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Interaction of hydrogen molecules on Ni-doped single-walled carbon nanotube*

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Adsorption of hydrogen molecules on an Ni-doped (8,0) single-walled carbon nanotube (SWNT) is investigated by using first-principles density functional calculations. The result shows that a single Ni atom adsorbed on the bridge site of the tube could cannot dissociate the H_2, however it can chemisorb three H_2 at most, with the average binding energy per H_2 suitable for the hydrogen storage at the room temperature. More H_2 would physisorb around an Ni atom weakly. As for the SWNT with an Ni dimer adsorbed, we find that when the H_2 approaches the Ni–Ni bond, it dissociates without overcoming any barrier and makes bonds with Ni atom.

Keywords: hydrogen storage, doped carbon nanotube, density functional theory
PACC: 8640K, 7125W, 7115M

1. Introduction

Hydrogen has been regarded as an ideal clean energy to replace the fossil fuel, but to apply it in diverse fields, the hydrogen storage needs improving. Carbon nanotubes (CNTs) have attracted much attention for hydrogen storage because of their high surface-to-volume ratio. Dillon *et al* [1] first used single-walled carbon nanotubes (SWNTs) to store hydrogen and estimated that 5–14 wt% of H_2 could be stored. Later, Chen *et al* [2] doped CNTs with alkali atoms to enhance hydrogen storage of CNTs. They reported that the doped CNTs had high H_2 uptake under an ambient pressure and a moderate temperature. However, the subsequent studies suggested that the interaction between the hydrogen molecules and SWNTs was a weak physisorption,[3,4] and that most of stored hydrogen reported by Chen *et al* was due to moisture.[5,6]

Recently, the focus has been on improving the hydrogen storage of SWNTs by doping transition metal (TM). Yildirim and Ciraci [7] reported that a single Ti atom coated on an SWNT could strongly bind up to four hydrogen molecules, and at a high Ti coverage an SWNT can adsorb up to 7.7 wt% hydrogen theoretically. Callejas *et al* [8] found that the hydrogen adsorption of the SWNT increased after the hydrogen reduction of Ni/Y catalyst at 623 K. Additionally, Kim *et al* [9] performed experiments and found that 6 wt% of Ni nanoparticle dispersed CNTs could store 2.8 wt% hydrogen, which is higher than that of pristine CNTs. The theoretical study done by Lee *et al* [10] showed that a single Ni doped on (5,5) SWNT could store $5H_2$ with an average binding energy of $-0.26\,\mathrm{eV}/H_2$. However, a further understanding is still expected of the interaction between H_2 molecules and Ni-doped CNT as well as the increase of the C–H_n stretching vibration peak after the hydrogen storage for the Ni-dispersed CNT in the experiment done by Kim *et al*.[9] Besides, Ni particles have often been used as a catalyst in the synthesis of SWNTs. The residual Ni atoms may influence the hydrogen storage of SWNTs.[11,12]

In this paper, we perform a systemic study on the interaction between H_2 molecules and Ni-doped semiconducting (8,0) SWNT through the first-principles total energy calculations. Starting from examining the interaction of H_2 molecules with a free Ni atom, the adsorption of H_2 molecules on single or dimer Ni-doped SWNTs is discussed. Our results show that the hydrogen storage of the SWNTs is enhanced by doping Ni atoms.

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2. Calculation method and simulation model

Our calculations are performed by using the DMol^3 package[13] within the framework of density-functional theory (DFT). All-electron calculation is used with the double numerical plus polarization basis set in the generalized gradient approximation (GGA) of PW91 for the exchange-correlation potential.[14] The adsorption of H_2 molecule on an Ni-doped (8,0) SWNT is treated in a triclinic supercell of a size $2.0\times2.0\times0.844\,\mathrm{nm}^3$. The lattice parameter c equals twice the periodicity of (8,0) SWNT and the lattice parameters a and b are large enough to ignore the effect of neighbouring tubes. The Monkhorst–Pack scheme[15] is used in the Brillouin zone with $1\times1\times5$ special K-points for all the geometry optimization.

