

## CHAPTER II

### BACKGROUND AND LITERATURE SURVEY

#### 2.1 Hydrogen Storage

##### 2.1.1 Compressed Hydrogen Gas

Hydrogen is compressed in classical high-pressure tanks that are made of fairly cheap steel. Its advantages include simplicity of design and room temperature compressed gas storage. They are tested up to 30 MPa and regularly up to 20 MPa (Schlapbach and Züttel, 2001). Novel high-pressure tanks made of carbon-fiber-reinforced composite material are being developed; these are tested up to 60 MPa. The drawbacks are high volume, high pressure, low density, and difficult to control pressure.

##### 2.1.2 Liquid Hydrogen Storage

Hydrogen is condensed into liquid hydrogen systems having the highest hydrogen density ( $70.8 \text{ kg/m}^3$ ), the lowest system volumes and acceptable safety characteristics. The drawback is high cost for liquefaction process (condensation temperature of hydrogen at 0.1 MPa is  $-252^\circ\text{C}$ ) and heat transfer through the container leads to hydrogen loss.

##### 2.1.3 Metal Hydride

Metal hydrides are chemical compound of hydrogen and metal. Metal can be used to absorb and retain hydrogen under specific temperature and pressure condition and release hydrogen under different conditions. Hydrogen is usually located in the form of atom on interstitial sites of the host metal lattice. Their options for storing hydrogen are very dense and safe. However, metal hydrides are heavy, expensive, and release heat during the hydrogen absorption process ([http://www.wtec.org/loyola/nano/US.Review/09\\_03.htm](http://www.wtec.org/loyola/nano/US.Review/09_03.htm))

#### 2.1.4 Nanostructure Material

Nanostructure materials are a new class of materials with unique properties that stem from their reduced length scale ( $1 < d < 100$  nm). They have both carbon base materials such as carbon nanofibers, carbon nanotubes, carbon nanohorn, fullerenes, and non-carbon-base nanomaterials made of other atoms. Hydrogen is stored by adsorbing on surface of material (for carbon nanostructure ranging from 0 to 60 mass%) and perform best at cryogenic temperature. All these new carbon structures exhibit a nanoscale extension giving rise to new interactions of carbon with hydrogen (Hirscher *et al.*, 2003).

An ideal solid hydrogen-storage material (HSM) for practical applications in both economic and environmental reasons (Grochala and Edwards, 2004).

- 1) High storage capacity: minimum 6.5 wt% and at least 65 g/L of hydrogen available from material
- 2) Temperature for desorption is 60 – 120°C
- 3) Reversibility of the thermal adsorption/desorption cycle: low temperature of hydrogen desorption and low pressure of hydrogen adsorption
- 4) Low cost
- 5) Low-toxicity and possibly inert storage medium

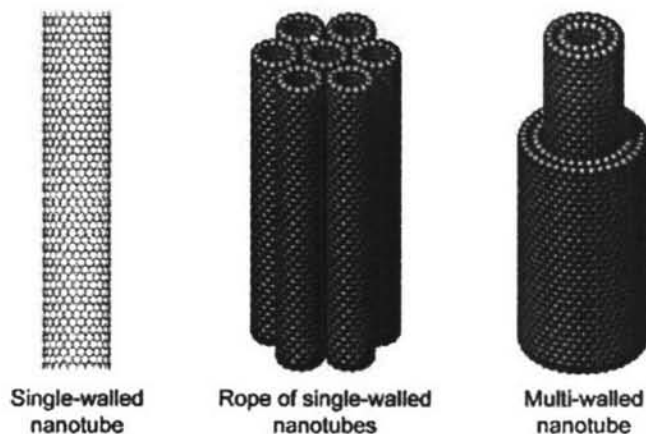
## 2.2 **Type of Carbon Based Material**

### 2.2.1 Activated Carbon

Activated carbon is normally made by thermal decomposition of carbonaceous material followed by activation with steam or carbon dioxide at elevated temperature. The structure of activated carbon consists of elementary microcrystallites of graphite, but these microcrystallites are stacked together in random orientation and it is the spaces between the crystals, which form the micropores. The graphite platelet structure gives the activated carbon its very large surface and porosity, which allows it to adsorb a wide range of compounds.

