Adsorption and dissociation of hydrogen molecules on bare and functionalized carbon nanotubes

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We investigated interaction between hydrogen molecules and bare as well as functionalized single-wall carbon nanotubes (SWNT) using first-principles plane wave method. We found that the binding energy of the H₂ physisorbed on the bare SWNT is very weak, and can be enhanced neither by increasing the curvature of the surface through radial deformation, nor by the coadsorption of Li atom that makes the semiconducting tube metallic. Though the bonding is strengthened upon adsorption directly to Li atom, yet its nature continues to be physisorption. However, the character of the bonding changes dramatically when SWNT is functionalized by the adsorption of Pt atom. Single H₂ is chemisorbed to Pt atom on the SWNT either dissociatively or molecularly. If Pt-SWNT bond is weakened either by displacing Pt from bridge site to a specific position or by increasing number of the adsorbed H₂, the dissociative adsorption of H₂ is favored. For example, out of two adsorbed H₂, first one can be adsorbed dissociatively, second one is chemisorbed molecularly. The nature of bonding is weak physisorption for the third adsorbed H₂. Palladium also promotes the chemisorption of H₂ with relatively smaller binding energy. Present results reveal the important effect of transition metal atom adsorbed on SWNT and advance our understanding of the molecular and dissociative adsorption of hydrogen for efficient hydrogen storage.

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I. INTRODUCTION

Fuel cells have been a real challenge for clean and efficient source of energy in diverse fields of applications with different size and capacity range. Once hydrogen molecule is chosen as potential fuel, its storage, easy discharge for consumption and dissociation into hydrogen atoms to complete the current cycle in the fuel cell to produce the desired electromotive force involve several problems to be solved. Dillon et al. have pioneered the idea that carbon nanotubes can be efficient, cheap and rechargeable storage medium for small-scale fuel cells with different size and capacity range. Once hydrogen molecule is chosen as potential fuel, its storage, easy discharge for consumption and dissociation into hydrogen atoms to complete the current cycle in the fuel cell to produce the desired electromotive force involve several problems to be solved. Dillon et al. have pioneered the idea that carbon nanotubes can be efficient, cheap and rechargeable storage medium for small-scale fuel cells with estimating 5-10 weight percent (up) H₂ adsorption in single-wall carbon nanotubes (SWNT). Later, Ye et al. and Liu et al. obtained H₂ storage capacities of 8.2 and 4.2 up, respectively.

Unfortunately, recent studies further exploring this idea have come up with controversial conclusions. In the mean time, adsorption of alkali atoms on SWNTs have been proposed to enhance the H₂-uptake. Nevertheless, carbon nanotubes have high surface-volume ratio and their functionalization to render them feasible for hydrogen storage through coverage of suitable adatoms has remained to be explored.

In this paper, we addressed following questions in order to clarify controversial issues related to the storage of hydrogen molecule on carbon nanotubes: Can H₂ molecule be adsorbed on the SWNT? What is the nature and strength of the bonding? Can the strength of the bonding be modified either by changing the curvature of the surface or by the coadsorption of metal atoms? In particular, can the H₂-uptake on SWNTs be promoted by their functionalization through transition elements? How can H₂ molecule be dissociated? To answer all these questions we investigated the interaction between H₂ molecule and bare, radially deformed and foreign atom adsorbed SWNTs by carrying out calculations within Density Functional Theory (DFT). Our results not only advance our understanding of H₂ adsorption on carbon nanotubes, but also suggest new ways for efficient hydrogen storage for rapidly growing research on fuel cells.

Our calculations have been carried out using first-principles plane wave method and ultrasoft pseudopotentials within Generalized Gradient Approximation (GGA). Adsorption and dissociation of H₂ is treated within the supercell geometry by optimizing atomic positions. The weak attractive Van der Waals (VdW) interaction becomes crucial in calculating binding energies of weak physisorption bonds, but is not well represented in DFT using GGA. Therefore, in the case of physisorption, weak and attractive VdW interaction energy, \( E_{VdW} \), is obtained from the Slater-Kirkwood approximation using the asymptotic form of the Lifshitz’s equation. However, this approach can not be suitable to determine the contribution of VdW interaction in the chemisorption of molecules. In the present calculations we take the zigzag (8,0) SWNT as a prototype tube.

