A plausible mechanism for the evolution of helical forms in nanostructure growth

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The observation of helices and coils in nano-tube/-fiber (NT/NF) syntheses is explained on the basis of the interactions between specific catalyst particles and the growing nanostructure. In addition to rationalizing nonlinear structure, the proposed model probes the interplay between thermodynamic quantities and predicts conditions for optimal growth. Experimental results on the effect of indium catalyst on affecting the coil pitch in NTs and NFs are presented. © 2007 The American Physical Society. [DOI: 10.1063/1.2723189]

I. INTRODUCTION

The synthesis of helical morphologies of nanotubes (NTs) and nanofibers (NFs), through chemical vapor deposition (CVD) techniques, has been widely reported and can be made practical for a wide variety of applications, e.g., nanoscale mechanical springs and electrical inductors. Additionally, the observed nano-coils/-helices (NC/NH) could be pertinent for observing interesting variants of electronic architecture. It was suggested, interestingly, that a coil could correspond to a sequence of junctions with alternating metallic and semiconducting character, adding to the possibilities of observing interesting electronic behavior in nonlinear nanostructures. NC/NH formation, mostly observed in carbon nano-tube/-fiber (CNT/CNF) syntheses, is also scientifically interesting in that helices abound in nature, e.g., DNA, proteins, etc. and a connection is being made at the nanoscale between carbon based inorganic and organic structures.

For application, it would be desirable to have control over the coil morphology and geometry- which has not been achieved, possibly due to an incomplete understanding of their growth mechanisms. Several models, none of them completely satisfactory, have been proposed to understand their synthesis. In this paper, we first briefly review the models in vogue and point out their shortcomings. Second, we introduce a thermodynamic model, based on exclusion volume principles, common in chemical and biological systems, that could potentially explain coiling in nanostructures. Third, we make specific predictions for the optimal growth of NC/NHs with the hope that these could be used as a guide for rational synthesis. Finally, our own experimental results conforming to the above model, on the role of indium catalyst particles and local CVD reactor temperature in influencing the coil pitch in NT/NFs, will be outlined.

For NC/NHs based on single walled CNTs, it has been found that it is necessary, based on theory and geometric considerations, to introduce pentagon-heptagon (P-H) pairs at the bends to account for the curvature. However, so far all experimental observations have been made on coiled multi-walled CNTs and noncrystalline carbon nanofibers (CNFs), and it is difficult to imagine the conditions necessary for the uniform and periodic introduction of the P-H pairs in such structures. The most widely accepted models for coiling, in NTs, are then related to (a) the anisotropic rates of carbon deposition and/or (b) nature and geometry of the catalyst particle. For example, it was proposed that nonuniform rates of extrusion of carbon from the catalyst (e.g., Ni) particle’s crystal facets, where the Ni is transported along with the growing CNT is responsible for nonlinear growth. A qualitative model, where the crystal faceting does not play a role but where stresses generated by uneven carbon deposition induce coiling, was also posited. Neither of these models makes any predictions nor gives specific reasons for helical growth, maintaining that “rather special conditions” would be needed for coiling. However, the faceting of the catalyst particle has never been explicitly shown, and coiled tubules have also been obtained where catalyst particles are either not present anywhere in the nanostructure or have been found, through high resolution transmission electron microscopy (TEM), to be embedded in the CNT. The above models also cannot explain the synthesis of amorphous carbon nanocoils, or compound (e.g., Boron Carbide) nanowires. Other mechanisms such as the (i) formation of superlattice structures from charged nanobelts, postulated for ZnO nanohelices, and (ii) oxide assisted growth are not applicable.

For NC/NH synthesis, many specific catalysts were also considered without sufficient rationale. A high yield of nanocoils was found to be promoted by the use of In and Sn either in catalyst or substrate form. Interestingly, it was also found that use of ultrasonic (Ref. 5)/microwaves (Ref. 25) increases the NC/NH yield. In this paper, we hope to provide...
a comprehensive explanation for all of these observed phenomena in terms of a unified model based on the thermodynamics and kinetics involved in the synthesis. This model has been motivated by the thought that the widespread occurrence of helices in NT/NF synthesis, demands a more fundamental explanation.

