydrogen and these materials, consistent with higher heats of adsorption than can be found with activated carbons.

In the 1995 Hydrogen Program Review Proceedings, we presented the results of our temperature programmed desorption (TPD) studies which showed significant H₂ adsorption near room temperatures. The adsorption energies on nanotube materials were estimated to be a factor of 2-3 times higher than the maximum that has been observed for hydrogen adsorption on conventional activated carbons. At the time these were the first results which demonstrated the existence of stable adsorbed hydrogen *on any type of carbon at temperatures in excess of 285 K*. We also analyzed the nanotube production yields versus rod translation rate in the electric arc.

In 1996 we performed a detailed comparative investigation of the hydrogen adsorption properties of SWNT materials, activated carbon, and exfoliated graphite. We also determined that the cobalt nanoparticles present in the arc-generated soots do not play a role in the observed hydrogen uptake. We determined the amount of hydrogen which is stable at near room temperatures on a SWNT basis is ~ 10 wt%, and found that an initial heating in vacuum is essential for producing high temperature hydrogen adsorption. Further experiments suggested that SWNTs are selectively opened by oxidation during this heating, and that H₂O is more selective in oxidation than O₂ due to hydrogen termination of dangling bonds at the edges of opened nanotubes. Purposeful oxidation in H₂O resulted in hydrogen storage capacities which were improved by more than a factor of three. We also correlated the measured nanotube densities produced by specific synthesis rod translation rates during arc-discharge with hydrogen storage capacities determined by TPD. Finally, we utilized NREL's High Flux Solar Furnace to form nanotubes by a new and potentially less expensive route for the first time.

In 1997 we confirmed that H₂ is stabilized by purely physical - rather than chemical - binding. The desorption of hydrogen was found to fit 1st order desorption kinetics as expected for physisorbed H₂, and the activation energy for desorption was measured to be 19.6 kJ/mol. This value is approximately five times higher than the value expected for desorption of H₂ from planar graphite and demonstrates that SWNT soots can provide very stable environments for H₂ binding. We also employed diffuse reflectance Fourier transform infrared (DRFTIR) spectroscopy to determine the concentrations and identities of chemisorbed species bound to the carbon surface as a function of temperature, and determined that “self-oxidation” allows high-temperature adsorption of hydrogen to occur in the arc-generated SWNT materials. We also began synthesizing SWNT materials in much higher yield than is currently possible with arc-discharge by using a laser vaporization process. We determined that the very long SWNTs made by this method could not be activated towards high-temperature H₂ physisorption by the same oxidative methods that were found to be effective for tubes produced by arc-discharge.

In 1998 we made significant advances in synthesis and characterization of SWNT materials so that we could prepare gram quantities of SWNT samples and measure and control the diameter distribution of the tubes by varying key parameters during synthesis. By comparing continuous wave (c.w.) and pulsed laser techniques, we learned that it is critical to stay in a vaporization regime in order to generate SWNTs at high yield. We also developed methods which somewhat purified the nanotubes and cut them into shorter segments. We performed temperature programmed desorption spectroscopy on high purity carbon nanotube material obtained from our collaborator Prof. Patrick Bernier, and finished construction of a high precision Seivert’s apparatus which will allow the hydrogen pressure-temperature-composition phase diagrams to be evaluated for SWNT materials.

This year we have significantly improved our laser-vaporization method for the production of SWNTs. We now employ pulsed laser vaporization to generate material containing between 20-30 wt% SWNTs at a rate of ~ 150 mg / hr or ~ 1.5 g / day. We have also developed a very simple 3-step purification technique for this material which results in single walled carbon nanotubes that are > 98 wt% pure as shown by thermal gravimetric analysis (TGA). The TGA method developed here at NREL is the first to accurately quantify nanotube wt% contents in carbon soots. Finally, we have simplified our previous nanotube cutting technique and have developed a process that allows for highly reproducible cutting of our purified laser-generated materials. The new cutting method enables the opening of laser-produced tubes which were unreactive to the oxidation methods that successfully opened our previously synthesized arc-generated tubes, and offers a path towards organizing nanotube segments to enable high volumetric hydrogen storage densities. Most importantly, this year we have employed TPD spectroscopy to demonstrate that purified cut SWNTs adsorb between 3.5 – 4.5 wt% hydrogen under ambient conditions in several minutes and that the adsorbed hydrogen is effectively “capped” by CO₂ making it stable for weeks in atmospheric conditions. The new cutting process now enables hydrogen adsorption on two separate sites in the SWNT samples.

Experimental

Pulsed Laser Synthesis of SWNTs

SWNT materials were synthesized by a laser vaporization method similar to that of Thess et al⁽¹¹⁾. A single Molelectron MY35 Nd:YAG laser was used which produced gated laser light ranging in duration from 300 to 500 ns at a frequency of 10 Hz. The gated laser light contained numerous short laser pulses of about 5 to 15 ns. The emission wavelength was 1064 nm at an average power

of 20 - 30 W/cm². An electronically rastered beam enabled material generation at rates of 75 - 150 mg / h. Typically production is ~ 1.5 g / day. It is important to stay in a vaporization regime ⁽¹²⁾ during synthesis so that graphite particles are not ejected. Targets were made by pressing powdered graphite (~ 1 μ particle size) doped with 0.6 at % each of Co and Ni in a 1 1/8" inch dye at 10,000 psi. Crude soot was produced between 850-1200 °C with 500 Torr Ar flowing at 100 sccm. Raw materials were estimated to contain ~ 20 - 30 wt% SWNTs by both a detailed analysis of numerous different TEM images⁽¹²⁾ and our newly developed highly accurate thermal gravimetric analysis method. Inductively coupled plasma spectroscopy (ICPS) was performed after complete air-oxidation of the carbon soots and thorough digestion of the residue in concentrated HNO₃. The same metal content was found in both the laser-generated crude and the initial target to be ~6 wt %. Thus the laser generated SWNT material was not enriched in metal as previously reported⁽¹¹⁾.

Purification of Laser-generated SWNTs

Approximately 80 mg of the above laser-generated crude was refluxed in 60 ml of 3M HNO₃ for 16 h at 120 °C. The solids were collected on a 0.2 μm polypropylene filter in the form of a mat and rinsed with deionized water. After drying, an ~82 wt % yield was obtained. The weight lost is consistent with the digestion of the metal and an additional ~12 wt % of the carbon impurities. The carbon mat was then oxidized in stagnant air at 550 °C for 10 min., leaving behind pure SWNTs. The SWNTs were shown to be > 98 wt% pure with thermal gravimetric analysis. Also, TGA revealed that no significant SWNTs were consumed in the purification process.

