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Length dependent stability of single-walled carbon nanotubes and how it affects their growth

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ABSTRACT

Using density-functional theory the stability of armchair and zigzag single-walled carbon nanotubes and graphene nanoribbons was investigated. We found that the stability of armchair and zigzag nanotubes has different linear dependence with regard to their length, with switches in the most stable chirality occurring at specific lengths for each nanotube series. We explain these dependencies by competing edge and curvature effects. We have found that within each series armchair nanotubes are the most stable at short lengths, while zigzag nanotubes are the most stable at long lengths. These results shed new insights into why (near) armchair nanotubes are the dominant product from catalytic chemical vapor deposition growth, if templating is not used. Paradoxically, the stability of armchair nanotubes at short lengths favors their growth although zigzag nanotubes are more stable at long lengths, resulting in the production of the least stable nanotubes.

1. Introduction

Since the discovery of single-walled carbon nanotubes (SWCNTs) [1–3] and their remarkable properties [4,5], huge amount of time and effort from both experimental and theoretical researchers has been spent in order to unravel their growth process [6]. A better understanding of the growth process is key in order to control it, which is the key to achieving a uniform product of SWCNTs, all with the same chirality (properties). A uniform product will in turn enable their full potential to be utilized in commercial/industrial applications, to push future technological advancements [7,8].

A long-standing question in the field of SWCNT growth has been the strong preference towards armchair and near-armchair SWCNT-chiralities found in experimental growth products. Great progress has been made in recent years towards answering this question, firstly by Yakobson's group who explained how chiral SWCNTs grow [9,10] and secondly in a recent paper by Hedman et al. [11] showing that the SWCNT-fragment stability dictates the product. In the latter paper, results from first principle calculations on short (6-layer) SWCNT-fragments showed that the relative energy of different chiral indices (n, m) strongly correlates to the product from catalytic chemical vapor deposition (CVD) growth. The authors showed that for high curvature SWCNT-series, $n+m \leq 10$ (diameter below ~ 7Å), the most stable short SWCNT-fragments are of zigzag type $(m=0)$. For lower curvature SWCNT-series, $n+m \geq 11$ (diameter above ~ 8Å), the relative energy switches towards armchair $(n=m)$ and near-armchair $(n \approx m)$ short SWCNT-fragments being the most stable. Surprisingly, this correlation with experiment is rather insensitive to other growth parameters, such as feed-stock, pressure, and catalytic particle composition, as long as the temperature is optimized for SWCNT growth and the metals catalytic ability is satisfied [12,13].

Here we present new results connecting the relative energy of armchair and zigzag SWCNT-fragments to their length, expanding on the results of our previous paper [11], and finally answering the question of why products from catalytic CVD growth shows a strong preference towards armchair and near-armchair chirality.

2. Computational model

We employed first principle calculations using density functional theory (DFT), to investigate the stability of hydrogen terminated SWCNT-fragments of the two extreme chiralities (armchair and zigzag) from the $n+m = 8$, 10, 12, 16 and 20-series. The investigated SWCNT-fragment lengths were 4, 7, 10, 13, 16, 19, 22

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and 25 layers, where each layer contains $2(n+m)$ carbon atoms. Curvature effects were studied using infinite length periodic armchair and zigzag SWCNTs, which have no edge effects. To study effects due to different edges (armchair and zigzag) without the influence of curvature periodic graphene nanoribbons (GNRs) was used, the GNR widths were matched to the SWCNT-fragment lengths (same number of layers).

The total energies for all structures (80 SWCNT-fragment, 10 periodic SWCNTs and 16 periodic GNRs) was calculated using DFT as implemented in the Vienna Ab initio Simulation Package (VASP) [14]. For all calculations we used a plane wave basis set, the projector-augmented wave method [15] and the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional [16]. The plane wave basis set energy cutoff (ENCUT) was set to 650 eV and the electronic self consistence loop was converged to 10^{-6} eV. The Methfessel-Paxton scheme (ISMEAR = 1) for partial occupancies was used and the smearing width was set to 0.2 eV, this gave an electronic entropy below 0.5 meV/atom. All calculations employed spin polarization (ISPIN = 2) and for SWCNT-fragments and GNRs with zigzag edges an anti-ferromagnetic initial magnetization (one edge spin up and the other spin down) was applied in order to match the ground state [17–19].

All structures were relaxed with no symmetry constraints using the conjugate-gradient algorithm (IBRION = 2), until all forces acting on the atoms were smaller than 10^{-3} eV/Å. For the periodic structures a gamma centered k-point grid of size ($1 \times 1 \times 16$) was used, for the finite SWCNT-fragments only the gamma point was used. The size of the simulation boxes was set to give at least 10 Å of vacuum separation between the periodic images (in the non-periodic directions of the structures) for all calculations.

