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Control the chirality of carbon nanotubes by epitaxial growth

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Abstract

We propose an idea for the chirality-selective growth of nanotubes by controlling the type of caps that form on the catalyst at the nucleation stage. Particular caps could be favored by their epitaxial relationship to the solid catalyst surface and the corresponding tubes grow preferentially. We show by ab initio calculations that lattice-matched caps and tubes are more stable next to a Ni surface than non-lattice-matched structures. This explains the dominance of certain chiralities in samples grown by low-temperature chemical vapor deposition.

Carbon nanotubes are nanomaterials with unique properties and a richness of physical phenomena [1]. They are extremely strong, some tubes are ballistic metals while others are semiconductors with a variable band gap. The chirality of a tube – its diameter and chiral angle or twist – determines whether a tube is a metal or a semiconductor, its band gap, and all other properties. For typical diameters of single-walled nanotubes (SWNTs), there are ~100 different chiralities. This variety makes nanotubes exciting, but also poses their greatest challenge [2,3]. Presently, we cannot control the chirality of a nanotube, or whether it will be semiconducting or metallic during growth.

The growth of single-walled carbon nanotubes is a catalytic process [4–14]. Experimental studies have focused on optimizing the catalyst particles for nanotube yield, purity and diameter [7,8]. Modeling studies have concentrated on the nature of the catalytic process, or on the energetics of tubes and caps neglecting the catalyst [4,10–13]. However, chiral selectivity during growth remains the true challenge. It is not known if the catalytic process can select nanotubes of specific chirality. We argue that chiral selectivity could occur by a control of the nucleation of the cap which then grows into the nanotube.

Our route to achieve chirality-selective growth of SWNTs is based on two key concepts: chiral selectivity could occur by controlling which carbon caps nucleate on the catalyst. A specific cap and thus specific tube can be selected by epitaxial growth on a *solid* metal surface. We show that the interaction between the carbon cap and metal particle drives the selection of nanotube structure.

SWNTs nucleate as carbon caps on the catalyst surface, by the root growth mechanism [9–11,14] except for ultralong tubes [15]. The tube then grows by adding carbon atoms to its root. Controlling nucleation is the key to chirality-selective growth. Carbon atoms can rearrange readily while still in contact with the catalyst surface, with a migration energy of ~0.2 eV [13]. Once away from the catalyst, the cap structure is *quenched-in*. The only way to change the chirality at this stage is via a costly rearrangement of the whole tube.

A cap consists of six pentagons and some hexagons, like a half fullerene. Small nanotubes such as (5,5) and (9,0) tubes have a single cap obeying the isolated pentagon rule. Larger nanotubes have many possible caps, increasing very rapidly with diameter [16,17]. A finished cap, however, can only grow into *one* (*n*,*m*) nanotube [17]. How can we use the relation between a cap and its matching tube for chiral selectivity? How can caps be selected? Of the three growth methods, the high temperatures in the laser or arc methods give a liquid catalyst and produce a uniform distribution of chiral angles. In contrast, the lower temperatures possible

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in CVD would allow a solid catalyst and thus the possibility of chirality control.

There is some debate about whether catalysts can be solid for SWNT growth. The small size of the catalyst droplet can greatly lower its melting point from its bulk value [18]. However, we have recently grown SWNTs by entirely thermal CVD at 350 °C [19], where the catalyst is unlikely to be molten. Also, Zhu et al. [14] have observed an epitaxial nucleation, which requires a solid catalyst surface.

We calculated the total energy of nanotube caps on a Ni(111) surface. We used the SIESTA ab initio code [20] within the PBE parameterization of the generalized gradient approximation (GGA). The real space mesh cutoff was 300 Ry. We described the valence electrons of C and Ni by a double-ζ and single-ζ polarized basis set, respectively, with a confinement shift of 250 meV. Caps were relaxed with a force tolerance 0.04 eV/A and the Ni atoms fixed. E_{cap} was found by joining two caps into a fullerene. Excess energies were corrected for the basis set superposition error.

In this Letter, all energies are expressed as *excess energies* compared to a perfect graphite and Ni sheet [11]. We model the growth of a cap as layer by layer growth and find the energy per atom in the last layer, E_{edge}. There are two contributions to the edge energy, the cap E_{cap} and the carbon-metal (C–M) energy E_{CM}, $E_{\text{edge}} = E_{\text{cap}} + E_{\text{CM}}$. C dangling bond energies are much larger (2.7–3.5 eV) than C–M bond energies, and they are critical to fullerene formation, favouring armchair edges [21]. However, they play no role in nanotube growth in the presence of metal by the root growth mechanism, because all dangling bonds have been transformed into C–M bonds. The cap energy is the excess energy of the cap neglecting C–M binding. Per atom, it scales roughly as d^{-2} or the number of hexagons in the cap [17]. It also depends on the cap structure (chirality of the tube), in particular, for very curved caps [4]. The carbon–metal binding energy is very complex. It varies with the metal, its surface, the position of the C atoms, and for armchair or zig-zag edges. Nickel is a frequently used catalyst, whose most stable surface is Ni(111). We use this configuration to explore whether carbon caps can grow epitaxially on it. In reality, catalyst particles are curved, facetted, stepped surfaces. However, we aim here to find the key energies for chiral selectivity, and later try to mimic the experimental situation.