### 2.2.2 Carbon Nanotubes

The discovery of carbon nanotubes (CNTs) is in 1991 by Iijima (1991). CNTs are formed by rolled graphite sheets, with an inner diameter starting from 1 nm up to several nm and a length of ten to one hundred  $\mu\text{m}$ . The CNTs are described as usually closed on both sides by a hemisphere, i.e. half of a fullerene. Tubes formed by only one graphite layer are called single wall nanotubes (SWNTs) and those consisting of multiple concentric graphite layers are called multi-wall nanotubes (MWNTs). The schematic diagrams of SWNTs and MWNTs are shown in Figure 2.1. The interlayer distance in MWNTs is close to the interlayer distance in graphite. The diameter of SWNTs varies from 1 to 3 nm, whereas MWNTs show typical diameters of 30 to 50 nm. Other features of CNTs are their chemical inertness and thermal stability. They are thermally stable up to over  $1000^\circ\text{C}$  in vacuum (Züttel *et al.*, 2001).



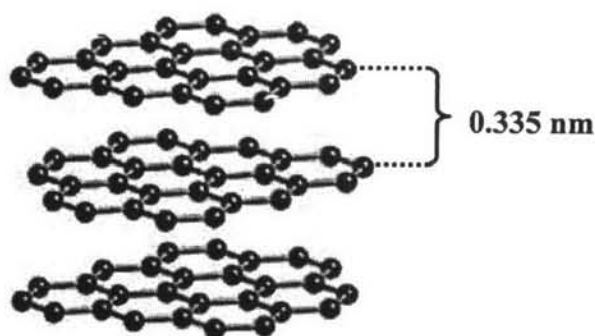
**Figure 2.1** Representation of the carbon nanotube structures.

([http://www.nanotechnologies.qc.ca/projets/hydrogene/images/en/nanotubes\\_large.jpg](http://www.nanotechnologies.qc.ca/projets/hydrogene/images/en/nanotubes_large.jpg))

### 2.2.3 Graphite

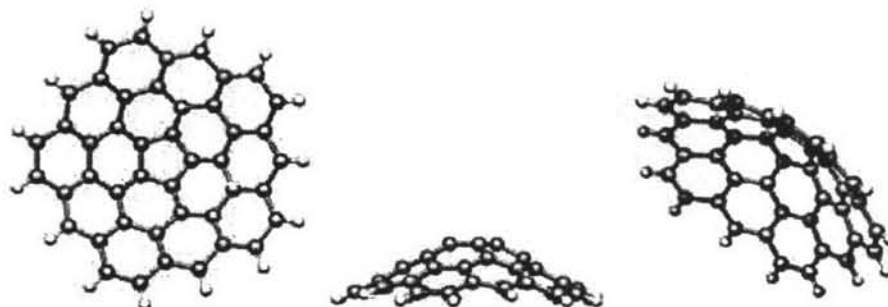
Graphite is one of the standard forms of carbon. The atoms are arranged in sheets, in a hexagonal pattern like chicken wire, as shown in Figure 2.2. The sheets lie on top of each other. Graphite is a layered solid in which the various

planes are bonded by van der Waals forces where the minimum distance between the carbon layers for single-crystal graphite is 0.335 nm. In this crystalline structure, delocalize  $\pi$  electrons form a cloud above and below the basal plane, and it is this arrangement that imparts a certain degree of metallic character to the solid that results in a relatively high electrical conductivity across each carbon layer. The interlayer spacing in graphitic materials is a property dependent on a number of parameters, including the nature and the thermal history of the precursor, and can vary between 0.335 and 0.342 nm, which by appropriate intercalation procedures can be expanded to values of 0.9 nm (Dressellhaus *et al.*, 1993). Unfortunately, in its conventional form, graphite has an extremely low surface area (about  $0.5 \text{ m}^2/\text{g}$ ), and this aspect tends to limit its usefulness as a practical selective adsorption agent.



