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

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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.

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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 \(\sim 7\AA\)), the most stable short SWCNT-fragments are of zigzag type \((m = 0)\). For lower curvature SWCNT-series, \(n + m \geq 11\) (diameter above \(\sim 8\AA\)), 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
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 $650 \text{ eV}$ and the electronic self consistence loop was converged to $10^{-6} \text{ eV}$. The Methfessel-Paxton scheme (ISMEAR = 1) for partial occupancies was used and the smearing width was set to $0.2 \text{ eV}$. 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 $10^{-3} \text{ eV/Å}$. 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

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

Here $E^{ac}$, $E^{zz}$ is the total energy of the armchair and zigzag SWCNT-fragments respectively. A negative value of $\Delta E$ 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 $\sim 1.16$ 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

$$\Delta E_c = E^{ac}_c - E^{zz}_c,$$  

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

Fig. 1a shows the relative energy, $\Delta E$, 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 $S \leq 5$. The same linear dependency can be seen in Fig. 1b where the relative energy per carbon atom $\Delta E_c$ 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

$$\Delta E = A \cdot S + B,$$  

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 $N_e = 2(n + m) \cdot S$, dividing Eq. (3) with the total number of carbon atoms will give the relative energy per carbon atom as

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

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

$$A = \Delta E_c \cdot 2(n + m).$$  

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

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

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 term $E_{H_2}$/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

$$\Delta E_e = E_e^{ac} - E_e^{zz}.$$  

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

$$B = N_e \cdot (\Delta E_e - \Delta E_c).$$
For SWCNT-fragments the number of edge atoms can be calculated by
\[ N_e = 2(n + m) \]
we can now write a final expression for the relative energy of armchair and zigzag hydrogen terminated SWCNT-fragments from within the same series as
\[
D_E = (\Delta E_c(S - 1) + \Delta E_e) \cdot 2(n + m).
\]
This simple linear model fits remarkably well with the relative energies obtained from the DFT calculations (points \( \bullet \), \( \circ \), \( \ast \), \( \circ \) and \( \ast \) in Fig. 1). Only small deviations from the model occurs at extremely short fragment lengths, \( S \leq S' \), were edge effects become non-linear due to the short fragment length.

A closer inspection of the calculated relative energies in Table 1 shows that for all five SWCNT-series investigated, the relative energy per carbon atom, \( \Delta E_c \), has a positive value, which means that the longer the SWCNT-fragment gets the more it will tend to favor a zigzag configuration. Furthermore it is clear that the relative edge energy per edge atom, \( \Delta E_e \), which at short fragment lengths contributes most to relative energy, is negative for all investigated SWCNT-series. Showing that for short SWCNT-fragments armchair configurations are the most favorable, this is especially clear for low curvature SWCNT-series and GNRs. The switching length denoted by \( S' \) can be calculated by \( S' = 1 - 0.5 \cdot \frac{\Delta E_e}{\Delta E_c} \) and is increasing (nonlinear) as the SWCNT-series is increasing. The impact of these results on the growth process is discussed below.

In catalytic CVD growth of SWCNTs there exists a number of tunable conditions such as temperature, pressure, carbon precursors, etc. Special techniques such as templating [22–24] has also been applied in order to control the chirality of the products. If constant conditions are employed and no special techniques are used we call this normal catalytic CVD growth of SWCNTs. For such normal catalytic CVD growth, it is well known that at early stages of the process an end-cap forms on the catalytic metal particle and an SWCNT starts to grow from this cap. Calculations on cap energetics, the total charge density (spin up + spin down) for armchair (left) and zigzag (right) edges of periodic GNRs, both figures have the same scale. We only show the total charge density between 10 and 15 Å to more clearly show the difference in bond strength.
by Penev et al. [25] show only small energy differences between the stable caps within each series. Molecular dynamics has, in addition, shown that a growing SWCNT can change its chirality during the early stages of growth [26,27], when the SWCNT has a very short length. It is also well known that the typical catalytic metal particles used are in a plastic state at growth temperature [28,29] and can thus adapt to fit the edge of the growing SWCNT [30].

These findings strengthen our conclusion that the stability of early stage short SWCNT-fragments dictates the chirality of the product (Hedman et al. [11]). Also note that when templating using cap-fragments have been successful (Sanchez-Valencia et al. [31]) cap-fragments with pre-existing 1.5-layer armchair walls was used as a template (not merely a cap).