In order to test the accuracy of the parameters, we study the interaction of an H_2 molecule with the exterior wall of the pristine (8, 0) SWNT. The hydrogen molecule is placed above the hexagon, parallel to the axis of the SWNT. After the optimization, the distance between the hydrogen molecule and the exterior wall of SWNT is 0.285 nm and the binding energy is −76 meV, which are similar to the previous studies.[3,16,17]

3. Results and discussion

3.1. Interaction between an H_2 and a free Ni atom

Optimized structures of H_2 molecules adsorbed to a free Ni atom are shown in Fig.1. Upon approaching a free Ni atom, the single H_2 molecule dissociates and makes bonds with Ni atom. This is denoted as Ni–H_2 shown in Fig.1(a). The Ni–H bond length $d_{\mathrm{Ni-H}}$ is 0.144 nm and the H–H bond length $d_{\mathrm{H-H}}$ is 0.199 nm. The binding energy for the free Ni atom and the H_2 molecule (namely $E_\mathrm{b} = E_\mathrm{T}[\mathrm{NiH_2}]–E[\mathrm{H_2}]–E[\mathrm{Ni}]$) is –1.55 eV. Using the Mulliken method, we find that about 0.13e charge is transferred from the Ni atom to two H atoms. When there are two H_2 molecules placed around the Ni atom, after the optimization these two molecules are both molecularly adsorbed without dissociation, denoted as Ni–$2H_2$, see Fig.1(b). Such an adsorption is considered as chemisorption with an average binding energy of $-1.27\,\mathrm{eV/H_2}$. The H–H bond length is 0.090 nm, which is slightly large compared with the bond length of the free hydrogen molecule. For the case of three or four H_2 molecules (denoted as Ni–$3H_2$ or Ni–$4H_2$) adsorbed to the Ni atom, the H_2 molecules are molecularly chemisorbed too. For Ni–$3H_2$ in Fig.1(c), the average binding energy is $-1.25\,\mathrm{eV/H_2}$ with $d_{\mathrm{H-H}}$=0.089 nm and $d_{\mathrm{H-Ni}}$=0.156 nm. While for Ni–$4H_2$ in Fig.1(d), the average binding energy is $-1.03\,\mathrm{eV/H_2}$ with $d_{\mathrm{H-H}}$=0.086 nm and $d_{\mathrm{Ni-H}}$=0.161 nm. Compared with the configuration of Ni–$2H_2$, the interaction between the hydrogen molecules and an Ni atom is weakened. When the fifth H_2 molecule is placed near Ni–$4H_2$, the optimized structure Ni–$5H_2$ in Fig.1(e) shows that four of them are molecularly chemisorbed, and the fifth hydrogen molecule is pushed away with an Ni-H distance of 0.361 nm. The isosurface of the

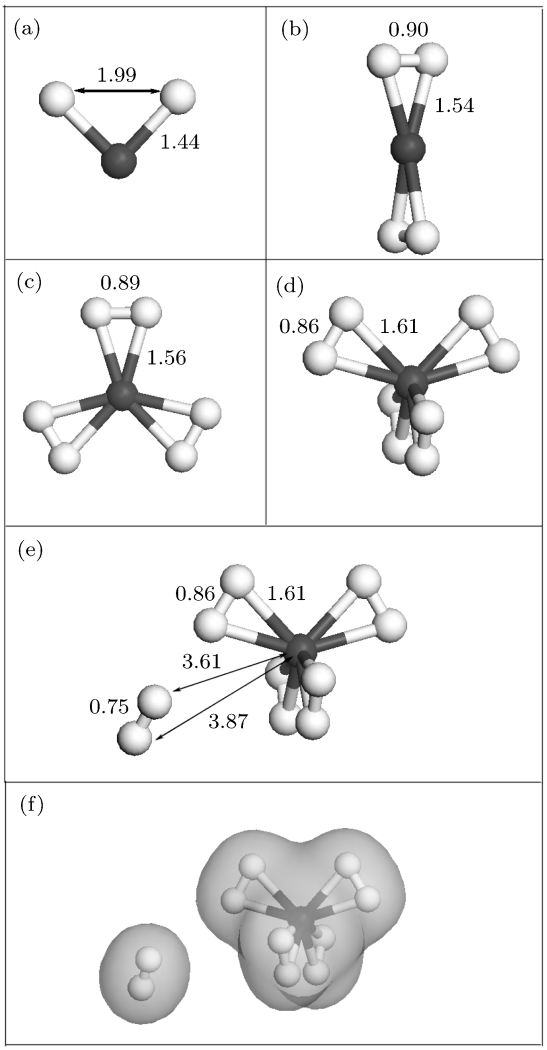


Fig.1. The optimized structures of one (a), two (b), three (c), four (d), five(e) H_2 molecules adsorbed to a free Ni atom separately, and isosurface of the charge density with a value of 0.08 for five H_2 molecules adsorbed to a free Ni atom (f).

