Nucleation model for chiral-selective growth of SWCNTs

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ABSTRACT:

Typical growth processes for single-walled carbon nanotubes (SWCNTs) produce a broad distribution of (n,m) chiralities that hinder their direct use in technological applications such as nanoelectronics. Among the various growth parameters that can be tuned to control SWCNT growth, the metal catalyst particle is generally assumed to play a key role in determining the chirality of SWCNTs. For example, it is well known that bimetallic catalysts can alter and even narrow the chirality distribution of as-grown SWCNTs. Here, we study epitaxial nucleation of nanotube caps on sliced icosahedral clusters of Ni. This structure resembles NiFe bimetallic catalysts and may explain growth preference of specific (n,m) chiralities. The energies associated with nanotube cap formation are calculated using density functional theory (DFT) on the VASP software. In our tests, we see that certain cap chiralities, such as (8,4), are more stably bound to a surface that resembles a NiFe bimetallic catalyst. Such results are in agreement with experimental observations and provide a route to bimetallic catalyst design in chiral-selective SWCNT growth.

INTRODUCTION:

Since their discovery in the latter half of the twentieth century, nanotubes have played an increasingly important role in the development of materials and nanoelectronics.
Pressure has been placed upon scientists and engineers alike to develop new ways of producing differing types of nanotubes efficiently and effectively. The better understanding of graphene (single sheeted honeycomb lattice of carbon atoms) and the effects of edge orientation and energy has provided new insights into the production of nanotubes of varying chirality. Chirality is simply a way to define the direction in which a graphene sheet must be 'rolled' to become a particular nanotube. I put rolled in quotations because nanotube nucleation usually happens very differently. The two basis vectors for describing chirality along a flat sheet of graphene are Armchair and Zig-Zag. They are defined to be sixty degrees apart. The unit vectors for armchair and zig-zag, \( u_a \) and \( u_z \) respectively along with weights \( m \) and \( n \) describe the chirality of an arbitrary nanotube, ie. \( C = mu_a + nu_z \). Armchair will have \( n=0 \) and zig-zag will have \( m=n \). From now on I will refer to a CNT’s chirality by the \((n,m)\). Now that it is clear what chirality is, why is it an important area of study? As a nanotube’s chirality changes so does its electronic properties. Zig-zag orientation has conducting properties while armchair has insulating. Any other chirality have some type of semi-conducting properties, whether that be low, medium, or low band gap. In classic production of CNT’s there is no control over the varying chirality of nanotubes, making it so anyone wanting to use them in electronics will have to apply a limited supply of methods to filter out the various types of nanotubes, most of which still only yield low purity. It is the goal of this study and those preceding it to somehow grow only a particular type of nanotube from the get go, rather than sorting through such a wide range.

The nucleation process of interest to us is the use of bimetallic catalysts as growth sites. The process is as follows, heated carbonic gas is bought into contact with nanoclusters of particular kinds of transition metal (for us it is iron and nickel). The carbon atoms then start to form a carbon cap on the surface of the catalyst clusters. From there the nanotube begins to grow up from edges of the cap. Theoretical work by theoretical work by experimentalists has shown there to be a homomorphic relationship between the type of cap and the chirality of the formed nanotube. Basically, once the cap is in place, the chirality is already determined. This allows researchers to look at the cap nucleation with the assumption that a particular chiral nanotube will be formed.
In an effort to study such structures Dr. Venkat’s group produced a paper addressing the correspondence between experimental nucleation and a computational model that utilized a Ni (111) surface. It was found that Ni and Ni0.67Fe0.33 bimetallic catalysts produce a relatively broad chirality distribution composed of (in order from smallest to largest diameter) (6,5), (8,3), (7,5), (8,4), (10,2), (7,6), (9,4) and (10,3), (8,6), (9,5), and (8,7) tubes, while Ni0.5Fe0.5 and Ni0.27Fe0.73 bimetallic catalysts yield a much narrower chirality distribution (in comparison) with mostly (6,5), (8,3), (7,5), (8,4), and (7,6) tubes (figure &). X-ray diffraction spectra of other nanoparticle catalysts are shown. Ni catalysts exhibit face-centered cubic (fcc) structure, in agreement with the crystal structure of bulk Ni.[1]

(Figure &) photoluminescence spectroscopy of catalysts by element composition

In computational models, after energy minimization, it was found that the nanotube cap changed shape and became elongated for the (8,4) cap. The dangling bonds were saturated by forming C-Ni bonds. This phenomenon was common to all 4
nanotube chiralities studied and indicate that the calculations reflect stable cap formation. Calculations for the (8,4) cap showed the best agreement with experiments. The lowest energy for cap nucleation \((E_b)\) occurs at the exact same bond length \((2.53 \text{ Å})\) as experimentally determined by XRD for Ni0.27Fe0.73 bimetallic catalysts which were found to preferentially grow \((8,4)\) tubes. In the case of the \((6,5)\) cap, the lowest energy occurred at \(d=2.57 \text{ Å}\).