Cutting of Laser-generated SWNTs

We previously reported a method for cutting SWNTs involving sonication for 24 hrs in the following solutions: concentrated H₂SO₄, HCl, Aqua Regia (4:1 HCl:HNO₃), 3:1 H₂SO₄:HNO₃, 5:18:1 HCl:H₂SO₄:HNO₃, and 5% Bromine and Iodine in methanol. However, we found these techniques to be both highly destructive and to result in highly irreproducible hydrogen storage results. This year we have developed a new less destructive method which cuts laser-generated SWNTs into segments several microns in length. We are currently filing a patent of this unique process. Importantly, the process enables reproducible activation of hydrogen adsorption on SWNT materials under ambient conditions at 3.5 – 4.5 wt%.

Transmission Electron Microscopy (TEM)

Samples were prepared for TEM by suspending ~ 0.2 mg in 10 ml of acetone. The solutions were sonicated for 5 min., and 6 drops were placed on Ted Pella Ultra-thin Carbon Type-A 400 mesh grids. TEM images were obtained on a Phillips CM-30 TEM/STEM operating at 200 kV with a 50 μm objective aperture for improved contrast. The images were recorded on a 1024 x 1024 CCD camera. Each sample was surveyed for ~45 min. and ~ 7 images were recorded between 4.4k and 160k to ensure a true representation of the material.

Thermal Gravimetric Analysis

TGA data were recorded on a Perkin Elmer TGS-2 interfaced with a MAC Centris 710 and controlled by a National Instruments Lab View program. The 1-2 mg SWNT samples were ramped from 25 – 875 C at 5 °C per minute in a platinum sample pan under an atmosphere of 100-sccm air. This procedure allowed for the determination of moisture content within the samples so that final yield could be determined accurately. Occasionally a TGA in-situ oxidation of a sample was necessary after the nitric acid reflux. This experiment involved; a step ramp to 550 C for 30 minutes, a cool-down to 25 °C within the furnace, and then the TGA experiment was performed as outlined previously.

Temperature Programmed Desorption

Details of the ultra high vacuum (UHV) chamber employed for the TPD studies have been reported previously⁽⁴⁾. Briefly, the sample is mounted at the bottom of a liquid nitrogen cooled cryostat, and a mass spectrometer provides for line-of-site detection of desorbing species. An ion gauge and capacitance manometer are employed to monitor pressure. Gas exposure is controlled with a variable conductance leak valve. Isolation gate valves separate the sample compartment during high-pressure gas exposures.

Carbon samples weighing ~1 mg were placed in a packet formed from 25 μm thick platinum foil. Pinholes in the foil enabled gas diffusion into and out of the packet. The packet could be cooled to ~90 K by the liquid nitrogen cryostat, and resistively heated with a programmable power supply. The sample temperature was measured with a thin thermocouple spot-welded to the platinum packet. The samples were heated in vacuum at 1 K/s to 970 K prior to TPD studies. Hydrogen (99.999% purity) exposures between 300-600 Torr at room temperature were employed to elucidate the H_2 adsorption properties of the samples. The samples were cooled to ~130 K prior to the evacuation of the hydrogen gas.

Results and Discussion

Optimization of Laser Synthesis of SWNTs

Last year we reported that for the efficient laser-generation of SWNTs, it is necessary to operate primarily in a vaporization regime⁽¹²⁾. We were also able to operate in the vaporization regime and achieve high yield production of SWNTs at room temperature using a continuous wave Nd:YAG laser process. Although SWNT contents under certain c.w. conditions were as high as ~78 wt%, the overall material generation rate was only several mg / hr. It was apparent that a method which balanced material production rate and nanotube content must be developed. The pulsed laser vaporization method described this year allows for the production of ~1.5 g / day of material containing between 20-30 wt% SWNTs. Figure 1 compares a) previous arc-generated SWNT materials with b) materials produced by the new method of pulsed laser vaporization. In both images bundles of SWNTs span between agglomerations of amorphous and nano-crystalline carbon, and metal nanoparticles. The laser-generated material, however, contains approximately three orders of magnitude more SWNTs than the arc-generated material. The fact that we can easily produce gram quantities of this high quality material everyday will greatly facilitate our development of a carbon nanotube based hydrogen storage system.

Three-Step Purification of Laser-generated SWNTs

Single-wall carbon nanotube materials produced in gram quantities with the Molelectron MY35 pulsed Nd:Yag laser vaporization methods were purified by a combination of refluxing in 3M nitric acid and subsequent air oxidation at 550 °C. Figure 2a) displays a TEM image of an initial relatively low-quality laser-generated SWNT material. Long bundles of SWNTs are clearly visible in Fig. 2a) however, the image also reveals a high concentration of amorphous carbon or nanocrystalline graphite as well as cobalt and nickel nanoparticles with diameters between 50-100 nm. Fig. 2 b) displays the same material following the reflux in nitric acid revealing that the SWNTs are now encased within a mat by a relatively thick and uniform carbonaceous matrix. The

metal nanoparticles have been completely removed. The carbon matrix was then completely removed by oxidation in stagnant air at 550 °C for 10 min., leaving behind pure SWNTs having a weight of ~20 % of the initial crude (Fig. 2c). The as-purified tubes were difficult to image at high magnification since the tubes were left disordered within their bundles after the acid reflux. However, a brief anneal to 1500 °C in vacuum was sufficient to re-order the tubes. The TEM image of Fig. 2d reveals the high-quality, final material after the vacuum anneal

This year we also developed a thermal gravimetric analysis technique which is the first to accurately quantify SWNT wt% in carbon soots. TGA in flowing air (100 sccm) showed that our purified SWNTs are quite stable (Fig. 3a). The decomposition temperature (T_d) at 735 °C, defined here as the inflection point during oxidation of the tubes, is ~125 °C higher than a recently reported value⁽¹³⁾. This result indicates a lack of dangling bonds or defects at which oxidation reactions can initiate. Since less than 1 wt % is consumed below 550 °C, and less than 1 wt % remains above 850 °C, the final purity is conservatively estimated to be >98 wt %. The TGA technique establishes these SWNTs as the purest reported to date. Furthermore, the metal content was measured by ICPS and found to be the lowest reported to date at 0.2 wt % for both Ni and Co.

