PHYSICAL REVIEW B **66**, 073415 (2002)

First-principles study of hydrogen adsorption on carbon nanotube surfaces

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(Received 21 March 2002; published 26 August 2002)

Based on first-principles theoretical calculations, we find that on pristine single-wall carbon nanotubes (SWNT's), the dissociative adsorption of H_2 molecules is severely suppressed due to very high energy barriers of about 3 eV, while H atoms have low-energy barriers less than 0.3 eV. On Li-doped SWNT's, the energy barriers for the dissociative adsorption of H_2 are lowered by about 0.3–0.5 eV due to the charge transfer to the tube, as compared to the pristine tube. However, these energy barriers are still too high for H_2 to be directly adsorbed, indicating that Li doping itself does not enhance significantly the H adsorption. On the other hand, LiH molecules are easily adsorbed and dissociated with no energy barrier.

DOI: 10.1103/PhysRevB.66.073415 PACS number(s): 61.48.+c, 68.43.−h, 71.20.Tx

After the discovery of carbon nanotubes by Iijima,[1] extensive studies have been done for various applications of these materials. In particular, much attention has been paid to their use as a hydrogen storage cell. Dillon and co-workers showed that soots containing single-wall carbon nanotubes (SWNTs) can absorb H_2 molecules of 0.01 wt % at 300 torr and room temperature.[2] Since the sample contains only 0.1 wt % SWNT's, this hydrogen storage capacity is regarded as 5–10 wt % per pure SWNT, assuming that the remainder of the soots is inert. In experiments using highly purified SWNTs and H_2, the amount of adsorbed H_2 was found to be 8.25 wt % at 80 K and 100 bars,[3] while other measured value of H_2 is 4.2 wt % at room temperature and about 10 MPa.[4] In Li- or K-doped carbon nanotubes, it was demonstrated that H_2 can be absorbed as much as 14–20 wt % under ambient pressure, while pristine carbon nanotubes only absorb H_2 molecules of 0.4 wt % at similar conditions.[5] In addition, it was reported that the amount of hydrogen stored electrochemically in SWNTs is 0.39 wt %.[6] Although experiments indicated that the hydrogen storage capacity of carbon nanotubes strongly depends on temperature and pressure, the mechanism for hydrogen storage has not been clearly understood yet.

In the absence of Li or K, a nondissociative adsorption of H_2 was suggested to be a dominant mechanism for hydrogen storage.[2,3] In Li-doped carbon nanotubes,[5] however, the dissociation of H_2 has been observed by Fourier transform infrared spectroscopy (FTIR), which would be one of the main reasons for why a large amount of hydrogen can be stored. Considering only the physisorption process without the dissociation of H_2, recent theoretical simulations[7] showed that SWNTs can store only 0.8 wt % hydrogen at 133 K and 300 torr. Although the hydrogen storage capacity increases to 1.9 wt % at 100 atm, theoretically estimated values from the H_2 physisorption are much lower than the measured values in Li-doped nanotubes. Thus, it is desirable to know the adsorption mechanism of hydrogen on carbon nanotubes for practical applications as a hydrogen storage cell.

In this work, we investigate the adsorption of hydrogen on SWNT surfaces through first-principles pseudopotential calculations. On the (5,5) SWNT, we find that H_2 has a very high adsorption energy barrier of about 3 eV, while that of atomic H is very small, i.e., 0.3 eV. On the Li-doped and negatively charged (5,5) SWNT's, the energy barriers for the dissociation of H_2 are only lowered by 0.3–0.5 eV, which results from the increase of the Fermi level due to charge transfer. This result indicates that the direct adsorption of H_2 is still severely suppressed even on Li-doped nanotubes. On the other hand, we find no energy barrier for the adsorption and dissociation of LiH molecules, the existence of which was identified experimentally in Li-doped nanotubes.[5]

The total energy calculations are performed using a first-principles pseudopotential method. Norm-conserving pseudopotentials are generated by the scheme of Troullier and Martins[8] and transformed into the separable form of Kleinman and Bylander.[9] The spin-polarized generalized gradient approximation is used for the exchange-correlation potential.[10] The Poisson and Kohn-Sham equations are expressed up to the 12th order based on a finite difference method, and solved by a real-space multigrid method.[11] The real-space grids are generated by the $80\times88\times80$ mesh for a supercell containing 120 atoms, with the spacings (h) of 0.312, 0.312, and 0.312 a.u., respectively. These grid spacings correspond to the effective kinetic-energy cutoff $[E_{\mathrm{cutoff}}=(\pi/h)^2]$ of about 101 Ry in the plane-wave-basis calculations, and are sufficient enough to ensure total-energy convergence to within 1.3 meV per atom. For the adsorption of H, H_2, and LiH, we test a 60-atom supercell, and find that the results remain unchanged, as compared to a 120-atom supercell. With the use of the conjugate-gradient technique, we relax ionic coordinates until the atomic geometry is fully optimized. The adsorption energy and its energy barrier are defined with respect to the total energy of the (5,5) SWNT with a free adsorbate.