II. ADSORPTION OF H₂ ON BARE AND RADIVALLY DEFORMED SWNT

To clarify whether H₂ can form stable bonding on the outer or inner surface of a SWNT, we calculated the chemical interaction energy between H₂ and the outer
surface of the (8,0) SWNT at different sites (i.e., H-site, above the hexagon; Z- and A-site above the zigzag and above the axial C-C bonds; T-site, a bridge site between two adjacent zigzag C-C bonds) as a function of spacing $d$. The chemical interaction energy is obtained from the expression, $E_C(d) = E_T[H_2+SWNT,d]−E_T[SWNT]−E_T[H_2]$, in terms of the total energies of bare nanotube ($E_T[SWNT]$), free $H_2$ ($E_T[H_2]$), and $H_2$ attached to SWNT at a distance $d$ ($E_T[H_2+SWNT,d]$). Here $E_C < 0$ corresponds to an attractive interaction. The stable binding occurs at the minimum of $E_C(d) + E_{VdW}(d)$, the negative of it is denoted as the binding energy $E_b$. The binding is exothermic when $E_b > 0$. In Fig. 1 we show the variation of $E_C(d)$ calculated for unrelaxed atomic structures at the H-site. Once the atomic structure of both SWNT and $H_2$ molecules are relaxed the minimum value of $E_C(d)$ is found to be -27 meV at $d_0 = 3.1 \text{Å}$ at the H-site. Minimum values of $E_C(d)$ calculated for A-, Z-, and T-sites are also very small and comparable to that of H-site. The long range VdW interaction energy calculated for the H-site at $d_0$ is $E_{VdW} \sim 30 \text{ meV}$. Then the binding energy associated with $H_2$ molecule adsorbed at H-site is calculated to be $E_b \sim 57 \text{ meV}$. This is a small binding energy and indicates physisorption.

Previous studies revealed that the physisorption of individual $H_2$ molecules with $E_b > 0$ cannot occur on the inner wall of SWNT. Hydrogen molecules prefer to stay either at the center of the tube or to form some cylindrical shells inside depending on radius of the tube. Owing to increased H-H interaction at high coverage, even the atomic hydrogen cannot form stable structure when it is adsorbed to the inner wall of small radius tube. For (8,0) tube we found that $H_2$ is trapped and stabilized at the center of the tube with a repulsive interaction energy $E_C = +0.34 \text{ eV}$. The implementation of $H_2$ inside the tube having radius in the range of 3 Å is expected to be hindered by this repulsive interaction.