charge density of the configuration Ni–5H_2 in Fig.1(f) clearly demonstrates that there is no hybridization between the fifth H_2 molecule and Ni atom, while a strong hybridization exists between the other four H_2 molecules and Ni atom. The binding energy of the fifth hydrogen molecule $E_b^{(5)}$ is –95 meV(here, $E_b^{(5)}$=E_T[Ni–5H_2]–E_T[Ni–4H_2]–E[H_2]), exhibiting a weak physisorption. All in all, a free Ni atom is able to chemically bind up to four H_2 molecules at most, and any more hydrogen molecules are only weakly physisorbed.

3.2. Adsorption of H_2 on one Ni-doped SWNT

To obtain the stable configurations for the adsorption of an Ni atom on the exterior wall of SWNT, the following four different sites are considered: the central site of the hexagon (H site), the top site of the carbon atom (T site), the bridge site over a zigzag C–C bond (Z site), and the bridge site over an axial C–C bond (A site). Among these configurations, the SWNT with the Ni atom on the bridge site over an axial C–C bond, that is A site, is the most stable one as shown in Fig.2. The binding energy of the Ni atom for this configuration is –2.95 eV and the C–Ni bond length is 0.191 nm. In the following calculations, we use this configuration (denoted in SWNTNi) as a prototype to further probe the interaction between the hydrogen molecules and Ni-doped SWNT.

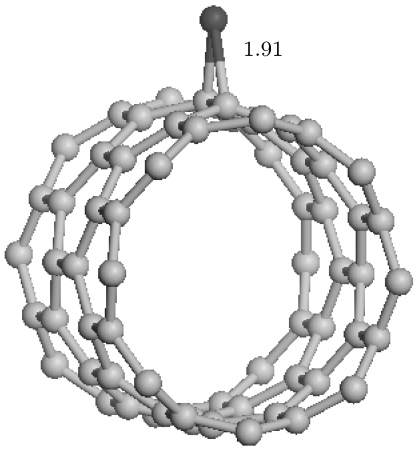


Fig.2. The optimized structure of one Ni atom adsorbed on the A site of the exterior wall of (8,0) SWNT.

Attaching an H_2 molecule to the configuration SWNTNi, several initial sites of the H_2 molecule with various directions and angles from the Ni atom are considered. After optimization, two different configurations are deduced as shown in Fig.3. In both configurations, the hydrogen molecules are molecularly adsorbed to the Ni atom with the H–H bond lengths slightly elongated. This is different from the interaction between an H_2 molecule and a free Ni atom, in which the H_2 is dissociated. For the configuration described in Fig.3(a), the Ni atom is located near the H site with an Ni–C distance of more than 0.202 nm. The H–H and the Ni–H bond lengths are 0.086 nm and 0.159 nm, respectively. The average binding energy per hydrogen molecule to the doped SWNT is calculated from the following formula:

$$E_b = (E_T[\mathrm{SWNTNi} - n\mathrm{H_2}] - E_T[\mathrm{SWNTNi}] - n\mathrm{E}[\mathrm{H_2}])/n, \quad (1)$$

where the SWNTNi-$n$$H_2$ represents the optimized configuration with $n$$H_2$ molecules adsorbed to SWNTNi, E_T[SWNTNi-$n$$H_2$] and E_T[SWNTNi] are the total energies of the optimized structures SWNTNi-$n$$H_2$ and SWNTNi respectively. The binding energy of H_2 molecule in Fig.3(a) is calculated to be –1.11 eV. For the configuration shown in Fig.3(b), an Ni atom is bound to the A site. The interaction between an Ni atom and SWNT in Fig.3(b) is relatively strong with a shorter bond length, d_{Ni-H}=0.196 nm as compared with that for the configuration in Fig.3(a). This relatively strong Ni–SWNT bond allows a weaker interaction between the Ni atom and H_2 molecule. In Fig.3(b), the H–H bond (0.085 nm) is shorter and the H–Ni bond (0.160 nm) is longer. The binding energy of H_2 to Ni-doped SWNT is –1.04 eV, which is 70meV smaller than that of the configuration of Fig.3(a).

