Hydrogen adsorption and storage in carbon nanotubes

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Abstract

A comprehensive studies on hydrogen adsorption and storage in carbon nanotubes CNTs have been done both experimentally and theoretically. Hydrogen atoms have been stored electrochemically in CNTs. We find that hydrogens exist as a form of H₂ molecule in an empty space inside CNTs, which was confirmed by Raman spectra. Several adsorption sites on CNTs are observed during the discharging process. We perform density-functional-based tight-binding calculations to search for adsorption sites and predict maximum hydrogen storage capacity. Our calculations show that the storage capacity of hydrogen, limited by the repulsive forces between H₂ molecules inside nanotubes, increases linearly with tube diameters in single-walled nanotubes, whereas this value is independent of tube diameters in multi-walled nanotubes. We predict that H storage capacity in 10,10 nanotubes can exceed 14 wt.% 160 kg H₂/m³.

Keywords: Hydrogen; Adsorption; Storage

1. Introduction

Carbon nanotubes CNTs reveal diverse physical properties depending on the diameter and chirality. Several potential applications have been demonstrated so far. Large aspect ratio and naturally formed nanoscale-diameter of CNTs make it possible to apply for efficient and stable electron field emitters. Field effect transistor operated at room temperature has been demonstrated using a single CNT. Covalently functionalized nanotubes could be prepared with different functional groups attached at the tip of CNTs.

Large empty space particularly inside the single-walled nanotubes SWNTs provides a possibility to be applied for hydrogen storage vehicle with large storage capacity. It is always desirable to develop a new storage material with high capacity, light mass, and high stability, which may be applicable for portable electronics and moving vehicles. CNTs seem to be an ultimate alternative for this, since nanotubes are chemically stable and have low mass density. Yet hydrogen storage capacity in nanotubes is still far from being clearly understood.

Hydrogen could be stored in bundles of SWNTs up to 5% to 10%, where H₂ molecules are physisorbed at the exterior surfaces of CNTs or interstitial spaces between CNTs, separating the intertube distances. Although graphite nanofibers or equivalently randomly oriented graphite platelets have been suggested to contain hydrogens up to 72 wt.%, this has not been corroborated. It has also been demonstrated that CNTs could also store electrochemically hydrogens less than 1%. Despite such efforts, understanding mechanistic detail of hydrogen adsorption sites, a form of hydrogen storage, maximum amount of stored hydrogens, and structural stability of CNTs upon H storage is a long standing problem.
main difficulty arises from i. the poorly prepared CNT samples and ii. lack of an atomistic model for H adsorptions and storage in CNTs, which is an essential ingredient for prediction of maximum storage capacity and an atomic-level interpretation of H adsorptions.

In this work, we have carried out a systematic study for the hydrogen adsorption and storage capacity in CNTs using charge–discharge cycling measurements, Raman measurements, and density functional DF calculations. Hydrogens were stored electrochemically in CNTs within KOH solutions. The existence of several slopes in discharge curves strongly indicates that the corresponding adsorption sites are present in CNTs. Raman spectra also suggest that hydrogens can exist as a form of H₂ molecule in the empty space inside CNTs, which was confirmed by the molecular dynamics simulations. Several intermediate key-adsorption sites of hydrogens i. at the exterior of the tube wall, ii. at the interior of the tube wall, and iii. in empty space inside SWNTs are identified by the DF calculations, whereas only exteriors of concentric shells are favored in multi-wall nanotubes MWNTs for large storage of hydrogens. In case of SWNTs, maximum hydrogen storage capacity increases with tube diameters, whereas in case of MWNTs, this value is independent of tube diameters. The maximum storage capacity is mainly determined by the repulsive forces between H₂ molecules and those between H₂ molecules and the tube wall.

2. Experiment

There are two methods to store hydrogens in CNTs. One is to store hydrogens under high pressure and the other is by electrochemical charge–discharge cycling method. The former usually involves physisorption of H₂ molecules between CNTs in most cases. We take the latter method in our approach. CNT-based composite electrodes were fabricated by mixing and grinding first with conductive Ni powders 99.8% for 50 min and later with the organic binder of polytetrafluoroethylene PTFE. for 20 min with a mixing composition ratio of CNT: Ni:PTFE = 40:50:10. The pellet was made by pressing the mixture into a mold of diameter of 10 mm by 2000 atmospheric pressure. This pellet was inserted into Ni metal mesh and used for working electrode. The counter electrode metal Ni was separated by a polymer separator, as shown in Fig. 1. The voltage across the two electrodes was measured in 6 M KOH solution as a function of time for 10 h, while maintaining a constant current at 0.4 mA.

