Titanium-Decorated Carbon Nanotubes as a Potential High-Capacity Hydrogen Storage Medium

T. Yildirim[1] and S. Ciraci[2]

[1]*NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, Maryland 20899, USA*
[2]*Physics Department, Bilkent University, 06800 Bilkent, Ankara, Turkey*

We report a first-principles study, which demonstrates that a single Ti atom coated on a single-walled nanotube (SWNT) binds up to four hydrogen molecules. The first H_2 adsorption is dissociative with no energy barrier while the other three adsorptions are molecular with significantly elongated H-H bonds. At high Ti coverage we show that a SWNT can strongly adsorb up to 8 wt % hydrogen. These results advance our fundamental understanding of dissociative adsorption of hydrogen in nanostructures and suggest new routes to better storage and catalyst materials.

PACS numbers: 81.07.De, 68.43.-h, 84.60.Ve

Developing safe, cost-effective, and practical means of storing hydrogen is crucial for the advancement of hydrogen and fuel-cell technologies [1]. The current state of the art is at an impasse in providing any material that meets a storage capacity of 6 wt % or more required for practical applications [1–8]. Here we report a first-principles computation of the interaction between hydrogen molecules and transition metal atoms adsorbed on carbon nanotubes. Our results are quite remarkable and unanticipated. We found that a single Ti atom adsorbed on a single-walled nanotube (SWNT) can strongly bind up to four hydrogen molecules. Such an unusual and complex bonding is generated by the concerted interaction among H, Ti, and SWNT. Remarkably, this adsorption occurs with no energy barrier. At large Ti coverage we show that a (8, 0) SWNT can store hydrogen molecules up to 8 wt %, exceeding the minimum requirement of 6 wt % for practical applications. Finally, we present high-temperature quantum molecular dynamics simulations showing that these systems are stable and indeed exhibit associative desorption of H_2 upon heating, another requirement for reversible storage.

Recent experiments [9,10] and calculations [11–14] suggest that it is possible to coat carbon nanotubes uniformly with Ti atoms without metal segregation problems [15]. Here we show that such Ti-coated carbon nanotubes exhibit remarkable hydrogen absorption properties. Below we will present our results in detail for a (8, 0) nanotube and briefly for four armchair (n, n) $(n = 4, 5, 6,$ and 7) and five zigzag $(n, 0)$ $(n = 7, 8, 9, 10, 11,$ and 12) nanotubes.

A single Ti atom on an (8, 0) SWNT has a magnetic ground state with $S = 1$ and a binding energy of 2.2 eV; this will serve as our reference system, denoted t80Ti. In order to determine different reaction paths and products between H_2 and t80Ti, we have carried out a series of single-energy calculations as H_2 molecules approach t80Ti, and when there are large enough forces acting on H_2 molecules we let the atoms evolve according to the quantum mechanical forces obtained from density functional theory (DFT) calculations [16]. We used the

conjugated-gradient (CG) minimization and optimized both the atomic positions and the c axis of the tube.

The energy calculations were performed within the plane-wave implementation [16] of the generalized gradient approximation [17] to DFT. We used Vanderbilt ultrasoft pseudopotentials [18] treating the following electronic states as valence: $Ti:3s^2 3p^6 3d^2 4s^2$; $C:2s^2 2p^2$; and $H:1s$. The Monkhorst-Pack special k point scheme [19] is used with 0.025 Å^{-1} k point spacing resulting in 5 k points along the tube axis. The cutoff energy of 350 eV is found to be enough for total energies to converge within 0.5 meV/atom. The calculations are carried out in a tetragonal supercell geometry of 20 Å $\times$ 20 Å $\times c$ where c is taken to be twice the lattice constant of SWNT along its axis.

