

Epitaxial growth of carbon caps on Ni for chiral selectivity

S. Reich^{*,1}, L. Li², and J. Robertson²

¹ Department of Materials Science and Engineering, Massachusetts Institute of Technology, 77 Massachusetts Ave, Cambridge, MA 02139, USA

² Department of Engineering, University of Cambridge, 9 JJ Thompson Avenue, Cambridge CB3 0FA, United Kingdom

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We suggest guiding principles for chirality-selective growth of single-walled carbon nanotubes. The chirality of a tube is determined by the carbon cap that forms during nucleation. Controlling the tube chirality requires controlling the nucleation stage. Certain caps can be favored by their epitaxial relationship to a metal surface. Lattice matched caps require ~ 0.1 eV/C less formation energy on a Ni surface than non-lattice matched cap structures.

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1 Introduction

Carbon nanotubes have many different microscopic structures or chiralities. Their physical properties change dramatically with chirality (diameter and chiral angle of the tube) [1]. The best known example for these changes is that one third of all carbon tubes are metals and two thirds are semiconductors [2].

The dependence of the tube properties on microscopic structure makes carbon nanotubes rich in physical phenomena and a very flexible nanomaterial. At the same time, however, the chirality dependence of the electronic properties, in particular, hinders the most promising applications of the tubes in nanotechnology [3]. Currently, nanotube growth methods – chemical vapor deposition (CVD), laser ablation, and arc discharge – produce a mixture of tube chiralities and of semiconducting and metallic species. For most applications, in contrast, we need either one type or the other, e.g., metallic tubes as interconnects and semiconducting tubes for transistors or infrared light emitters. For applications of semiconducting tubes we further need to control their band gap, which depends on diameter and chiral angle. Controlling the chirality of carbon nanotubes is therefore a key for using carbon tubes as a building material for nanotechnology.

The growth of carbon nanotubes is a catalytic process [4–8]. Past experimental effort concentrated on nanotube yield, length, and purity [6, 7]. After mastering these initial challenges, the focus turned recently towards controlling the ratio of metallic versus semiconducting tubes and enriching certain chiralities by catalyst design and low-temperature CVD [4, 5, 8]. Theoretical studies considered the nature of the catalytic process or the energetics of various tubes to understand the formation of tubes [9–12]. Currently, we lack guiding principles of how to achieve chiral selectivity.

We suggest two key concepts for chirality-selective growth: (i) chiral selectivity can only be achieved during nucleation when a carbon cap is formed on the catalyst and (ii) the varying carbon–metal binding energy on a catalyst surface could help in driving chiral selectivity by lattice-matched growth [13].

* Corresponding author: e-mail: sreich@mit.edu

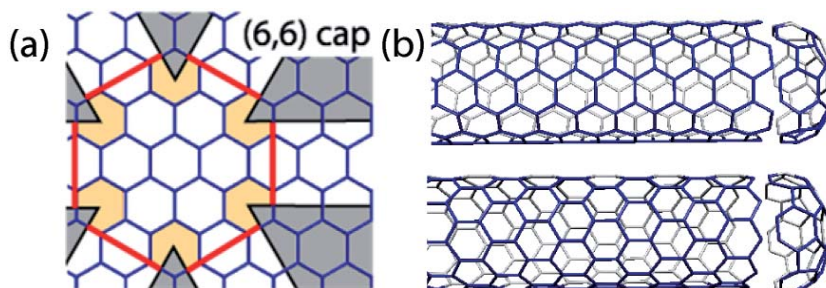


Fig. 1 (online colour at: www.pss-b.com) (a) Construction of the (6, 6) nanotube cap by the flattening method [14]. The dark grey areas are cut and the black lines joined to form a half sphere. The orange hexagons thereby become the six pentagons of the cap. The red line goes around the circumference of the final cap. It defines the chiral vector of the tube. (b) The cap in (a) fits onto the (6, 6) nanotube (top), but not on the (10, 0) tube (bottom).

