An extensive first-principles study of fully exo-hydrogenated zigzag \((n,0)\) and armchair \((n,n)\) single wall carbon nanotubes \((C_nH_n)\), polyhedral molecules including cubane, dodecahedrane, and \(C_{60}H_{60}\) points to crucial differences in the electronic and atomic structures relevant to hydrogen storage and device applications. \(C_nH_n\)'s are estimated to be stable up to the radius of a \((8,8)\) nanotube, with binding energies proportional to \(1/R\). Attaching a single hydrogen to any nanotube is always exothermic. Hydrogenation of zigzag nanotubes is found to be more likely than armchair nanotubes with similar radius. Our findings may have important implications for selective functionalization and finding a way of separating similar radius nanotubes from each other.

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lations the Brillouin zone integration is carried out at the Γ-point. For nanotubes, we used k-point spacing of $dk \approx 0.02 \text{ Å}^{-1}$, generating 5 and 10 special k-points along the tube axis for zigzag and armchair nanotubes, respectively [25]. All carbon and hydrogen positions were relaxed without assuming any symmetry. For nanotube calculations, the c-axis of the supercell (corresponding to the tube axis) is also optimized.

Fig. 2 Energy curves as a CH-bond is rotated towards the indicated arrows for armchair (top) and zigzag nanotubes (bottom) starting from $\theta = \alpha$. The minimum energy is found when the CH-bond is tilted toward the shaded hexagons. Zero of energy was taken to be arbitrary.

In principle, there are an infinite number of isomers depending on the locations of hydrogen atoms (i.e. endo if they are inside the tube and exo if they are outside) as well as amount of hydrogen coverage. Endo-hydrogenation, alternating endo-exo hydrogenation, and various half coverage cases are being studied and the results will be published elsewhere [24]. Here, we consider the case of full coverage where all carbon atoms in a nanotube are hybridized with hydrogen atoms from outside of the tube as shown in Fig. 1c. We refer to this isomer as a fully exo-hydrogenated carbon nanotube.

First, the equilibrium orientations of the CH bonds were determined starting with all the CH-bonds radially outward (Fig 1c). Using this configuration, we studied a single CH-bond orientational dependence of the potential energy surface. Figure 2 shows the calculated energy curves as a single CH-bond is rotated along two high symmetry directions for both zigzag and armchair nanotubes. For armchair (n,n) nanotubes, the optimum orientation is obtained when the CH-bond is tilted about the tube axis (i.e c-axis). Hence in the fully optimized structure, CH-bonds tilt in opposite directions around the c-axis alternatively. For the zigzag nanotubes, the optimum orientation is obtained when the CH-bond is tilted towards the c-axis. Therefore, the lowest energy configuration for zigzag tubes has CH-bonds tilted towards plus and minus c-axis alternatively. Having located the CH-bond orientations in this way, we next let all the carbon and hydrogen atoms along with c-axis vary to obtain the final optimum structures.

Table 1 summarizes the parameters obtained for fully optimized structures. Upon hybridization of carbons with hydrogens, the C-C bond length ($d_{CC}$) increases from $\approx 1.4 \text{ Å}$ to $\approx 1.55 \text{ Å}$. The latter is typical for sp$^3$ CC-bonds. The increase in $d_{CC}$ results in an increase in the tube radius ($R_{HC}$) by about 13 - 16% for armchair nanotubes and by about 15 - 17% for zigzag nanotubes. Interestingly, these values are almost twice of those found for the polyhedral molecules. Moreover, the value of $d_{CC}$ increases slightly (by about 0.03 Å) with increasing tube radius. The CH-bond length ($d_{CH} \approx 1.09 \text{ Å}$) is also found to have weak dependence on the tube radius. Using projection techniques we estimated the total charge transfer from hydrogen to carbon to be around 0.26 electrons for nanotubes and 0.3 electrons for polyhedral molecules.

The most important difference between zigzag and armchair nanotubes is found in the local CCH angles ($\alpha_{CCH}$). Even though one of these angles is about the same for both types of nanotubes, the second angle in zigzag nanotubes is always larger than those in armchair nanotubes. This implies that the CCH-bond angles are more frustrated in armchair nanotubes than in zigzag nanotubes and therefore deviate more from the ideal tetrahedral sp$^3$ bond angle of 109.5°. This observation suggests that hydrogenated armchair nanotubes will have higher energy and therefore they are less stable than zigzag nanotubes. Unlike CCH-bond angles, CCC-bond angles have weak radius dependence and are about the same for both types of nanotubes.
Table 1 Various parameters of the fully optimized structures of exo-hydrogenated armchair and zigzag carbon nanotubes and other polyhedral molecules. For graphene (i.e. $R_{HC} \rightarrow \infty$) $d_{CH}$ and $d_{CC}$ are 1.066 Å and 1.622 Å, respectively.