From a thermodynamic point of view the growing SWCNT will favor a low energy configuration. The possibility of chiral reconfiguration at short lengths on a reformatable catalyst particle surface, suggests that a growing short SWCNT can change its chirality from a high energy configuration to a more favorable low energy armchair or near-armchair configuration. Thus our previous results [11] combined with the new insights presented here explains the preference for the production of (near) armchair SWCNTs in normal catalytic CVD growth experiments [32–36]. Note that in experimental growth data there is a clear abundance of near-armchair SWCNTs as compared to armchair, even though SWCNTs with armchair chiralities are more stable. This discrepancy can be explained by the fact that armchair and zigzag SWCNTs grow significantly slower compared to chiral SWCNTs, due to their different growth mechanisms [9,10]. The faster growth rate of near-armchair SWCNTs will not create more near-armchair SWCNTs compared to armchair, but longer ones. And since the signal strength of the most common detections techniques (Raman spectroscopy and photoluminescence) scales with the number of atoms in the SWCNT. The longer length of the near-armchair SWCNTs will give a stronger signal compared to the shorter length armchair SWCNTs, thus showing a higher abundance of near-armchair SWCNTs.

At a later stage, as the length of the growing SWCNT increases it reaches a switching region where the most stable configuration changes from armchair to zigzag, as shown in Fig. 1. When this switching region is reached the SWCNT length of all but the high curvature SWCNT-series is large enough that reconfiguration is unlikely i.e. the armchair geometry has been locked-in and the SWCNT continues to grow with an armchair chirality. However, it would be theoretically possible to produce SWCNTs with zigzag chirality by stimulating a rearrangement from armchair to zigzag after the initial growing SWCNT has passed the switching length. This stimuli could be provided by temperature, plasma, or similar.

Interesting new results by Zhao et al. [37] shows an example of this. Using a stimuli of periodically changing the temperature during CVD growth, they manage to perturb the growth process, resulting in production of mostly (72%) near zigzag (15,2) SWCNTs. This perturbation of the growth process may have promoted SWCNTs of longer length to change their chirality to a more stable zigzag configuration, the possible nature of this reconfiguration is discussed in Refs. [26,27,37]. This would be an example of perturbation of the normal catalytic CVD growth process using a stimuli.

An interesting idea is to target zigzag SWCNTs through diameter-selective growth, however current diameter-selective growth experiments reports a diameter selectivity of ~2 Å [38–40]. This is a too broad interval for singling out zigzag SWCNTs since in that diameter range (2 Å) there will always exist (near) armchair SWCNTs from the same or a close by series within ±0.34 Å in diameter (using analytical equation for SWCNT, \( d = \sqrt{2/9} \sqrt{n^2 + m^2 + nm} \)). Thus a diameter selectivity narrower than 0.34 Å is required in order to single out zigzag SWCNTs, which is currently not experimentally feasible. We propose a more viable method of producing zigzag SWCNTs using normal catalytic CVD growth, by targeting high curvature SWCNTs (SWCNT-series where \( n + m \leq 10 \)). For these high curvature SWCNTs, zigzag chiralities are the most stable even down to lengths of only 5–5 layers. Particularly promising for growth experiments would be to target the \((10,0)\) SWCNT \((S^2 = 5.5)\) as the dominant product using normal catalytic CVD growth, since SWCNTs of similar diameters are frequently observed. SWCNTs with even smaller diameters have shorter switching lengths and would thus be more likely to produce zigzag SWCNTs. However the growth rate of zigzag SWCNTs are significantly slower compared to chiral SWCNTs as discussed previously.

4. Conclusions

We have performed first principle calculations on periodic SWCNTs, GNRs and hydrogen terminated SWCNT-fragments. Our calculations show that the relative energy for armchair and zigzag fragments have a linear dependence on the number of layers (length) of the fragment, due to a combination of curvature and edge energy. The edge energy for armchair is lower than that of zigzag, causing the armchair chirality to be the most stable at short lengths. As the length increases the lower curvature of the zigzag chirality causes a switch to occur in the relative energy, which means that at long fragment lengths zigzag chirality is the most stable. These new results explain the preference towards (near) armchair chiralities in growth products and, paradoxically, also means that the least stable nanotube (armchair at microscopic length) is the most dominant in experimental growth products. New insights was also gained on how one can promote zigzag chiralities by the use of different stimuli (temperature, plasma, or similar), in order to drive a rearrangement from armchair to zigzag chirality after the growing SWCNT-fragment has passed the switching length. In light of our new results, diameter-selective growth was discussed. We concluded that a much narrower diameter distribution than the currently achievable (2 Å) is required in order to single out zigzag SWCNTs. We also propose that growth of zigzag SWCNTs can be achieved, by targeting high curvature zigzag SWCNTs such as (10,0) which have short switching lengths.

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References
