

Hydrogen Storage on Carbon Nanotubes
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Single-walled carbon nanotubes are remarkable forms of elemental carbon. Their unique properties have stimulated the imaginations of many scientists and engineers to propose a wide range of applications. At NETL, the Advanced Materials Research team has looked at one of the proposed applications which is relevant to fuels for the future, and that is hydrogen storage.

Carbon nanotubes struck the fancy of chemists immediately on the first report of their existence by Iijima. It is interesting to look back on some of the connections that go along with this story. First, the discovery of nanotubes came out of an investigation of the soot left behind during the production of fullerenes by the arc discharge process. Even if fullerenes had no other practical value, we have the intense interest they generated to thank for the advent of the era in carbon nanotubes. Fullerenes were first identified by mass spectroscopy. This follows in the decades old tradition of chemists, that is the use of spectroscopic evidence as a prime tool to determine the structure of new molecules. The structure of nanotubes was obtained by a different approach, direct physical observation using transmission electron microscopy (TEM). Perhaps the full recognition and appreciation of this new form of elemental carbon had to await the development of powerful tools for visualization of objects on the nanoscale.

Nanotubes do have a dramatic visual impact. If beauty rests on symmetry, nanotubes have inherent beauty. Further, their cylindrical structures led to suggestions that they would be ideal gas storage materials. The appearance of these potential storage materials conveniently coincided with the revivification of interest in the hydrogen economy. The potential for coupling carbon-based storage materials to supply pure hydrogen to automotive fuel cell power plants was quickly seen. Initial reports of experiments showing high levels of hydrogen storage were encouraging. Theoreticians were then quick to calculate the possible amounts of hydrogen that could be stored using arrays of tubes of various sizes and packing parameters. Since the appearance of the initial reports, the results have been varied and controversial. Some are higher, some lower; some imply physisorption, and some chemisorption. It is clear that storage is a complex issue, partly because the materials are more far complex than the visual comprehension of the single ideal nanotube would allow.

Single-walled carbon nanotubes do not come to the laboratory experimentalist as ideal structures. Rather than being the perfect and straight cylinders typically depicted in illustrations, they more often look like piles of cooked spaghetti. If made by laser ablation or arc discharge, several forms of carbon besides nanotubes are typically present. Carbon clutter composed of amorphous carbon, fullerenes, "bucky onions", and graphitic debris may be present to a greater or lesser degree. Depending on their post-synthesis treatment there are variable numbers of defects in the structures. Not every sidewall may be perfect. There are holes here and there. Functional groups are attached to the edges of the holes and at the uncapped ends of the graphene walls. The metals used as catalysts in the synthesis are encapsulated in graphitic sheets, entwined in nanotube bundles, and resistant to efforts to separate them. Various methods have been developed to remove the

metals, but none is perfectly selective. Further, the tubes can be damaged when the metals are removed during the purification process.

Experimentalists engaged in hydrogen storage research are learning to deal with carbon nanotubes and their far from fully understood characteristics. Together with my colleagues at NETL, Drs. Edward Bittner and Milton Smith, an investigation of hydrogen adsorption was begun that has developed two main aspects. One aspect is analytical. Other than visual inspection by TEM, how does one learn about the complexity of the particular sample of nanotubes in question? Temperature programmed oxidation is one way to characterize samples of tubes based on chemical reactivity. An example is shown in Figure 1. During thermal gravimetric analysis (TGA) using air it is seen that the rate of weight loss varies as the temperature is increased. The differential of this weight loss curve can be fit by a series of peaks, thus indicating that the oxidation proceeds in defined stages. If different parts of the sample required different temperatures for oxidation, it seemed logical that peaks in the differential of the TGA could be manipulated by choice of the gas stream used in the analysis. In fact, each peak shifts to lower temperature when pure oxygen is substituted for air, and to higher temperatures when carbon dioxide is used. Significantly, some peaks were well separated under carbon dioxide, suggesting that part of the sample could be selectively removed by limiting the oxidation temperature at a value between the low and high temperature regions. In fact, this idea worked quite well when it was transposed from an analytical to a larger scale using samples on the order of a fraction of a gram. That result led in turn to a pleasing discovery about hydrogen storage capacity.