Both the zig-zag and armchair edges of graphite are closely lattice-matched to Ni(111), because the lattice constant of graphene (2.46 Å) is close to the 2.49 Å Ni bond length. There are four high-symmetry sites of a zig-zag edge on Ni(111) and two of an armchair edge (Fig. 1). The C–Ni binding energy varies by up to 0.5 eV/C depending on the position of the C atoms. The lowest-energy zig-zag site, a bridge site (X), and the armchair bridge site (B1), have similar energy. These two configurations (X, B1) resemble diamond bonding, which makes them quite stable. (This contrasts with dangling bond energies, which are much lower for armchair edges [21,22].)

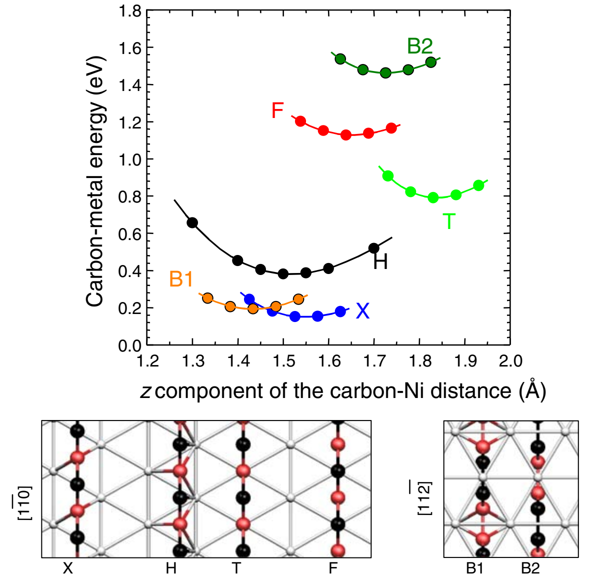

Fig. 1. Lattice-matched sites for zig-zag (a) and armchair (b) edges. The C–Ni excess energy is given in eV/C.

The edges of achiral caps are similar to the zig-zag and armchair edges of infinite graphene, except for the curvature. For such caps to be lattice-matched on a metal surface, the caps must be matched locally and globally. The local match is fulfilled, since the C–C distance is the same as in graphite. The global match requires the cap's diameter and symmetry to match Ni. This is illustrated in Fig. 2a,b for zig-zag (9,0) and (10,0) tubes. In each case, one carbon atom (arrowed) lies in the stable X site. The neighboring edge atoms also lie at the X site (local match). The (9,0) cap in Fig. 2c matches Ni(111) in symmetry and diameter. All edge atoms lie in the most stable position. In contrast, a

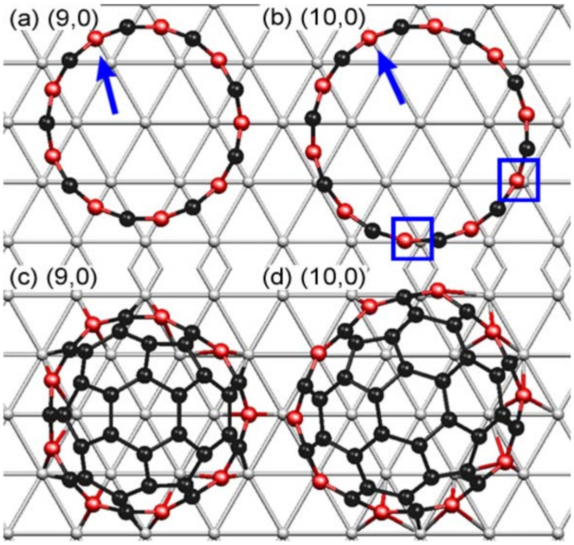

Fig. 2. Lattice matching of (a) (9,0) and (b) (10,0) edge on Ni. Grey (red) atoms are edge atoms. Arrowed atoms lie in the stable zz-X site, squared atoms in the costly zz-T site. Relaxed (c) (9,0) and (d) (10,0) cap on Ni. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 1
Cap energy (E_{cap}), C–Ni excess energy of the edge atoms (E_{CM}) and total excess energy of the edge atoms $E_{\mathrm{edge}} = E_{\mathrm{cap}} + E_{\mathrm{CM}}$

