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Hydrogen storage in single-walled carbon nanotubes

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We perform density-functional calculations to search for hydrogen adsorption sites and predict maximum storage capacity in single-walled carbon nanotubes. We find two chemisorption sites at top sites of the exterior and the interior of the tube wall. We further find that a form of H_2 molecule can exist in an empty space inside nanotubes. The storage capacity of hydrogen in an empty space increases linearly with tube diameter. The maximum storage capacity is limited by the repulsive energies between H_2 molecules inside nanotubes and those between H_2 molecules and the tube wall. We predict that hydrogen storage capacity in (10,10) nanotube can exceed 14 wt % (160 kg H_2/m^3). © *2000 American Institute of Physics.* [S0003-6951(00)04520-4]

Carbon nanotubes (CNTs) reveal diverse physical properties depending on the diameter and chirality.[1] The large aspect ratio and naturally formed nanoscale-diameter of CNTs make them efficient and stable electron field emitters.[2–4] The large empty space, particularly inside the single-walled nanotubes (SWNTs), opens a new application for the hydrogen storage vehicle with high capacity. It is always desirable to develop a new storage material with high capacity, light mass, and high stability, which may be applicable for portable electronics and moving vehicles. Carbon nanotubes seem to be an ultimate alternative for this, since nanotubes are chemically stable and have low mass density.

Hydrogen could be stored in bundles of the SWNTs up to 5%–10%, where H_2 molecules are physisorbed at the exterior surfaces of CNTs or interstitial spaces between CNTs, separating the intertube distances.[5,6] Although graphite nanofibers or equivalently randomly oriented graphite platelets have been suggested to contain hydrogens up to 72 wt %, this has not been corroborated.[7] It has also been demonstrated that the hydrogens could also be stored electrochemically less than 1% in the CNTs.[8] Despite such efforts, the hydrogen adsorption sites, a form of stored hydrogens, maximum storage capacity, and the structural stability of CNTs upon *H* storage are far from being clearly understood. The main difficulty arises from the lack of an atomistic model for the *H* adsorption and storage in CNTs, which is an essential ingredient for prediction of maximum storage capacity and atomic-level interpretation of *H* adsorption.

In this work, we have carried out density functional (DF) calculations to find the adsorption sites and storage capacity in the SWNTs. We found two chemisorption sites at top sites of (i) the exterior and (ii) the interior of the tube wall. We further found that hydrogens can exist in an empty space inside nanotube as a form of H_2 molecules. The maximum storage capacity is mainly determined by the steric hindrance between H_2 molecules and that between H_2 molecules and the tube wall. Excessive hydrogen storage will result in large repulsive energies and eventually breakdown the tube wall.

For our calculations, we use a self-consistent-charge density-functional-based tight-binding method (SCC-DFTB). The SCC-DFTB method uses a basis of numerically described *s* and *p* atomic orbitals for a carbon atom and *s* orbital for a hydrogen atom. Charge transfer is taken into account through the incorporation of a self-consistency scheme for Mulliken charges based on the second-order expansion of the Kohn–Sham energy in terms of charge density fluctuations. Further detail of the SCC-DFTB method has been published elsewhere.[9]

In order to check the validity of our approach, we also perform the DF total energy calculations based on the local density approximation (LDA) and the generalized gradient approximation (GGA).[10] The exchange-correlation energy in LDA is parameterized by Perdew and Wang's scheme[11] and Becke's corrected exchange functional[12] is adopted in GGA calculations. All-electron Kohn–Sham wave functions are expanded in a local atomic orbital basis. All orbitals including core electrons, are taken into account throughout the calculations. Double-numerical basis set is used to describe the polarization. The convergence criterion for the structure optimization is that all forces be $\leqslant 0.001$ a.u. Structure optimization is done by the SCC-DFTB and LDA schemes. The GGA calculations are done with structures optimized by the LDA whenever necessary.

We first perform benchmark tests for CH_4 and H_2 molecules. The SCC-DFTB describes well the bond lengths of C–H (1.10 Å) and H–H (0.75 Å), compared to the experimental values of 1.1 and 0.74 Å, respectively. The binding energies of C–H bonds (-5.69 eV) and H–H bond (-6.53 eV) are overestimated compared to the respective experimentals values of -4.54 and -4.51 eV. Our GGA results for binding energies (-4.53 and -4.47 eV) are in excellent agreements with experimental values.