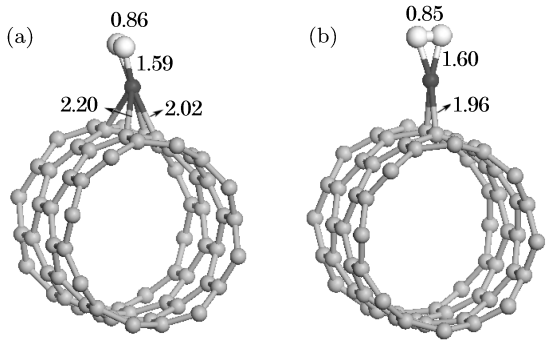


Fig.3. The optimized structures of one hydrogen molecule adsorbed to one Ni atom, where an Ni atom is adsorbed near the H site (a) and an Ni atom on the A site (b) of (8,0) SWNT separately.

To understand the characteristics of the adsorption of the first H_2 molecule on the SWNTNi, we analyse the projected density of states (PDOS) for

H atom and Ni atom. Figure 4(a) shows the PDOS for the initial configuration in which the H_2 molecule is unbound to the SWNTNi. We denote this configuration as SWNTNi+H_2. Figure 4(b) presents the PDOS of the final configuration SWNTNi–H_2 (Fig.3(b)), where the H_2 molecule is bound to the SWNTNi. For the unbound SWNTNi+H_2, the doubly occupied H_2 bonding state shows a single peak about 6 eV below the Fermi level E_F. For the bound SWNTNi–H_2 (Fig.4(b)), this peak disappears and an overlap of density state between H 1s orbital and Ni 3d, 4s, 3p orbitals appears at about 8 eV below E_F, which indicates that the hybridization takes place mainly between H_2 bonding state and Ni 3d, 4s state. Additionally, in Fig.4(b), we can find the overlap of the density state between Ni 3d, 4s and H 1s orbitals at about 1.2 eV below E_F. The isosurface plot of the Ni and H orbitals at about 1.2 eV below E_F (in Fig.5) suggests that this overlap is due to the hybridization between a filled Ni 3d orbital and an antibonding molecular orbital of H_2. The above analysis suggests

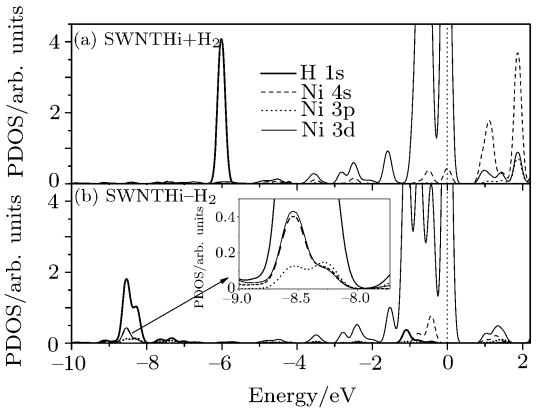


Fig.4. The PDOS for an Ni atom and H atom of the Ni-doped SWNT with unbound H_2 (a), and the Ni-doped SWNT with bound H_2 (b).

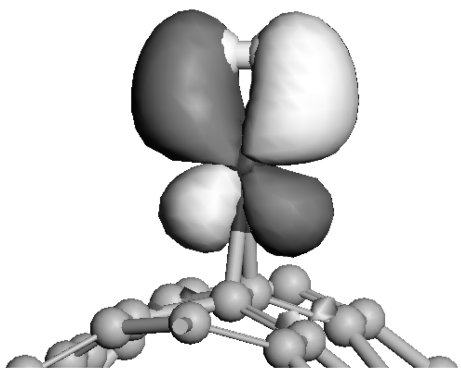


Fig.5. Isosurface plot of the Ni and H orbitals about 1.20 eV below the Fermi energy at a value of 0.03.

that the adsorption of the first H_2 molecule to SWNTNi comes from the electronic hybridization between Ni orbitals and H_2 molecular orbitals.

We now reach the question of how many H_2 molecules could be chemically bound to a single Ni atom doped on the exterior wall of the SWNT. We place a second H_2 molecule around the Ni atom to which one H_2 has already attached. The optimized structure in Fig.6(a) illustrates that both of the H_2 molecules are molecularly adsorbed around the Ni atom with the H–H bond lengths increasing to 0.082 and 0.084 nm, and the average binding energy E_b is –0.78 eV/H_2. By adding a third H_2 to the SWNTNi–$2H_2$ as shown in Fig.6(b), this H_2 is just physisorbed with a binding energy of –0.15 eV. The Ni–H distance increases to 0.331 nm.

