HYDROGEN STORAGE ON ACTIVATED CARBON NANOTUBES

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The invention is related to hydrogen storage on single and multi-wall activated carbon nanotubes (CNT). Hydrogen is clean and renewable energy carrier and an H energy system is expected to progressively replace fossil fuels in future. Due to compressed gas, containers in vehicles have less volume than the classic ones. A clear picture of the true capacity of nanotubes for hydrogen storage is still being developed by efforts in experiment and theory. Because CNT received directly after synthesis, generally, have closed caps, methods for chemical activation are required to achieve their full potential. Results for SWCNT in which different forms of oxidation were used for activation and the MWCNT cleaned by PmPV used for H storage medium are presented. The whole process comprises activation of medium and hydrogen storage steps. Storage capacity of CNT for H can be calculated from the difference in pressure before and after equilibrium.

1. Introduction

In the late 20th century, fullerenes and carbon nanotubes (CNT) were discovered as new allotropic modifications of carbon [1,2]. Since then, the knowledge of new carbon structures and its derivates grows. The variety of new species is diverse, such as endo- [3], exo- [4] and heterohedral [5] fullerenes, functionalized [6] or filled single-walled (SWCNT) [7] and multi-walled (MWCNT) [8] carbon nanotubes, leaving a vast field of diverse new applications to be developed [9]. SWCNT are considered to be one-dimensional (1D) molecules due to their high length to diameter ratio [10], while MWCNT are a collection of concentric SWCNT, and as such, it is of great importance to understand and explore the possibilities of purifying the material on nanoscale level, with a special curiosity in size of tubes.

Recent publications concerning the hydrogen storage capacity of new nano-structured carbonic materials gave rise to the hope that energy problem of running out fossil fuels could be solved. An appropriate and safe hydrogen storage device would enormously push the application of hydrogen as the clean alternative fuel. The high energy value and the lack of environmental pollutants make the use of hydrogen very attractive.

Carbon nanotubes are unique nanoscale objects representing p-conjugated molecules whose dimensionality is intermediate between the 0D fullerenes and the 2D graphene layer. The extraordinary properties of this carbon allotrope largely originate from the graphite-like arrangement of the carbon atoms in the shells, and have enabled CNTs to promote and shape the field of nanotechnology to an unprecedented extent.

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Several reviews have reported a comprehensive overview with respect to the synthesis, characterization, as well as the basic mechanical and electronic properties of CNTs [11–20].

Their ultrahigh surface-to-volume ratio makes CNTs highly suited for investigating fundamental aspects of gas adsorption. For instance, the interior region of nanotubes offers a deep well for physical adsorption, which provides an ideal example of a micro-porous material. In particular, nanotubes represent an optimal testing ground for theoretical predictions on adsorption mechanisms within 1D matter, for which only a few physical realizations exist. Moreover, the fact that all carbon atoms of an SWCNT are exposed to the surface imparts a high sensitivity of its electronic properties against binding of atoms or molecules, whereby promising perspectives for sensor applications are opened.

The electronic properties of CNTs are unique in so far as the presence or the absence of an energy gap depends on the precise way in which the carbon hexagons match up around the circumference of these cylinders with diameters in the nanometer range. Hence, either quasi-1D metals or 1D semiconductors can be realized merely by altering the tubes geometrical structure, without the need to introduce dopants into the system. CNTs have allowed approaching the originally formulated goals of molecular electronics more closely than any other material to date. The concepts envisioned in the early 1970s comprised, for instance, molecular diodes and switches implemented into individual p-conjugated carbon chains [21]. Indeed, rectifying diodes [22,23], memory devices [24,25], and photo-induced switches [26,27] have recently been demonstrated on the basis of SWCNTs. In the meanwhile, the great success of carbon nanotubes in the realization of nanoscale electrical devices appears to be generally acknowledged [28–30].

Despite the exceptional electrical characteristics of CNTs, doubts have arisen concerning their real technological applicability in ultra-small electrical devices, which is largely due to the fact that the controlled synthesis of one specific type of tubes is hard to achieve. Furthermore, no reliable method is currently available to produce extended ensembles of aligned nanotubes, in which each tube would be located at a desired location and connected to its neighbors in a well-defined manner. Nonetheless, recent advances in linking specific groups or molecules to the nanotubes clearly testify the strong potential of chemical functionalization not only for tuning the tubes electronic properties, but also to enable their assembly into more-complex architectures required for integrated device operation [31].

Chemical functionalization furthermore imparts increased solubility to the nanotubes, thus opening new perspectives for solution-based chemical transformations and spectroscopy. The fast progress made in these directions has led to the prediction that the field of nanotube chemistry will successfully rival that of the fullerenes [32].

In this paper, the effect of adsorption of hydrogen on the activated SWCNT and MWCNT is addressed. The most of the chemical modifications are understood as the physisorption or chemisorption of atoms, ions or molecules inside the interior space or on the exterior wall of the tubes.

