

Encapsulation and polymerization of acetylene molecules inside a carbon nanotube

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Abstract

We study the energetics of acetylene (C_2H_2) molecules inside a carbon nanotube (CNT) using the ab initio pseudopotential method. The encapsulation energy of a single C_2H_2 molecule into the nanotube and the formation energy of $(C_2H_2)_n@CNT$ are calculated. We investigate whether a polyacetylene chain can be produced by fusion of the close-packed acetylene molecules inside the CNT and find that there is practically no activation barrier to polymerization. We propose to employ this method to obtain straight, perfectly isolated, and single-stranded polyacetylene chains encapsulated inside CNTs, which may be used for molecular electronic devices.

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1. Introduction

Due to the presence of the inner hollow space, the CNT can be an ideal container for atoms or small molecules. Recently, Takenobu and co-workers [1] reported that organic molecules predominantly occupy the inner space of the nanotubes. Atoms and molecules engaged in the nanotube are isolated from the environment and their chemical reaction could be triggered by electron beam irradiation. Among alkynes (organic molecules with carbon triple bonds), acetylene (C_2H_2) is the simplest and a good model system to study pressure-induced polymerization which arises at pressures above 3 GPa at room temperature [2,3]. On the other hand, under pressure or in the presence of copper, it can be converted to carbon and hydrogen with explosion. This instability causes problems in the handling and storage of the material and the commercial acetylene is stabilized with acetone and phosphine to prevent explosion.

McIntosh and co-workers [4,5] proposed to insert the polyacetylene (PA) chains inside carbon nanotubes and avoid interchain coupling and complicated morphology of the bulk materials. Because of the entropic effect, however, the PA (polymer) is not straight and cannot reach the deep inside of the CNT at room temperature. Here we propose a method to store acetylene molecules and convert them into PA using the CNT as a chemical reactor as well as a container. Through this process, we can obtain a straight, perfectly isolated, and single-stranded PA encapsulated inside a CNT. Carbon fullerenes were already found to be converted into a CNT inside the host nanotube by the coalescence process [6,7]. A collection of PA chains under such a morphological control may be used for future molecular electronic devices. In this work, we calculate the energetics of acetylene insertion into a nanotube and find that the reaction is exothermic resulting in a static capillary force [4,8]. This force compresses incorporated acetylene molecules with an effective pressure of the order of sub-GPa. Once acetylene molecules are aligned compactly inside the tube, polymerization of them is predicted to take place practically without an activation energy barrier.

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2. Computational details

We perform ab initio electronic structure calculations for C_2H_2 molecules inside the CNT based on the density functional theory (DFT) within the Local Density Approximation for the exchange-correlation energy. We also checked the energy shift by employing the Generalized Gradient Approximation for some important geometries, and found that overall results are the same. For the large supercell calculations, norm-conserving pseudopotentials [9] are employed in the Kleinman–Bylander form [10]. The wave functions are expanded using the numerical atomic orbital basis set [11,12] and an energy cutoff of 100 Ry. To calculate the activation energy barrier in polymerization of the acetylene molecules which require heavier computational loads, the nudged elastic band (NEB) method [13,14] implemented in the PWSCF package [15] is used. Ionic cores are described by ultrasoft pseudopotentials and the Kohn–Sham orbitals are expanded in plane waves with a kinetic energy cutoff of 30 Ry. We have done test calculations for diamond and C_{60} , and obtained converged results for electronic and structural properties with two cutoff energies, 100 and 30 Ry, for norm-conserving and ultrasoft pseudopotentials, respectively. The NEB method enables us to find the optimal reaction pathway with the minimum energy when both the initial and final states are known. Seven replicas are chosen including the initial and final ones to construct the elastic band in this method. The atomic positions of the CNT, acetylene, and polyacetylene chain are relaxed, respectively until the atomic force becomes less than 0.05 eV/Å.

3. Results and discussion

We first discuss the energetics of C_2H_2 insertion into a CNT. The dangling bonds of the open (5,5) nanotube of 2 nm in length are passivated by hydrogen atoms and the C_2H_2 molecular axis is assumed to be initially aligned with the tube axis as shown in Fig. 1a. The supercell size in the lateral (xy) direction is chosen to be as large as 20 Å to avoid interaction between (5,5) CNTs with ~ 7 Å in diameter and that in the axial direction (z -axis) is 70 Å to allow for sufficient vacuum regions. The abscissa in Fig. 1b represents the position of the center of C_2H_2 from the edge carbon atoms of the CNT along the tube axis. A static capillary force associated with the energy gain during encapsulation may compress other C_2H_2 molecules inside the CNT. The energy lowering by the axial insertion of an acetylene molecule into the (5,5) CNT is ≈ 0.65 eV as shown in Fig. 1b, indicating an exothermic reaction. The energy slope along the tube axis in Fig. 1b corresponds to a static capillary force of ≈ 0.22 nN. The energy is further lowered by 0.1 eV when C_2H_2 is tilted by about 45° with respect to the axis of the (5,5) nanotube. In this situation, the distance between a H atom on C_2H_2 and the tube wall is ≈ 2.3 Å. Because of the limitation of the computational resource,

