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RESEARCH ARTICLE



Theoretical study of hydrogen adsorption in Ti-decorated capped carbon nanotube

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ABSTRACT

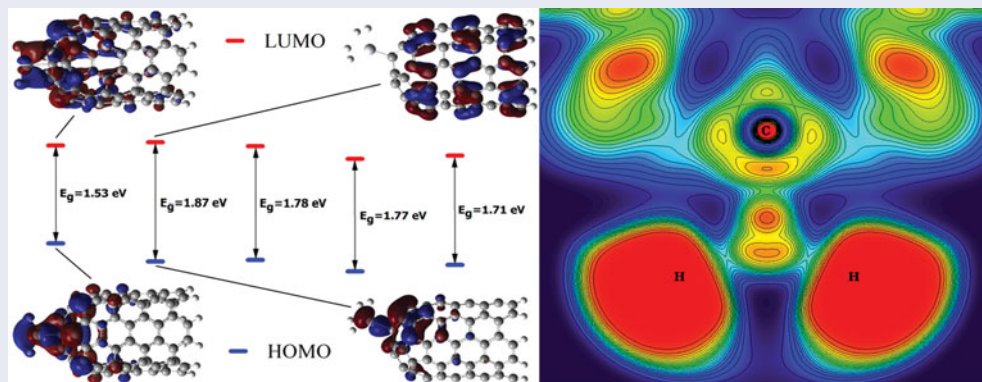
We present *ab initio* study using dispersion-corrected density functional theory calculations to investigate the hydrogen interaction with Ti-coated, one end closed, single-walled carbon nanotube (SWCNT). Our results demonstrate that a single Ti atom binds up to five hydrogen molecules on SWCNT cap top, whereas adsorption of four hydrogen molecules is energetically more favourable. The analyses from adsorption energy profile, highest occupied molecular orbital–lowest unoccupied molecular orbital gap and Mulliken charge distribution show contrast in first hydrogen molecule adsorption compared with the rest of four configurations. This is clearly due to the strongly different bonding nature of first hydrogen adsorption among others, between hydrogen molecules and Ti-coated SWCNT. These results not only support our understanding of adsorption nature of hydrogen in Ti-coated SWCNTs but also suggest new directions for smart storage techniques.

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KEYWORDS

Hydrogen storage; single-walled carbon nanotube; density functional theory; adsorption energy; dispersion correction





1. Introduction

Carbon nanotubes (CNTs) have attracted the attention of scientists and engineers since their discovery in 1993 [1], due to their unique and promising structural, mechanical and electronic properties, as well as their application potential [2,3]. Numerous research projects have been performed to work on the properties and applications of these fascinating novel materials. They have a wide range of potential applications, ranging from the field of nanoelectronics to nanoscale biotechnology. They also, because of their size, large surface area and hollow geometry, are being considered as prime

materials for gas adsorption [4–6], biological, chemical, electromechanical sensors and nanoelectronic devices [7,8]. Generally, nanostructures play an important role in the area of hydrogen storage. Hence, among the nanomaterials identified for hydrogen storage, carbon nanomaterials are the preferred ones. In particular, CNTs are one of the possible hydrogen storage media useful, for example, for fuel cell applications. Many studies support the importance of CNTs for storing hydrogen in many convenient ways [9–12]. However, as it is known that pristine CNTs have very poor hydrogen storage capacity [13], functionalisation in an appropriate way is

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required to improve the H₂ storage capacity. Formerly published works [14,15] indicated that single-walled carbon nanotubes (SWCNTs) and fullerenes coated with Ti can enhance the hydrogen storage capacity; and it has also been proven that heavy transition metals like Mn, Fe and Co are not suitable to store/deliver hydrogen at ambient conditions [14]. Indeed, light transition metal atoms have a better chance to promote hydrogen binding [16]. Hence, in this study, a light transition metal, titanium, has been chosen for functionalisation.

There are various practical ways for CNTs production; because of their lower energy configuration, CNTs produced by most standard chemical vapour deposition techniques with having a capped (closed) end. Such closed end can be opened by a water-assisted selective etching method [3]. The presence of both capped and open-end CNTs has attracted extensive research activities because of their geometrical-dependant properties; for example, experimental observations have shown that, in an end-contact configuration, the thermal/electrical conductance at a CNT/metal interface is tightly related to the tube tip geometry [17,18].