An overview of the most important hydrogen addition reactions that have been developed so far for the covalent sidewall functionalization of SWCNTs is provided in Table 1.

The dissociative chemisorption of a hydrogen molecule, resulting in two hydrogen atoms bonded to nearest-neighbor carbon atoms is defined as the fraction of carbon atoms bearing a covalently bonded moiety. Its value is usually determined from elemental analysis, thermo-desorption spectroscopy (TDS) [33,34] used in this work. However, this chemisorption state is difficult to reach because of the existence of a substantial activation barrier, which has been calculated to be 3 eV for typical nanotube diameters [35,36]. As a consequence, direct thermal reaction with hydrogen is not a viable route to functionalize SWCNTs. This task has instead been reached by adding hydrogen in the form of separate electrons and protons, specifically through protonation of nanotubes subsequent to chemical reduction with an alkali metal dissolved in liquid ammonia (modified Birch reduction) [37] or during electrochemical reduction [38].

An alternative possibility to hydrogenate CNTs consists of treatment with atomic hydrogen, which has been accomplished with the help of microwave discharge [39] or a heated tungsten filament [40].

The high reactivity of hydrogen atoms towards the sidewall is confirmed by theoretical studies, which predict the chemisorption of a single hydrogen atom on the exterior wall to be an exothermic process, associated with only a small kinetic barrier (0.3 eV) [34-36]. For the corresponding binding energy, values ranging between 0.3 eV [36] and 2.7 eV [41] have been calculated, depending on the chirality and diameter of the nanotube.

This paper gives a report on the state of art hydrogen storage in activated carbon nanotubes. The measured storage capacities of these materials in our experiments were 24% for SWCNT and 5% for MWCNT. The exterior surface, is only slightly endothermic by 0.4–0.5 eV according to first principles calculations ''functionalization degree''. Hydrogen storage capacity is a function of several parameters like the tube diameter, alignment, length of nanotubes, and structure (multi-walled or single-walled, open or closed tubes). If the variation of storage capacity with different parameters could be quantified it would help in predicting the storage capacity and remove some of the ambiguities in the experimental results.

SEM and TEM images can serve as a good tool to find the diameter distribution. To analyze the SEM images and to get the distribution of diameters, a semi-automated digital image processing techniques have been used. The technique of digital image processing is routinely used to determine the distribution of particle sizes.

2. Experimental

Characterization of SWCNT and MWCNT was made on SEM (JEOL JSM 6460 LV Japan, 2003) and TEM (TEM measurements were performed using Philips EM 400 microscope, operated at 120 kV). The adsorption – desorption cycles and hydrogen capacity were done on a mass spectrometer MS-1-MT (home design).
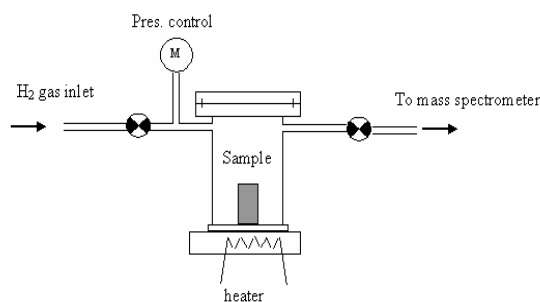

Fig. 1.Schematic diagram of chamber for hydrogen adsorption studies

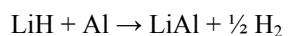## 3. Results and discussion

Measured mass of SWCNT= 0.0732 g
Measured mass of MWCNT= 0.3215 g
Nanotubes were filled with hydrogen up to pressure to 3 atm.
$LiAlH_4$ was used for calibration.

Reactions

$3 LiAlH_4 \rightarrow Li_3AlH_6 + 3H_2 + 2Al$

$Li_3AlH_6 \rightarrow 3LiH + 3/2 \; H_2 + Al$

$LiH + Al \rightarrow LiAl + \frac{1}{2} \; H_2$

The final reaction: 3 mol $LiAlH_4 \rightarrow$ 6 mol $H_2 + (3 \; LiAl)$

$Mr(LiAlH_4)$= 38 g/mol

Measured mass of $LiAlH_4$ 0.53g produces mass of hydrogen 0.055g.

Pressure in the chamber, which released H_2 in the combustion reaction of $LiAlH_4$, p= 0.63 atm H_2.