2 Carbon cap determines chirality

Carbon nanotubes nucleate as carbon caps on the catalyst surface. The tube then grows by adding carbon atoms to its base in the root-growth mechanism [7, 9]. A carbon cap resembles half a fullerene; the half-spherical carbon structure contains five pentagons and a number of hexagons, see Fig. 1 for an example. A cap is uniquely specified by indicating the position of the pentagons on an hexagonal network [15]. Typical carbon nanotubes with diameters on the order of 1 nm have $10^3 - 10^4$ different cap structures that fit on them [16]. A given cap, however, fits only onto one specific (n, m) nanotube as illustrated in Fig. 1(b).

The close relation between a cap structure and tube chirality can be understood when considering the cap hexagon [15]. The cap hexagon defines the rim of the cap; it is the smallest hexagon on the flat lattice that includes all six pentagons, see red line in Fig. 1(a). The cap hexagon will form a line around the cap circumference after joining the black lines in Fig. 1(a) into a spherical structure. The line around the circumference or the so-called chiral vector $c = na_1 + ma_2$, on the other hand, uniquely defines an (n, m) nanotube (a_1 and a_2 are the lattice vectors of graphene).

The cap that forms at the beginning of the tube growth thus uniquely defines the chirality of the tube. The first key to chiral selectivity is to control the cap structure during nucleation.

3 Lattice matched growth

One idea for controlling nanotube caps is by growing them epitaxially on a metal catalyst. Epitaxial or lattice-matched growth is a powerful tool, e.g. in the growth of semiconductor heterostructures. We want to find out whether the differences in the formation energy for lattice-matched and mismatched carbon caps could drive chirality selection. Epitaxial growth requires a solid catalyst. During the growth at high temperature as typical for laser ablation and arc discharge the catalytic particle is liquid. Very low growth temperatures were recently realized in chemical vapor deposition allowing for a solid catalyst [12]. Our idea of epitaxial growth is consistent with the preference of certain chiralities found in low-temperature CVD [4, 5].

3.1 Method

The formation energy E_f of a nanotube cap on a catalyst has two contributions, curvature energy E_c and carbon–metal binding energy E_{C-M} [13]

$$E_f = E_c + E_{C-M}. \quad (1)$$

Table 1 Cap energy E_c , carbon–metal binding energy E_{C-M} , and total formation energy E_f for caps fitting five chiral (n, m) nanotubes. d is the tube diameter, n_c the number of carbon atoms in the cap, and yield indicates the yield of the corresponding tubes in low-temperature CVD growth [4, 5, 13, 20].

(n, m)	d Å	n_c	E_c eV/C	E_{C-M} eV/C	E_f eV/C	yield %
(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

Both E_c and E_{C-M} are on the order of 0.1–1 eV/C when expressed as excess energies with respect to graphene (a single sheet of graphite). Additionally, carbon dangling bonds were suggested to be important in nanotube growth; the dangling bond energies are large (2.7–3.5 eV) and favor armchair edges, which led to the idea of the preference of (10, 10) nanotubes [17]. In the presence of a catalyst all dangling bonds are replaced by carbon–metal bonds. As shown by Fan et al. [10] the presence of the metal leads to the growth of nanotubes as opposed to fullerenes or graphene flakes, because the catalyst saturates the costly dangling bonds.

We calculated the formation energies of nanotube caps on nickel from first principles. Ni is one of the most frequently used catalysts for nanotube growth. To make the calculations computationally less demanding we used a flat Ni(111) surface and placed various caps in different positions and orientations [13]. The total energy of the caps was found by a conjugate gradient minimization. We used the SIESTA [18] *ab-initio* package 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 [19]. Caps were relaxed with a force tolerance 0.04 eV/Å and the Ni atoms fixed. The cap formation energy E_c was found by joining two caps into a fullerene [15]. The carbon–metal excess energies E_{C-M} were corrected for the basis set superposition error. In this paper we concentrate on caps for five semiconducting nanotubes with diameters between 6.9 and 8.2 Å, see Table 1. Further examples can be found in Refs. [13, 15].