TGA was also used to evaluate the crude and acid-refluxed materials to illuminate the key features of the purification process. The data for the crude soot (Fig. 3a) shows a slight increase in weight at low temperatures due to the oxidation of the Ni and Co metals. The carbonaceous fractions begin to combust at ~370 °C and are mostly removed by oxidation below 600 °C. A small final weight loss at ~650 °C is due to the oxidation of surviving SWNTs (~4 wt %). Consistent with observations by others⁽¹⁴⁾, the majority of SWNTs are combusted at lower temperatures concurrently with other carbonaceous materials. The weight remaining at 875 °C corresponds to the weight expected for the oxidized metals (~ 8 wt %).

The TGA data from acid-refluxed material is also displayed in Figure 3a. A first thing to note is that refluxed samples getter as much as 10 wt % water from lab air, while purified and crude samples remain relatively dry. More importantly, non-nanotube decomposition occurs at a lower temperature and is completed before the onset of SWNT combustion. A plateau extending from 550 to 650 °C is evident in the TGA data because the oxidation now occurs in two separate regimes. The sample weight is reduced to approximately zero by 850 °C since all carbonaceous materials have been removed and very little metal is left (0.2%). The acid treatment not only removes the metal but also produces carboxyl, aldehyde, and other oxygen – containing functional groups⁽¹⁵⁾ on the surfaces of the non-nanotube carbonaceous fractions. As a result, the coating is extremely hygroscopic and reactive towards oxidation. This enables the oxidative purification of the SWNTs that could not be achieved with the crude material.

The combustion of non-nanotube carbons in the refluxed soot is essentially complete at the inflection point in the TGA curve at 560 °C. At this temperature, the sample contains pure SWNTs amounting to ~26 wt % of the dry refluxed material, or ~21 wt % of the pre-reflux weight. This latter value is in excellent agreement with the yield after refluxed material was heated to 550 °C in stagnant air (~20 wt %), and considerably higher than the tube content determined by TGA analysis of the crude material (~4 wt %). The quantitative agreement between the bulk oxidation in stagnant air and the TGA measurements under dynamic conditions suggests that neither route consumed SWNTs appreciably. In fact, neither longer times in stagnant air at 550° C (up to 1 h) nor holding at 550 °C during TGA experiments produced further significant weight loss. Since the weight-loss proceeds as expected for oxidation of a single phase above 550 °C, and the TEM images of Fig. 2c) and 2d) show only SWNTs, we can conclude that the final product is pure. It is important to note that the yields determined by purification and analysis are reproducible within 2 percentage points both for samples from a given laser run, and for samples produced in different runs using the same target/laser parameters.

To determine the extent to which tubes are damaged or consumed during the acid reflux, TGA was performed on materials refluxed for 4, 16, and 48 h in 3M HNO₃ (Fig. 3b). Materials for these experiments were produced with 30 W/cm² of laser power. The data were adjusted for the dry-weight lost during reflux so the y-axis represents the wt % remaining of the initial crude material. The data for the 4 and 16 h refluxes overlay at temperatures above ~450 °C, and a plateau associated with SWNT stability is observed at 540 °C and a SWNT content of 17 wt %. It is striking that the TGA curves are virtually identical at the higher temperatures considering the difference in masses consumed during the reflux step. Since the SWNT content is determined to be the same in both cases, it is likely that neither reflux consumed a significant number of tubes. As discussed earlier, tubes are evidently not consumed by oxidation below 550 °C, so the 17 wt % value can be taken as an accurate assessment of the SWNT content in the crude soot. Once again, this value is in good agreement with the yield obtained from batch oxidation at 550 °C after a 16-h reflux in 3M HNO₃. Unlike the 16-h process, the 4-h reflux did not always permit good purification by oxidation. In these cases a TGA curve very similar to that of the crude material was observed.

The oxidation reactions are no longer well separated after a 48 h reflux (Fig. 3b) so only a small SWNT stability plateau is seen at ~ 625 °C. The affinity for water is considerably less than in either the 4 or 16-h samples. The uniform, hydrophilic carbon matrix produced after 16 h of refluxing was not observed by TEM. Instead, a patchier coating was observed along with occasional agglomerations, and some tubes appeared clean and uncoated. The TEM images revealed the non-nanotube carbons to be distributed much like as in the crude soot. Unlike the crude, however, some of the tubes were observed to be sharply angled, cut and damaged. The extended reflux apparently digests most of the non-nanotube carbon and also begins to attack the SWNTs. These cut and defective tubes are then more susceptible towards air oxidation such that only ~8 wt %, or < 50 % of the tubes known to be present remain at the onset of the SWNT stability plateau (Fig. 3b).

Thus, we have developed a non-destructive purification technique which results in SWNTs of > 98 wt% purity. The dilute HNO₃ reflux / air oxidation procedure described here appears to be a simpler and more effective purification process than any previously reported. The reflux must be performed for sufficient time to produce a carbon coating on the SWNTs which can be removed by oxidation. However, exposures which are too extensive or in concentrated acids result in damage and digestion of SWNTs. Also the initial material should not contain large graphite particles ≥ 1μ or metal heavily encased by carbon. Details of the underlying mechanisms which enable this simple purification procedure may be found in our recent paper appearing in *Advanced Materials*⁽¹⁶⁾. We have also applied for a patent on this unique process.

Cutting of Laser-generated SWNTs

Previously a degas to 973 K in vacuum was sufficient to activate hydrogen adsorption on arc-generated SWNTs⁽¹⁷⁾. However in applying the same experimental methods to the very long laser-generated nanotube bundles no significant H₂ adsorption was observed for either the crude or purified materials. The 10-15 Å diameter SWNTs produced at high yield by pulsed laser vaporization are 100's of microns in length. The poor hydrogen uptake by these materials may be attributed to very slow hydrogen diffusion down the long nanotube walls resulting in an effective blockage at the ends of the tubes. In order to activate the hydrogen adsorption properties we have developed a very simple method of cutting the long SWNTs that we have recently submitted to be patented. We have employed this process to samples of our purified material resulting in a significantly increased hydrogen uptake.