**Figure 2.2** Representation of the graphite structure.

<http://www.science.org.au/nova/024/024img/graphite.jpg>



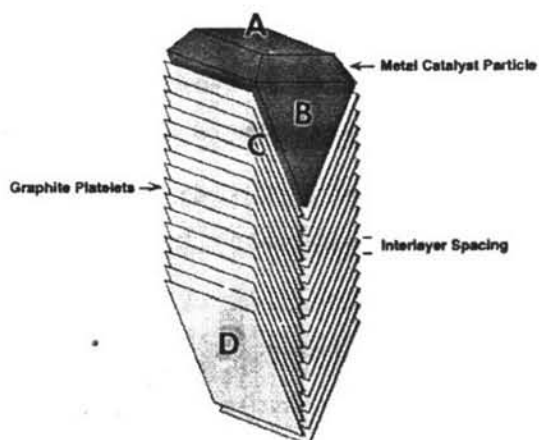
**Figure 2.3** Inserting a 5-sided pentagon into a sheet of 6-sided hexagons in graphite same structure from different angles.

(<http://www.ewels.info/img/science/graphite/penthept/p2.jpg>)

Recently, much attention has been paid to the investigations of the hydriding properties of carbon-related materials with specific nanometer-scale structures. Orimo *et al.* (1997) applied the mechanically milling method to prepare nanostructured materials. Formation of a nanostructure graphite by mechanical milling method had also been reported (Fukunaga *et al.*, 1998). With this method, the nanostructure can be modified continuously and homogeneously by optimizing the operating parameters, like the milling atmosphere, and the amount of additional elements, and so on. Therefore, the property of high surface area can be obtained. Moreover, hydrogen in the mechanically prepared nanostructure graphite provides a very interesting system from the viewpoint of basic research as well as for design of new carbon-related materials.

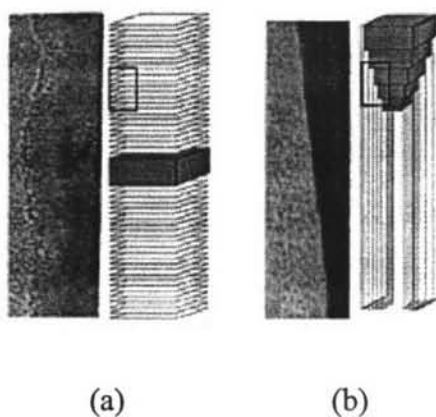
#### 2.2.4 Graphite Nanofiber

Graphite nanofibers (GNFs) are the product of the decomposition of certain hydrocarbons over selected metal particle (Rodriguez *et al.*, 1995). The material consists of graphene sheets. Graphene has a similar structure to graphite but it is a single isolated sheet of carbon, the orientation of which can be controlled by the choice of the catalyst used in the preparation procedure. Three distinct structures may be produced: 'tubular' (90°), 'platelet' (~0°) and 'herringbone' (45°) where the angle in parentheses indicates the direction of the nanofiber axis relative to the vector normal to graphene sheets, as shown in Figures 2.4 and 2.5, respectively.



**Figure 2.4** Schematic diagram of a catalytically grown carbon nanofiber, herringbone.

([http://www.wtec.org/loyola/nano/US.Review/fh09\\_02.gif](http://www.wtec.org/loyola/nano/US.Review/fh09_02.gif))

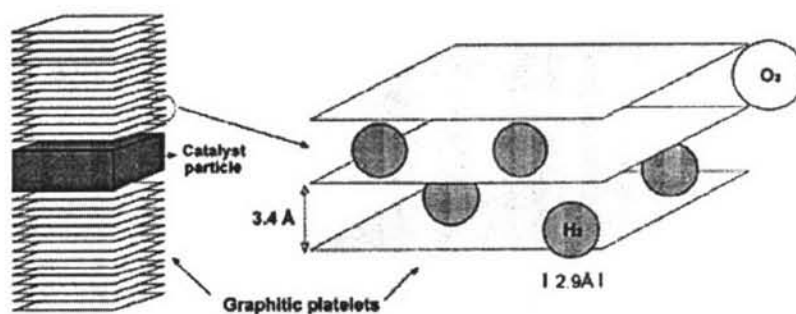


**Figure 2.5** High resolution electron micrographs and schematic representation of carbon nanofibers with their graphite platelets, (a) "platelet" and (b) "tubular" to the fiber axis.