A brief description of our measurement of hydrogen storage capacity is necessary before discussing the results. In general, determinations of gas uptake have been made based on either pressure change or gravimetric methods. Each method has advantages and disadvantages. We chose to use a recently developed instrument, a tapered-element pulse mass analyzer, for the determination of isotherms. Attractive features of this instrument include a flow through design that promotes good contact of the gas stream with the sample in the packed bed and good time resolution with the measurement of small mass changes. This allows both the amount of gas that is adsorbed and the rate of its adsorption to be probed. The latter is an important consideration in discerning physisorption from chemisorption. We have found that in progressing through a programmed pressure experiment, the weight of the sample bed reaches equilibrium within seconds after each pressure jump. This is consistent with a purely physisorption process. Five examples of isotherms obtained with this instrument are given in Figure 2. The first is for a sample of single-walled nanotubes made by the laser ablation method. They were purchased in the "raw" and the purified forms. The nitric acid treatment used in the purification reduces the metals content and removes extraneous carbon material. For both the raw and purified tubes, the storage capacity is lower than that of an activated carbon when measured at 25 C and 700 psia, the upper pressure limit of our instrument. Still it is evident that higher pressures would lead to greater storage. The adsorption capacity increased significantly after partial oxidation under temperature controlled conditions with carbon dioxide. A further increase was found after the oxidized samples were heated to 700 C in helium, which drove off a large fraction of the oxygenated functional groups. This combination of CO₂ oxidation and mild pyrolysis increased the hydrogen capacity of the original sample by a factor of nearly three. Thus, nanotubes are

amenable to activation. Many techniques have been developed to activate conventional carbons over the years. Perhaps a similar array of methods can be employed to tailor the adsorption properties of nanotubes as well.

This work has a theoretical as well as experimental dimension. Prof. Karl Johnson of the University of Pittsburgh has been simulating the physisorption of hydrogen and other gases on nanotubes for several years. He is now modeling these experimental results with his graduate student Wei Shi. The more refined models take into account complex arrays of nanotubes and the introduction of functional groups. The Monte Carlo simulation for an array of tubes of similar dimensions as the purified sample that was used at NETL agrees with the experimental results quite well. The next step is to identify the physical and chemical features of a nanotube array that would lead to the result obtained with the carbon dioxide activated materials. This coordinated approach leads to the design of better experiments both in the laboratory and on the computer.

Where does this leave us and what are the prospects? A storage capacity of 1 wt % hydrogen is considerably short of the stated DOE target of 6 wt%. Going to higher pressures with this sample would bring us closer, but probably not to the target level. Nonetheless, avenues for improving storage capacity remain open. Methods for chemical activation are a long way from being exhausted or optimized. The reasons for the improved performance we have seen are not yet clear, but further experiments can tell us more. Much attention has been devoted to single-walled nanotubes, but multi-walled tubes may offer potential as well. One thing may already be evident. The best material for gas storage may not be the ideal nanotube structures and arrays frequently assembled in theoretical studies, but a chemically and physically disordered array engineered to provide molecular nooks and crannies better able to trap and retain hydrogen. Build a better hydrogen trap and the world will drive to your house in a fuel cell powered car.

Having spent a good bit of time working in a national laboratory that has devoted considerable attention to coal, the whole new field of nanotube research brings special associations to mind. The inherent problems in characterizing both materials are in many ways strangely similar. Both are black, insoluble materials. Both contain an inorganic component that originated in the formative process; the intimately mixed mineral matter in coal and the encapsulated catalytic metals in nanotubes. Both have intriguing pore structures that have sparked controversy. The "blind" pores of coal have their answer in capped carbon nanotubes. Oxygenated functional groups play a big role for both. Pyrolysis has been used to release these groups in both cases. The potential for making derivatives at carboxylic and phenolic sites has been well explored for coal and is now beginning to be exploited for tubes. Both are held together strongly by intermolecular forces and associative bonds that are not totally understood. Both swell and take in solvents to various degrees. Considering these parallels it seems displaced coal chemists would find characterization of carbon nanotubes a fruitful area to work in. Techniques that have been developed over the last few decades to investigate the structure of coal would undoubtedly be helpful. Some valuable insights have been recently reported that resulted from using techniques reminiscent of those used in coal characterization and one anticipates far greater progress in the near future.