1g $LiAlH_4 \rightarrow$ 0.104 g H_2
1g SWCNT $\rightarrow$ 0.314 g H_2
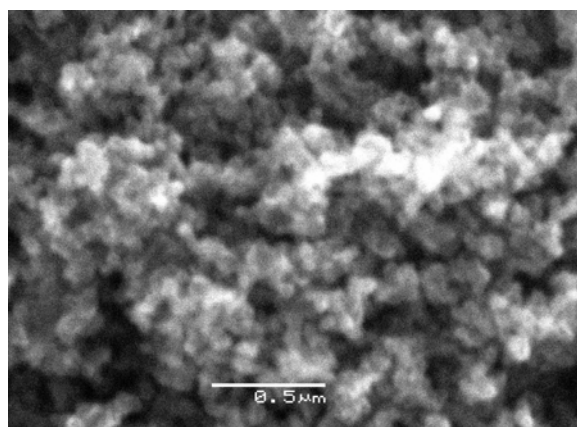1g MWCNT$\rightarrow$ 0.053 g H_2

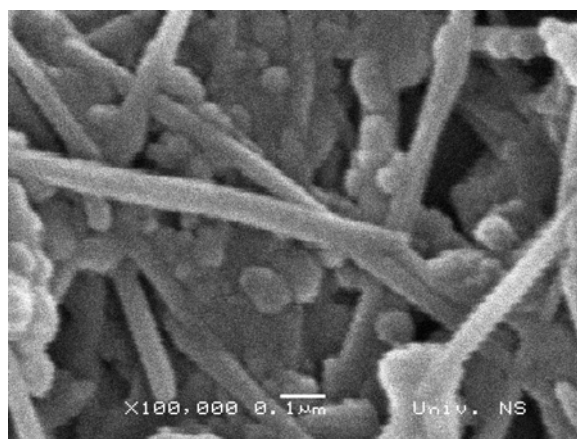Fig. 2. SEM image of not-purified SWCNT

Fig. 3. SEM image of MWCNT after PmPV purification. The content of impurities in non-treated nanotubes compared with acid treated nanotubes is higher. The diameter of MWCNT appears to be uniform

For pressure higher than 1 atm the hydrogen storage is confirmed in SWCNT. The storage capacity probably can be increased by applying higher hydrogen pressures or by lowering the temperature. In future studies, an emphasis should be given to develop reliable purification and characterization methods for carbon nanotubes [42].
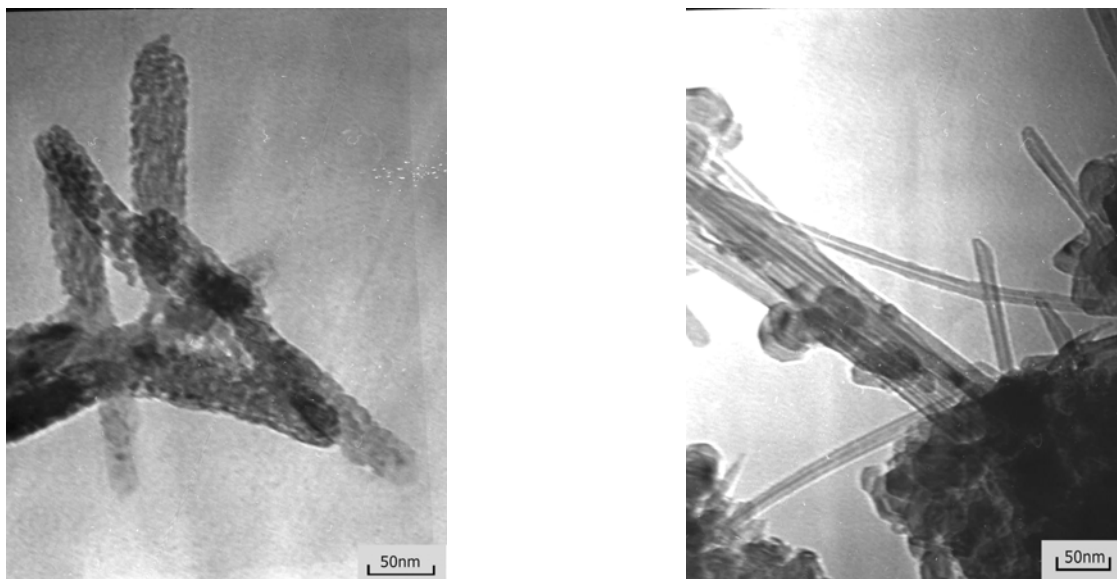

Fig. 4. a) TEM image of MWCNTs after PmPV purification; b) TEM image of SWCNTs after heating in nitric acid.

Table 1. Covalent functionalization schemes for SWCNT and MWCNT via addition to the sidewall.

Reaction type	Reagent(s)	Maximal FD(%)	Reference(s)
Hydrogenation SWCNT	Hydrogen plasma	~50	[40, 43, 39]
Hydrogenation SWCNT	Electrochem. red; protonation;	~20	[38]
Hydrogenation SWCNT	Alkali metal in NH_3; protonation;	~10	[37]
Hydrogen SWCNT	Adsorption of H_2	34	This work
Hydrogen MWCNT	Adsorption of H_2	5	This work

4. Conclusion

In this work, we have shown that carbon nanotubes have good properties for hydrogen storage. The experiment shows that CNT possess possibilities for multi adsorption-desorption cycles, without material damage.

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