On the other hand, difficulties in CNTs production and especially elicitation of functionalised CNTs characterisation have made computational studies of these systems indispensable. Even though experimental techniques have advanced, theoretical calculations have preserved their significant role in predicting geometries and energy levels of novel materials.

Thus, first principle studies have shown [14] that each Ti atom adsorbed on wall of SWCNT can bind up to four hydrogen molecules. It was also reported that TiO₂ bonded to CNT can form an appropriate functionalisation for hydrogen storage in CNTs [19]. There is a recently published report in which adsorption of atoms has investigated on different parts of capped (5,5) SWCNT and they ended up with results indicating that adsorption energies on the tube are lower than those on the cap, implying that the adsorptions on the cap are more stable [20]. Considering these assumptions, in present work, we investigate interaction energies of hydrogen molecules with Ti decorated on the cap top of (5,5) SWCNT along with structural and electronic properties.

2. Computational method

All *ab initio* calculations are based on hybrid Becke's 3-parameter functional combined with Lee, Yang, and Parr's correlation functional (B3LYP) [20] including dispersion correction for density functionals using Grimme's DFT-D3 approach [21] and with the Becke–Johnson damping. The method has recently been refined

regarding higher accuracy, broader range of applicability and less empiricism. It has also been established that DFT is able to accurately treat such systems due to incorporation of the exchange–correlation effects. For both heavy and light atoms, i.e. carbon, hydrogen and titanium, we used double- ξ quality plus polarisation basis sets def2-SVP [22]. Convergence criteria for the Self Consistent Field (SCF) energies and for the electron density (rms of the density matrix) were placed at 10⁻⁷ a.u., whereas for the Cartesian gradients the convergence criterion was set at 10⁻⁴ a.u. The whole system was relaxed in the geometry optimisation at the same time by demanding that the total force (average and maximum) on each atom be practically zero, i.e. smaller than 10⁻⁴ a.u. All DFT and frequency calculations were performed using ORCA 4 [23] *ab initio* quantum chemistry program package.

3. Results and discussion

3.1. Structural properties

We constructed armchair (5,5) SWCNT and closed one end by placing a part of fullerene C₆₀ at top in order to achieve one closed-end SWCNT. Thus, nanotube contains 90 carbon atoms and 10 hydrogen atoms, hence a total of 100 atoms which is much feasible for computational calculations using DFT. Furthermore, in the absence of periodic boundary conditions of molecular calculations, it is necessary to saturate the carbon dangling bonds with hydrogen atoms; so we designed a hydrogen terminated SWCNT.

Initially, a Ti atom was placed at the top of pentagon ring of SWCNT and optimised, then H₂ molecule was added to Ti atom and geometry optimisation was again performed. Progressively, second H₂ molecule was added and all steps of geometry optimisation were repeated up to five hydrogen molecules successfully. Hence, all five SWCNTs are denoted as C₉₀H₁₀(Ti+1H₂), C₉₀H₁₀(Ti+2H₂), C₉₀H₁₀(Ti+3H₂), C₉₀H₁₀(Ti+4H₂) and C₉₀H₁₀(Ti+5H₂). Some selected optimised geometries of which are shown in Figure 1. In addition to these five SWCNTs, we have also performed calculations for 10 hydrogen molecules attached to two titanium atoms, therefore result of which is not shown in this article (one can see optimised geometry of C₉₀H₁₀(2Ti+10H₂) in Figure S1 (online supplemental data)). It is worth mentioning that the geometry optimisation was failed for six hydrogen molecules, hence was assumed saturation point (i.e. up to five hydrogen molecules). Furthermore, as is mentioned earlier, we performed frequency calculations along with geometry optimisation, which confirms that all systems included in this study are stable (with