Figure 1(a) shows the energy variation from *non-spin-polarized* calculations as a single H_2 molecule approaches t80Ti. The energy first decreases slowly as the hydrogen gets closer to the nanotube and Ti. However, as the charge overlap gets large, the H_2 molecule is attracted towards the Ti atom with a sudden decrease in the energy. At this point, the H_2 molecule is still intact with a significantly increased H-H bond length of 0.86 Å. The second sudden decrease in energy is achieved by dissociating the H_2 molecule into 2 H atoms. At this point, the H-H distance increases from 0.86 to 2.71 Å. The interaction between H_2 and t80Ti is always attractive and therefore H_2 is absorbed onto a Ti atom without any energy barrier. The final geometry is shown in the inset to Fig. 1(a), with relevant structural parameters given [20]. In order to calculate the binding energy for this dissociative adsorption, we calculate the total energies of the initial t80Ti and H_2 state [dashed line in Fig. 1(a)] and the final t80TiH_2 state [dotted line in Fig. 1(a)] from spin-polarized calculations. We obtain the binding energy to be 0.83 eV (Fig. 1). We note that spin-polarized calculation lowers the total energy by about 0.6 eV with respect to non-spin-polarized calculations and yields a triplet magnetic ground state (i.e., $S = 1$) for the initial t80Ti and the H_2 system. However, once the
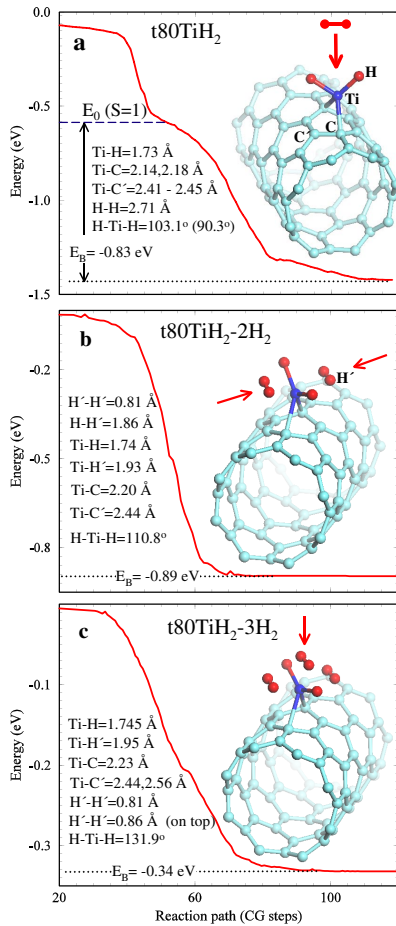
FIG. 1 (color online).   Energy vs reaction paths for successive dissociative and molecular adsorption of H_2 over a single Ti-coated   (8, 0)   nanotube.   (a) H_2 + t80Ti → t80TiH$_2$. (b) $2H_2$ + t80TiH$_2$ → t80TiH$_2$ − 2H$_2$.   (c) H_2 + t80TiH$_2$ − $2H_2$ → t80TiH$_2$ − 3H$_2$. The zero of energy is taken as the sum of the energies of two reactants. The relevant bond distances and binding energies (E_B) are also given.

hydrogen molecule is attached to Ti, the system is non-magnetic and spin-polarized calculations are not necessary.

Remarkably, it is also energetically favorable for the TiH$_2$ group to complex with additional hydrogen molecules. Figure 1(b) shows the energy variation as two hydrogen molecules approach the Ti atom, one from each side of the TiH$_2$ group. As in the case of single adsorption, the energy always decreases, first slowly and later very rapidly, at which point both hydrogen molecules are strongly attached to the t80TiH$_2$ system. We denote the final product as t80TiH$_2$-2H$_2$, which is shown in Fig. 1(b). The total-energy change upon adsorption is about 0.89 eV (i.e., 0.45 eV/H$_2$). Unlike the first adsorption, the two hydrogen molecules are in intact but with a rather elongated bond length of 0.81 Å. This 10% increase is rather reminiscent of the elongated H-H bonds observed in the metal-dihydrogen complexes first synthesized by Kubas [21].