We now choose armchair nanotubes with different diameters in our calculations. Supercells of eight layers along the tube axis of (5,5) and (10,10) nanotubes are used. The periodic boundary condition is applied along the tube axis. Figure 1 shows top views of various adsorption sites of hydrogens on the SWNT. The diameter of fully relaxed (5,5) SWNT is 6.88 Å similar to that of C_{60}, with the average bond lengths of 1.44 Å, as shown in Fig. 1(a). We consider

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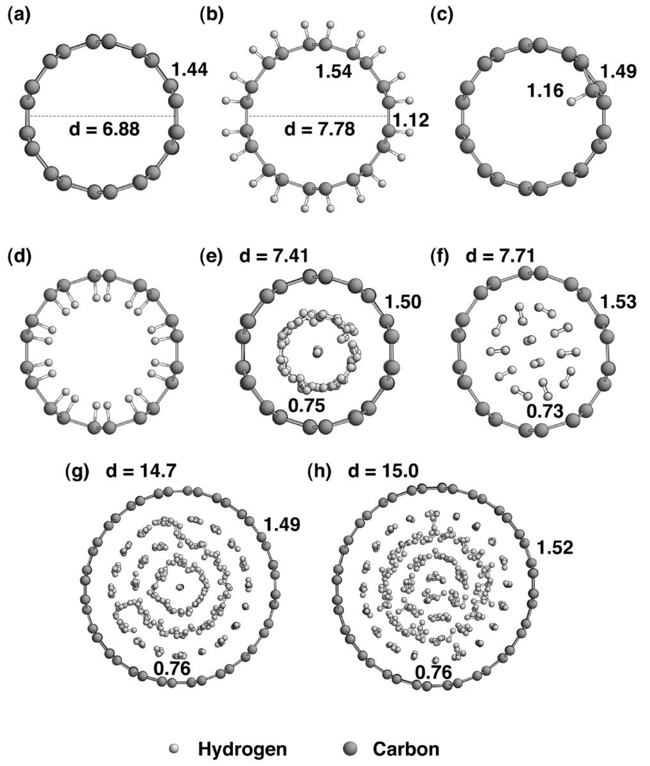

FIG. 1. Top views of various hydrogen adsorptions in SWNTs; (a) clean (5,5) CNT, (b) hydrogens adsorbed at the exterior of the tube wall with $\theta = 1.0$, (c) adsorption of a single hydrogen atom at the interior of the wall, (d) the initial geometry of hydrogens adsorbed at the interior of the wall with $\theta = 1.0$, (e) the fully relaxed geometry of (d), (f) H_2 inside the tube with $\theta = 1.2$, (g) H_2 inside (10,10) CNT with $\theta = 2.0$, and (h) with $\theta = 2.4$. Bond lengths are in unit of Å.

hydrogen adsorption at the exterior of the tube wall in Fig. 1(b), where all top sites of carbons are taken by H atoms. This chemisorption could occur during the electrochemical storage process. The diameter and average C–C bond lengths are expanded to 7.78 and 1.54 Å, respectively, due to the enhancement of the sp^3 rehybridization. The C–H bond length is 1.12 Å, similar to that of a CH_4 molecule. Geometries optimized by LDA were not much different from those optimized by SCC-DFTB. The binding energy (E_b) of the C–H bond is calculated as follows:

$$E_b(\text{C–H}) = E_t(\text{CNT}+H) - E_t(\text{CNT}) - n_{\text{H}} E_{\text{at}}(H), \qquad (1)$$

where $E_t(\text{CNT}+H)$ and $E_t(\text{CNT})$ are the total energy of CNT with and without hydrogens inside, respectively. The $E_{\text{at}}(H)$ is the self-energy of hydrogen atom and n_H is the number of hydrogens. The binding energy of the C–H bond is -2.65 (-2.10:-1.75) eV/C–H bond from SCC-DFTB (LDA:GGA) results, about half the C–H bond energy of CH_4 molecule. Adsorption of a hydrogen atom at the interior of the tube wall pulls inward the carbon atoms nearby [Fig. 1(c)], enhancing sp^3 rehybridization. The binding energy of the C–H bond in this case is -0.83 (-1.50:-1.28) eV/C–H bond. Severe lattice distortions are involved in this geometry. It is noted that hydrogens are chemisorbed with relatively strong binding energy in both cases.

One may imagine hydrogen atoms to be adsorbed at all top sites of the interior wall with a coverage of $\theta = 1.0$, as shown in Fig. 1(d), where the coverage is defined as the ratio of the number of hydrogen atoms to that of carbon atoms.

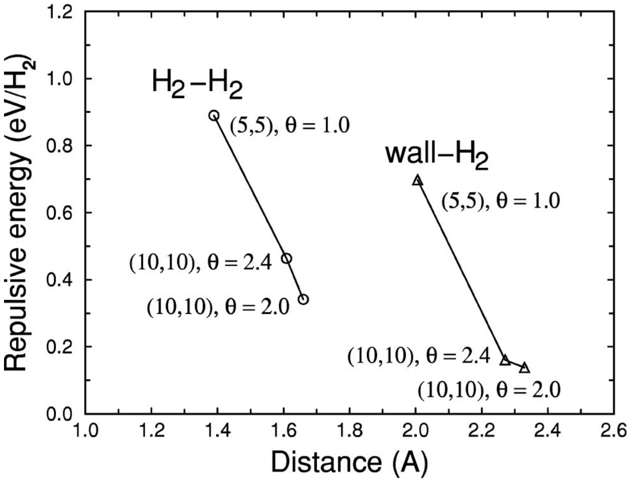

FIG. 2. The repulsive energies between CNT wall-H_2 molecules (triangles) and between H_2–H_2 molecules (circles) inside the CNT.