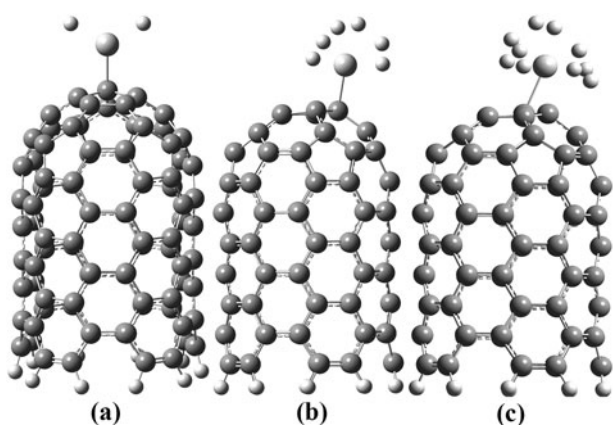


Figure 1. Fully relaxed geometries of (a) $C_{90}H_{10}(Ti+1H_2)$, (b) $C_{90}H_{10}(Ti+3H_2)$ and (c) $C_{90}H_{10}(Ti+5H_2)$ single-walled carbon nanotube using B3LYP-D3/def2-SVP level of density functional theory.

no negative frequency peaks and their minimum of energy).

The average Ti-C bond length is 2.09 Å while considering nearest neighbour carbon atom of cap top pentagon and titanium atom for each SWCNT. Titanium-carbon and hydrogen-hydrogen atom bond length values can be seen in Table 1, whereas average bond lengths of hydrogen molecules can be seen in Figure 2 for all five configurations of SWCNTs. In all cases, interaction between H_2 and SWCNT is always attractive; hence, H_2 is absorbed on Ti atom without any energy constraints. Therefore, from Figures 1(a) and 2, it is clear that during the first adsorption, hydrogen molecule has a bond length of 2.93 Å. However, in the second case, i.e. $C_{90}H_{10}(Ti+2H_2)$, two hydrogen molecules are intact but with a rather short H-H bond length of 0.95 Å which has also been reported earlier [14] (the same is true for next adsorptions). It has also been observed that bond length of hydrogen molecule (H-H) is continuously decreasing as far as more H_2 molecules are added to the system. An interesting and rather important point is that the nature of bond between near neighbouring hydrogen and titanium atom is chemically different in the case of $C_{90}H_{10}(Ti+1H_2)$ compared with last four configurations. Thus, strong Ti-H bonding

Table 1. Bond lengths between titanium and nearing neighbour carbon, average bond length between hydrogen-hydrogen and titanium and closest most hydrogen atoms in Angstroms (Å) for all five configurations of Ti-decorated capped SWCNTs.

Cluster	$d(Ti-C)$	$d(H-H)$	$d(Ti-H)$
$C_{90}H_{10}(Ti+1H_2)$	2.07	2.93	1.72
$C_{90}H_{10}(Ti+2H_2)$	2.09	0.95	1.80
$C_{90}H_{10}(Ti+3H_2)$	2.07	0.94	1.81
$C_{90}H_{10}(Ti+4H_2)$	2.13	0.84	1.91
$C_{90}H_{10}(Ti+5H_2)$	2.11	0.82	1.93

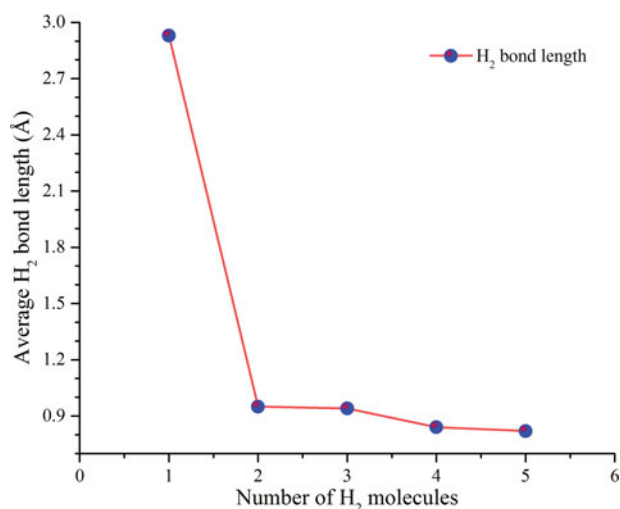


Figure 2. Average hydrogen molecule bond length as the number of hydrogen molecules on the top of Ti atom is increasing for each set of SWCNT, i.e. $C_{90}H_{10}(Ti+1H_2)$, $C_{90}H_{10}(Ti+2H_2)$, $C_{90}H_{10}(Ti+3H_2)$, $C_{90}H_{10}(Ti+4H_2)$ and $C_{90}H_{10}(Ti+5H_2)$.

changes adsorption energy and electronic gap drastically (further discussion is included in Section 3.2).