In summary, they have used DFT calculations in combination with lattice matching criterion to relate the stability of various cap chiralities on a model catalyst surface that represents a bimetallic catalyst. The results of the calculations provide fundamental insight into why the growth of certain nanotube chiralities such as the \((8,4)\) tube is preferred on bimetallic catalysts of a particular composition. Future studies will allow us to use lattice matching as a guide to design new catalysts for the growth of desired chiralities, including ones that are not often observed in experiments such as large diameter semiconducting tubes, metallic species, and zig-zig structures\(^\text{[1]}\).

Their results serve as a jumping off point for a new part of the project. Instead of looking at a flat surface of only Ni, I looked at full three dimensional structures of varying concentrations of NiFe.

METHODS:

The production an testing of computer model took place on a multitude of utilities. First the production of the coordinates of the 3D nanoclusters was made possible through the alteration of a colbalt icosahedrons cluster C++ code compiled with the g++ compiler available on the CIRCE network. The alteration produced clusters of pure Ni, NiFe, NiFe, and NiFe of a pseudo random dispersion. A model of a Ni faced cluster with an Fe core was produced as an effort to bolster results. Most attention was paid to clusters of fifty five or one hundred and forty seven atoms with distances varied from 2.45 to 2.57 angstroms. Through the vi text editor, the format of the coordinates were changed to .xyz to be read into the Crystal Maker software. Here the individual atom type could be altered and the overall structure coordinates could be amended with a carbon cap of a specific Chirality. The coordinates were then exported to a new file containing a chiral
cap and once again altered in vi to fit the specifications of the VASP software (POSCAR, INCAR, POTCAR, KPOINTS) or the Gaussian software (.com files). When new clusters were generated with the caps they were run into either of those two pieces of software. VASP was used in the following way: First, a cluster with the cap was run under energy optimization selective dynamics where the cluster was held fixed but the carbon atoms were free to move. Then, the cluster by itself was run through the energy optimization but this time all cluster atoms could move. This can be altered in the POSCAR file by including the words ‘selective dynamics’ before the coordinates, then placing three spaced T’s or three spaced F’s next to the coordinates, where F means fixed and T means free. Both calculations are done to get the energy difference between the binding energy of the cap to the cluster and the energy of the cluster itself. This difference tells us how stable the cap lies. The Gaussian software was used for visualization and preliminary single point energy calculations for the clusters and caps. Once the calculations are complete they are to be compared to the work mentioned in the introduction.

DISCUSSION:

Before any calculations were run, it was found that the icosahedral structure with 55 atoms was too small for an (8,4) cap to stably bond to. This is due to the bond distance between the dangling carbons and the catalysts being too large (figure $).
Although this does not help our inquiry of specific nanotube formation, the likelihood of nanoclusters of this size in experiment is plausible, making the 55 atom cluster a pertinent if not trivial case to explore. Moving up to the larger 147 cluster, the sheer number of atoms was not conducive to short term computational simulation. The Gaussian program would use far too much memory to process all of this. This forced us to primarily use VASP, because of less required memory to run. After the clusters were sliced, it became apparent that such a structure would not remain stable on its own, so the fully 147 cluster need still be processed and optimized without the cap. As we are unsure of the exact atomic coordinates for these NiFe clusters, it would be good to explore less randomized structures such as a NiFe cluster with a Ni surface and Fe core (figure *)

(Figure *) NiFe cluster with Ni surface and Fe core

CONCLUSION

The research is still a work in progress. As far as we can tell, the icosahedral structure is a viable approximation of a NiFe nanocluster for nanotube nucleation. Future work utilizing the various structures mentioned above could yield a better understanding of nanotube nucleation and further bolster previous computational results. The goal would be to find a simplified but accurate model to base experimental production of CNTs.

[1] Epitaxial nucleation model for chiral-selective growth of SWCNTs on bimetallic catalyst surfaces (pre-publication)
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