| Material      | Formula | $R_{HC}$ (Å) | $d_{CH}$ (Å) | $d_{CC}$ (Å) | $\alpha_{CCH}$ (deg.) | $\alpha_{CCC}$ (deg.) |
|---------------|---------|--------------|--------------|--------------|-----------------------|-----------------------|
| (4,4) C_{16}H_{16} | 3.103 (2.734) | 1.090 | 1.541, 1.567 | 96.70, 98.60 | 12.77, 120.69 |
| (5,5) C_{20}H_{20} | 3.885 (3.394) | 1.087 | 1.549, 1.575 | 94.82, 97.15 | 113.18, 121.50 |
| (6,6) C_{24}H_{24} | 4.698 (4.061) | 1.084 | 1.557, 1.594 | 93.35, 96.30 | 113.30, 122.00 |
| (8,8) C_{32}H_{32} | 6.228 (5.400) | 1.079 | 1.567, 1.594 | 92.16, 94.85 | 114.62, 121.95 |
| (10,10) C_{40}H_{40} | 7.780 (6.755) | 1.077 | 1.574, 1.600 | 91.40, 94.00 | 115.40, 121.76 |
| (7,0) C_{28}H_{28} | 3.180 (2.765) | 1.092 | 1.549, 1.553 | 96.40, 102.25 | 113.95, 125.90 |
| (8,0) C_{32}H_{32} | 3.641 (3.146) | 1.090 | 1.553, 1.557 | 95.22, 101.60 | 114.12, 127.00 |
| (9,0) C_{16}H_{16} | 4.111 (3.557) | 1.089 | 1.553, 1.566 | 94.32, 101.14 | 114.27, 127.58 |
| (10,0) C_{40}H_{40} | 4.571 (3.912) | 1.087 | 1.556, 1.572 | 93.60, 100.54 | 114.48, 128.75 |
| (12,0) C_{48}H_{48} | 5.467 (4.695) | 1.084 | 1.557, 1.576 | 92.66, 99.340 | 115.11, 127.67 |
| Cubane C_{8}H_{8} | 1.345 (1.267) | 1.087 | 1.553 | 125.26 | 90.0 |
| Dodecahedrane C_{20}H_{20} | 2.157 (2.0) | 1.090 | 1.539 | 110.9 | 108.0 |
| Fullerene C_{60}H_{60} | 3.827 (3.510) | 1.088 | 1.536, 1.550 | 101.1, 101.9 | 108.1, 120.0 |

The stability and energetics of CH-bond formation are derived from the average binding energy per atom for exo-hydrogenated nanotubes defined as

$$E_B = (E_{C_nH_n} - E_C - nE_H) / n.$$  

Here $E_{C_nH_n}$, $E_C$, and $E_H$ are the total energies of the fully optimized exo-hydrogenated nanotube, nanotube alone, and hydrogen atom, respectively. According to this definition, a stable system will have a negative binding energy. Fig. 3a shows the radius dependence of $E_B$ for nanotubes and polyhedral molecules (see inset). Two interesting observations are apparent. First, as shown by solid and dotted lines, the binding energies can be very well described by a one parameter fit:

$$E_B = E_0 - C(n,m)/R_{HC},$$

where $E_0$ is the limit $R_{HC} \rightarrow \infty$ (i.e. graphene) and calculated to be -1.727 eV. The fit results for $C(n,m)$ are given in Fig. 3a for zigzag and armchair nanotubes. The inset to Fig. 3a shows that while $E_B$ for cubane falls on the same curve as nanotubes, dodecahedrane and C_{60}H_{60} have lower energies than nanotubes due to their more spherical shape.

The second interesting observation in Fig. 3a is that the binding energies of zigzag nanotubes are always lower than those in armchair nanotubes with similar radius by about 30 meV/atom. As discussed above, this is a natural result of the fact that the CCH-bond angles in zigzag nanotubes are closer to the optimum tetrahedral sp^{3} bonding than those in armchair nanotubes. We expect this observation is also valid for hybridization of nanotubes with other elements, such as Cl and F and this may have important implications for separating similar radius nanotubes from each other by selective chemical functionalization.