3. Theoretical approaches

For our calculations, we use a self-consistent charge density-functional-based tight-binding method SCC-DFTB. The SCC-DFTB method uses a basis of numerically described s and p atomic orbitals for carbon and s orbital for hydrogen. Hamiltonian and overlap matrix elements are evaluated by a two-center approach. Charge transfer is taken into account through the incorporation of a self-consistency scheme for Mulliken charges based on the second-order expansion of the Kohn–Sham energy in terms of charge density fluctuations. The diagonal elements of the Hamiltonian matrix employed are then modified by the charge-dependent contributions in order to describe the change in the atomic potentials due to the charge transfer. The off-diagonal elements have additional charge-dependent terms due to the Coulomb potential of ions. They decay as 1/r and thus account for the Madelung energy of the system. Further detail of the SCC-DFTB method has been published elsewhere. Although the SCC-DFTB approaches are very efficient to describe the systems quantum mechanically, the accuracy test is demanded in some cases. In order to check the validity of SCC-DFTB approach, we also perform state of art technique, the DF total energy calculations based on the local density approximation LDA, and generalized gradient approximation GGA. The exchange-correlation energy in LDA is parameterized by Perdew and Wang’s scheme and Becke’s corrected exchange functional is adopted in GGA calculations. All-electron Kohn–Sham wavefunctions are expanded in a local atomic orbital basis. All orbitals including core electrons, are taken into account throughout the calculations. In the double-numerical basis set, C-2s and C-2p orbitals are represented by two basis functions each, and a 3d-type wave function on carbon atom is used to describe polarization. The convergence criterion for the structure optimization is that all forces be \( F \leq 0.001 \text{ a.u.} \) Structure optimization is done by the SCC-DFTB and LDA schemes. The GGA calculations
Table 1

Benchmark test of CH₄ and H₂ molecules. $E_b$ and $l$ are the binding energy and bond length, respectively.

<table>
<thead>
<tr>
<th>Method</th>
<th>CH₄</th>
<th>H₂</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$l$ Å</td>
<td>$E_b$ eV.</td>
</tr>
<tr>
<td>SCC-DFTB</td>
<td>1.095</td>
<td>5.69</td>
</tr>
<tr>
<td>LDA</td>
<td>1.10</td>
<td>5.94</td>
</tr>
<tr>
<td>GGA</td>
<td>y4.53</td>
<td>4.47</td>
</tr>
<tr>
<td>Expt.a</td>
<td>1.087</td>
<td>5.54</td>
</tr>
</tbody>
</table>

aRef. 46x

are done with structures optimized by LDA whenever necessary.

Table 1 shows results of benchmark test for CH₄ and H₂ molecules. The SCC-DFTB describes well the bond lengths of each molecule, whereas the binding energies of C–H bonds and H–H bond are overestimated compared to the experimental values 46x. Our GGA results for binding energies are in excellent agreements with experimental values for both molecules.

4. Results and discussion

Fig. 2a shows charge–discharge behaviors of SWNTs as a function of time at a constant current of 0.4 mA,

\[
\text{CNT} + x\text{H}_2\text{O} \rightarrow x\text{H}_2 + \text{C}_{\text{NT}} + x\text{OH}^-, \quad 1
\]

where the time axis was converted into the charge storage capacity. In the working electrode, the reaction is as follows:

\[
\text{CNT} + x\text{H}_2\text{O} \rightarrow x\text{H}_2 + \text{C}_{\text{NT}} + x\text{OH}^-, \quad 1
\]

where hydrogen ions are inserted into CNTs during the charging process. Repeating charge–discharge cycle, which involves activation process of working electrode, gives rise to the saturation of charge storage capacity. It is noted that several slopes appear in the discharge curves, as shown in

Fig. 3. Top and the corresponding side views of various hydrogen adsorptions in 5,5 SWNT; a–b, clean 5,5 CNT, c–d, hydrogens adsorbed at the exterior of the tube wall for $u \approx 1.0$, and e–f, adsorption of a single hydrogen atom at the interior of the wall. Bond lengths are expressed in Å.