In the adsorption process of atomic H, an energetically favorable path is along the vertical line on top of a C atom. Relaxing all the C atoms for each position of H, we find that H has the lowest energy for the C—H bond distance of 1.104 Å, with the adsorption energy of -1.64 eV. In this case, the C atom bonded to H is displaced outward by 0.35 Å from its ideal position, increasing the sp^3 hybridization, as compared to other C atoms. The calculated C—H bond length is slightly larger than the value of 1.087 Å for C_2H_4 and CH_4.[12] When H is located at 1.96 Å from the underlying C atom, the energy barrier is estimated to be 0.3 eV. Since the adsorption reaction of atomic H is exothermic and the associated energy

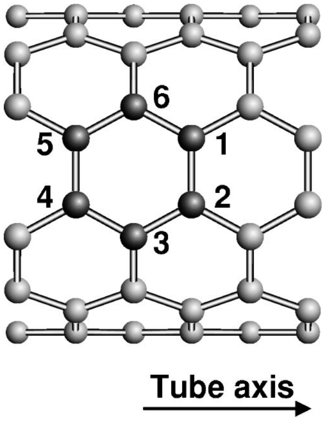

FIG. 1. An hexagon ring formed by six carbon atoms on the (5,5) nanotube surface.

barrier is sufficiently low, H atoms are expected to be easily adsorbed on carbon nanotubes. On the inner surface of the tube, it costs a higher energy for H to be adsorbed due to the curvature effect. In fact, the adsorption energy is calculated to be higher by 1.32 eV than on the outer surface, thus, our calculations are mainly focused on the outer-surface adsorption.

For the dissociative adsorption of molecular H_2, we choose two different reaction paths. In reaction path 1, H_2 is adsorbed on the C(1) and its nearest C(2) atoms (see Fig. 1), with keeping the molecule parallel to the nanotube surface. For each position of the center of mass of H_2 along the vertical line on top of the C(1)—C(2) bond, we fully relax both the C and H atoms. As H_2 approaches the tube, the total energy increases very rapidly. For a distance of 1.43 Å between the H_2 and tube, we find an energy barrier of 3.07 eV. In this case, the H—H bond is weakened, and the H_2 molecule starts to dissociate symmetrically to form new C—H bonds. When the center of mass of H_2 is located at 1.06 Å from the tube, the H—H ($d_{\mathrm{H—H}}=2.09$ Å) and C(1)—C(2) bonds are almost broken, and some charges are transferred from the C(1)—C(2) bond to the C—H bonds, as shown in Fig. 2. In this geometry, the adsorption energy is estimated to be 0.50 eV, indicating that the adsorption of H_2 is a slightly endothermic reaction.

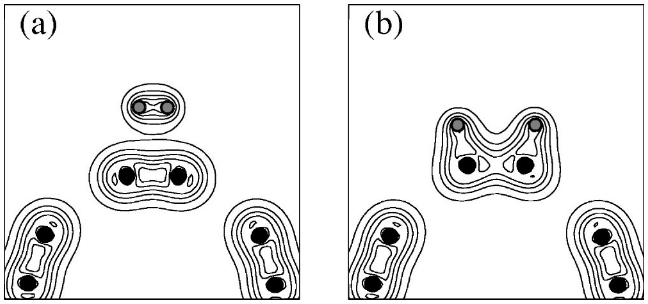

FIG. 2. (a) Contour plots of the charge densities for H_2 adsorbed at 1.85 Å above a C—C bond of the (5,5) SWNT, with a contour spacing of 0.05 a.u. In (b), H_2 is dissociatively adsorbed at 1.06 Å above the nanotube. Charges are transferred from the C—C bond to the C—H bonds. Black and gray dots denote the C and H atoms, respectively.

TABLE I. The adsorption energies (E_d) of Li (a) above and (b) below a hexagon site, (c) above and (b) below a carbon atom, and (e) on the tube axis of the single-wall (5,5) tube.