Figure 4 a) displays a TEM image of crude laser-generated SWNT material cut by the previous method involving sonication in 5:18:1 HCl:H₂SO₄:HNO₃. Individual nanotubes with lengths between ~0.25 - 1 μ are clearly visible in the image. However, the image is also clearly dominated by impurities or perhaps remnants of destroyed SWNTs. Figure 4 b) displays a TEM image of purified laser-produced SWNTs cut by our new less aggressive process. Here the as-synthesized seemingly endless ropes of SWNTs have been “cut” into compact bundles ~ 1-5 microns in length. No impurities have been introduced by the cutting process indicating that the SWNTs are simply severed and not destroyed. The average bundle diameter has also been increased which should facilitate the development of a compact lightweight vehicular hydrogen storage system.

Improved Hydrogen Uptake in Purified Cut SWNTs

Upon degassing the purified cut SWNT samples in vacuum, the unique hydrogen adsorption properties were activated. Figure 5 displays the H₂ TPD spectrum of a degassed sample following a brief room temperature H₂ exposure at 500 torr. The spectrum is characterized by two separate desorption signals peaked at 470 and 630 K indicating at least two unique hydrogen adsorption sites. The peak desorption temperatures of these signals can be as much as 100 K lower depending on the SWNT sample and the specific cutting conditions. The total hydrogen adsorption capacity corresponds to ~ 4 wt%.

The hydrogen corresponding to the signal peaked at 470 K can be evolved by holding the sample at room temperature overnight in vacuum. Also holding the SWNT sample at 423 K for only 8 minutes results in complete evolution from the low temperature site which corresponds to ~ 1.5 wt%. In order to desorb all of the hydrogen from the higher temperature site it is necessary to heat the sample between 475-850 K. Figure 5 also displays the hydrogen desorption signal from a cut crude laser generated sample as well as the previously reported hydrogen desorption signal from arc-generated SWNT material. The signal peaked at 133 K in the spectrum of the arc-generated material is attributed to physisorbed hydrogen on impurities present in the carbon soot. The very significant increase in SWNT adsorption capacity on a material weight basis is readily apparent from Fig. 5. The development of a new hydrogen adsorption site as evidenced by the H₂ desorption signal at 630 K is also observed following the new cutting process.

Both of the SWNT hydrogen adsorption sites are effectively “capped” by the adsorption of carbon dioxide. This phenomena was revealed in an experiment where a standard hydrogen exposure to cut SWNTs was followed by a room temperature 10 min. 500 torr exposure to CO₂. Figure 6a) displays the hydrogen desorption signal from the SWNT sample following a 500 torr hydrogen exposure at room temperature without any subsequent cooling of the sample. Here two peaks at ~ 420 K and 602 K are observed. However, the lower temperature peak is slightly shifted to a higher temperature due to the absence of cooling during the hydrogen exposure. If the sample had been cooled the lower temperature peak in this case would have been observed at 370 K.

Figure 6b) and c) display TPD desorption signals of CO₂ and H₂ respectively when an identical hydrogen exposure was followed by a CO₂ exposure. The small CO₂ desorption signal peaked at 400 K demonstrates the existence of a small population of CO₂ adsorption sites on the SWNT sample. Surprisingly, however the H₂ desorption signals are both shifted to higher temperature by ~ 50 K. It appears from Figure 6 that the hydrogen does not begin to desorb from the SWNTs until a significant portion of the CO₂ has already evolved suggesting that the CO₂ in fact blocks the hydrogen desorption. In a subsequent experiment the sample was exposed to CO₂ for 10 min at 500 torr at room temperature and then exposed to H₂ under the same conditions. Subsequent TPD revealed only a CO₂ desorption signal demonstrating that carbon dioxide completely blocks hydrogen adsorption as well. CO₂ also apparently “caps” the SWNTs upon exposure to air. Samples charged with hydrogen and exposed to atmosphere were shown to desorb first CO₂ and

then H₂ several weeks later without a significant loss in the stored hydrogen. This effective “capping” of the SWNTs by CO₂ may prove significant to the commercial development of SWNTs for a hydrogen storage system. It is also highly interesting that there are relatively few adsorption sites for CO₂ compared with H₂.

Conclusions / Future Work

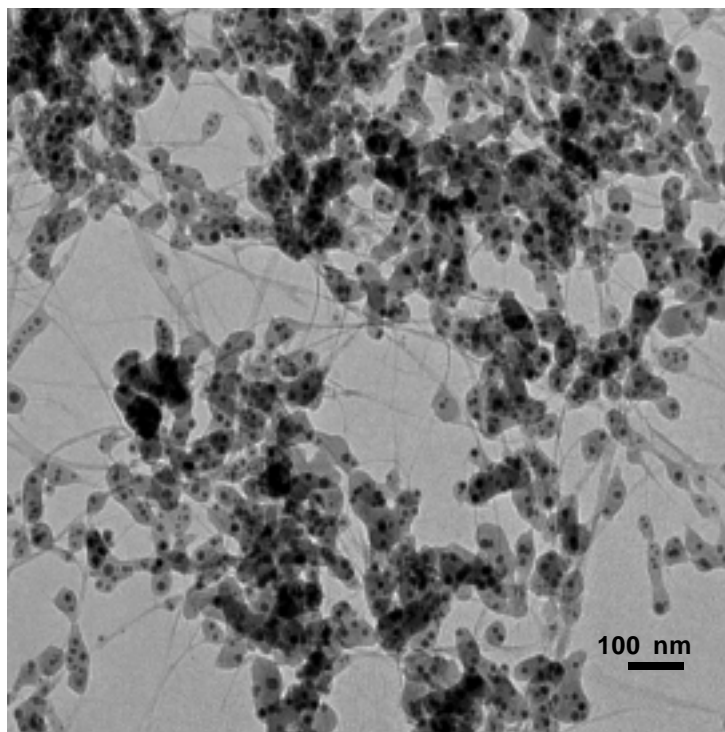
This year we have made significant advances in the synthesis, purification and cutting of SWNT materials resulting in greatly increased hydrogen adsorption on a sample wt% basis. We now can produce 1.5 g / day of material containing ~ 20–30 wt% SWNTs using the method of pulsed laser vaporization. We have developed a simple 3-step method which results in SWNTs that are > 98 wt% pure without a significant loss in SWNT content. We have also developed a thermal gravimetric analysis method that for the first time enables highly accurate determination of SWNT wt% content in carbon soots. Finally we have pioneered a gentle cutting process which enables 3.5 – 4.5 wt% hydrogen adsorption on our purified laser materials. The adsorption occurs in two separate sites and conveniently, all of the adsorbed hydrogen is effectively capped by CO₂ resulting in the hydrogen’s stability under atmospheric conditions for several weeks. The temperature at which hydrogen desorption occurs appears to vary with material and specific cutting conditions. In the future we will explore the hydrogen adsorption properties on materials with SWNTs of highly specific diameters, and we will also vary the parameters of our cutting scheme in order to further optimize H₂ adsorption properties. Presently our cutting method is suitable only for mg sized samples. We will endeavor to scale-up the method so that large scale measurements may be made on our high precision Seivert’s apparatus which will allow hydrogen uptake to be measured at increased pressures. We will explore methods of further aligning the SWNTs so that a compact storage system may be achieved. Finally we will employ Raman, nuclear magnetic resonance and conductivity measurements on the initial and hydrogen charged SWNT samples in order to gain a better understanding of the two unique hydrogen interactions. We anticipate that all of these exploratory efforts will enable increased hydrogen adsorption on larger SWNT samples.