([http://www.wtec.org/loyola/nano/US.Review/fh09\\_03.gif](http://www.wtec.org/loyola/nano/US.Review/fh09_03.gif))

The GNFs are packed closely together. They consist of stacks of graphite platelets and vary from 5 to 100 mm in length and from 5 to 100 nm in

diameter. The spacing between graphite layers in each case is the same value found in conventional graphitic carbon,  $\sim 3.4 \text{ \AA}$  while the hydrogen molecules have a diameter of 0.26 nm. Multiple layers of hydrogen could be squeezed into the gap if the molecules interact strongly with the electrons in the graphite. When the hydrogen is adsorbed by the graphite, they lose a lot of rotational energy and shrink to an effective radius of 0.064 nm. Scientists predict that they could probably produce five layers of hydrogen through one graphite slit. This will allow a dramatic increase in hydrogen storage (<http://www.rdg.ac.uk/~scscharip/tubes.htm>).



**Figure 2.6** Schematic representation of the structure of a graphite nanofiber and details of the hydrogen absorption process.

([http://www.wtec.org/loyola/nano/US.Review/fh09\\_04.gif](http://www.wtec.org/loyola/nano/US.Review/fh09_04.gif))

Pretreatments of GNFs may induce changes in carbon structure and lead to increased hydrogen storage capacity. Park *et al.* (1999) attributed the increase in hydrogen storage levels following high-temperature inert gas treatment of herringbone GNFs to remove oxygen functional groups that blocked access of hydrogen to the internal graphite surfaces as shown in Figure 2.6. Support for this concept was provided in a related study with SWNTs that showed that high-temperature pretreatment removed surface functionalities responsible for the blocking pore (Kuznetsova *et al.*, 2000). These procedures included heat treatments in oxidative, reductive, and inert atmospheres.

### 2.3 Hydrogen Storage in Nanostructure Graphite and Related Materials

Isobe *et al.* (2004) examined the catalytic effect of 3d transition method on hydrogen storage properties in nanostructural graphite prepared by ball milling under H<sub>2</sub> atmosphere (1 MPa and room temperature). The Fe-, Co-, Ni- and Cu-doped nanostructure graphite resulted in the hydrogen adsorption up to ~4 wt% by milling for 32 h (~7 wt% for 80 h), and two peak of H<sub>2</sub> were desorbed around 460 and 780°C by Thermal Desorption Spectroscopy (TDS) method. On the other hand, the Co-doped graphite indicated that adsorbed H<sub>2</sub> reached up to ~2 wt% by milling for 32 h. The Ni- and Cu-doped graphites did not show any improvement for hydrogen storage. Therefore, the catalytic effect on hydrogen storage properties strongly depended on the affinity of graphite and doped metals.

Orimo *et al.* (1999) showed that nanocrystalline graphite is able to store a large quantity of hydrogen (7.4 wt %) for graphite ball milled for a maximum of 80 h in 1 MPa H<sub>2</sub> atmosphere. The hydrogen adsorbed in the sample was determined by means of oxygen-combustion hydrogen analysis. However, they found that the hydrogen is at least partially covalently bond to the graphite.

Hirscher *et al.* (2002) studied the milling process, which affected hydrogen storage in carbon nanostructures, graphite, GNFs and SWNTs. The microstructure of all starting materials was modified by ball milling. They found that SWNTs could adsorb lower than 0.1 wt% of H<sub>2</sub> under 0.08 MPa D<sub>2</sub> atmosphere at room temperature after they were ball milled 24 h under Ar using TDS apparatus, which D<sub>2</sub> was desorbed at 285°C. For reactive ball milling under D<sub>2</sub>, they found that adsorbed D<sub>2</sub> on GNFs and SWNTs was desorbed at 450°C, whereas graphite reached its maximum desorption at 630°C. In addition, a hydrogen capacity for SWNTs was 1.0 wt%, 0.5 wt% for GNFs and 0.3 wt% for graphite. Ball milled graphite, GNFs and SWNTs showed a small reversible hydrogen uptake for SWNTs. However, Orimo *et al.* (1999) reported a storage capacity of 5 wt% for graphite ball milled 24 h under 1 MPa H<sub>2</sub> atmosphere.