	(a)	(b)	(c)	(d)	(e)
E_d (eV)	−1.71	−1.62	−1.32	−1.47	−0.90

In reaction path 2, we examine the adsorption of H_2 onto the C(1) and its second-neighboring C(5) atoms (see Fig. 1). Similarly, H_2 moves along the vertical line on top of the middle point between C(1) and C(5), maintaining the molecular orientation parallel to the tube surface. The energy barrier is calculated to be 2.70 eV, which is lower by 0.37 eV than for the path 1. When H_2 is adsorbed, we also find that the dissociated H atoms form two new C—H bonds, while the H—H ($d_{\mathrm{H—H}}=2.49$ Å) bond is broken. When the C(1) and C(5) atoms are bonded to the H atoms, they undergo individually outward relaxations that increase the strain energy, while adjacent outward relaxations of the C(1) and C(2) atoms greatly reduce the strain energy for the path 1. Thus, the calculated adsorption energy of 1.25 eV is much higher than that for the path 1.

The energy barriers for the adsorption paths 1 and 2 of H_2 are found to be comparable to a theoretically predicted value of 3.56 eV for the H_2 adsorption on graphite.[13] These high-energy barriers may be attributed to a symmetry forbidden reaction,[14] which was suggested to cause a high activation barrier for the adsorption of H_2 on metal surfaces.[15] When H_2 approaches the tube surface along the path 1, the σ_g electrons of H_2 start to interact with the π electrons of the underlying C(1) and C(2) atoms, forming the bonding and antibonding states. As the coupling between the σ_g and π orbitals is enhanced, the energy of the occupied antibonding state increases very rapidly, resulting in the high-energy barrier, while the bonding state moves slowly to lower energies. On the other hand, the σ_u state of H_2 decreases due to the hybridization with the unoccupied π orbitals in the tube, and eventually crosses with the increasing antibonding state of the σ_g and π orbitals. Then, electrons are transferred to the unoccupied σ_u orbital, weakening the H—H bond, and H_2 is easily dissociated. As the Fermi level increases, since the charge transfer occurs before reaching the maximum energy barrier, the energy barrier is expected to be lowered. To see such a reduction in the adsorption barrier of H_2, we examine a negatively charged (5,5) tube, which has an extra electron per 20 carbon atoms. The energy barriers are found to be reduced by 0.49 and 0.30 eV for the reaction paths 1 and 2, respectively, as compared to the neutral tube. Nevertheless, since these energy barriers are still too high, it may require sufficiently high temperatures or pressures for H_2 to be adsorbed on pristine carbon nanotubes. Previous calculations also predicted that H_2 adsorption only occurs on very thin nanotubes such as the (3,3) SWNT.[16]

Next we examine the effect of Li doping on the dissociative adsorption of H_2. The calculated adsorption energies of Li are listed in Table I for various positions on the (5,5) SWNT. The adsorption energy is found to be lowest when Li is located at 1.79 Å above the hexagon center. However, since the energy of Li below the hexagon center is only higher by 0.09 eV than that above the hexagon center, Li atoms can be adsorbed both inside and outside the tube. We note that Li atoms are positively ionized on the SWNT, donating electrons to the tube, consistent with previous calculations.[17,18] Since this charge transfer raises the Fermi level, the energy barrier for the H_2 adsorption is also expected to be reduced. Recent experiments have shown that SWNT's can store Li atoms up to the stoichiometry of $Li_{1.6}C_6$, while the Li capacity of multiwall carbon nanotubes is similar to that of graphite (LiC_6).[19,20] For our 120-atom supercell with 8 additional Li atoms just above hexagon sites, which is equivalent to the measured Li/C ratio of 1/15,[5] we estimate the Li adsorption energy to be -1.68 eV/atom, close to the value of -1.71 eV for a single Li adsorption on the pristine SWNT. This result indicates that the Li ions are separated sufficiently enough to minimize repulsive interactions between the Li ions. In the Li-doped SWNT, the energy barrier is calculated to be 2.63 eV for the dissociation of H_2 over the two nearest-neighbor C atoms. Although this energy barrier is lower by 0.44 eV than for the pristine SWNT, it is too high for H_2 to be directly adsorbed. On the other hand, we may expect that the Li ions on the tube facilitate the dissociation of H_2 via the reaction, $2Li^+ + H_2 \rightarrow 2LiH^+$. However, this reaction is found to be endothermic by 4.19 eV. In addition, since it costs a very high energy to form LiH^+, the Li ions are unlikely to dissociate H_2 molecules. Although a Li ion can form several complexes with H_2 molecules,[18] it was shown that it is still difficult to dissociate directly H_2 molecules.[21]

