Hydrogen Adsorption on Single Walled Carbon Nanotubes (SWNT)

B. K. Pradhan, A. R. Harutyunyan, G. U. Sumanasekera and P. C. Eklund
Dept. of Physics, 104 Davey Laboratory, The Penn State University,
University Park, PA-16801, USA

Introduction

The ever-growing demand for energy, mediated by the 1990 Clean Air Act and 1992 Energy Policy Act in the United States has pointed out the need for the developments of cleaner fuels and more efficient engines. Because of a limited supply and adverse environmental problems, fossil fuels must be replaced with pollution-free fuels derived from renewable resources. For these reason, Hydrogen is an ideal candidate providing more energy than fossil fuel on a weight basis. Carbon materials may provide an inherently safe and potentially high energy density hydrogen storage method, and they are now under serious study. Recently reports of very high, reversible adsorption of molecular hydrogen in nano-carbon materials, i.e., pure carbon nanotubes, alkali-doped graphites, and pure and alkali-doped graphite nanofibers (GNFs) have generated tremendous interest in the research community, stimulating much experimental works and many theoretical studies worldwide[1]. In this study, we demonstrate that significant amounts of hydrogen can be stored in SWNTs, depending on post synthesis treatment.

Experimental

The SWNTs materials (arc-discharge derived: Ni-Y catalyzed) were obtained from Carbolex. This raw material was processed to remove amorphous and multi-shell carbon and residual catalyst. To accomplish this, the materials were first subjected to a high temperature oxidation under flow of dry air, then refluxed with mild mineral acid (HCl) in order to remove the exposed catalyst particles. The details of the purification is described elsewhere[2]. These samples were characterized by HRTEM, TPO, Raman scattering and N_2 and CO_2 adsorption isotherms. Hydrogen uptake/storage measurements were carried out by using a gravimetric sorption analyzer (300-77K), which operates from 10^{-8} Torr to 20 bar pressure range. Ultra high purity H_2 was flowing through an oxygen/moisture trap was maintained at fixed pressure to abtain an isotherm. Prior to the hydrogen adsorption, the sample was degassed under high vacuum (10^{-8} torr) at 220-1000 °C overnight. Equilibrium at any pressure was usually achieved in less than 20 min. Most of the experiments were replicated to determine the reproducibility of the adsorption and desorption isotherms.

Results & Discussion

Figure 1 shows the transmission electron micrographs of the purified SWNTs. The typical rope diameter is 15-20 nm, containing 100-200 SWNTs with a length of a few microns. The average diameter of the individual SWNT is 1.4 nm, similar to (10,10) tube[3]. After selective oxidation to remove amorphous carbon, the metal catalyst was removed by acid treatments. Figure1 shows the TEM images of the purified sample, without any wall damage (Fig. 1a:C-SWNTs, with 2 metal at %)

and with extensive wall damage (Fig 1b:O-SWNTs, with 0.2 metal at %). The purity and amount of the SWNTs in the sample were evaluated semi-quantitatively by TPO and TEM[3]. A typical specific surface area (SSA) measured by BET was 270 m^2/g, which is 5 times lower than the outer surface area of individual tubes (1300 m^2/g). After purification, the SSA of the purified tubes increased for the C-SWNTs, while it decreased for O-SWNTs. Once these materials were heat treated, the SAA increases with heat treatment with temperature. The microporosity in the samples were measured by CO_2 adsorption isotherms at room temperature. O-SWNTs showed the highest degree of microporosity among the samples[2].

Figure 1c shows the hydrogen uptake at T=77K in different SWNTs sample containing different wt % of SWNTs. The wt % of SWNTs was estimated by DTPO[2]. Some of the samples subjected to post-synthesis treatments showed a factor of 3 increase of hydrogen storage over untreated samples. During these treatments, the sample wt loss was calculated to be as high as 15-40 wt %, and is tentatively assigned to the loss of surface oxygen groups on the carbon nanotube surface and attendant oxidation to CO/CO_2.

Conclusion

A systematic study has been done on SWNTs (as prepared and purified) for storage of hydrogen at 77 K and upto 16 bar of pressure. The post synthesis treatment of the purified SWNT material has been found to be critical for the high hydrogen uptake. However, we could not correlate the specific surface area of the SWNT samples with hydrogen uptake. In the open SWNTs, saturation of hydrogen adsorption takes place at pressures (P < 2 atm).

References:

1. M. S. Dresselhaus, K. A. Williams, P. C. Eklund, *MRS Bull.*45, 1999, 24
2. B. K. Pradhan *et al.,* under preparation.
3. M. S. Dresselhaus, G. Dresselhaus, P. C. Eklund*, Science of Fullerenes and Carbon Nanotubes*, (Academic Press, San Diego, 1996).

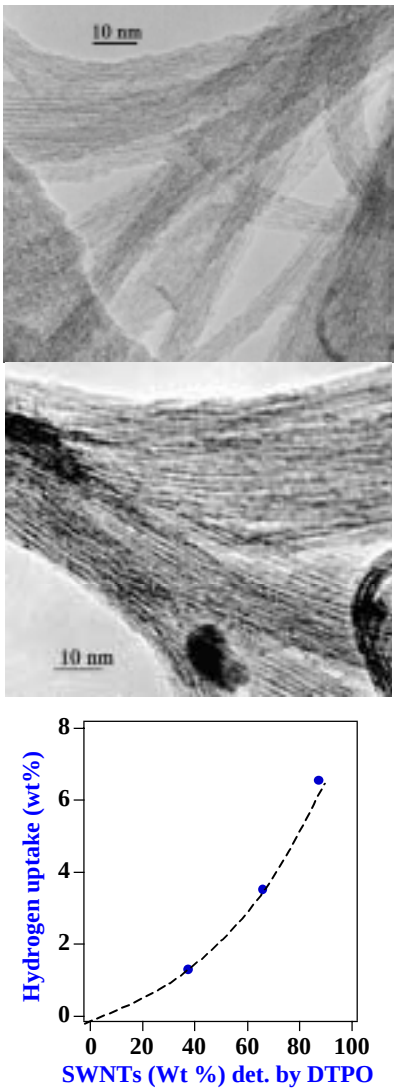

Figure 1. (a) and (b) are the TEM images for closed and open SWNTs respectively, (c) the relation between the hydrogen uptake and wt % of SWNTs in the samples.