Figure 1(c) shows the energy evolution when a fourth hydrogen molecule approaches the t80TiH$_2$-2H$_2$ system

from the top. The energy again decreases continuously, indicating a zero-energy barrier. The final product, denoted as t80TiH$_2$-3H$_2$, is shown in the inset with the relevant structural parameters. The energy gained by the fourth adsorption, 0.34 eV/H$_2$, is slightly smaller than for the other cases but is still substantial. The H-H distance of the top H$_2$ is 0.86 Å. Several attempts to add a fifth hydrogen molecule at a variety of positions failed, suggesting a limit of 4H$_2$/Ti.

The final optimized structures shown in Fig. 1 need not be the global minimum. Among many different isomers tried for the 4H$_2$ system, we found a very symmetric configuration (denoted as t80Ti-4H$_2$) [Fig. 2(a)] that is 0.1 eV lower in energy than t80TiH$_2$-3H$_2$. Here all four hydrogen molecules stay intact and benefit equally from bonding with the Ti atom. The average H-H bond distance is about 0.84 Å and each molecule has an excess charge of about 0.15e. The average binding energy per H$_2$ molecule
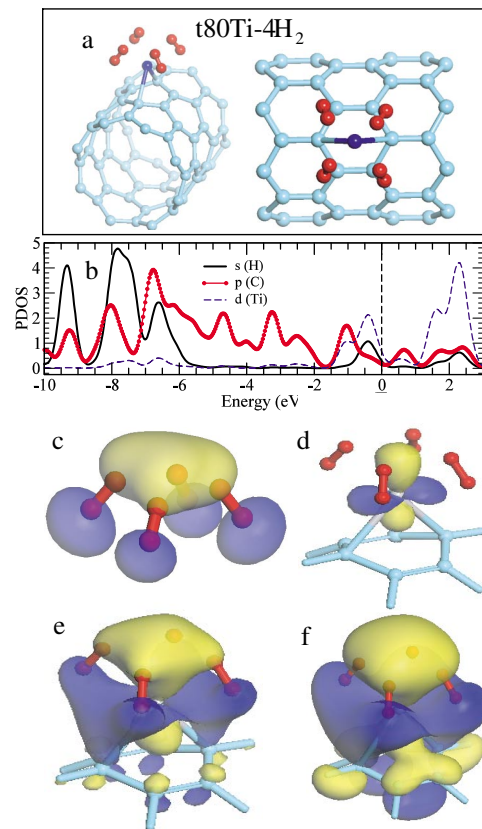

FIG. 2 (color).   (a) Two different views of the optimized structure of t80Ti-4H$_2$. The relevant structural parameters are H-H = 0.84 Å, Ti-H = 1.9 Å, Ti-C = 2.17 Å, Ti-C′ = 2.4 Å. (b) The PDOS at the Γ point contributed from Ti, four H$_2$ molecules, and the six carbons of the hexagon on which Ti and H$_2$ molecules are bonded. (c) The σ^* antibonding orbital of four H$_2$ complex; (d)–(f) isosurface of the state just below E_F at three different values: at $\Psi = 0.08$, it is mainly Ti-d orbital; at $\Psi = 0.04$ the hybridization between the d orbital, two carbon π orbitals, and 4H$_2$ σ^* antibonding is apparent. At $\Psi = 0.02$ it is clear that the other four carbon atoms are also involved in the bonding.

is 0.54 eV, which suggests that the bonding is an unusual combination of chemisorption and physisorption.

To test system stability, we performed high-temperature quantum molecular dynamics (MD) simulations on t80TiH$_2$-3H$_2$ [20]. In total, we have carried out 1.5 ps MD simulations with a Langevin thermostat for temperatures ranging from 200 to 900 K. We observe an associative desorption of a H$_2$ molecule (i.e., 2 H atoms come together to form H$_2$ and leave the system) at around 800 K [20]. While a 1.5 ps time MD simulation is already computationally quite costly, it is not long enough to get statistically meaningful values for the temperature. However, it does suggest that the system is quite stable and that it is possible to extract the H$_2$ molecules without breaking the Ti-C bonding or removing the TiH$_2$ from the nanotube.