3.2. Adsorption energies

The adsorption energy ΔE_{ads} of H_2 is calculated using Equation (1):

$$\Delta E_{ads} = E(CNT + Ti + H_2) - [E(CNT + Ti) + E(H_2)] \quad (1)$$

where $E(CNT + Ti + H_2)$, $E(CNT + Ti)$ and $E(H_2)$ represent the total energy of the system including hydrogen molecules, total energy of the system without the presence of hydrogen molecules and total energy of hydrogen molecule, respectively. It is important to emphasise that in all the above total energies, we include zero-point energy (ZPE) corrections; that is, $E(CNT + Ti + H_2) = E_0(CNT + Ti + H_2) + ZPE(CNT + Ti + H_2)$, $E(CNT + Ti) = E_0(CNT + Ti) + ZPE(CNT + Ti)$ and $E(H_2) = E_0(H_2) + ZPE(H_2)$ where E_0 , in an obvious notation, is the total electronic energy without ZPE.

Figure 3 shows hydrogen adsorption energies with respect to increasing number of hydrogen molecules for $C_{90}H_{10}(Ti+1H_2)$, $C_{90}H_{10}(Ti+2H_2)$, $C_{90}H_{10}(Ti+3H_2)$, $C_{90}H_{10}(Ti+4H_2)$ and $C_{90}H_{10}(Ti+5H_2)$ CNTs. Values of adsorption energy have also been mentioned in Table 2 along with highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) gaps for all systems.

In general, hydrogen atoms can be absorbed on carbon nanostructures surfaces physically (physisorption)

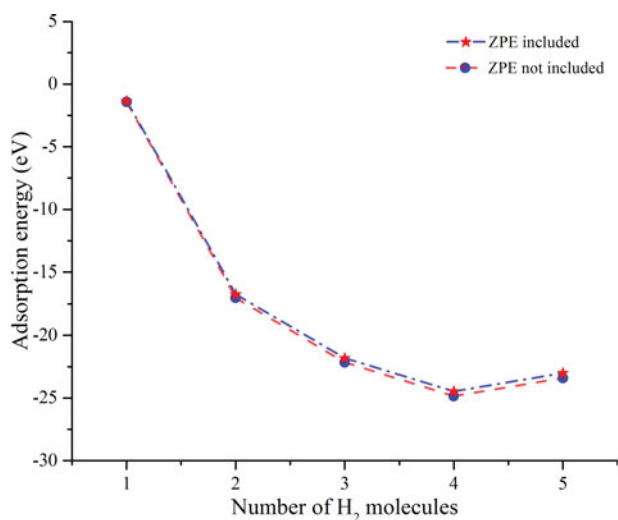


Figure 3. Adsorption energy of hydrogen molecule compared with the number of hydrogen molecules for each system studied in this work, i.e. $C_{90}H_{10}(Ti+1H_2)$, $C_{90}H_{10}(Ti+2H_2)$, $C_{90}H_{10}(Ti+3H_2)$, $C_{90}H_{10}(Ti+4H_2)$ and $C_{90}H_{10}(Ti+5H_2)$.

or chemically (chemisorption). For physisorption, adsorbates react with the system through weak Van der Waals forces [24], so they are highly reversible via changes in temperature and pressure in contrast with the chemisorption process in which chemical bonds are formed between the adsorbates and the surface of the adsorbent. Practically, hydrogen adsorption in carbon nanostructure at room temperature is a combination of reversible physisorption and irreversible chemisorption. Predomination of each of the aforesaid mechanisms depends on the practical condition under which the system is gone through. And it is also established recently, for pressures of up to 20 bar, the physisorption and chemisorption have relatively the same magnitude in multi-walled carbon nanotubes (MWCNTs), whereas above 20 bars, physisorption becomes the primary adsorption mechanism [25].