Fig. 4. Top and the corresponding side views of various hydrogen adsorptions in 5,5 SWNT; a–b, the initial geometry of hydrogens adsorbed at the interior of the wall for $u \approx 1.0$, c–d, the fully relaxed geometry of a, and e–f, the fully relaxed geometry for $u \approx 1.2$. Bond lengths are expressed in Å.
layers of tubes. No appreciable changes were observed in the difference of the total energies. The periodic boundary condition is applied along the tube axis. Fig. 3 a–f shows top and the corresponding side views of various adsorption sites of hydrogens on the 5,5-SWNT. The diameter of fully relaxed 5,5-SWNT is 6.88, similar to that of C_{60}, with the average bond lengths of 1.44 Å, as shown in Fig. 3 a–b. We consider hydrogen adsorptions at the exterior of the tube wall in Fig. 3 c–d, where all top sites of carbon atoms are taken by hydrogen atoms. C–H bond length is 1.12 Å, close to that of CH_{4} molecule. The diameter and average C–C bond lengths are expanded to 7.78 and 1.54, respectively, enhancing the sp^{3} rehybridization in the tubes. Geometries optimized with LDA were not much different from those optimized with SCC-DFTB for all cases. The binding energy of the C–H bond is calculated as follows:

\[ E_{b} = E_{total\, \text{CNT}} - n_{H} E_{atom\, H} - E_{H-H} \]

where \( E_{atomic\, H} \) is the self energy of hydrogen atom and \( n_{H} \) is the number of hydrogens. GGA calculations are done with geometries that are fully optimized with LDA. The \( E_{b} \) C–H for 5,5-SWNT is 2.65, 2.10, and 1.75 eV C–H bond from SCC-DFTB LDA/GGA results, about half the C–H bond energy of CH_{4} molecule. Adsorption of a hydrogen atom at the interior of the tube wall Fig. 3e–f pulls inward the carbon atoms nearby, again enhancing sp^{3} rehybridization. The binding energy in this case, however, is 0.83 \( \gamma_{1.50} \) 1.28 eV C–H bond, where SCC-DFTB underestimates the binding energy. Severe lattice distortions are involved in this geometry.

One may imagine hydrogen atoms to be adsorbed at all top sites of the interior wall with a coverage of \( \gamma_{1.0} \), as shown in Fig. 4 a–b, where the coverage is defined as the ratio of the number of hydrogen atoms to the number of carbon atoms. However, this structure is not stable after full relaxation, resulting in the formation of H molecules, as shown in Fig. 4 c–d. The energy is minimized by forming H_{2} molecules with the binding energy of 4.57 \( \gamma_{3.16} \) 2.24 eV H_{2} molecule, calculated similarly to the previous C–H binding energy, and further reducing the

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**Table 2**

<table>
<thead>
<tr>
<th>Coverage</th>
<th>E_{b} eV/H_{2}·</th>
<th>E_{rep} H_{2}·– H_{2}· eV/H_{2}·</th>
<th>E_{rep} wall–H_{2}· eV/H_{2}·</th>
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</thead>
<tbody>
<tr>
<td>5,5 (-ext) u=0.0</td>
<td>y9.14</td>
<td>y8.41</td>
<td>y7.48</td>
</tr>
<tr>
<td>5,5 (-ext) u=1.0</td>
<td>y2.65</td>
<td>y2.10</td>
<td>y1.75</td>
</tr>
<tr>
<td>5,5 (-int) u=1.0</td>
<td>y4.57</td>
<td>y3.16</td>
<td>y2.24</td>
</tr>
<tr>
<td>10,10 (-int) u=2.0</td>
<td>y5.91</td>
<td>0.34</td>
<td>0.14</td>
</tr>
<tr>
<td>10,10 (-int) u=2.4</td>
<td>y5.64</td>
<td>0.46</td>
<td>0.16</td>
</tr>
</tbody>
</table>

* The binding energy are expressed in eV \( \times \) C–H bond.

* The binding energy are expressed in eV \( \times \) C–C bond.