References

- (1) Cannon, J.S. in *Harnessing Hydrogen* INFORM, Inc., New York, 1995
- (2) N.E.S., 1991/1992,
- (3) Flavin, C. and Lessen, N. in *Power Surge* W.W. Norton & Co., New York, 1994
- (4) Dillon, A.C., Bekkedahl, T.A., Cahill, A.F., Jones, K.M. and Heben, M.J. *Carbon Nanotube Materials for Hydrogen Storage* 1-521 (Coral Gables, FL, 1995).
- (5) Carpetis, C. and Peschka, W., *Int. J. Hydrogen Energy* 1980, 5, 539.
- (6) Schwarz, J.A. *Modification Assisted Cold Storage (MACS)* .
- (7) Schwarz, J.A. *Activated Carbon Based Storage System* 1-271 (Honolulu, HI., 1992).
- (8) Gregg, S.J. and Sing, K.S.W. in *Adsorption, Surface Area and Porosity* Academic Press, London, 1982
- (9) Breck, D.W. in *Zeolite Molecular Sieves: Structure, Chemistry and Use* Wiley, New York, 1974
- (10) Pederson, M.R. and Broughton, J.Q., *Phys. Rev. Lett.* 1992, 69, 2689.
- (11) Thess, A., Lee, R., Nikolaev, P., Dai, H., Pitit, P., Robert, J., Xu, C., Lee, Y.H., Kim, S.G., Rinzler, A.G., Colbert, D.T., Scuseria, G.E., Tomanek, D., Fischer, J.E. and Smalley, R.E., *Science* 1996, 273, 483.
- (12) Dillon, A.C., Parilla, P.A., Jones, K.M., Riker, G. and Heben, M.J., *Mater. Res. Soc. Conf. Proc.* 1998, 526, 403.

- (13) Rinzler, A.G., Lui, J., Dai, H., Nikolaev, P., Huffman, C.B., Roderiguez-Macias, F.J., Boul, P.J., Lu, A.H., Heymann, D., Colbert, D.T., Lee, R.S., Fischer, J.E., Rao, A.M., Eklund, P.C. and Smalley, R.E., *Appl. Phys. A* 1998, 67, 29.
- (14) Tohji, K., Goto, T., Takahashi, H., Shinoda, Y., Shimizu, N., Jeyadevan, B., Matsuoka, I., Saito, Y., Kasuya, A., Ohsuna, t., Hiraga, K. and Nisshina, Y., *Nature* 1996, 383, 679.
- (15) Kinoshita, K. in *Carbon: Electrochemical and Physicochemical Properties* John Wiley and Sons, New York, 1988 Ch. 3.
- (16) Dillon, A.C., Gennett, T., Jones, K.M., Alleman, J.L., Parilla, P.A. and Heben, M.J., *Adv. Mat.* 1999, 11, 1354.
- (17) Dillon, A.C., Jones, K.M., Bekkedahl, T.A., Kiang, C.H., Bethune, D.S. and Heben, M.J., *Nature* 1997, 386, 377.

a)



b)

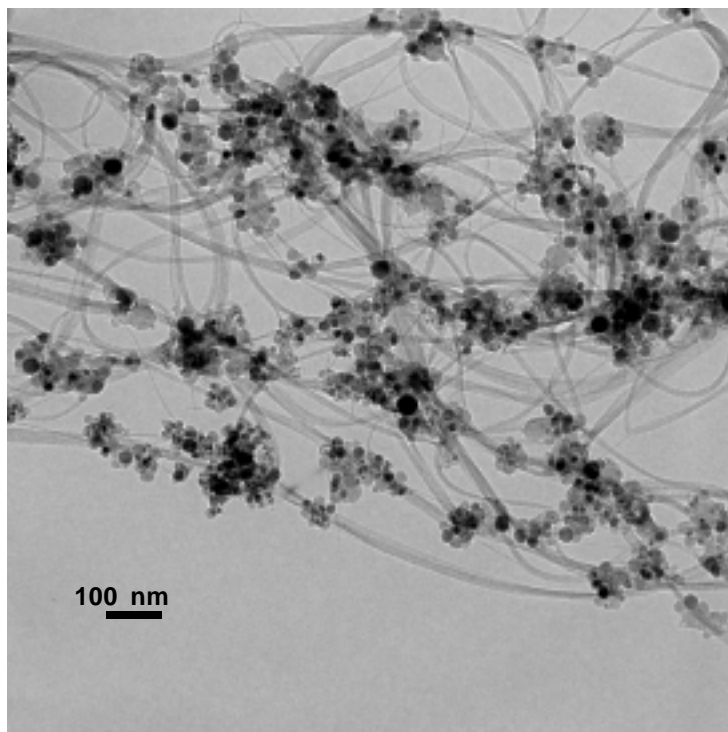


Figure 1: TEM images of SWNT soots produced by a) arc discharge and b) pulsed laser vaporization.