Tube	*d* (A)	n_{cap}	E_{cap} (eV/C)	E_{CM} (eV/C)	E_{edge} (eV/C)	Experiment (%)
(9,0)	7.1	39	0.49	-0.15	0.34	
(**10**,**0**)	7.9	42	0.38	0.07	0.45	
(**11**,**0**)	8.7	45	0.33	0.10	0.43	
(12,0)	9.5	48	0.33	0.01	0.34	
(5,5)	6.9	30	0.42	0.00	0.42	
(6,6)	8.2	36	0.39	0.09	0.48	
(7,7)	9.6	56	0.29	0.08	0.37	
(**6**,**4**)	6.9	30	0.44	0.21	0.65	1
(**6**,**5**)	7.6	43	0.33	0.10	0.43	17
(**8**,**3**)	7.8	65	0.31	0.13	0.44	9
(**7**,**5**)	8.2	52	0.31	0.09	0.40	20
(**9**,**1**)	7.6	42	0.35	0.22	0.57	1

d is the diameter and n_{cap} the number atoms in the cap. Exp. is the relative abundance of semiconducting chiral tubes from PL [4,5,17,22]. The index of semiconducting tubes are indicated in bold.

(10,0) cap has the wrong diameter and symmetry to match to Ni(1 1 1). Two of its edge atoms lie at the costly on-top (T) site and some at the less stable hole (H) sites.

The calculated excess energy of the edge atom is 0.11 eV/C lower for the relaxed (9,0) cap than for the (10,0), Table 1 and Fig. 2c,d. This is due to the lattice-matching of the (9,0) cap, as the cap energies show the opposite trend, Table 1. Since the (9,0) cap is lattice-matched to Ni, it lowers its energy by 0.15 eV/C, whereas the non-matched (10,0) cap increases in energy by 0.07 eV/C. Growth on a solid catalyst thus strongly favors caps and hence tubes that match the metal surface. The calculated energies of other armchair and zig-zag caps confirm these ideas. Their cap energies vary by up to 0.15 eV/C, but no cap is particularly stable. We find the armchair (5,5) cap to be more stable than the zig-zag (9,0) cap, in agreement with Ref. [4], but for (6,6) and (10,0) this is reversed. The C–Ni binding energies of achiral caps fall into two classes in Table 1. Lattice-matched caps with $E_{\mathrm{CM}} \sim 0$ eV/C ((9,0), (5,5) and (12,0)) and non-matched caps with $E_{\mathrm{CM}} > 0.1$ eV/C. Including E_{CM} re-orders the excess energies per atom, Table 1. The lattice matched (9,0) and (12,0) caps are most stable, followed by the (5,5).

The (12,0) cap matches Ni(1 1 1) in symmetry, but not in diameter, Fig. 3a. It lies at stable H sites, after being strained to a larger diameter. On the other hand, the (5,5) cap has the wrong symmetry for Ni(1 1 1), but a good diameter. The (5,5) cap maximizes E_{CM} by finding a position not possible for infinite armchair graphene: Two of its edge atoms lie at the B1 site; the other six atoms move to a site like X, the most stable configuration, Fig. 3b.

The energetics of chiral caps follows slightly different rules. Their irregular edges forbid a global match, but a local match is still possible. The question arises if the differences in edge energies are large enough for chiral selectivity. For small-diameter chiral tubes, we know the approximate abundance in low-temperature CVD [4,5,17,23], see Table 1. We consider three caps with a large (10–20%) abundance, (6,5), (7,5), and (8,3), and two caps, (6,4) and (9,1), with 1% or less abundance.

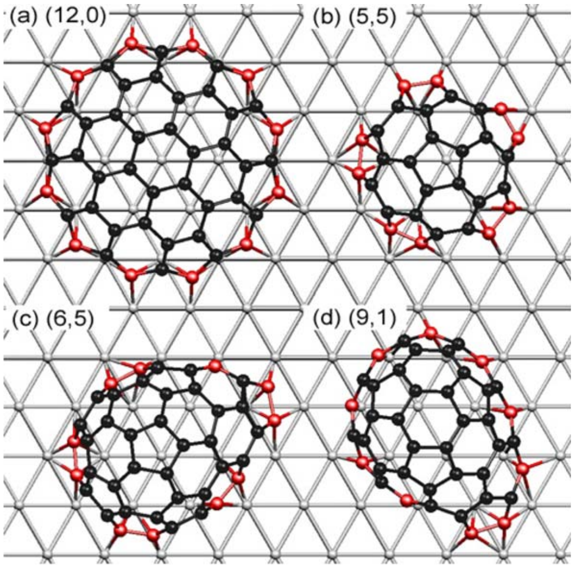

Fig. 3. Relaxed caps on Ni(1 1 1). Grey (red) atoms are edge atoms; black atoms are away from the metal. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