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Fig. 5. Top and the corresponding side views of various hydrogen adsorptions in 10,10-SWNT: a–b, the geometry of 10,10-CNT for \( u_{2} = 2.0 \), and c–d, for \( u_{2} = 2.4 \). Bond lengths are expressed in Å.

Fig. 2 a, indicating the existence of different adsorption sites. Fig. 2 b shows the cyclic voltammetry CV for the CNT electrode at a scan rate of 10 mV/s. Ag\_AgCl standard electrode was used as a reference electrode in this measurement. Sharp peaks were observed at 0.31 and 0.19 during the respective extraction and insertion processes of hydrogens from CNTs. The amount of H and H\_out may be expressed as an integrated area below and above the zero current, respectively, indicating controllability of hydrogen storage in CNTs by electrochemical method.

We choose armchair nanotubes with different diameters in our calculations. Supercells of eight layers of 5,5 and 10,10 CNTs are used in our SCC-DFTB calculations, as shown in Figs. 3 and 5. For LDA and GGA calculations, four layers are chosen in order to save the computing time. The convergence on the supercell size was tested with six layers of tubes. No appreciable changes were observed in the difference of the total energies. The periodic boundary condition is applied along the tube axis. Fig. 3 a–f shows top and the corresponding side views of various adsorption sites of hydrogens on the 5,5-SWNT. The diameter of fully relaxed 5,5-SWNT is 6.88, similar to that of C\(_{60}\), with the average bond lengths of 1.44 Å, as shown in Fig. 3 a–b. We consider hydrogen adsorptions at the exterior of the tube wall in Fig. 3 c–d, where all top sites of carbon atoms are taken by hydrogen atoms. C–H bond length is 1.12 Å, close to that of CH\(_{4}\) molecule. The diameter and average C–C bond lengths are expanded to 7.78 and 1.54, respectively, enhancing the sp\(^{3}\) rehybridization in the tubes. Geometries optimized with LDA were not much different from those optimized with SCC-DFTB for all cases. The binding energy of the C–H bond is calculated as follows:

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One may imagine hydrogen atoms to be adsorbed at all top sites of the interior wall with a coverage of \( u_{2} = 1.0 \), as shown in Fig. 4 a–b, where the coverage is defined as the ratio of the number of hydrogen atoms to the number of carbon atoms. However, this structure is not stable after full relaxation, resulting in the formation of H molecules, as shown in Fig. 4 c–d. The energy is minimized by forming H\(_{2}\) molecules with the binding energy of 4.57 \( \gamma_{3.16} \) 2.24 eV H\(_{2}\) molecule, calculated similarly to the previous C–H binding energy, and further reducing the
lattice distortions at the tube wall. This calculation strongly suggests that H\textsubscript{2} molecule can exist stably in the vacant space inside the nanotubes. Binding energy of the H\textsubscript{2} molecule inside the CNT is reduced compared to that of a gaseous H\textsubscript{2} molecule due to the repulsive forces between H\textsubscript{2} molecules and between the tube wall and H\textsubscript{2} molecules. Higher coverage of \( u \leq 1.2 \), as shown in Fig. 4 e–f, results in larger repulsive energies, as listed in the Table 2. The repulsive energy between the tube wall and H\textsubscript{2} molecules is calculated by

\[ E_{\text{rep \ wall--H}_2} = E_{\text{tot \ CNT \ H}_2} - y E_{\text{tot \ CNT}} \]

and similarly that between H\textsubscript{2} molecules,

\[ E_{\text{rep \ H}_2--H}_2 = E_{\text{tot \ H}_2} - y n_{\text{H}_2} E_{\text{H}_2} \]

where \( E_{\text{tot \ H}_2} \) is the total energy of H\textsubscript{2} only within CNT, and \( n_{\text{H}_2} \) and \( E_{\text{H}_2} \) are the number of gaseous H\textsubscript{2} molecule and the total energy of a single gaseous H\textsubscript{2} molecule, respectively. LDA and GGA calculations consistently reproduce SCC-DFTB results of repulsive energies. The average distance between H\textsubscript{2} molecules with \( u \leq 1.0 \) is 1.4 Å, whereas that between the tube wall and H\textsubscript{2} molecules is 2.0 Å. Repulsive energies become larger for higher coverages, increasing the diameter and eventually break the tube walls. We conclude that these repulsive energies determine the maximum storage capacity of hydrogens inside tubes and the stability of the tubes.