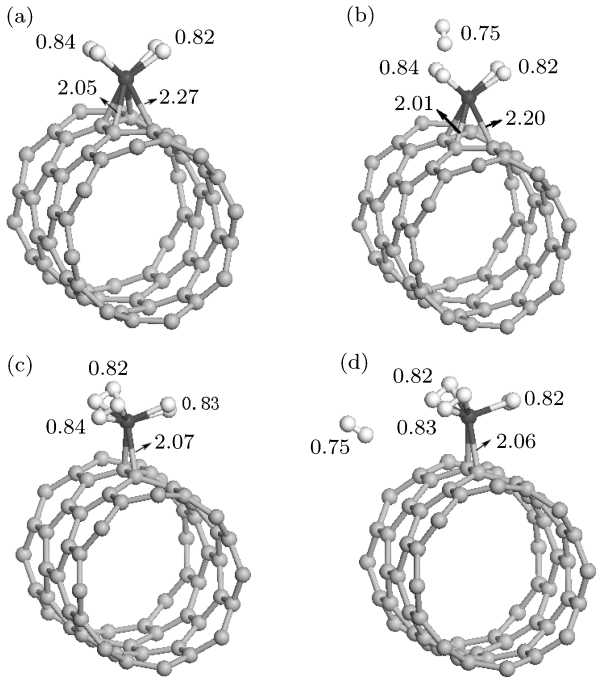


Fig.6. The optimized structures of $2H_2$ (a), $3H_2$ ((b) and (c)), and $4H_2$ (d) adsorbed to the Ni atom on exterior wall of (8, 0) SWNT.

In fact, the configuration in Fig.6(b) is not the only configuration with three H_2 molecules adsorbed to the SWNTNi. Among many different isomers tried for $3H_2$ system, we find a symmetric configuration SWNTNi–$3H_2$ as shown in Fig.6(c), where three hydrogen molecules are symmetrically chemically adsorbed around the Ni atom with an average binding energy of –0.67 eV/H_2. The average H–H bond length increases to 0.083 nm, and the Ni–C bond lengths are all elongated to 0.207 nm. Its total energy is 0.29eV lower than that of the asymmetric configuration in

Fig.6(b).

Setting a fourth hydrogen molecule to SWNTNi–$3H_2$, the optimizing procedure indicates that only former three hydrogen molecules keep chemically bound to the Ni atom and the fourth one moves away as in Fig.6(d). The distance between the fourth H_2 and the Ni atom is 0.374 nm and the binding energy is –0.12 eV, which indicates that the fourth hydrogen molecule is weakly physisorbed around the Ni atom.

The above results imply that at most three H_2 can be chemisorbed to the Ni atom which is adsorbed on the exterior wall of SWNT. The average binding energy of –0.67 eV/H_2 reveals that the three chemisorbed H_2 molecules are significant for the hydrogen storage at a moderate temperature, while the physisorbed hydrogen molecules may escape from the SWNT.

Using Mulliken method, we find that the Ni atom transfers 0.34e to the SWNT when it is adsorbed on the A site of exterior wall. This charge transfer leaves the Ni atom in the cationic form. It is reported that the Ni cation is difficult to donate electrons to H_2 molecule, but it can polarize the H_2 molecules and bind them by the electrostatic interaction.[18] And it is this polarization that makes the hydrogen molecules transfer a small number of electrons to the Ni cation. As the number of the H_2 increases, the Ni cation becomes close to the neutral state which in turn reduces polarization. Such an average binding energy decreases as the number of H_2 molecules increases. Apart from the electrostatic interaction, electronic hybridization also plays an important role in the adsorption process.

3.3. Adsorption of H_2 molecule to Ni dimer on SWNT

Most probably, nickels stay with the nanotube as clusters. Here we just probe the case of Ni dimer. In the initial structure, two Ni atoms are placed on the adjacent A sites of (8,0) SWNT. As discussed above, the A site is the most stable site when single Ni atom is adsorbed on SWNT. After geometrical optimization, one of the Ni atoms is still on the A site and another one moves to near the H site (Fig.7(a), named SWNT2Ni). The average binding energy between the Ni dimer and SWNT is –2.87 eV/Ni. The bond length of Ni–Ni is 0.237 nm and it elongates compared with that of the free Ni dimer. These changes indicate that the interaction between Ni dimer and SWNT is weakened with the number of Ni atoms increasing and conversely the interaction between SWNT and Ni dimer weakens the Ni–Ni bond.