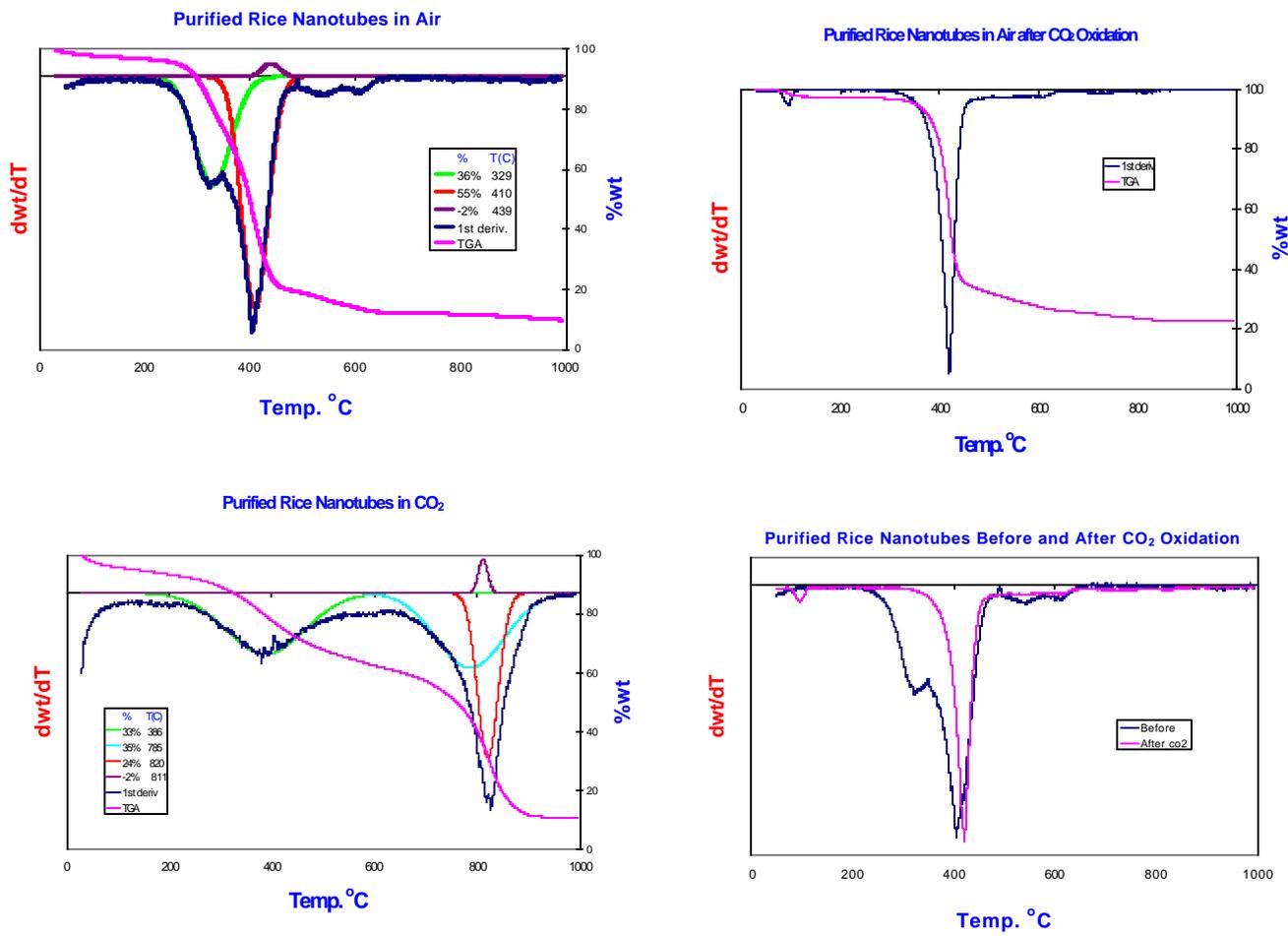


Figure 1. Investigation of single-walled carbon nanotubes by TGA. Carbon dioxide provides better resolution and can be used to selectively remove the most reactive components of a purified nanotube sample.

Activation improves hydrogen adsorption on nanotubes

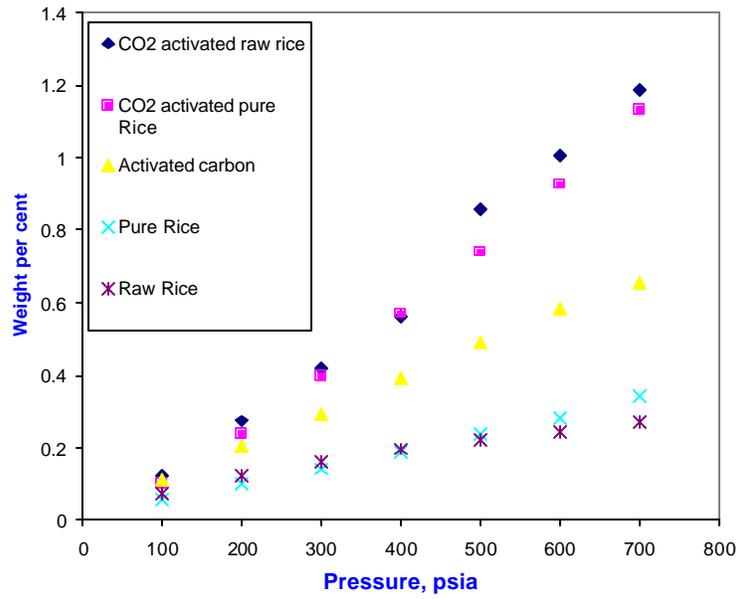


Figure 2. Activation of carbon nanotubes using CO₂ improves their hydrogen storage capacity.