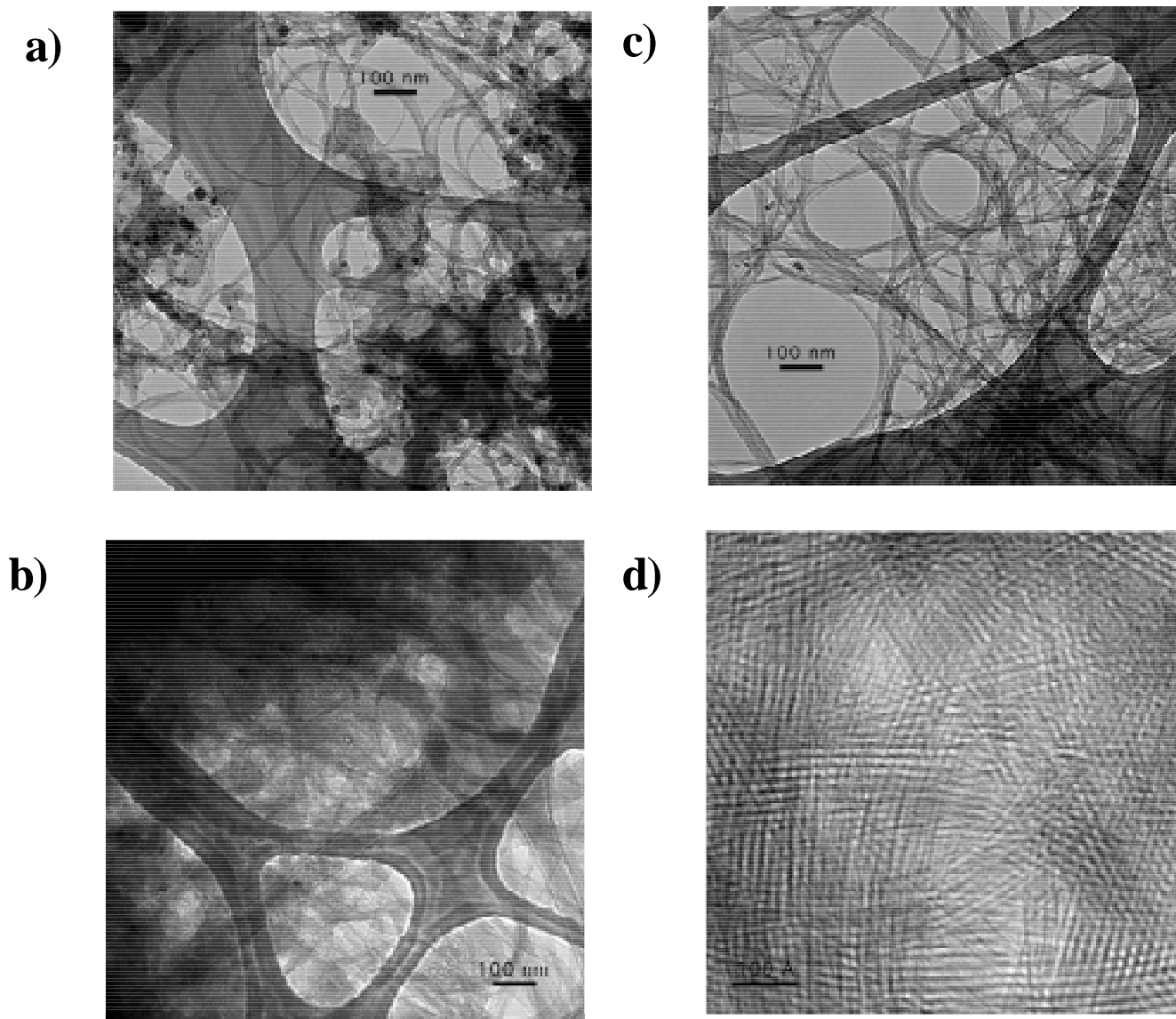


Figure 2: TEM images of: (a) as-produced $\sim 20 \text{ W/cm}^2$ laser-generated SWNT soot. (b) crude material which was refluxed for 16 h in 3M HNO_3 . (c) purified SWNTs produced by oxidizing the acid treated sample for 30 min. in air at $550 \text{ }^\circ\text{C}$, and (d) purified SWNTs at high magnification following a brief $1500 \text{ }^\circ\text{C}$ vacuum anneal.

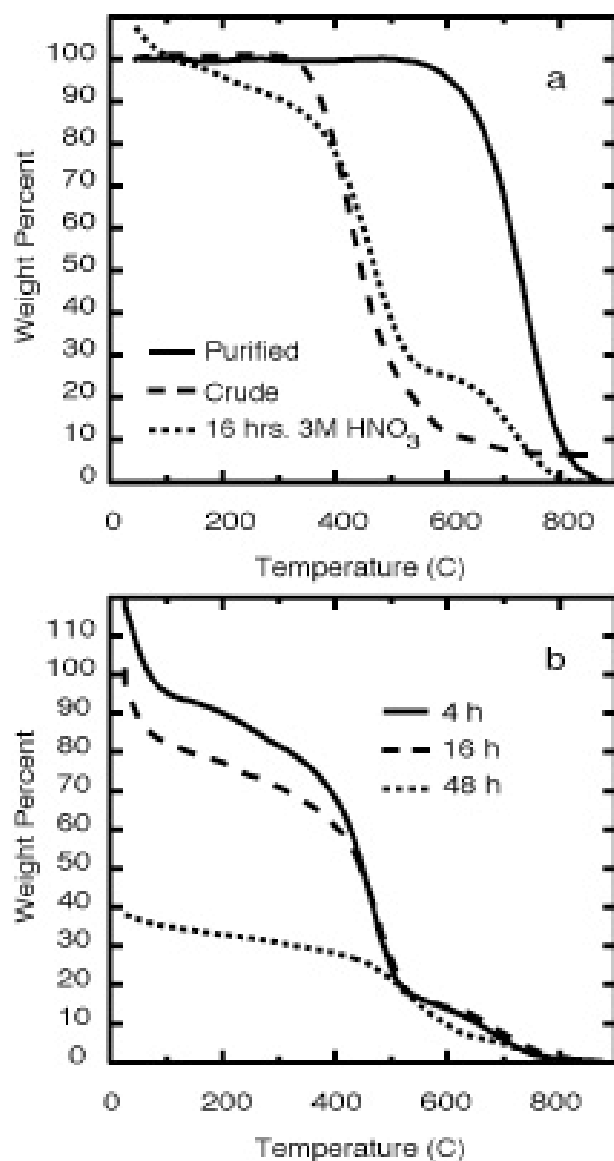
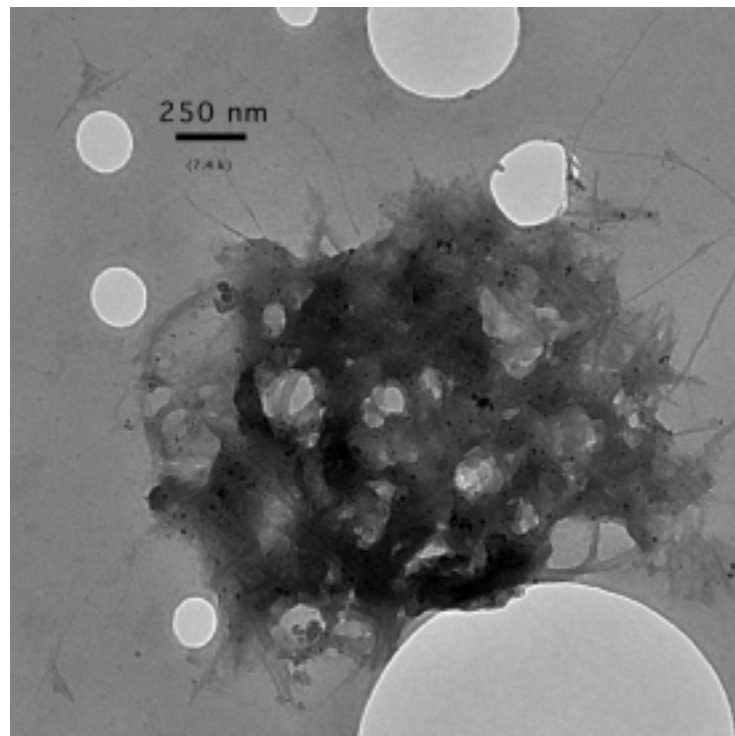