II. THEORETICAL ANALYSIS

It has been found in computational studies\(^{26,27}\) that the optimal configuration for strings incorporates spontaneous helical chirality, due to entropic interactions\(^{28}\) and is energetically preferred. On this basis, we postulate that the formation of helical nanostructures could be explained through basic thermodynamic principles incorporating minimization of the configurational entropy. Two scenarios would have to be considered in terms of nanocoil evolution and growth: (1) regular nanotube growth\(^{29}\) convoluted with a subsequent coil/helix inducing mechanism, or (2) nucleation and growth of a coiled structure. It is generally seen, in experiments\(^{7,20}\), that (2) is favored, where the initial turn itself is a helix. We hypothesize that the consequent entropy reduction is offset by the influence of the increased excluded volume interactions, brought about by the conditions in the CVD chamber and/or the influence of the catalysts.

We consider energy minimization in nanocoil growth through a simple model. The Gibbs free energy, \(\Delta G\), consists of: (a) the elastic energy per unit length \(E_c\) of the NT/NW \((=Y/2R^2)\) \([Y\) is the Young modulus, \(\Pi\), the moment of inertia, is proportional to \((r_o^4-r_i^4\), where \(r_o\) and \(r_i\) are the outer and inner radius of the tube \((r_o-r_i\), for a nanowire), and \(R_c\) the radius of curvature], (b) the enthalpy of interaction \((\Delta H)\) between the nanocoil and the ambient, and (c) entropy of the system \((\Delta S=\Delta S_c+\Delta S_s)\), which includes the contributions from the coiling \((\Delta S_c)\) and the ambient \((\Delta S_s)\).

In this model, coiling or nonlinear growth is favored if the increased elastic energy and the decreased entropy \((\Delta S_c)\) due to coiling is compensated by a decreased energy through coil-ambient interactions and increased \(\Delta S_s\), i.e., if \(\Delta G=\Delta E_c+\Delta H-T(\Delta S_c+\Delta S_s)\)<0. We suggest that such conditions can be favored by the use of specific catalyst particles and ambient agitation.

The enthalpy \((\Delta H)\) is modeled through the interaction between the ambient \((\pi)\) with catalyst particles of concentration, \(X_C\), and the growing nanotube \((X_T)\) as \(\Delta H=\Omega X_C X_T\), where \(\Omega\) is parametrized in terms of the interaction energies\(^{30}\) as proportional to \(E_{C-T}^{-1}/2(E_{C-C}+E_{T-T})\). \(E_{C-T}\) is related to the adhesive energy of the catalyst \((C)\) particles \(v/s\) the nanotube \((T)\), and \(E_{C-C}\) and \(E_{T-T}\) are the respective cohesive energies. Consequently, \(\Omega (\Delta H)\) can be negative if the ambient conditions promote a nonwetting behavior, i.e., through catalyst particles that have a greater tendency for cohesion than adhesion onto the growing NT/ NF. Increased ambient entropy, say through agitation, in ultrasonic\(^{5}\) or microwave\(^{25}\) CVD, or use of sublimating compounds,\(^{31}\) can have a similar effect. One can confirm specific cases where the above situations are plausible through comparison with experiment.