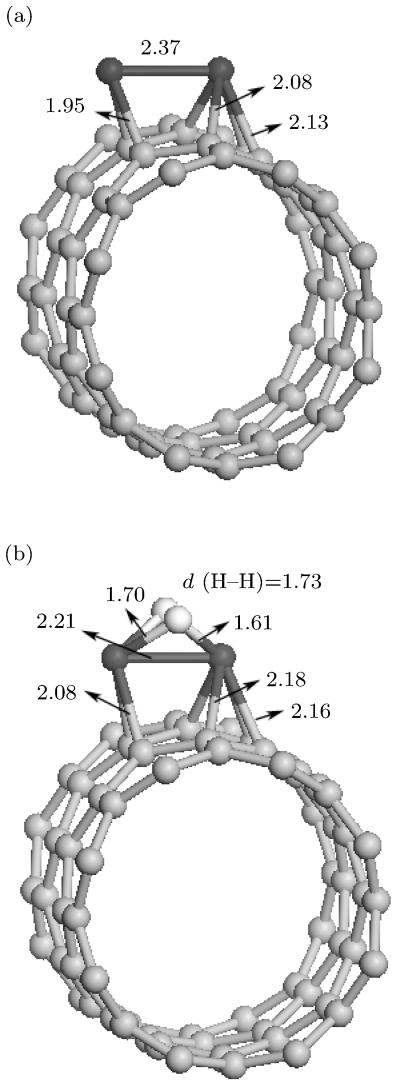


Fig.7. The optimized structure of two Ni atoms adsorbed on the exterior wall of (8,0) SWNT (a), and the optimized structure of one hydrogen molecule adsorbed to the Ni dimer on exterior wall of (8,0) SWNT (b).

For the adsorption of the H_2 molecule on SWNT2Ni, different initial positions of H_2 around the Ni atoms are taken into account. We find that when the H_2 molecule perpendicularly approaches the Ni–Ni bond, the H_2 dissociates without overcoming any barrier, which is different from the case of H_2 attached to SWNT doped by one Ni atom. The optimized structure is shown in Fig.7(b). The H–H bond is broken, with each H atom adsorbed to the two Ni atoms. The Ni–H distances are 0.170 nm and 0.161 nm. The H–H bond length is 0.173 nm with a binding energy of –0.53 eV/H. This result indicates that the Ni atom can

work as a catalyst to make the H_2 dissociate automatically.

In the experiment performed by Kim *et al* [9] compared with the pristine nanotubes, there is a prominent increase of the C–H_n stretching vibration peak after interacting with hydrogen for the Ni-dispersed nanotubes, which means that there are more H atoms bound to the surface of the SWNT. While our results have proved that the H_2 molecule can dissociate without energy barrier upon approaching the Ni dimer adsorbed on the SWNT. Therefore we suggest that the dissociated H atoms adsorbed on the Ni dimer may diffuse onto the surface of SWNT and make bonds with C atoms. As the diffusion is a dynamic process, which is affected by many factors, such as the number and the dispersion condition of the Ni atoms, the temperature, the pressure and so on. By optimizing these factors, the hydrogen storage of Ni-doped SWNT may reach the Department of Energy (DOE) target (6.5 wt%).

4. Conclusions

We have investigated the adsorption of the hydrogen molecules on Ni-doped SWNT. For the exterior wall of SWNT, a single Ni atom tends to occupy the bridge site above the C–C bond and this Ni atom can bind up to three H_2 at most. The average hydrogen binding energy of –0.67 eV indicates that the binding results from the physisorption and chemisorption, which is suitable for the reversible hydrogen storage at a moderate temperature. For the SWNT doped with Ni dimer, the Ni atoms can work as a catalyst to make the hydrogen molecule automatically dissociate into two H atoms, thereby making bonds with Ni atoms. In certain conditions, the H atoms are supposed to diffuse onto the surface of SWNT and make C–H bonds. All in all, the Ni atoms doped on SWNT can affect the hydrogen storage by directly molecularly chemisorbing the H_2 molecules or dissociating the H_2 molecules as a catalyst.

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