Figure 3: TGA curves for: (a) Materials produced at a laser power of $\sim 20 \text{ W/cm}^2$; purified, crude and crude soot after a 16 h reflux in 3M HNO_3 . The data for the refluxed material was normalized to 100 wt % at 100 °C to compare dry weights. (b) Materials produced with 30 W/cm^2 of laser power. Samples were refluxed in 3M HNO_3 for 4, 16 and 48 h. These curves were normalized to 100 wt % at 100 °C to compare dry weights, and then re-normalized to account for the different weight losses in the HNO_3 refluxes.

a)



b)

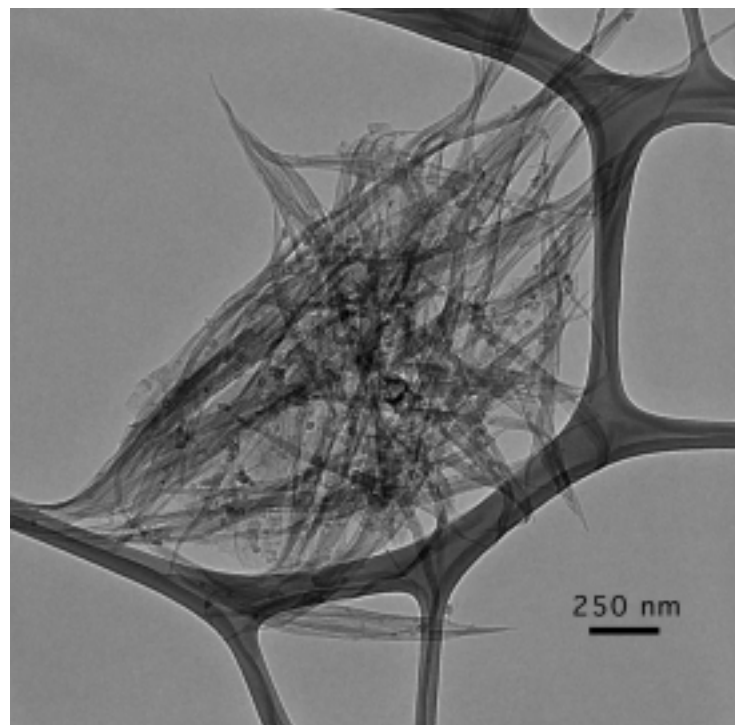


Figure 4: TEM images of a) previously cut SWNT crude materials and b) cut purified materials with the newly developed non-destructive method.