3.2 Cap formation energy

The cap formation energies E_c in Table 1 vary little from cap to cap with the exception of the (6, 4) cap [13, 15, 16]. Caps for the (6, 4) tube violate the isolated pentagon rule, because of the small tube diameter [16]. Neighboring pentagons cost an energy of 1.5 eV/pair and increase the cap formation energy, see Table 1 and Ref. [15]. The additional energy needed for the formation of adjacent pentagons can explain the very low yield of tubes with diameters below $d_p = 7.3$ Å in low-temperature CVD [4, 5]. Tubes with diameters below d_p have only caps that violate the isolated pentagon rule and are energetically expensive.

For tubes with isolated pentagons the cap formation energy scales by the number of hexagons in the cap or as $1/d^2$. E_c depends also on tube chirality and the exact cap structure for caps that fit on one and the same tube. However, these differences tend to be quite small, especially, when compared to the typical thermal energies during nanotube CVD growth $k_B T \sim 0.08$ eV. We thus conclude that the small energetic differences in the cap formation energies ~ 0.01 eV are unlikely to help in chirality-selective growth.

3.3 Carbon–metal binding energy

The carbon–metal binding energy is much more complex than the cap formation energy. It varies with the metal surface and the position of the carbon atoms on the surface. To understand the contribution of

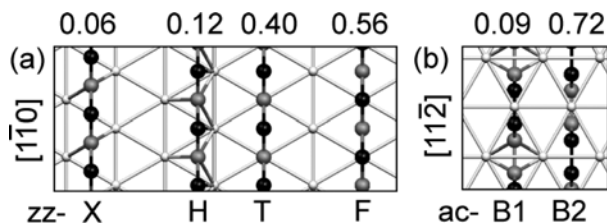


Fig. 2 Lattice matching of (a) zigzag and (b) armchair graphene edges on Ni(111). Light gray carbon atoms are at the C–Ni interface. The formation energies are given in the upper part of the figures (in eV/C). (a) Zigzag edges have four lattice-matched high-symmetry positions on Ni. They are ordered by increasing formation energy. The most stable (smallest excess energy) position is the zz-X position with $E_{C-M} = 0.06$ eV/C. (b) Two lattice matched sites for an armchair edge; the most stable position is ac-B1.

E_{C-M} to the formation energy of nanotube caps on a catalyst we first consider epitaxial relationships between graphene edges and Ni(111).

Graphene is lattice matched to Ni(111), because the graphene lattice constant $a_0 = 2.461$ Å is very similar to the Ni–Ni bond length 2.49 Å. There are four lattice-matched high-symmetry positions for a zigzag edge on Ni and two for armchair edges, see Fig. 2. Favorable sites are on top of a Ni–Ni bond, zz-X, and the positions in the center of the Ni triangles, zz-H and ac-B1 in Fig. 2.

It is impossible to fully lattice match chiral caps to Ni(111), because the caps have steps in their edges. Moreover, the configuration of the edge will change during growth when carbon atoms are added to the tube. In the following we discuss whether characteristics of the edge structure make some caps more stable (smaller E_f) than others.

The edge of a chiral cap can be viewed as being composed of armchair-like and zigzag-like parts. The total number of edge atoms in an (n, m) cap is $n + m$. Out of these atoms $n - m$ atoms have a zigzag-like configuration. By this we mean that a carbon atom with a dangling bond (or a carbon–metal bond on the surface) is surrounded by carbon atoms *without* dangling bonds. For example, the (6, 5) cap in Fig. 3 has one atom in the zigzag configuration (in the upper part of the cap shown in Fig. 3), the (9, 1) cap has eight. The remaining $2m$ atoms form the armchair-like part of the edge; a carbon atom with a dangling bond has one neighbor with a dangling bond, see Fig. 3.