3. Results and discussion

From the total energies obtained using the method described in Section 2, we can define the relative energy (stability) for a structure as

$$\Delta E = E^{ac} - E^{zz}. \tag{1}$$

Here E^{ac}, E^{zz} is the total energy of the armchair and zigzag SWCNT-fragments respectively. A negative value of ΔE means that the armchair chirality is the most stable and a positive value means that zigzag chirality is the most stable. Worth noting is that for periodic SWCNTs the armchair layer is ~ 1.16 times longer than the zigzag layer, but for both chiralities one layer contains the same number of carbon atoms. Thus armchair and zigzag SWCNT-fragments with the same number of layers (length) and from the same series have an equal amount of carbon and hydrogen atoms, even though their curvature and edge is different. For periodic SWCNTs we can define the relative energy per carbon atom as

$$\Delta E_c = E_c^{ac} - E_c^{zz}, \tag{2}$$

here E_c is simply the total energy divided by the number of carbon atoms in the structure.

Fig. 1a shows the relative energy, ΔE, as a function of the fragment length (number of layers) S. It is clear that for all investigated SWCNT-series the relative energy follows a linear dependency on S except at very short fragment lengths $S \lesssim 5$. The same linear dependency can be seen in Fig. 1b where the relative energy per carbon atom ΔE_c is plotted as a function of the inverse fragment length $1/S$, for which we also can include the values of periodic SWCNTs and GNRs.

We assume that the relative energy of two SWCNT-fragments are governed by two effects; the difference in curvature and the difference in edge energy and that these two effects combine linearly as shown in Fig. 1a. Thus we start by assuming a simple linear relationship for the relative energy

$$\Delta E = A \cdot S + B, \tag{3}$$

were A and B are coefficients and S is the fragment length (number of layers). For an SWCNT-fragment the total number of carbon atoms in the structure can be defined as $N_c = 2(n+m) \cdot S$, dividing Eq. (3) with the total number of carbon atoms will give the relative energy per carbon atom as

$$\Delta E / N_c = \frac{A}{2(n+m)} + \frac{B}{2(n+m)} \cdot \frac{1}{S}. \tag{4}$$

It is clear that the quotient $1/S \to 0$ as $S \to \infty$, the left hand side of Eq. (4) will then equal the relative energy per carbon atom, $\Delta E/N_c \underset{S\to\infty}{\to} \Delta E_c$, for periodic systems. Here we have isolated the curvature effect on the relative energy, ΔE, since periodic SWCNTs have no edges. This implies that the quotient $\frac{A}{2(n+m)}$ is purely a curvature effect and given by the relative energy per carbon atom for periodic armchair and zigzag SWCNTs, ΔE_c. It is now trivial to find that the slope, A, of Eq. (3) can be written as

$$A = \Delta E_c \cdot 2(n+m). \tag{5}$$

The remaining coefficient, B, in Eq. (3) can now be thought of as accounting for the difference in edge energy for armchair and zigzag edges. To investigate this in the extreme case of zero curvature we used periodic GNRs with armchair and zigzag edges.

Looking at the relative energy per carbon atom for GNRs, points ● in Fig. 1b we can see that for all investigated GNR widths the relative energy is negative, which means that the armchair edge is the most stable, in agreement with previously published work [20,21]. To understand why this is we look at the electronic structure at the edge of the GNRs. The electronic structure (total charge density) is shown in Fig. 2 for both armchair and zigzag GNR edges. From the figure it is clear that the armchair edge has carbon-carbon bonds with higher charge density as compared to that of the zigzag edge. A higher charge density points to a stronger and shorter bond and thus a lower energy. From the charge density plots we conclude that the armchair edge always has a lower energy than the zigzag edge when unstrained.

To incorporate this edge effect into Eq. (3) we start by defining edge energy per edge atom for both SWCNTs and GNRs as

$$E_e = \frac{E - E_c \cdot (N_c - N_e)}{N_e} - \frac{E_{H_2}}{2}. \tag{6}$$

Here E is the total energy of the structure, E_c the energy per carbon atom of the representative periodic structure, N_c the total amount of carbon atoms in the structure and N_e is the number of edge carbon atoms. For completeness we also include the therm $\frac{E_{H_2}}{2}$ which accounts for the hydrogen termination of the edge atoms. Worth noting is that this term is arbitrary when comparing energies for edges with the same type of termination *e.g.* in our case it cancels out in Eq. (7) below. We now define the relative energy per edge atom for armchair and zigzag edges as

$$\Delta E_e = E_e^{ac} - E_e^{zz}, \tag{7}$$

here E_e^{ac}, E_e^{zz} is given by Eq. (6). To get an expression for the coefficient B in Eq. (3) we combine Eqs. (1), (2), (6) and (7) and solve for B, to get

$$B = N_e \cdot (\Delta E_e - \Delta E_c). \tag{8}$$