Experimentally, it is debated whether C—H bonds are formed in Li-doped nanotubes. In Li-doped nanotubes, Chen and co-workers observed the FTIR spectrum, which is first developed between 3000 and 3350 cm^{-1}, and gradually broadened into the band ranging from 2600 to 3400 cm^{-1}.[5] They suggested that this FTIR spectrum reveals the formation of C—H bonds by the dissociation of H_2. On the other hand, it was suggested that this spectrum is attributed to that of $LiOH \cdot H_2O$, and the high capacity of hydrogen observed by Chen and co-workers arises from the adsorption of water molecules.[22] For the C—H stretch mode, we calculate the vibrational frequency of 2686 cm^{-1}, close to the lower edge of the observed FTIR spectrum.[5] Nevertheless, because of the very high energy barrier for the adsorption of H_2, the direct adsorption of H_2 is not expected even on Li-doped nanotubes.

Finally, we investigate the adsorption of LiH molecules on carbon nanotubes. In Li-doped nanotubes, the existence of LiH was identified in the process of hydrogen storage.[5] When a LiH molecule is adsorbed on the (5,5) SWNT, we find that the adsorption energy is lowest at the center of a hexagon, with the H atom bonded to one of the neighboring C atoms, as shown in Fig. 3. In this adsorption process, the center of mass of LiH is constrained to move along a vertical line on the tube, and all the atoms are fully relaxed for each position of the center mass of LiH. The LiH adsorption does not follow the symmetry forbidden reaction, because of the ionic bonding character. When the H atom of LiH approaches the C atom, the C atom undergoes an outward relaxation similar to the H atom adsorption. The adsorption energy of LiH is -0.96 eV and no energy barrier is found. In other adsorption path [see Fig. 2(b)], where the Li and H atoms are adsorbed on the C(1) and C(2) atoms, respectively, no energy barrier is also found, while the adsorption energy is -0.73 eV. Thus, it is expected that LiH is easily dissociated and adsorbed on the tube surface. Since the dissociation of LiH is energetically determined by the formation of the C—H bond, it is almost independent of the position of Li. Because of the repulsive interaction between the adsorbed H and Li atoms, the energies of the hexagon sites (S sites in Fig. 3) near the H atom are higher by about 0.2 eV, as compared to other hexagon sites (U sites in Fig. 3). We calculate the energy barrier for the diffusion of Li on the (5,5) tube surface, where a single H atom is adsorbed. When Li diffuses from the S_1 site to the U_3 site, passing either through the intermediate C atom or the bond-centered site of the C—C bond, the energy barriers are about 0.25 eV. For other diffusion paths from S sites to U sites, such as S_2-U_4 and S_3-U_1, we find similar energy barriers to within 0.1 eV, while the energy barrier is slightly increased to 0.44 eV along the path from U_2 to U_1. In the desorption process of hydrogens, since Li is very mobile on the tube, H atoms are expected to be desorbed from the surface, leading to the delivery of H_2 molecules, which result from the reaction between H atoms.

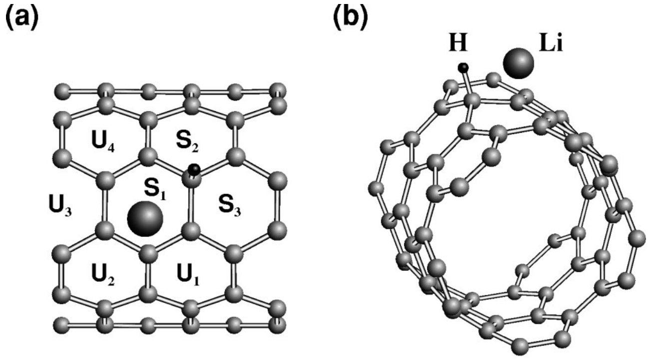

FIG. 3. (a) Top and (b) side views of LiH adsorbed on the (5,5) SWNT. Unstrained hexagon sites are denoted by U, while S sites for the strained hexagon sites in the neighborhood of the adsorbed H atom.

In conclusion, we have investigated the adsorption of hydrogen on the (5,5) SWNT surface. On the pristine nanotube, very high activation energies of 2.70–3.07 eV are found for the dissociative adsorption of H_2, while atomic H has a very small adsorption barrier of 0.3 eV. In the Li-doped (5,5) SWNT, we find that Li atoms can be adsorbed both outside and inside the tube, donating electrons to the tube. However, the energy barriers for the dissociation of H_2 are slightly lowered by the charge transfer, similar to those for negatively charged nanotubes, while LiH can be easily adsorbed and dissociated with no energy barrier.

We would like to thank H.-S. Sim and Y.-H. Kim for helpful discussions. This work was supported by the QSRC at Dongkuk University and the supercomputing center in KISTI.

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