Projecting the plane waves on the pseudoatomic orbitals [Fig. 2(b)] gives detailed information on the nature of the bonding. The density of states indicates that Ti 3s and 3p orbitals are mostly intact and lie below -20 eV. In the energy range of from -10 eV to zero, Ti contributes only d electrons, while Ti 4s electrons are almost absent, probably promoted to Ti d orbitals. Figure 2(b) shows that the binding state just below E_F has a major contribution from Ti d orbitals, together with the carbon p orbitals and hydrogen s orbitals. In Fig. 2, we showed the isosurface plot of this state. From this figure it is clear that a filled Ti d orbital is hybridized simultaneously with the $\sigma*$ antibonding molecular orbital of the 4H$_2$ complex [see Fig. 2(c)] and the π_4^* antibonding orbital of the C6 ring of the SWNT. The Mulliken analysis indicates that there is about 1e transfer to the 4H$_2$ antibonding orbital. Similarly, projected density of states (PDOS) in Fig. 2(b) show that the σ bonding of the 4H$_2$ group forms a band between -10 and -6 eV and weakly hybridized with d orbitals. Integrating these peaks over energy and k points suggests that there is about 0.4e electron transferred to the Ti empty d orbitals. Hence the bonding mechanism for t80Ti-4H$_2$ seems to be very similar to the Dewar, Chatt, and Duncanson model [22], where the interaction has often been viewed as a donation of charge from the highest occupied orbital of the ligand to the metal empty states and a subsequent back donation from filled d orbitals into the lowest unoccupied orbital of the ligand. Finally, the second peak around -1 eV in PDOS corresponds to the hybridization of one d orbital with the π orbital of the C6 hexagon of SWNT, which is responsible for the bonding of the Ti atom to the nanotube.

In summary, our analysis of PDOS and molecular orbitals clearly indicates that we need two occupied d orbitals: one for molecular bonding of the hydrogens and the other to bind the metal to the nanotube. We also expect that the ionization potential (IP) of the metal is important, which controls the amount of back charge transfer to the hydrogen antibonding state. When a single H$_2$ molecule is introduced to t80Ti, it seems that Ti is able to donate just enough charge to the σ^* antibonding state, causing dihy-

drogen to be unstable against dissociation of H$_2$ [Fig. 1(a)]. However, when more hydrogen molecules are added to the system, the charge transfer per H$_2$ molecule is not enough to destabilize the dihydrogen state, and therefore the absorption becomes molecular [Fig. 2(a)].

From the above discussion it is clear that we need both filled and empty d orbitals for the metal-hydrogen complex formation. We tried the same thing with alkali and alkaline earth metals, such as Li and Mg, and failed. Heavy transition metals with diffusive d orbitals, such as Pt and Pd, are also not good candidates for the molecular absorption. Such metals are known to interact with the $\sigma*$ antibonding of the hydrogen molecules strongly, destabilizing dihydrogen structure against classical hydride formation. Our preliminary results based on a structural optimization starting from t80TiH$_2$-3H$_2$ with Ti replaced by Pt/Pd indeed indicate that the side hydrogen molecules are not bonded and leave the system immediately [23]. We did observe that two H$_2$ do indeed bind to Pt/Pd forming a PtH$_4$ (or PdH$_4$) classical hydride cluster, which was not bonded to the nanotube. However, we expect the light transition metals like Sc and V to show similar behavior since they have both occupied and empty d orbitals with a similar IP to Ti. We are currently investigating a large number of transition metals and the results will be published elsewhere [23].