Zigzag edges can be energetically most stable, because they can occupy the X position of graphene, see Fig. 2, with its low excess energy. However, this type of edge is rather inflexible and rigid. A zigzag-like edge atom in a zz-X position can have an edge neighbor in the costly zz-T site. An example for this

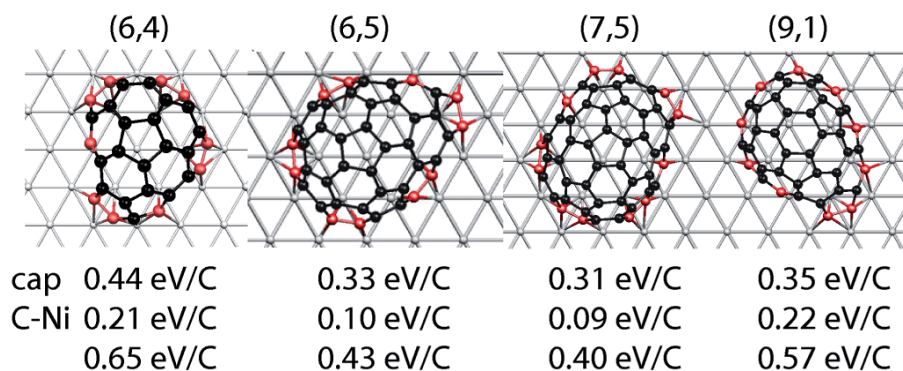


Fig. 3 Carbon caps for four chiral nanotubes on Ni(111). Red atoms are at the cap-metal interface and participate in the carbon-metal binding. In the lower part of the figure we compare the cap formation energy (cap), the carbon-metal binding energy (C–Ni), and the total formation energy (third row). The caps with the lowest formation energies are the (6, 5) and (7, 5) caps in the middle. These tubes grow with a high yield in low-temperature CVD, see Table 1.

configuration is the topmost edge atom of the (9, 1) cap in Fig. 3 and its left neighbor. The lattice matching for zigzag edges is determined by the global structure of the caps, its diameter and symmetry [13].

Lattice matching and carbon-metal binding energies for armchair-like configurations are more sensitive to the local structure of the edge. Placing one armchair-edge atom into a low-energy site such as an X or hole position, we find its neighbor in the same low-energy position. A good example for this are the armchair like parts of the (6, 5) and (7, 5) caps in Fig. 3, which are all in X and H sites. Although a single carbon atom gains less energy in the armchair than in the zigzag configuration, the overall carbon-metal excess energy is lower for the armchair edges due to the proximity of low-energy positions for two carbon atoms, the so-called “two-good sites” rule.

The carbon-metal excess energy for the chiral caps in Table 1 varies between 0.09 eV/C for the (7, 5) and 0.22 eV/C for the (9, 1) cap, see also Fig. 3. This results in $E_f \sim 0.45$ eV/C for the (6, 5), (7, 5), and (8, 3) cap and $E_f \sim 0.6$ eV/C for the (9, 1) and (6, 4) cap. The difference in formation energy is on the order of the thermal energy. The experimental yields agree very nicely with the much lower formation energy of the (6, 5), (7, 5), and (8, 3) caps. The two-good sites rule favors the formation of caps close to the armchair structure.

4 Conclusion

Controlling the chirality of carbon nanotubes during their growth requires controlling the tube nucleus, a carbon cap on a metal surface. Lattice-matched growth of caps on Ni can preferentially produce tubes with large chiral angles (close to armchair). For this the catalyst needs to be solid, which agrees with the non-homogeneous chirality distribution reported in low-temperature CVD [4, 5]. True chiral selectivity, i.e., growing only one chirality, needs larger difference in the carbon-metal binding energies as a function of the position of a carbon atom than found for Ni(111). Further theoretical studies also need to consider steps and the curvature of the catalytic nanoparticles. On the experimental side, it would be highly desirable to measure the chirality-distribution in a variety of nanotube samples produced by different growth methods and under varying conditions (catalyst, temperature etc.).

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