Energetics of the oxidation and opening of a carbon nanotube

M. S. C. Mazzoni,* H. Chacham,† P. Ordejón,‡ D. Sánchez-Portal,† J. M. Soler,† and E. Artacho†
*Departamento de Física, ICEx, Universidade Federal de Minas Gerais, C.P. 702, 30123-970 Belo Horizonte, MG, Brazil
†Departamento de Física, Universidad de Oviedo, 33007 Oviedo, Spain
‡Departamento de Física de la Materia Condensada, C-III, Universidad Autónoma de Madrid, 28049 Madrid, Spain
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We apply first principles calculations to study the opening of single-wall carbon nanotubes (SWNT’s) by oxidation. We show that an oxygen rim can stabilize the edge of the open tube. The sublimation of CO₂ molecules from the rim with the subsequent closing of the tube changes from endothermic to exothermic as the tube radius increases, within the range of experimental feasible radii. We also obtain the energies for opening the tube at the cap and at the wall, the latter being significantly less favorable.

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The possibility of filling carbon nanotubes [1] with a variety of substances has fascinated the materials science community since they were first observed [2] and synthesized in promising quantities [3], but the fact that the tube tips are closed represented a severe limitation for it. Ajayan and Iijima [4] observed the cap removal and filling of nanotubes in which they were first oxidized in air to remove the caps. In this process, 60% of the tube walls remaining intact. Ugarte et al [7] described a method of filling nanotubes in which they were first oxidized in air, suggesting a chemical reaction between oxygen and the tube ends. This was confirmed by Ajayan et al [5] who showed that the tubes were open exclusively at the caps. Simultaneously, Tsang, Harris and Green [6] described the thinning and opening of nanotubes by carbon dioxide. They also observed corrosion at the cap region, the tube walls remaining intact. Ugarte et al [7] described a method of filling nanotubes in which they were first oxidized in air to remove the caps. In this process, 60% of the tubes were open. The above mentioned experiments used multi-walled nanotubes. In a recent experiment, however, Dillon et al [8] observed the physisorption of H₂ in bundles of small-diameter SWNT’s. They suggested that these tubes were open by oxidation in the same way as multi-walled tubes. Individual open-ended SWNT’s were also obtained experimentally [9] by treating SWNT rope material with a mixture of acids.

The filling and opening of nanotubes have also been subjects of theoretical studies. Pederson and Broughton [10] predicted the tendency of the nanotubes to attract molecules to their interior. More recently, Miyamoto et al [11] reported first-principles calculations that showed the ionic cohesion between carbon nanotubes and potassium atoms linearly arranged inside them. The reactivity of the open end of SWNT’s was studied by Charlier et al [12]. They showed that the unsaturated tip of small diameter SWNT’s closes spontaneously at typical growth temperatures. However, first principles calculations also indicate that these tubes may stay open during growth in the presence of a catalyst, such as Ni [13].

The detailed description of the burning and opening processes, and of their kinetics, is a formidable problem beyond the scope of state-of-art ab initio techniques. In the present work, we apply first principles calculations to address two specific, but relevant questions on the energetics of these processes: (i) why does O₂ attack preferentially the tube caps? and (ii) how and why do the tubes remain open (if at all) after the O₂ supply has been cut? To address the first question, we compare the opening of oxidized holes at the cap of the tube with their chemical equivalents at the wall, finding that the cap oxidation is much more favorable, due to the release of its curvature strain. On the second question, we find that the presence of an oxygen rim at the edge of the open tube results in a very stable configuration, even in the absence of O₂. Smaller holes with favorable energetics allow us to obtain an estimate of the activation barrier of the closing process.

Our calculations were performed with the SIESTA program [14-16], using density-functional theory [17], within the generalized gradient approximation (GGA) for exchange-correlation [18], and norm-conserving pseudopotentials [19,20]. The basis set is a linear combination of pseudoatomic orbitals [19,21,22]. We always used a split-valence double-ζ (DZ) basis [23], and convergence tests were performed by adding polarization functions [24]. This resulted in changes in formation energies of only a few meV/atom. All the geometries were optimized, with remanent forces of less than 0.1 eV/Å. Test calculations were performed on graphite, nanotubes, and fullerenes. The calculated nearest-neighbor distances of C₆₀ (1.42 and 1.47 Å) and graphite (1.42 Å) reproduce the experimental values (1.40, 1.46, and 1.42 Å, respectively) within 2%. Also, the energy per atom of C₆₀ relative to that of graphite (0.38 eV/atom) agrees very well with the experimental result (0.392 - 0.433 eV/atom) [25]. Our calculations were performed for (4,4), (6,6), and (8,8) armchair SWNT’s, with diameters 5.6, 8.3, and 11.1 Å, containing up to 166 carbon atoms. However, for the sake of clarity in the exposition, we will refer to the specific (6,6) case throughout the paper, leaving the analysis of the size effects to the end.

In order to understand why O₂ produces a selective ox-
oxidation of the tube caps, rather than a generalized burning, we compare the energies of similar holes at the tube’s cap and wall. Figure 1 shows these structures for the (6,6) tube. The closed tube, hereafter denoted by C120, is shown in Fig. 1(b). The other end of the tubes is bulk-like and saturated by hydrogen atoms. This termination is used in all the structures, except the infinite tubes used to calculate the carbon chemical potential \( \mu_C \), for which we used periodic boundary conditions [Fig. 1(a)]. The hole geometries, shown in Fig. 1(c)-(j), were chosen as plausible low energy structures for specific hole sizes and not necessarily to simulate the actual oxidation process.