However, this structure is not stable after full relaxation, resulting in the formation of H_2 molecules, as shown in Fig. 1(e). The energy is minimized by forming H_2 molecules with the E_b of -4.57 (-3.16:-2.24) eV per H_2 molecule. This strongly suggests that the H_2 molecule can exist stably in the vacant space inside the nanotubes. The E_b of the H_2 molecule inside CNT is reduced by about 2 eV, compared to that of a gaseous H_2 molecule, due to the repulsive forces between H_2 molecules and between the tube wall and H_2 molecules. Higher coverage of $\theta = 1.2$, as shown in Fig. 1(f), results in larger repulsive energies. The repulsive energy (E_{rep}) between the tube wall and H_2 molecules is calculated by

$$E_{\text{rep}}(\text{wall}-\text{H}_2) = E_t(\text{CNT}+H_n) - E_t(\text{CNT}) - E_t(H_n), \qquad (2)$$

and similarly that between H_2 molecules is calculated by,

$$E_{\text{rep}}(\text{H}_2-\text{H}_2) = E_t(\text{H}_n) - n_{\text{H}_2} E_{\text{H}_2}, \qquad (3)$$

where $E_t(H_n)$ is the total energy of H_n only in CNT, and n_{H_2} and E_{H_2} are the number of gaseous H_2 molecule and the total energy of a single gaseous H_2 molecule, respectively.

The repulsive energy between tube wall and the H_2 is 0.7 (0.47:0.74) eV/H_2 and that between H_2 molecules is 0.89 (0.81:1.19) eV/H_2 for $\theta = 1.0$. The LDA and the GGA calculations consistently reproduce the SCC-DFTB results. The average distance between H_2 molecules is 1.4 Å, and that between the tube wall and H_2 molecules is 2.0 Å for $\theta = 1.0$. Figure 2 shows the repulsive energies as a function of average distances between H_2–H_2 molecules and tube wall-H_2 molecules. Repulsive energies become larger for higher coverages, increasing the diameter and eventually break the tube walls. We conclude that these repulsive energies determine the maximum storage capacity of hydrogens inside tubes and the stability of the tubes. The tubes containing H_2 with $\theta = 1.0$ remained stable from the molecular dynamics simulations at room temperature.[13]

To estimate the maximum storage capacity, we assume the hydrogen density (n_H/volume) to be nearly constant inside the tube. The volume and the number of the hydrogen atoms increase with square of the radius, whereas the number

TABLE I. Hydrogen storage capacity in SWNTs in different units. Cavity volume of the tube is used to calculate the density.

	θ	H wt %	ρ (mA h/g)	ρ (atoms/Å^3)	ρ (kg/m^3)
(5,5)	1.0	7.7	2200	0.19	160
(5,5)	1.2	9.1	2700	0.23	190
(10,10)	2.0	14.3	4500	0.19	160
(10,10)	2.4	16.7	5400	0.22	190

of carbon atoms increases linearly with the radius. Therefore, we expect hydrogen storage capacity to be linearly proportional to the radius or diameter. To validate this prediction, we now take (10,10) SWNT. Figure 1(g) shows the optimized structure with a coverage of $\theta=2.0$ or equivalently 14.3 wt %. This value is much higher than the estimated value of 3.3 wt % from the geometrical model.[14] In spite of higher coverage, the C–C bond lengths are smaller and H_2 bond lengths longer compared to (5,5) SWNT resulting from smaller repulsive energies,[13] as shown in Fig. 2. One may increase the coverage to $\theta=2.4$ but still the tube wall is stable, as shown in Fig. 1(h). By choosing the coverage $\theta=2.0$ for (10,10) nanotube, we generalize the hydrogen storage capacity H wt % $\geqslant 14.3$ (D/D_0) for SWNTs, where D_0 is the diameter of (10,10) nanotube.[15] Table I summarizes the storage capacity in various units. We emphasize here that the experimentally well observed (10,10) nanotubes[16] can have superb charge storage capacity up to 4500 mA h/g, which is much greater than 100–400 mA h/g of a conventional metal-hydride battery.[17] This suggests potential applications for an electrode in secondary battery for moving vehicles or fuel cells. We also considered hydrogen adsorptions in multi-wall nanotubes. The hydrogen storage capacity is independent of the tube diameter and is expected to have lower storage capacity than SWNTs. The detail will be described elsewhere.[13]

In summary, we found two hydrogen chemisorption sites in SWNTs by DF calculations; top sites at the exterior and interior of the tube wall. We predict that hydrogen molecules can exist in the empty space inside the nanotube. The maximum hydrogen storage capacity increases linearly with diameter in SWNTs, i.e., H wt %$\geqslant 14.3$ (D/D_0), [D_0 is the diameter of (10,10) nanotube].

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