Earlier it has been shown that binding energy of foreign atoms adsorbed on SWNT increase with increasing curvature. Tada et al. have argued that the potential barrier associated with the dissociative adsorption of $H_2$ on SWNT is lowered with increasing curvature of the tube. It has been proposed that the potential barrier for the dissociation of $H_2$ adsorbed in the interstitial region between tubes can be lowered by applying radial deformation to the rope or SWNT. It is known that under radial deformation the circular cross section changes and consequently the curvature varies at different locations on the surface. Motivated with those effects of curvature, we examine whether the attractive interaction energy $E_C$ can be enhanced by changing the curvature of the tube via radial deformation. Radial deformation is realized by pressing the tube between two ends of a given diameter. It, in turn, changes the circular cross section of the bare tube with radius $R_0$ to an elliptical one with major and minor axes $2a$ and $2b$, respectively. The atomic structure of (8,0) tube is optimized under radial strain $\epsilon_r = (R_0 - b)/R_0 \approx 0.3$ by fixing row of carbon atoms at the end of minor axis. The deformation is reversible so that the tube goes back to its original, undeformed form upon the release of radial strain. The deformation energy (that is the difference between the total energies of
deformed and undeformed SWNTs) is calculated to be $E_D = 1.4$ eV per unit cell. We examined whether the binding energy of H$_2$ molecule changes under the radial deformation of SWNT. Figure 11 shows the variation of $E_C(d)$ for H$_2$ approaching toward the high curvature site of the tube (i.e. one end of the major axis) at the H-site. The minimum value of the attractive interaction, $E_C$ is -30 meV and occurs at $d_o = 2.9$ Å. For $e_r = 0.25$, we also obtained very small enhancement of $E_C(d)$. Hence, the effect of curvature on the binding energy of H$_2$ is negligible due to relatively large $d_o$. This result also suggests that the physisorption energy does not vary significantly depending on the radius of SWNT. Apparently, the binding of H$_2$ on the outer surface of SWNT is weak and corresponding physisorption energy is small. The binding cannot be enhanced by increasing the curvature locally through radial deformation. Curvature effect or radial deformation may be significant at small $d$ when H$_2$ is forced towards SWNT surface.

III. COADSORPTION OF HYDROGEN MOLECULE AND LITHIUM ATOM ON SWNT

Next, we examine whether the binding of H$_2$ is enhanced by the coadsorbed foreign atoms. To this end we first consider Li atom adsorbed on the (8,0) SWNT, since the adsorption of an alkali atom has been proposed to enhance the H$_2$-uptake. Li atom is chemisorbed at the H-site, 1.5 Å above the surface of SWNT with a binding energy of 0.8 eV. Self-consistently calculated electronic structure shown in Fig. 2 reveals that chemisorbed Li atoms donate their 2s-valence electrons to the lowest conduction $\pi^*$-band so that the semiconducting (8,0) SWNT (having band gap $E_g = 0.6$ eV) becomes metallic. This is a behavior common to the other alkali atoms adsorbed on SWNTs. In order to examine the indirect effect of coadsorbed Li we considered H$_2$ as attached at the opposite site to Li. The optimized structure of the physisorbed H$_2$ is shown in Fig. 2 together with relevant structural parameters. We found $E_C$ has a minimum value of -35 meV at $d_o = 3.4$ Å. Similar study has been also performed for Li atom adsorbed on the inner wall of SWNT while H$_2$ is on the external wall directly above the coadsorbed Li as shown in Fig. 2. In this adsorption configuration minimum value of $E_C$ practically did not change. The local density of states calculated on Li atom and H$_2$ refuse the possibility of any significant interaction between adsorbates. As a result, our calculations for both external and internal adsorption of Li rule out any indirect effect of coadsorbed Li to enhance the binding of H$_2$ on SWNT. The occupation of empty conduction band by the alkali electrons and hence metallization of SWNT did not affect the bonding of H$_2$. These results are in agreement with the first principles calculations by Lee et al. However, the effect of Li on the adsorption of H$_2$, whereby H$_2$ is attached directly to Li atom is found significant. The minimum value of $E_C$ has increased to -175 meV, while $d_o$ decreased to 2.1 Å. Briefly, the coadsorption of Li does not have any indirect effect on the binding of H$_2$, but the energy associated with direct binding to Li is enhanced. However, the nature of bonding remains physisorption in direct and indirect cases.

IV. COADSORPTION OF HYDROGEN MOLECULE AND PLATINUM ATOM ON SWNT

A single transition metal atom adsorbed on the outer surface of SWNT has shown interesting properties, such as high binding energy and magnetic ground state with high net magnetic moment. For example, transition element atoms (Ti, V, Cr, Mn, Fe, Co, Pt, etc.) have crucial adsorption states on nanotubes and some of them (Ti, Ni, Pd) form continuous or quasi-continuous metal coating on the SWNT. As for Pt atom, it is known to be a good catalist in various chemical processes. While SWNTs offer high surface/volume ratio, the interaction between H$_2$ and Pt atom adsorbed on SWNT may be of interest. Now we investigate the character of the bonding between H$_2$ and Pt adsorbed on SWNT and address the question of how many H$_2$ molecules can be attached to an adsorbed Pt atom and how strong is the binding.