These hole structures will provide estimates of the energy released, for a given hole size, during the tube opening process. Figure 2 shows the potential energy change during oxidation as a function of the hole size, measured by the number of carbon atoms lost by the tube in the process. These atoms are removed from the tube according to the reaction \( C + O_2 \rightarrow CO_2 \), while extra oxygen is used to saturate the resulting holes. The initial structure is Fig. 1(b) and the oxidized structures are Fig. 1(c)-(j). The general trend is linear with the number of C atoms missing in the hole, as it should, but the energy released by oxidizing the cap is larger than for the wall, as shown in Fig. 2(b) [26]. As we will see, the origin of the difference is the extra elastic energy accumulated at the cap. It is remarkable that the wall-cap difference for removing the first carbon atom (2.4 eV), is already very close to that for a full hexagonal hole. Thus, the cap’s strain energy is substantially released from the very beginning of the oxidation.

Addressing the stability of the open tube after oxidation, Fig 1(c) shows the most efficient chemical saturation of the open tube with oxygen. In this oxidized open tube, denoted by \( C_{120}O_6 \), every O atom saturates two carbon “dangling bonds”, giving a slightly stretched C-O bond distance of 1.43 Å and a C-O-C angle of 105°. The bond stretching produces an inward relaxation (18°) of the rim structure as a consequence of the pulling of the O atoms, diminishing the tube perimeter at the rim. The structure is very stable: the sublimation of oxygen atoms in the form of \( CO_2 \), resulting in an unsaturated open tube [Fig. 1(k)], is found to be energetically unfavorable by 17.8 eV. This highly endothermic reaction indicates that, if open tubes are present, they will have an oxygen rim at the edge even at typical oxidation temperatures (∼1000K) [27].

Starting with this oxidized open tube, we consider a reaction in which the tube closes and \( CO_2 \) molecules evaporate:

\[
\text{oxidized open tube} \rightarrow \text{closed tube} + 3\text{CO}_2.
\]  

The energy of this reaction is \( \Delta E = (E_{C_{120}} + 3E_{\text{CO}_2}) - (E_{C_{120}O_6} + 3\mu_C) \) The result is \( \Delta E = 0.2 \text{ eV} \) with the DZ basis, and \( \Delta E = 0.3 \text{ eV} \) including polarization orbitals. Thus, the oxidized open tube is slightly favorable energetically over the closed one for this tube diameter. However, it has to be stressed that the system composed by the closed tube and the carbon dioxide gas has larger entropy and will thus predominate in thermodynamic equilibrium at a high enough temperature.

In addition to its genuine stability, the oxidized open tube can be further stabilized by the energy barrier of the closing process, which requires substantial rebonding. The actual rebonding is extremely hard to guess or simulate. We search for an estimate of the energy barrier as follows: first we consider a “closing coordinate” that the system must necessarily follow during the
We can understand the origin of the distinct cap and wall behaviors by defining a cap energy $E_{\text{cap}}$, as the energy of the capped tube minus that of the same number of atoms in the bulk of the tube. Since chemical bonds are similarly saturated at the cap and at the wall, the origin of $E_{\text{cap}}$ must be the larger elastic energy of the cap. It amounts to 9.0 eV for the (6,6) tube, which is comparable to the 9.2 eV energy obtained for the opening of the large hole at the tube wall.

Since the release of the strain energy, which plays a crucial role in the opening process, is related to the tube diameter, narrower tubes should be more easily open due to their larger cap curvature. Our calculations on the (4,4) and (8,8) armchair tubes confirm this trend: with CO$_2$ molecules used as an oxygen atom reservoir, as in equation (1), the closing energy amounts to 1.2 eV for the (4,4) tube, 0.2 eV for the (6,6) tube (as we have already shown), and -0.3 eV for the (8,8) tube, allowing us to estimate a value of $\sim -0.6$ eV for the (10,10) tube. Therefore, within the range of experimental feasible radii [28] the CO$_2$ sublimation changes from endothermic to exothermic, always within tenths of eV.

The presence of an oxygen rim may have a strong influence on the ability to fill the tubes. In some cases, it may be desirable to replace it by a possibly more inert hydrogen rim. Therefore, we have studied the energetics of reducing the oxidized open tube with H$_2$. Simply replacing O with H, followed by O$_2$ evaporation, is slightly endothermic (by 0.3 eV for the (6,6) tube). However, the reaction becomes strongly exothermic, by 9.1 and 9.5 eV, when we consider CO$_2$ and H$_2$O as byproducts, respectively. Thus, we expect that the reduction of the oxygen rim should be quite possible. We shall mention that the saturation of the tube ends with other molecular terminations rather than O or H could result in even lower
formation energies.

In conclusion, we have studied the energetics of opening SWNT’s by oxidation. We show that an oxygen rim can stabilize the edge of the open tube. The sublimation of CO$_2$ molecules from the rim with the subsequent closing of the tube changes from endothermic to exothermic as the tube radius increases, within the range of experimental feasible radii. Our results also show that the opening reaction occurs preferably at the tube cap, due to the release of its strain energy.

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