In our case, we performed all calculations assuming 298.15 K temperature and pressure of 1 atm. Clearly, adsorption energy profile in Figure 3 shows that $C_{90}H_{10}(Ti+1H_2)$ is in favour of chemisorption because of the strong bond between titanium and hydrogen atom, i.e. 1.72 Å (details of which are also mentioned in Section 3.1). Whereas, further hydrogen adsorptions up to five molecules indicate physisorption with larger Ti-H bond lengths around 1.93 Å. Furthermore, the first hydrogen adsorption leads system to higher energy with respect to the initial geometry (also compared with further absorptions) and, once again, this may be because of dissociating H_2 in two hydrogen atoms; however, configurations with further addition of hydrogen molecules have minimum energy in comparison.

Table 2. Hydrogen adsorption energies, ΔE_{ads} (eV/ H_2) and highest occupied molecular orbital–lowest unoccupied molecular orbital gap energies (eV) for all five configurations of Ti-decorated capped SWCNTs. For adsorption energies, zero-point energy (ZPE) corrections are also considered.

Cluster	ΔE_{ads}		HOMO–LUMO gap
	Without ZPE	With ZPE	
$C_{90}H_{10}(Ti+1H_2)$	−1.42	−1.36	1.53
$C_{90}H_{10}(Ti+2H_2)$	−17.01	−16.74	1.87
$C_{90}H_{10}(Ti+3H_2)$	−22.16	−21.82	1.78
$C_{90}H_{10}(Ti+4H_2)$	−24.85	−24.47	1.77
$C_{90}H_{10}(Ti+5H_2)$	−23.40	−23.01	1.71

3.3. Electronic properties

Electronic charge distribution has an important role while understanding the molecular interactions. Figure 4 shows colour map of Mulliken charge distribution for last four SWCNT configurations, respectively, whereas exact values of which can be seen in Tables S1–S5 (online supplemental data). It is shown in Figure 4(a–d) that the titanium atom is positively charged, which is obviously due to relatively higher electronegativity of carbon atoms. Positive charges distributed on Ti atom allow it to induce charge to nearing neighbour hydrogen atoms of H_2 molecules which is the obvious phenomenon for sorption. As it is clear from the figure, the amount of positive charges collected on Ti atom is maximum in Figure 2(a) because Ti atom is bonded to C and H atoms while both have higher electronegativity with respect to Ti atom. Progressively positive charge decreases as new H_2 molecules are introduced to the system. It is clear from Figure 4 that atoms of hydrogen molecules in

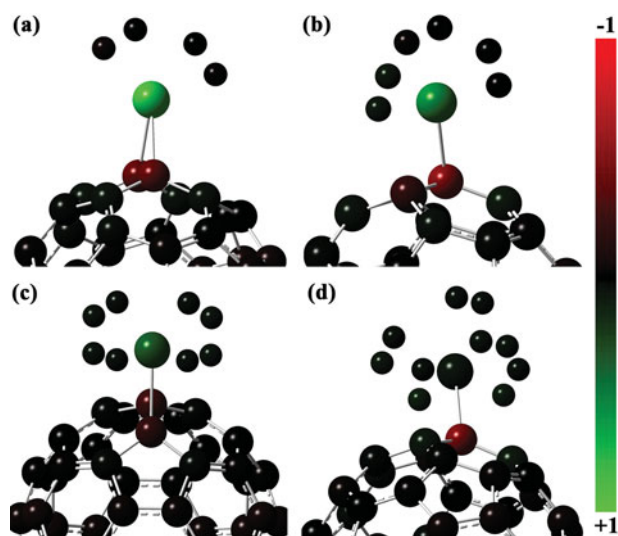


Figure 4. Mulliken charge distribution for (a) $C_{90}H_{10}(Ti+2H_2)$, (b) $C_{90}H_{10}(Ti+3H_2)$, (c) $C_{90}H_{10}(Ti+4H_2)$ and (d) $C_{90}H_{10}(Ti+5H_2)$. The amount of charge can be seen in Tables S1–S5 (online supplemental data).