A. Adsorption of Pt atoms on SWNT

We first examine the adsorption of Pt atom(s) on (8,0) SWNT. The character of the bonding has been investigated by placing Pt atoms on the A-sites of (8,0) tube (that is known to yield highest binding energy) and then by optimizing the structure. Three different adsorption configuration have been examined, namely one, two and three Pt atoms adsorbed on the adjacent sites to represent a small cluster on SWNT as described in Fig. 3. Calculated binding energies of Pt atoms have increased as the number of Pt atoms increases from one to three in the same neighborhood. On the other hand, the C-Pt distance gradually increases with increasing number
B. Adsorption of H₂ to a free Pt atom

We now consider the interaction between H₂ molecules and a free Pt atom. Optimized binding structures are shown in Fig. 4. Upon approaching to a free Pt atom, single H₂ molecule dissociates and form PtH₂ with Pt-H bond distance \(d_{Pt-H} = 1.51 \text{ Å}\) and \(d_{H-H} = 2.08 \text{ Å}\). The total energy \(E_T\) relative to the energies of free Pt and H atoms is calculated -9.88 eV. The binding energy relative to H₂ molecule and free Pt atom is \(E_b = 3.09\) eV. As for the adsorption of H₂ to PtH₂, there are several minima on the Born-Oppenheimer surface: The first minimum corresponds to a configuration in Fig. 4(b) where PtH₂ preserves the dissociated configuration while second H₂ is molecularly adsorbed. Even if H-H interaction of adsorbed H₂ is weakened and hence the H-H distance has increased to 0.87 Å, we identify it as molecular adsorption. We denote this configuration as PtH₂+H₂. The adsorbed H₂ molecule is perpendicular to the plane of PtH₂. The binding energy of the second H₂ to PtH₂ is calculated to be \(E_b = 0.87\) eV. Under these circumstances the average binding energy of each H₂ is 1.98 eV. In the second configuration, identified as Pt-2H₂ as shown in Fig. 4(c), both H₂ are molecularly adsorbed. As H-H molecular bonds are weakened, \(d_{H-H}\) is increased to 0.96 Å and all Pt-H bonds have uniform length with \(d_{Pt-H} = 1.65\) Å. Here ad-
sorbed H₂ molecules are perpendicular. The binding energy of each molecules is calculated to be 1.94 eV slightly less than the average binding energy in PtH+H₂ configuration. The configuration PtH₂+2H₂ shown in Fig. 4(d) involves the adsorption of three H₂ molecules; one dissociatively, remaining two are molecularly adsorbed. Here Pt-H₂ planes of two molecularly adsorbed H₂ are perpendicular. The binding energy of the third H₂ relative to the energy of PtH₂+H₂ in Fig. 4(b) is found to be 0.81 eV. Accordingly, the average binding energy of each H₂ is 1.6 eV relative to free H₂ and free Pt atom.

Fig. 4(e) compares four distinct configurations related with the adsorption of two molecules on the same free Pt atom. It appears that these configurations correspond to local minima on the Born-Oppenheimer surface and the configuration in Fig. 4(b) appears to have lowest energy.