For the chiral tubes considered, E_{cap} is similar for armchair and zig-zag caps of similar diameters except for the (6,4) cap, Table 1 and Fig. 4a. The (6,4) cap is less stable, because it contains adjacent pentagons [17]. The energy differences between the other chiral caps are very small 0.02 eV/C and cannot explain the large difference in experimental abundance. However, by including E_{CM} we find that the (9,1) and (6,4) caps are 0.1 eV/C less stable than other chiral caps, Fig. 4b. This is in excellent agreement with experiment, in that the less stable (9,1) and (6,4) tubes are an order of magnitude less abundant than the (6,5), (7,5), and (8,3) tube, Table 1.

According to the E_{edge} in Table 1, metallic zig-zag tubes ((9,0) and (12,0)) seem to be preferred over semiconducting achiral and chiral caps. However, the very low E_{edge} of some armchair and zig-zag caps is somewhat artificial, because we always modelled the achiral edges with completed layers, see Figs. 2c,d and 3a,b. A complete armchair or zig-zag edge has no steps, which allows a global lattice

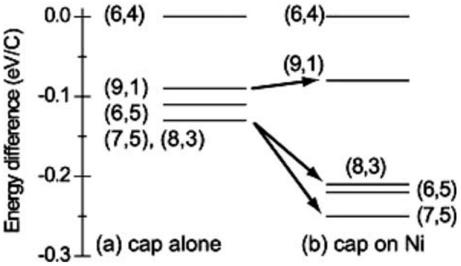

Fig. 4. (a) Excess energies per layer for chiral caps without Ni and (b) on Ni(1 1 1). Energies are referred the (6,4) cap.

match and strongly lowers their formation energies. However, if we remove some carbon atoms from the edges of (9,0) and (10,0) caps to form steps and mimic a growing edge layer, this increases E_{edge} by ∼0.15 eV/C after relaxation. It makes these caps less favourable than the chiral (6,5), (7,5), and (8,3) caps. Thus, achiral and chiral E_{edge} in Table 1 cannot be directly compared to each other.

Chiral caps can only have a local C–Ni match, not a global match. The local match favors tubes with large chiral angles (armchair like) as we explain now. The edge of a chiral cap or tube is composed of both armchair and zig-zag segments, see Fig. 3c,d. An armchair edge always has two neighbors forming C–Ni bonds. When one of them lies on a favorable H or X site, its neighbor lies in a similar site, see the (5,5) and (6,5) caps in Fig. 3. We call this the 'two good sites' rule. In fact, we typically find a two-X/two-H sequence for the relaxed armchair segments, i.e. four favorable sites for placing one atom into a good site. In contrast, for zig-zag edges, lattice matching is sensitive to the exact cap structure. A zig-zag edge can have the largest E_{CM} in a global match, the (9,0) in Fig. 2c, but changing the structure a little looses the advantage completely, as for (10,0) in Fig. 2d.

The dependence of the C–Ni energy on the type of edge is seen in the relaxed (6,5) and (9,1) caps in Fig. 3 and for all chiral caps in Table 1. It is crucial to explain (6,5) and (9,1) caps, which have very different abundances despite having the same diameter [4,5]. The armchair segments in both relaxed caps are in low-energy sites. Parts of the zig-zag segment in (9,1) are on good sites as well, but the cap curvature forces others onto costly T and F sites, Fig. 3d. The (9,1) cap has a much larger excess energy 0.57 eV/C than the (6,5) cap, 0.43 eV/C, Table 1. Only 14% of this difference comes from E_{cap}, the C–Ni energy accounts for 86%. The chiral (7,5), (6,5) and (8,3) caps have a low excess energy on Ni(1 1 1) due to their good local C–Ni lattice match, Fig. 4b. Thus, the C–Ni bonding is accounts for the high abundance of these tubes, not the cap energy. It would be interesting to obtain abundances for armchair and zig-zag tubes, which do not show luminescence.

In conclusion, we suggested two key concepts for chirality-selective growth of SWNTs: Selectivity must start during nucleation. Once a cap is formed, it is quenched in and grows into a unique nanotube. Epitaxial growth favors certain caps and tubes. We find C–Ni bonding favours armchair edges by a local lattice matching of neighboring C atoms. Some zig-zag configurations can be very stable due to a global match, but this depends critically on the diameter and symmetry of the cap.

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