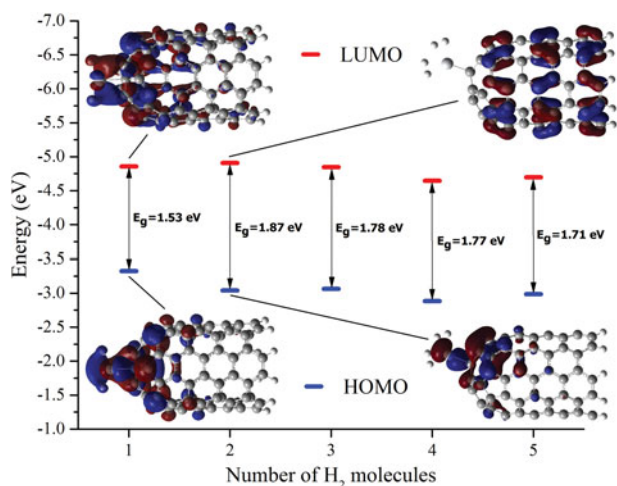


Figure 5. Highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs) of $C_{90}H_{10}(Ti+1H_2)$, $C_{90}H_{10}(Ti+2H_2)$, $C_{90}H_{10}(Ti+3H_2)$, $C_{90}H_{10}(Ti+4H_2)$ and $C_{90}H_{10}(Ti+5H_2)$ with respect to the increasing number of hydrogen molecules. Graphical representation of HOMO and LUMO is shown for first two H_2 adsorptions with isoval = 0.02.

$C_{90}H_{10}(Ti+2H_2)$, $C_{90}H_{10}(Ti+3H_2)$, $C_{90}H_{10}(Ti+4H_2)$ and $C_{90}H_{10}(Ti+5H_2)$ have been charged differently since they are in different distances of Ti being dictated to place in certain symmetry arrangements with respect to Ti atom. The calculated transferred charge for each atom can be determined by the amount of charge transferred between the CNT and the attached atoms.

We have shown electronic gaps for all configurations, whereas graphical representation of HOMO and LUMO is also included for first two adsorptions in Figure 5. The capped (5,5) SWCNT coated with Ti has HOMO and LUMO of 1.24 eV. As Figure 5 shows, hydrogen molecules' sorption changes electronic gap of the nanostructures significantly. First H_2 adsorption in Ti-SWCNT increases HOMO–LUMO gap by 0.29 eV and even increases in the case of second adsorption with 0.63 eV which is significant too. The difference of 0.34 eV between $C_{90}H_{10}(Ti+1H_2)$ and $C_{90}H_{10}(Ti+2H_2)$ configurations is quite large which is due to the different chemical bond nature of first H_2 adsorption. Since large gap indicates that it is difficult to add electrons to a high LUMO and remove electrons from deep HOMO [26]. Therefore, one can conclude that kinetic stability of the system changes as hydrogen molecules are added to it. Therefore, adding more H_2 molecules to the system then lowers electronic gap with only small differences.

In graphical representation of HOMOs and LUMOs, both HOMO and LUMO are localised at the top of SWCNT for $C_{90}H_{10}(Ti+1H_2)$ including cap top of nanotube, Ti atom and hydrogen atoms. In the case of $C_{90}H_{10}(Ti+2H_2)$, HOMO is localised at the top of

SWCNT including Ti atom but excluding hydrogen molecules, whereas LUMO is distributed only on the wall of nanotube. This may indicate significant charge transfer during excitation. For third, fourth and fifth adsorption, similar trend has been observed.

4. Conclusions

The DFT-D3 (B3LYP/def2-SVP) optimised structures of titanium decorated capped armchair (5,5) SWCNTs structures were obtained and their hydrogen adsorption energies are reported along with Mulliken charges and HOMO–LUMO gaps. Our results determine that a single Ti atom binds up to five hydrogen molecules on SWCNT cap top, whereas adsorption of four hydrogen molecules is energetically more favourable. The analyses from adsorption energy profile, HOMO–LUMO gap and Mulliken charge distribution show contrast in first hydrogen molecule adsorption compared with the rest of four configurations. Mulliken charge distribution shows that positive charge on Ti atom decreases as new H_2 molecules are introduced to the system. First H_2 adsorption in Ti-SWCNT increases HOMO–LUMO gap by 0.29 eV and even increases in the case of second adsorption with 0.63 eV which is significant. This is clearly due to the strongly different bonding nature of first hydrogen adsorption among others, between hydrogen molecules and Ti-coated SWCNT. These results not only support our understanding of adsorption nature of hydrogen in SWCNTs with titanium decoration on cap top but also suggest new directions for smart storage techniques. This study suggests to enhance scope of the subject on 2D systems such as rippled graphene sheets; hence, work is in progress.

Disclosure statement

No potential conflict of interest was reported by the authors.

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