C. Adsorption of H₂ to a Pt atom on SWNT

We deduced two configurations for the adsorption of a single molecule to a Pt atom adsorbed on the (8,0) SWNT as described in Fig. 5. While these two chemisorption configuration look dramatically different, their total energies differ only by 6 meV (that is smaller than the accuracy range of DFT). In the configuration described in Fig. 5(a) H₂ is dissociatively adsorbed with binding energy $E_b=1.1$ eV relative to free H₂ and Pt adsorbed on SWNT, i.e. $E_T[H_2]$ and $E_T[Pt+SWNT]$, respectively. The H-H and Pt-H distances are 1.86 Å and 2.3 Å, respectively. Whereas in the configuration in Fig. 5(b) H₂ is molecularly adsorbed with a significantly weakened H-H bond. H₂ approaching from different directions and angles results in a chemisorption state with binding energy $E_b=1.1$ eV and Pt-H distance 1.7 Å. The length of H-H bond has increased from 0.75 Å to 0.95 Å upon adsorption. Whereas, this configuration appears to be less energetic than the former one, the energy difference between them is only 6 meV. Notably, while in the first configuration leading to dissociative adsorption Pt atom is located near hollow H-site, in the "molecular" adsorption of H₂ Pt atom is adsorbed at the A-site. As compared to the average binding energy calculated for H₂ adsorption to a free Pt atom, the molecular adsorption of H₂ to Pt atom adsorbed on SWNT is relatively weaker due to the Pt-SWNT bond.

Adsorption of H₂ to a single Pt atom attached to the surface of graphite is of interest in order to reveal how the binding energy and binding configuration of H₂ depends on the radius of SWNT. We considered two configuration, namely single Pt atom is adsorbed near hollow H-site, as shown in Fig. 5(c) and Pt at the A-site as shown in Fig. 5(d). For both location of Pt atom on the graphite surface, H₂ molecule approaching the adsorbed Pt atom is dissociated and eventually Pt atom formed two Pt-H bonds with individual H atoms. In this case the binding with the graphite surface is weaker than that on SWNT, and thus $d_{Pt-C}$ is increased to 2.4 Å. Relatively weaker interaction between Pt and graphite surface allows stronger interaction between H₂ and Pt, as in the case of free Pt atom, and hence leads to the dissociation of the molecule. In view of two limiting case in Fig. 5 one can expect that dissociation of H₂ may occur for SWNTs having larger R.

FIG. 6: Optimized structure of H₂ molecules adsorbed to the Pt atom on the SWNT. (a) One H₂ adsorbed to PtH₂. The inset show the regions of charge depletion ($\Delta \rho < 0$) and charge accumulation ($\Delta \rho > 0$) as a result of the bonding between SWNT and PtH₂+H₂ in (a). (b) Another local minima where two H₂ is molecularly adsorbed to the Pt atom. (c) One H₂ is chemisorbed two H₂ are weakly bound. (d) four H₂.
FIG. 7: Dissociative adsorption of single H\textsubscript{2} on a small Pt cluster adsorbed on SWNT (a). One H\textsubscript{2} is approaching two adjacent Pt atoms adsorbed on SWNT. (b) Optimized geometry after dissociative adsorption of H\textsubscript{2}. (c) Variation of total energy with distance \(z\). Small circles correspond to \(E_T\) for unrelaxed H\textsubscript{2} and unrelaxed SWNT. Dotted curve corresponds to \(E_T\) of the geometry relaxed at certain distances. (d), (e) and (f) same as (a), (b) and (c) except the Pt cluster consists of 3 Pt atoms. \(z\) is the distance from the surface of SWNT. Variation of \(E_T(z)\) is amplified by inset.