It is important to know if the results reported above for (8, 0) SWNT hold for other nanotubes and how they depend on the chirality and tube radius. Therefore we have also studied four (n, n) ($n = 4, 5, 6,$ and 7) and five $(n, 0)$ ($n = 7, 8, 9, 10, 11,$ and 12) nanotubes and details will be published elsewhere [23]. Briefly we find that the binding energies of the TiH$_2$, TiH$_2$-3H$_2$, and Ti-4H$_2$ groups have a weak but complicated dependence on the tube radius, conduction, and valence band energy levels and band gaps. Therefore we did not find a simple trend like $1/R$ for the binding energies. This suggests that nanotubes with larger diameters can also show the similar effect. For the largest nanotubes that we have studied, the binding energy of Ti is reduced to 1.8 and 1.6 eV for (12, 0) and (7, 7), respectively. The binding energy for the first H$_2$ for (7, 7) is about 0.66 eV/H$_2$, slightly reduced from 0.83 eV/H$_2$ for the (8, 0) nanotube. We find that those nanotubes with significant band gaps [like (8, 0), (10, 0), and (11, 0)] show the strongest hydrogen absorption. For example, (10, 0) has 2.5 eV/4H$_2$ binding energy for TiH$_2$-3H$_2$ while the binding energy for (11, 0) and (8, 0) is about 2.1 eV/4H$_2$. We also find interesting small differences between (n, n) and $(n, 0)$ nanotubes. For example, the TiH$_2$-3H$_2$ configuration [Fig. 1(c)] is the ground state for the (n, n) nanotubes, while it is Ti-4H$_2$ [Fig. 2(a)] for $(n, 0)$ nanotubes. In conclusion, the phenomena that *a single Ti atom absorbed on hexagonal phase of SWNT can bind up to four molecular hydrogen* is a very general and novel result and holds for a very large number of nanotubes and for other carbon-based nanoclusters (i.e., C$_{60}$ [24]).

To this point we have discussed the interaction of H$_2$ with a single Ti atom bonded to a nanotube, but clearly one

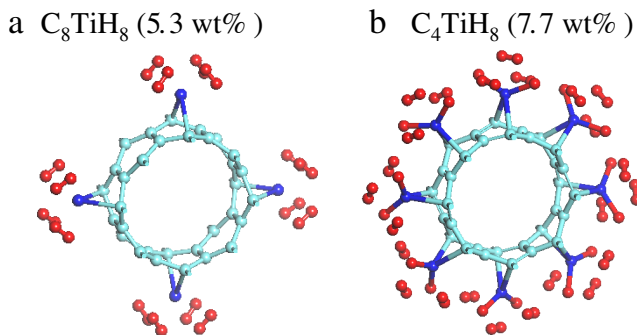**a** C_8TiH_8 (5.3 wt%)   **b** C_4TiH_8 (7.7 wt%)

FIG. 3 (color online).   Two high-density hydrogen coverage on a Ti-coated $(8, 0)$ nanotube.

can imagine attaching more Ti to a nanotube, thereby increasing the hydrogen storage capacity. In order to show the feasibility of this approach, we present two simple cases where Ti covers $\frac{1}{4}$ and $\frac{1}{2}$ of the hexagons. The optimized bond lengths and other parameters of the structures shown in Fig. 3 are very similar to those in the single-Ti case, indicating that the system has the capacity to have many Ti and hydrogen. In fact, these configurations, which have the chemical formulas, C_8TiH_8 and C_4TiH_8, store approximately 5 and 8 wt % hydrogen, respectively. These numbers are based on the assumption that t80TiH$_2$ group will also release the hydrogen molecule without difficulty. This is a good assumption, since the binding energy of H$_2$ in t80TiH$_2$ is about $1/3$ of the binding energy of t80Ti.

The calculated binding energy [25] for C_8TiH_8 is 0.43 eV per H$_2$, which is somewhat reduced from the average binding energy of 0.54 eV in t80Ti-4H$_2$. For C_4TiH_8, the binding energy is further reduced to 0.18 eV. This reduction is due to the Ti-Ti interaction which is also responsible for the increased binding energy of Ti on nanotubes [i.e., 2.8 eV/Ti compared to 2.2 eV for a single Ti on a $(8, 0)$ SWNT]. The stability of C_4TiH_8 is further checked by MD simulations on a $1 \times 1 \times 2$ supercell, which did not show any Ti metal segregation. Furthermore, we checked the stability of the system against releasing one and eight of the top hydrogen molecules [see Fig. 3(b)]; both yielded a binding energy of 0.13 eV/H$_2$. This is the weakest bond in the system and yet it is 4–5 times stronger than the van der Walls interactions between hydrogen and SWNT [26].