To estimate the maximum storage capacity, we assume the hydrogen density \( n_{\text{H}_2} \)  volume \( \cdot \) to be nearly constant inside the tube. The volume and the number of the hydrogen atoms increases with a square of the radius, whereas the number of carbon atoms increases linearly with the radius. Therefore, we expect hydrogen storage capacity to be linearly proportional to the radius or diameter. To validate this prediction, we now take experimentally well observed 10,10. SWNT synthesized by the laser ablation synthesis. Fig. 5 a–b. show the optimized structure with a coverage of \( u \leq 2.0 \). In spite of higher coverage of hydrogen compared to \( 5,5 \). SWNT, C–C bond lengths are smaller and H\textsubscript{2} bond lengths are longer, implying smaller repulsive forces, as confirmed in the Table 2. The average distance between H\textsubscript{2} molecules with \( u \leq 2.0 \) is 1.66 Å, whereas that between the tube wall and H\textsubscript{2} molecules is 2.33 Å. Fig. 6 shows the general trend between repulsive forces and the average separation distances between H\textsubscript{2} molecules and between the tube wall and H\textsubscript{2} molecules.

One may increase the coverage to \( u \leq 2.4 \) but still the tube wall is stable, as shown in Fig. 5 c–d. By choosing the coverage which gives lower repulsive energies, \( u \leq 2.0 \) for 10,10- nanotube, we generalize the hydrogen storage capacity in wt.% , H wt.% \( 14.3 \) for SWNTs, where 14.3 H wt.% is equivalent to the hydrogen coverage \( u \leq 2.0 \) and \( D_0 \) is the diameter of 10,10- nanotube. We also calculate the lower bound of kinetic diameter from 10,10- with a coverage \( u \leq 2.0 \). The kinetic diameter of

### Table 3
Hydrogen storage capacity in CNTs in different units

<table>
<thead>
<tr>
<th></th>
<th>u</th>
<th>H wt%</th>
<th>( \varepsilon ) mA h g\textsuperscript{-1}</th>
<th>( \varepsilon ) atoms cm\textsuperscript{-3}</th>
<th>( \varepsilon ) kg H\textsubscript{2} cm\textsuperscript{-3}</th>
</tr>
</thead>
<tbody>
<tr>
<td>SWNT</td>
<td>5,5</td>
<td>1.0</td>
<td>7.7</td>
<td>2200</td>
<td>0.19</td>
</tr>
<tr>
<td></td>
<td>5.5</td>
<td>1.2</td>
<td>9.1</td>
<td>2700</td>
<td>0.23</td>
</tr>
<tr>
<td></td>
<td>10,10</td>
<td>2.0</td>
<td>14.3</td>
<td>4500</td>
<td>0.19</td>
</tr>
<tr>
<td></td>
<td>10,10</td>
<td>2.4</td>
<td>16.7</td>
<td>5400</td>
<td>0.22</td>
</tr>
<tr>
<td>MWNT</td>
<td>5.5- ( @ ) 10.10</td>
<td>0.33</td>
<td>2.7</td>
<td>740</td>
<td>0.053</td>
</tr>
<tr>
<td></td>
<td>5.5- ( @ ) 10.10</td>
<td>1.0</td>
<td>7.7</td>
<td>2200</td>
<td>0.16</td>
</tr>
</tbody>
</table>

Fig. 7. Top and the corresponding side views of various hydrogen adsorptions in 5,5-@ 10,10- MWNT; a–b, clean MWNT, c–d, the hydrogen adsorption at the exterior of the inner shell, and e–f, the hydrogen adsorption at the exteriors of both walls. Bond lengths are expressed in Å.
H₂ molecule should be greater than 2.42 Å, comparable to the previously reported 2.89 Å. Table 3 summarizes the storage capacity in various units. We emphasize here that the experimentally well observed 10,10 nanotubes can have superb charge storage capacity up to 4500 mA h/g, which is much greater than 100–400 mA h/g of a conventional metal-hydride battery, suggesting potential applications to an electrode in secondary battery for moving vehicles or fuel cells.