Fig. 3 (a) Binding energies $E_B$ of (n,m) (square) and (n,0) (circle) nanotubes as a function of $R_{HC}$. The solid and dashed lines are one parameter fits to $E_B = E_0 - C(n,m)/R_{HC}$ as discussed in the text. Inset shows the binding energies of cubane, dodecahedrane, and C_{60}H_{60}. (b) Full circles indicate the energy ($\Delta E_B$) to break a single CH-bond to form a C_{n}H_{n−1} zigzag nanotubes as depicted in the top inset. Full squares indicate energy gain $\Delta E_C$ by attaching a single H atom to a nanotube to form a C_{n}H as depicted in the bottom inset. The solid and dashed lines are two parameter fits as discussed in the text, indicating 1/$R_{HC}$ behavior.
Even though $C_nH_n$ nanotubes are found to be stable with respect to a pure carbon nanotube ($C_n$) and $n \times H$ atoms for all values of the radius, it is of interest to see if they are also stable against breaking a single CH-bond. We, therefore, calculated energies of fully optimized hydrogenated nanotubes after breaking one of the CH-bonds and putting the H atom at the center of supercell as shown in the top inset to Fig. 3b. Calculated values of the energy differences $\Delta E_B$, for zigzag nanotubes were fitted to $\Delta E_B = E_0 + A/R_{HC}$ where $E_0$ and $A$ are 2.506 eV and -15.671 eVÅ, respectively. We note that for radius around $R_{HC} \approx 6.25 \text{ Å}$, the $\Delta E_B$ becomes negative, suggesting instability [27]. Hence, (12,0) and (8,8) nanotubes are at the limit for stable, fully exohydrogenated nanotubes. We are currently studying this problem for half-coverage case as well.

![Diagram](image_url)

**Fig. 4** (a) Electronic band structure of a (9,0) exo-hydrogenated carbon nanotube (left panel) and the corresponding density of states (DOS) (right panel). (b) Band gap as a function of tube radius $R_{HC}$. Inset shows the full scale plot to include the band gaps of the polyhedral molecules.

The energy, $\Delta E_G$, gained by attaching a single H atom to a carbon nanotube is calculated by performing structure optimization of a $C_nH$-nanotube as depicted in the bottom inset to Fig 3b. It is seen that $\Delta E_G$ can be also well described by $\Delta E_G = E_0' + A'/R_{HC}$ (dashed line) where $E_0'$ and $A'$ are -1.161 eV and -4.952 1 eVÅ, respectively. Unlike $\Delta E_B$, there is no change in the sign of $\Delta E_G$, suggesting that for any radius of carbon nanotube hybridization of a single carbon atom is always stable. However the energy gain from two such processes is around 5–6 eV which is slightly less than the dissociation energy of $H_2$, 6.65 eV. Hence $C_n$ nanotube plus $H_2$ system is stable against forming a $C_nH_2$ hydrogenated nanotube. Therefore, in order to realize the CH-bonding discussed here, one first has to break $H_2$ molecules into hydrogen atoms, probably by using a metal catalyst or electrochemical techniques.

Hydrogenation of nanotubes is also important in the modification of the electronic structure for device applications. Figure 4 shows the band structure and the corresponding density of states (DOS) for a (9,0) exo-hydrogenated nanotube, which is typical to other nanotubes that we studied. Using projected DOS, we find that the bottom of the conduction bands are mainly derived from hydrogen while the top of the valence bands are mainly carbon-origin. In contrast to pure nanotubes which are metal or semiconductors depending on their structure, the $C_nH_n$ nanotubes are found to be direct band insulators with a gap of 1.5–2 eV at the Γ-point. This value is about one-third of those for the molecular polyhedrals, indicating less stability of hydrogenated nanotubes than molecules (Fig. 4b). The band gaps decrease with increasing tube radius but unlike binding energies there is no apparent $1/R_{HC}$ type behavior. Interestingly, the band gaps of armchair nanotubes are higher in energy by about 0.2 eV than those in zigzag nanotubes. This is surprising because the band gap is usually higher for more stable saturated hydrocarbons.

The observed band gap opening via hydrogenation of nanotubes can be used for band gap engineering for device applications such as metal-insulator heterojunctions. For example, various quantum structures can easily be realized on an individual carbon nanotube, and the properties of these structures can be controlled by partial hydrogenation of carbon nanotubes. If the different regions of a SWNT are covered with hydrogen atoms, the band gap and hence the electronic structure will vary along the axis of the tube. This way various quantum structures of the desired size and electronic character can be formed. In this respect, present scheme is quite similar to our previous constructions of nanotube heterostructures or quantum dots, where periodic applied transverse compressive stress is used for band gap opening [28].

In summary, we have presented first-principles calculations of the structural and electronic properties of various nanotubes which are fully protonated by sp$^3$ hybridization of carbons. We find that $C_nH_n$ nanotubes are stable for tube radius $R_{HC}$ smaller than 6.25 Å, roughly corresponding to a (8,8) nanotube. Hybridization of a single carbon atom is found to be always exothermic regardless of tube radius. Weak but stable CH-bonding in nan-
tubes may be an important consideration for possible hydrogen storage applications. We also found that hybridization of zigzag nanotubes is more likely than armchair nanotubes with the same radius, suggesting a possible selective chemical functionalization of nanotubes. The fact that other carbon clusters such as cubane, docosahedrane, and C_{60}H_{32} have been synthesized successfully, suggest that it may possible in the near future to hydrogenate carbon nanotubes, yielding new structures with novel properties.

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