Li *et al.* (2001) studied amount of hydrogen uptake by graphitize MWNTs. They discovered that MWNTs can be used for hydrogen storage under 10 MPa and



at room temperature. The structure and crystallinity of the CNTs appeared to have an important effect on the hydrogen storage capacity. Proper crystallinity with some discontinuous graphene sheets and gaps may be propitious for hydrogen spreading into CNTs, and a stable structure is helpful for hydrogen reacting with the wall of CNTs. Moreover, they found that heat treatment at high temperature resulted in a high H<sub>2</sub> storage capacity because its degree of order was significantly improved.

Poirrier *et al.* (2001) obtained less than 1 wt% of H<sub>2</sub> adsorption on carbon nanofibers and activated carbon at 10.5 MPa and room temperature using volumetric method. The nanofibers were synthesized by catalytic decomposition of acetylene on a nickel-copper catalyst. At 10.5 MPa, the quantity of hydrogen adsorbed per unit surface area was much larger on nanostructures than on activated carbon. This suggested that increasing in the surface area could possibly lead to interesting hydrogen storage capacity. They found that the presence of different nickel-copper ratios in the catalyst led to changes in crystalline structure and specific surface area. Therefore, the proportional of metallic components could play a role in optimization of the hydrogen storage capacity of these materials.

Strobel *et al.* (1999) focused on the hydrogen adsorption on carbon materials at hydrogen pressure up to 12.5 MPa and ambient temperature (27°C) using isothermal gravimetric analysis. The measured hydrogen adsorption capacities were a maximum of 1.6 wt% H<sub>2</sub> in activated carbon and 1.3 wt% H<sub>2</sub> in nanofibers.

Züttel *et al.* (2001) synthesized MWNTs by pyrolysis of acetylene. The MWNTs and the high surface area graphite as well adsorbed hydrogen up to 5.5 wt% at -196°C and 1 MPa. The hydrogen desorption was investigated by the TDS method. However, at room temperature, the capacity dropped to 0.6 wt% under 6 MPa and 27°C. They discovered that large storage densities at room temperature were possible; however, the hydrogen tends to covalently bind to the carbon when the adsorption and desorption took place at elevated temperature and higher than 80°C and 300°C, respectively.

Chambers *et al.* (1998) described their findings on various carbon nanostructures. Hydrogen gas applied at 11.35 MPa was adsorbed at room temperature (25°C) measured by the constant volumetric method. The hydrogen

storage capacity was found to be for tubular CNTs 11.26 wt%, for herringbone carbon nanofibers 67 wt%, for platelet carbon nanofibers 53 wt%, and finally for graphite 4.5 wt%.

Park *et al.* (1999) confirmed their results of an important hydrogen molecule intercalation between the graphene sheets of the nanofibers. Unfortunately, these extraordinary high values, until today nobody has been able to reproduce these results, neither experimentally nor theoretically. Nevertheless, there have also been suggestions that the presence of defects in the GNFs structure may play a role in the dissociation of H<sub>2</sub> leading to subsequent intercalation (Browning, 2002).

Fan *et al.* (1999) investigated the hydrogen adsorption of vapor-grown carbon nanofibers with a diameter of 5 nm to 300 nm. The fibers adsorbed hydrogen up to 12.38 wt% when hydrogen pressure of 12 MPa and 25°C were applied by the constant volumetric method. The adsorption equilibrated upon 200 – 300 min.

Nijkamp *et al.* (2001) presented a survey of the storage capacities of the large number of different adsorbents for H<sub>2</sub> at -196°C and 0.1 MPa. Results were evaluated to examine the feasibility and reversible storage systems based on physisorption of H<sub>2</sub> on adsorbents. It was concluded that microporous adsorbents, e.g. zeolites, activated carbon, displayed appreciable sorption capacities. Based on their micropore volume (~ 1 mL/g) carbon-based sorbents displayed the largest adsorption (238 mL (STP)/g) because their intrinsic interaction with H<sub>2</sub> seems to be slightly stronger than that with oxidic adsorbents, and their micropore volume could probably be increased to a value above 1 mL/g.