We next consider hydrogen adsorption in MWNTs. We choose 5,5 @ 10,10 double-walled nanotube with an inner-tube distance of 3.4 Å, as shown in Fig. 7 a–b. Adsorption of hydrogen atoms at the exterior of the inner wall again enlarges the diameter to 7.56 Å and C–C bond lengths to 1.51 Å, slightly smaller than the respective 7.78 Å and 1.54 Å of SWNT due to repulsive forces from the outer wall, as shown in Fig. 7 c–d. The binding energy is 2.56 eV C–H bond, again slightly weaker than 2.65 eV of SWNTs. Further saturation of top sites at the exterior of the outer wall reduces the repulsive forces, extending both diameters to 7.80 and 16.0 Å and C–C bond lengths to 1.54 and 1.57 Å, respectively, as shown in Fig. 7 e–f. The peak position is shifted slightly to lower energy side 1580 cm⁻¹. This trend is similarly observed in the MWNT-samples. This may be attributed to the enlargement of tube diameters with hydrogen storage, as clearly seen from Figs. 4 and 5. We note that a new peak near 4226 cm⁻¹ appears after charging, as shown in Fig. 9 b. This peak position is similar to 4161 cm⁻¹ from a gaseous H₂ gas. It is very unlikely that H₂ molecules

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1 Intercalated H₂ molecule which is aligned parallel to the c axis in graphite dissociates and takes two top sites on upper and lower graphitic layers, enlarging the interlayer distances.
are stable inside the Ni or carbonaceous particles. 2 We annealed samples up to 750°C for 30 min in N₂ ambient but the peak intensity was not changed, showing that H₂ molecules were not physisorbed on or in-between the tube surfaces. 3 This strongly suggests that H₂ molecules exist inside nanotubes. It is of note that the integrated area of the peak at 4226 cm⁻¹ of SWNTs is greater than that of MWNTs, indicating that more hydrogens are stored in SWNTs.

The existence of molecular hydrogens in the vacant space inside CNTs could be further confirmed theoretically. We calculate vibrational frequencies by choosing SWNT with hydrogen coverage of 5.5. The vibrational frequency is obtained by taking the Fourier transform of velocity–velocity autocorrelation functions which are calculated from tight-binding molecular-dynamics simulations in a microcanonical ensemble. The time step was 2.42 × 10⁻¹⁶ s. The total energies were kept constant within 0.001 a.u. during the simulation at 100 K. The total simulation time was 2.5 ps. The peak position of a gaseous H molecule is located at 4349 cm⁻¹, as shown in Fig. 10. This is overestimated, compared to the experimental value of 4161 cm⁻¹, as expected from typical TB approaches. The average bond length of H₂ molecules inside the tube is 0.75 Å. We calculate vibrational frequencies by choosing H₂ molecules with shorter and longer bond lengths separately than the average bond length of 0.75 Å. H₂ molecules with shorter bond show the higher vibrational peak at 4514 cm⁻¹, whereas those with longer bonds show the lower peak at 4226 cm⁻¹, as expected. It is therefore expected that the observed Raman frequency, which is slightly higher than that of a gaseous molecule, is due to the contraction of H₂ bond lengths from the repulsive forces between H₂ molecules. This strongly suggests that the frequency becomes with increasing the hydrogen coverage due to the repulsive forces between hydrogen molecules and therefore Raman measurement of H₂ mode could be a way to monitor hydrogen storage capacity.

5. Summary

We have stored hydrogen atoms inside CNTs electrochemically. Several adsorption sites are observed experimentally. We have identified the adsorption sites from our calculations: top sites at the exterior of the tube wall as atomic H, in the interior of the tube wall as atomic H, and in the empty space inside the SWNTs. From Raman spectroscopy we observe that H₂ molecules exist in the empty space of CNTs and these are further confirmed by the tight-binding molecular-dynamics simulations. The maximum hydrogen storage capacity increases linearly with diameter in SWNTs, i.e., H wt.% G 14.3 D₂D₀. D₀ is the diameter of 10,10 nanotube. In MWNTs, hydrogen atoms favor to adsorb at the exterior of concentric tube walls, where hydrogen storage capacity is independent of diameters. We conclude that SWNTs are better than MWNTs for higher hydrogen storage. This paper presents the experimental demonstration for the hydrogen storage in CNTs in a controllable manner. This observation, aided by DF calculations identifying the key intermediate adsorption sites, provides adequate atomistic interpretation of the hydrogen adsorption and storage in CNTs.

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