To answer the questions of how many H\textsubscript{2} molecule can be attached to a single Pt atom we perform a systematic study outlined in Fig. 6. First we let a second H\textsubscript{2} approaches to Pt atom on SWNT that already has one H\textsubscript{2} molecule attached as in Fig. 5(b). The final optimized geometry of Pt and adsorbed H\textsubscript{2} molecules in Fig. 6(a) is similar to the configuration PtH\textsubscript{2}+H\textsubscript{2} described in Fig. 4(b). This situation is explained by the weakening Pt-C bond between PtH\textsubscript{2} and SWNT shown in Fig. 5(a) which is followed by the increase of \(d_{Pt-C}\). First H\textsubscript{2}, which was initially chemisorbed to Pt as a molecule has dissociated upon the molecular adsorption of the second H\textsubscript{2}. The dissociation of H\textsubscript{2} is an indirect process and is mediated by the weakening of the Pt-C bonding through the molecular adsorption of second H\textsubscript{2}. The difference charge density \(\Delta\rho(r) = \rho_T(r) - \rho_{SWNT}(r) \approx \rho_{PtH_2+H_2}(r)\) calculated from the difference of total charge density \(\rho_T(r)\) of SWNT+PtH\textsubscript{2}+H\textsubscript{2} in Fig. 6(a) and those of SWNT and PtH\textsubscript{2}+H\textsubscript{2} indicates that while the charge of Pt-\textit{d}\textsubscript{xy} and C-\textit{p}\textsubscript{x,y} orbitals are depopulated, the Pt-\textit{d}\textsubscript{z} and C-\textit{p}\textsubscript{z} orbitals become populated to form Pt-SWNT bond. This result suggests that in a reverse situation the weakening of the Pt-SWNT bond would lead to the transfer of charge from Pt-C bond to Pt-H bonds resulting in increased population of \(d_{xy}\)-orbitals in favor of the dissociation. Interestingly, exactly the same configuration has been obtained even when two H\textsubscript{2} molecule approach concomitantly the bare Pt adsorbed on SWNT. Another configuration related with two molecularly adsorbed H\textsubscript{2} is shown in Fig. 6(b), which appears to be a local minima on the Born-Oppenheimer surface and \(\sim 0.4\) eV less energetics than that in Fig. 6(a). The configuration of Pt+2H\textsubscript{2} has remained even after SWNT is removed.

In Fig. 6(c), two H\textsubscript{2} approaching from both sites of PtH\textsubscript{2} already adsorbed on SWNT have been attached by weak physisorption bonds resulting PtH\textsubscript{2}+2H\textsubscript{2}. Their distances to Pt atom are relatively larger (2.1 Å and 3.2 Å) than that occurred for molecularly chemisorption of H\textsubscript{2}. The latter Pt-H distance is too long and the binding energy is \(\sim 20\) meV; the binding energy can increase slightly by the VdW interaction but the adsorbed molecule can desorb and escape from Pt at high-temperature. Note that due to weak interaction between PtH\textsubscript{2} and both H\textsubscript{2} molecules, the Pt-C bond becomes stronger, and consequently H-H distance of PtH\textsubscript{2} is closed to be associated in H\textsubscript{2}. The attempts to attach more than three molecules to the Pt atom have failed. For example, as shown in Fig. 6(d), from four H\textsubscript{2} brought at the close proximity of Pt atom, only three were attached (one dissociatively chemisorbed, one molecularly chemisorbed, one physisorbed and the forth escaped). At the same time the Pt-SWNT bond has weakened and hence \(d_{Pt-C}\) distance has increased to 2.3 Å. We define the interaction energy between Pt+nH\textsubscript{2}, where \(n=2\) (one of H\textsubscript{2} is dissociated), 3 and 4 (one of H\textsubscript{2} is dissociated) and SWNT in Fig. 6(a-c) as \(E[Pt-nH_2]+E_T[SWNT]-E_T[Pt+nH_2+SWNT]\). Here
and H2 action and smaller binding energies. For example, the calculated for different H2 from the normal value 0.7˚ 
while the H-H bond length is stretched a little in this case, while the H-H bond length is stretched a little.