In conclusion, using the state of the art first-principles total-energy calculations, we have shown that each Ti atom adsorbed on a SWNT can bind up to four hydrogen molecules, a remarkable and totally unanticipated finding. The mechanism of the bonding is explained by a unique hybridization between Ti-d, hydrogen σ^* antibonding, and SWNT C-p orbitals (Fig. 2). These results advance our fundamental understanding of dissociative and molecular chemisorption of hydrogen in nanostructures, a fundamental step towards novel materials needed for hydrogen production, storage, and consumption in the fuel cells. They

also suggest a possible method of engineering new nanostructures for high-capacity storage and catalyst materials.

[1] See the special issue *Towards a Hydrogen Economy*, by R. Coontz and B. Hanson, Science **305**, 957 (2004).
[2] S. P. Chan, G. Chen, X. G. Gong, and Z. F. Liu, Phys. Rev. Lett. **87**, 205502 (2001).
[3] K. Tada, S. Furuya, and K. Watanabe, Phys. Rev. B **63**, 155405 (2001).
[4] Y. Miura *et al.*, J. Appl. Phys. **93**, 3395 (2003).
[5] G. Lu, H. Scudder, and N. Kioussis, Phys. Rev. B **68**, 205416 (2003).
[6] P. Dubot and P. Cenedese, Phys. Rev. B **63**, 241402 (R) (2001).
[7] E. C. Lee, Y.-S. Kim, Y.-G. Jin, and K. J. Chang, Phys. Rev. B **66**, 073415 (2002).
[8] O. Gulseren, T. Yildirim, and S. Ciraci, Phys. Rev. B **66**, 121401(R) (2002).
[9] Y. Zhang and H. Dai, Appl. Phys. Lett. **77**, 3015 (2000).
[10] Y. Zhang, N. W. Franklin, R. J. Chen, and H. Dai, Chem. Phys. Lett. **331**, 35 (2000).
[11] O. Gulseren, T. Yildirim, and S. Ciraci, Phys. Rev. Lett. **87**, 116802 (2001).
[12] C. K. Yang, J. Zhao, and J.P. Lu, Phys. Rev. B **66**, 041403(R) (2002).
[13] E. Durgun *et al.*, Phys. Rev. B **67**, 201401(R) (2003).
[14] S. Dag, E. Durgun, and S. Ciraci, Phys. Rev. B **69**, 121407 (2004).
[15] This is due to compatible ionic radius and the Ti-Ti and Ti-C interactions which are similar in strength.
[16] M. C. Payne *et al.*, Rev. Mod. Phys. **64**, 1045 (1992).
[17] P. J. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).
[18] D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990).
[19] H. J. Monkhorst and J. D. Pack, Phys. Rev. B **13**, 5188 (1976).
[20] The animations of the reaction paths and simulations can be found at http://www.ncnr.nist.gov/staff/taner/h2.
[21] *Metal Dihydrogen and Bond Complexes—Structure, Theory, and Reactivity*, edited by G. J. Kubas (Kluwer Academic/Plenum Pub, New York, 2001).
[22] *Modern Coordination Chemistry: The Legacy of Joseph Chatt*, edited by G. J. Leigh and N. Winterton (Royal Society of Chemistry, Cambridge, 2002).
[23] T. Yildirim, J. Íñiguez, S. Ciraci, and S. Dag (to be published).
[24] T. Yildirim, J. Íñiguez, and S. Ciraci, cond-mat/0505046.
[25] We defined the binding energy as the energy sum of the individual H$_2$ molecules and the tube-Ti spin-polarized optimized structure minus the energy of the final optimized structure.
[26] T. Yildirim and A. B. Harris, Phys. Rev. B **67**, 245413 (2003).