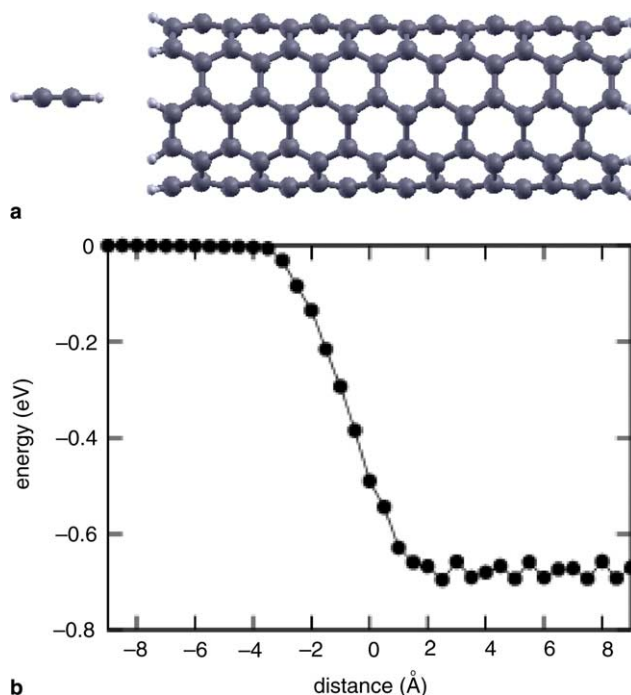


Fig. 1. Energetics of acetylene insertion into a CNT. (a) Atomic model of a C_2H_2 molecule entering a (5,5) nanotube. (b) Energy profile during the insertion of C_2H_2 along the tube axis.

the data presented in Fig. 1b are obtained without optimization for the whole system. According to our test calculation, the full relaxation lowers the total energy by only 0.03 eV (30 meV). Thus we believe that we can do without complete optimization for the supercell containing the whole system (i.e., the nanotube and acetylene molecule).

Small but finite energy variation for positive values of the abscissa in Fig. 1b implies that the acetylene molecule inside the tube feels the lattice structure of the CNT. The periodicity of the variation is almost the same as that of the armchair CNT (~ 2.5 Å). In addition, the tilting of the encapsulated C_2H_2 molecule indicates the nonbonding interaction between the nanotube wall and C_2H_2 . The recent density functional calculations show that the long organic molecules such as tetracyanop-quinodimethane (TCNQ) and tetrafluorocyanop-quinodimethane (F4TCNQ) encapsulated in the bigger CNT are tilted by about 30° with respect to the tube axis [16,17].

We then calculate the activation energy barrier along the reaction path between two locally stable configurations using the NEB method. Two stable configurations are the one-dimensional close-packed array of C_2H_2 molecules (Geometry A) and the PA chain (Geometry B) inside the (5,5) CNT, respectively, displayed in Fig. 2a,b. As mentioned above, the acetylene molecule prefers to be tilted by 45° to the tube axis inside the (5,5) CNT (Geometry A). First of all, the formation energy of Geometry A is calculated. We define the formation energy of the close-packed array of acetylene molecules in the (5,5) CNT,

$$E_{\text{form}} = E[\text{CNT} + (C_2H_2)_n] - E[\text{CNT}] - E[(C_2H_2)_n], \quad (1)$$