dissociation process schematically shown in Fig. 7(c) by plotting the variation of total energy E_z as a function of z for two different cases. The curve by small circles corresponds to the total energy of SWNT+Pt2 and H2 calculated for different H2-tube distance z by keeping the atomic configuration at z = ∞ frozen for all z. The continuous curve is obtained by relaxing the atomic configuration at certain values of z. We see that for z < 4.2 Å E_z starts to lower upon the onset of dissociation. We note very small barrier at about z ~ 4.5Å. Upon overcoming this energy barrier, the process is exothermic with an energy gain of ~ 1.2 eV. As described in Fig. 7(d-f), the adsorption of single H2 on a Pt cluster consisting of three Pt atoms also results in dissociation of the molecule. As the size of cluster increased by inclusion of the third Pt atom, the small potential barrier at z ~ 4.5Å is further lowered, the binding energy increased to 1.5 eV. Also one of the Pt atoms which binds both H atom is detaches from the SWNT surface. This situation confirms that Pt-SWNT bonds are weakened upon the (molecular or dissociative) adsorption of H2 to Pt.

The interaction between Pd atoms adsorbed on SWNT and H2 molecule is somehow similar to that with Pt atom. However, the latter case leads relatively less strong interaction and smaller binding energies. For example, the interaction between H2 and a single Pd atom adsorbed on SWNT results in a binding between chemisorption and physisorption with a binding energy of 0.6 eV. In this case, while the H-H bond length is stretched a little from the normal value 0.7 Å to 0.8 Å, the C-Pd bond is stretched from 2.1 Å to 2.2 Å. Small changes after the adsorption of H2 are manifestations of relatively weak H2-Pd interaction. In contrast to adsorbed two Pt atom in Fig. 7(a) breaking the H2 molecule, two adsorbed Pd atoms give rise to chemisorption of molecule with more stretched H-H bonds.

### V. CONCLUSIONS

In this work we presented a detailed analysis of the interaction between hydrogen molecule and a SWNT. We found that the binding energy between H2 and outer surface of a bare SWNT is very weak and the physisorption bond can easily be broken. We showed that the binding of H2 to the outer surface cannot be enhanced by applying radial deformation to increase curvature effects at the site facing H2 molecule. In contrast, the interaction between the inner surface of (8,0) tube and H2 is repulsive which can prevent molecules from entering inside the tube. The repulsive interaction may turn to be attractive for large tube radius. To promote H2 uptake on SWNT surface we considered functionalized tubes through adsorption of foreign atoms. The binding energy of H2 on SWNT surface did not increase by the coadsorption of Li. However, the binding energy increased if H2 is directly attached to adsorbed Li; yet the nature of the bonding remained physisorption.

The situation with Pt atom, which can make strong chemisorption bonds with the outer surface of SWNT is found to be interesting from the point of view of H2 storage. We showed that H2 molecule can form chemisorption bonds with free Pt as well as Pt adsorbed on SWNT. Single H2 adsorbed on a free Pt atom dissociates and forms two strong Pt-H bonds. On the other hand, while single H2 molecule is molecularly chemisorbed to a single Pt atom at the A-site of SWNT surface, it can dissociate if Pt atom adsorbed near the hollow site. Even the molecular adsorption of single H2 can turn dissociative if a second H2 is molecularly adsorbed to the same Pt atom. The dissociative adsorption is mediated by the weakening of Pt-C bonds either due to a specific location of Pt on SWNT or due to the second H2 molecularly adsorbed to Pt. Dissociative adsorption of single H2 to a single Pt atom on the graphite surface suggests that the dissociation of H2 is favored on SWNTs having large radius. Our analysis suggests that single Pt adsorbed on SWNT can bind up to two H2 molecules with significant binding energy in the chemisorption range. Beyond two adsorbed H2, additional molecules form weak physisorption bonds with Pt. Single Pd atom adsorbed on SWNT exhibits similar effects but in relatively weaker manner as compared to that of Pt. Interesting interaction between H2 and Pt and resulting bonding mechanisms justifies similar investigations of SWNTs functionalized by other transition elements (in particular Ti, Ni, Cr, V) for a higher up H2 storage.
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27. Since, the bond distance of H$_2$ is extended by 20%, the H-H interaction is weaker than that in free H$_2$. For d$_{H−H} ≈ 1\AA$ the adsorption may be considered as an intermediate stage between molecular and atomic adsorption.