Lueking *et al.* (2004) studied pretreatment of the GNFs. A herringbone GNFs structure possessing a relatively short-range crystalline order and a significant number of dislocations was found to exhibit the highest H<sub>2</sub> adsorption capacities, which were exposed to several pretreatment procedures, including oxidative, reductive, and inert environments. The procedure that ultimately resulted in the highest desorption was an in situ H<sub>2</sub> pretreatment of herringbone GNFs for 1 h at 700°C. The hydrogen capacity has ranged from 3.3 to 3.8 wt% after exposure at 6.9 MPa and room temperature (25°C) using constant volumetric method. Moreover,

they claimed that carbon materials have been highly disputed due to artifacts such as water contamination, metal contamination and/or temperature effect.

Tibbetts *et al.* (2001) claimed that utilizing relatively low pretreatment temperatures did not improve the ability of nanofibers to store hydrogen. On the other hand, it should be noted that both Gupta and Srivastava (2000) and Browning *et al.* (2002) were able to achieve significant hydrogen uptakes in GNFs material (10-15 and 4.16 wt%, respectively) after only a 150°C vacuum pretreatment.

Terres *et al.* (2005) synthesized spherical nanoporous carbons by pyrolyzing spherical MCM-48 (Schumacher *et al.*, 1999), impregnated homogenously with sucrose ( $C_{12}H_{22}O_{11}$ ), at 1000°C in an Ar atmosphere. They demonstrated that spherical nanoporous carbons exhibiting periodic arrays of channels and large surface area (1646 m<sup>2</sup>/g) can be stored H<sub>2</sub> up to 2.7 wt% under 0.2 MPa and at -196°C using a constant volumetric method. Moreover, they discovered that an alternative way to increase the amount of H<sub>2</sub> physisorbed occurred by optimizing the morphology of nanostructures of the adsorbent.

Cooper *et al.* (2004) studied the capacity of H<sub>2</sub> on carbon-based compositions by a reversible chemical hydrogenation/dehydrogenation process under pressure/temperature swing conditions in the presence of suitable catalysts. They found that one composition showed the ability to adsorb over 3.5 wt% H<sub>2</sub> at 110°C under 6.9 MPa H<sub>2</sub> and released the H<sub>2</sub> by decreasing in H<sub>2</sub> pressure to 0.12 MPa and increase in temperature to 180°C.

Chen *et al.* (1999) reported that a high H<sub>2</sub> uptake of 20 and 14 wt% can be achieved in milligram quantities of Li-doped and K-doped MWNTs adsorbed H<sub>2</sub> at room temperature, but they were chemically stable, and required elevated temperature (200 to 400°C) for maximum adsorption and desorption of H<sub>2</sub>. In their experiment, hydrogen uptake was measured by thermogravimetry analysis (TGA).

In contrast, Yang (2000) revisited these data. He prepared the doped nanotubes following the same procedure and also measured the adsorption-desorption using a thermogravimetric analyzer. His conclusion was that special caution needed to be taken to remove any moisture contamination of the hydrogen in measuring the adsorption. Moisture, which drastically increased the weight gain,

picked up and then put the results in error. So, for dry hydrogen, the adsorption is of 2.5 wt% for Li-doped and 1.8 wt% for K-doped CNTs. Results were confirmed by Pinkerton *et al.* (2000).

Dresselhaus *et al.* (1999) presented two geometrical estimates for the filling of a rope (crystalline lattice) of SWNTs. They assumed that hydrogen was a completely deformable fluid that filled the space not occupied by the CNTs, and the other was packed with H<sub>2</sub> molecules of kinetic diameter 0.29 nm on the inner walls and in the interstitial volume of the nanotubes. Using the geometrical model with close-packing of H<sub>2</sub> molecules led to 3.3 wt% H<sub>2</sub> adsorption within the tube and 0.7 wt% within the interstitial space, or a total of 4.0 wt% H<sub>2</sub> adsorption under 10 MPa. They concluded that for SWNTs hydrogen was stored in both pores formed by the inner tube cavities and the inter-tube space, and the storage density was possibly higher than that on a planar graphene surface.