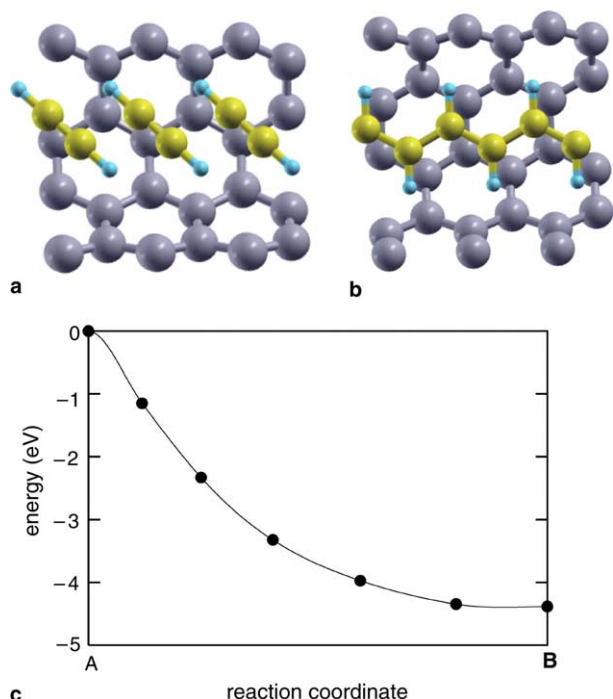


Fig. 2. Polymerization process of acetylene in the CNT. (a) Atomic model of a one-dimensional close-packed array of acetylene molecules inside a (5,5) CNT (Geometry A). (b) Atomic model of the *trans*-polyacetylene formed inside a (5,5) CNT (Geometry B). (c) Energy diagram along the reaction pathway of polymerization from Geometry A to B.

where $E[\text{CNT}]$ and $E[(\text{C}_2\text{H}_2)_n]$ are the energies of the isolated nanotube and C_2H_2 while $E[\text{CNT} + (\text{C}_2\text{H}_2)_n]$ is the energy of the whole encapsulated system. For the plane-wave calculation, the unit cell size in the lateral (xy) direction is chosen to be 15 Å and that in the axial direction (z -axis) is 2.5 Å with the periodic boundary condition. The formation energy is -0.4 eV per C_2H_2 (exothermic reaction). We do not consider a Peierls distortion in calculating the energy of the PA chain. Fig. 2c reveals that Geometry B has a lower energy than Geometry A by 4.3 eV per C_2H_2 and there is no activation barrier. In this reaction process, a π -electron in the triple bonding rapidly hops to form a new carbon–carbon bond with the nearest-neighbor C_2H_2 . The initial and final dots in (c) indicate the energies of Geometries A and B, respectively. Therefore, close-packed acetylene molecules are driven to be polymerized by fusion in the tube. During the process of polymerization, the carbon–carbon bonds of the acetylene molecule are elongated (from 1.2 to 1.4 Å) and the angles between carbon and hydrogen atoms are changed. We have also tested the acetylene encapsulation and polymerization inside a larger diameter nanotube, (6,6) CNT. Insertion of C_2H_2 into the (6,6) tube is more favorable than that of the (5,5) tube energetically. However, the (6,6) tube has a region of a constant potential inside [4] and the randomness caused by the lateral freedom of the C_2H_2 position in that region (owing to the entropic effect) makes polymerization a little bit less favorable. For dense C_2H_2 molecules in the (6,6) tube, the equilibrium angle of the C_2H_2 axis

with the tube axis is found to be 90° before polymerization. Other than these differences, we obtain similar energetics to the (5,5) tube case, including the absence of the activation barrier to polymerization.

Even if there is practically no activation energy barrier, it is very hard for the molecules to react with the neighbor molecule spontaneously inside the CNT before arranging themselves into a one-dimensional close-packed array (Geometry A). The isomers of C_4H_4 cannot be created from acetylene molecules at room temperature because C_2H_2 molecules are not dissociated. In addition, some isomers of C_4H_4 such as cyclobutadiene (ring-shaped) are energetically unstable. When the encapsulated C_2H_2 molecules form the one-dimensional close-packed array by the effective pressure of the order of sub-GPa associated with the capillary force, polymerization of acetylene takes place without activation energy barrier. Interestingly, it is known that the equilibrium spacing between C_{60} molecules in the nanotube is smaller by $\sim 4\%$ than in the three-dimensional C_{60} crystal by the high resolution transmission electron microscopy (HRTEM) [18], electron diffraction [19], and Raman measurements [20]. It indicates that incorporated molecules inside the CNT may be subject to an axial compressive force due to the energy change along the tube axis during the insertion [8]. In the same manner, acetylene molecules may be close-packed in the nanotube.

4. Conclusion

We have performed ab initio pseudopotential calculations to investigate the energetics of acetylene (C_2H_2) molecules inside a CNT. The encapsulation process of a single C_2H_2 molecule in the nanotube is an exothermic reaction and the static capillary force produced by entering C_2H_2 is a fraction of a nanoNewton. It is found that there is practically no activation barrier to the polymerization reaction, implying that a PA chain can be easily produced inside the CNT by fusion of the close-packed acetylene molecules in it. Thus, we propose a method to fabricate a straight and isolated PA chain inside a CNT, by which we can avoid the interchain coupling and understand the intrinsic properties of the individual PA chains. In addition, it is a promising way to investigate and control the interaction between the CNT and the polymer. We believe that this study sheds light on physical and chemical properties of organic molecules and leads to an application of the nanotube as a nano-sized chemical reactor.

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