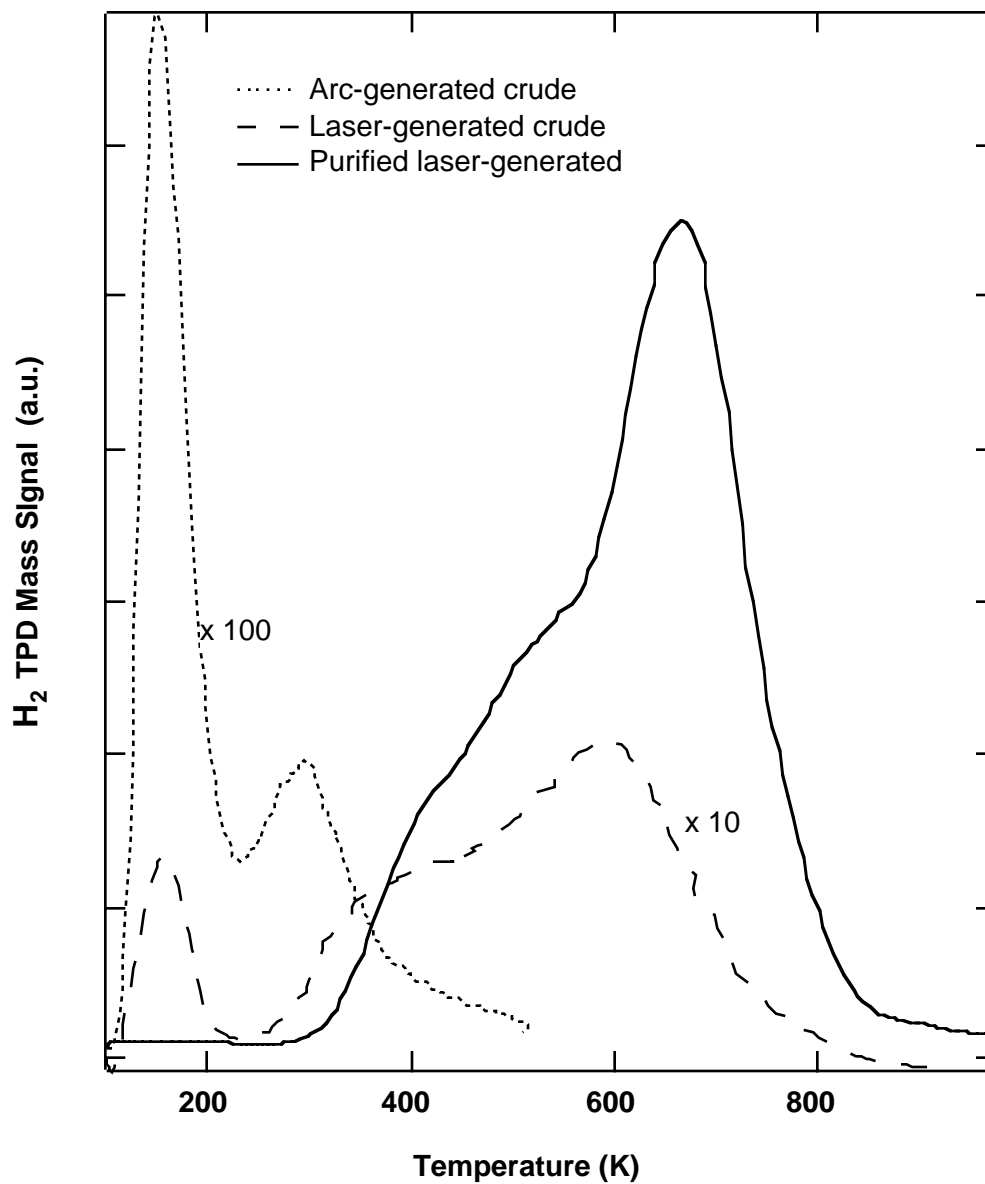


Figure 5: Hydrogen TPD spectra of degassed samples following a brief room temperature H_2 exposure at 500 torr for arc-generated crude, laser-generated crude and purified laser-generated SWNT materials .

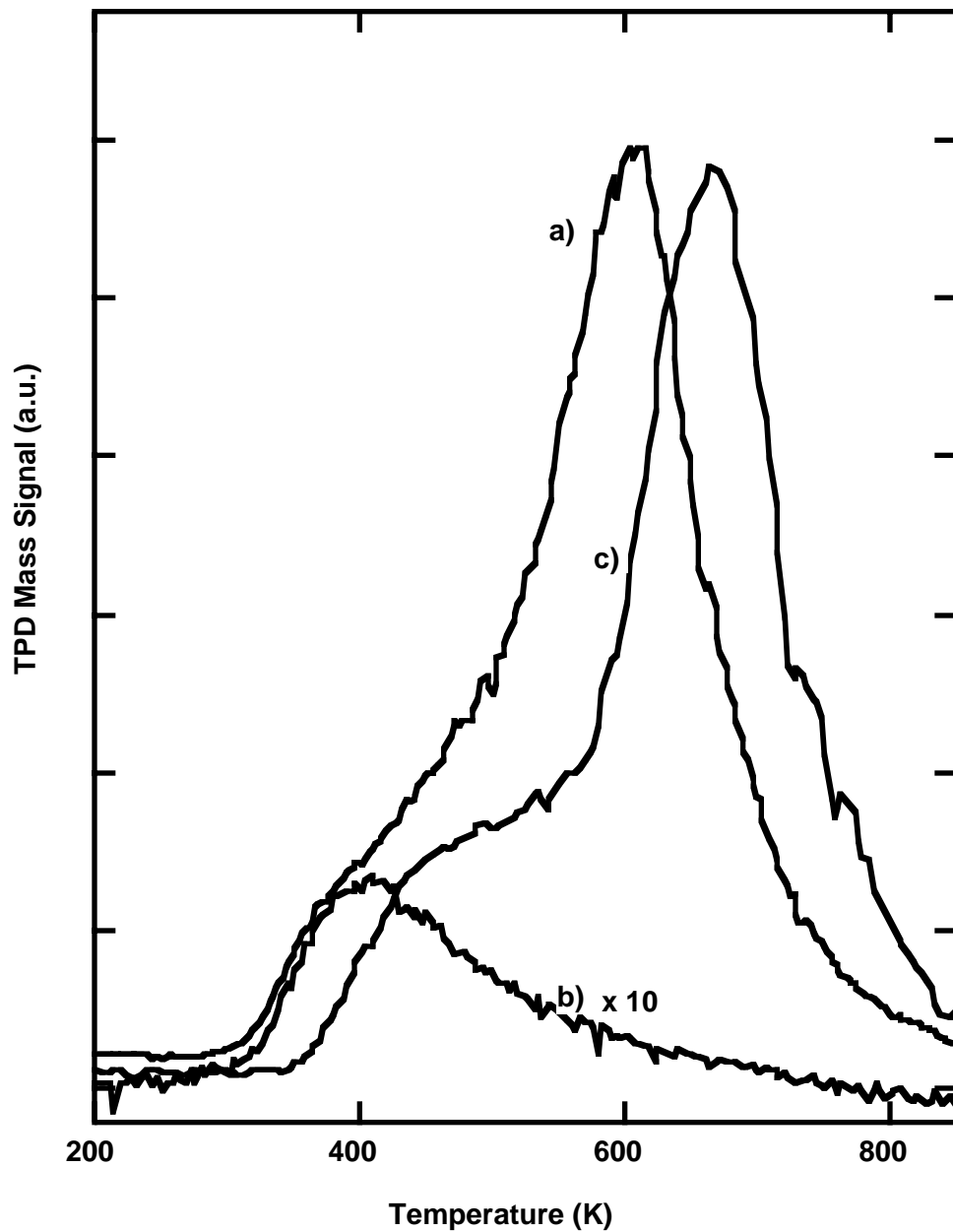


Figure 6: TPD spectra of a) the hydrogen desorption signal from an SWNT sample following a 500 torr hydrogen exposure at room temperature without any subsequent cooling of the sample, b) and c) display TPD desorption signals of CO_2 and H_2 respectively when an identical hydrogen exposure was followed by a CO_2 exposure.