III. WETTABILITY OF A NANOSTRUCTURE SURFACE

As mentioned earlier, it has been observed that the use of certain catalysts \((Sn^{32}, \text{ or both}^{24} \text{ In and Sn})\) or substrates \([ITO,^{2,24} \text{ powdered Ni,}^{1} \text{ or Cu,}^{33} \text{ Ge,}^{34} \text{ Al}_2O_3\) \((\text{Ref. 35})\)] enhances the nanocoil yield. One can explain this observation by positing the degree of wettability of the NT/NF surface by the catalysts/substrates as a criterion for coiling. It is seen that the wetting angle \(\theta=\cos^{-1}(\gamma_{SV}/\gamma_{LV})\) of liquid metals with graphite surfaces\(^{36}\) \([\gamma\) represents the relative surface energies of the surface \((s)\), liquid \((l)\) metal, and the ambient \((v)\) phases] is large for the interaction of In \((159°)\), Sn \((156°)\), Cu \((156°)\), Ge \((164°)\), Al \((159°)\) while Fe, Co, and Ni, used for straight NT/NF growth all have smaller wetting angles \(<75°\). Consequently, the latter elements have a net attractive interaction with the growing nanostructure (exemplified through the Baker model\(^{29}\) surface while the former elements, by inducing a repulsive interaction through nonwetting, promote nonlinear growth. Note that this model implies that the specific catalyst particles, say In/Sn, are only indirectly, and externally, responsible for the coiling and hence are not/need not be found in/on the nanostructure itself—as has been observed through TEM and Energy Dispersive Spectroscopy (EDS). The above model is summarized, for the case of In particles, in Fig. 1. Figure 1(a) schematically illustrates ambient conditions in the CVD chamber while Fig. 1(b) shows that the nonwetting In catalyst particles induce coiling/helix formation. A larger pitch is obtained when the In concentration in the CVD feedstock is reduced [Fig. 1(c)].

IV. COMPARISON TO EXPERIMENT

We have verified some of the above hypotheses through CVD experiments. Indium, in the form of indium isopro- poxide, was used as a catalyst dissolved in a xyleneferrocene feed gas mixture. These precursors, along with an acetylene carbon source and Ar carrier gas, were cojected into the CVD reaction chamber at \(-1000\text{ K. Further experimental details have been published elsewhere.}^{7} \text{ In addition to the observed coiling, catalyzed by Indium addition, it was noted that when the In/Fe ratio \((R_{In/Fe})\) in the feedstock mix-
A THERMODYNAMIC MODEL FOR COIL/HELIX GROWTH

To justify the above experimental observations more rigorously, we formulate an empirical model for the synthesis of NC/NH forms. The overall growth and density of packing, in a nonlinear structure, is decomposed into the following: (a) a linear growth mode, (b) a bending mode, and (c) a twist mode. In a Cartesian coordinate system, the $x$, $y$, and $z$ directions are related to the in-plane nanostructure growth, while the $z$ axis refers to the vertical/out-of-plane growth direction. The degree of growth (parametrized by $A$) is dictated by the supply of the growth catalyst (typically Fe, Co, and Ni) and is given by

$$\nabla \cdot \mathbf{n} = A,$$

where $\mathbf{n}$ denotes the directorial vector of growth and

$$\nabla = i \frac{\partial}{\partial x} + j \frac{\partial}{\partial y} + k \frac{\partial}{\partial z}.$$  

In an a priori assumption, the bending is

$$n_x(\nabla n_x) = -A n_x,$$  

which seems to be borne out from experimental considerations (i.e., the bending increases with the length of the tube/fiber)\textsuperscript{20,21,39}. Finally, the overall twist, $n \cdot (\nabla n) = A[\nabla \cdot (n_x + n_y)]$. \textsuperscript{30}

Equation (3) follows from the observation that in nonlinear growth the rates of carbon deposition are very likely to be different in orthogonal directions. This relation also makes a connection to a previous growth model,\textsuperscript{21} where compressive and tensile stresses caused by the uneven deposition of carbon were thought to be responsible for coiled growth. The coiling (bending and twist) are induced by nonwetting catalyst particles, as outlined earlier.

We note that the above terms, viz., $\nabla \cdot \mathbf{n}$, $n_x(\nabla n_x)$, and $n \cdot (\nabla \mathbf{n})$ would contribute to the net elastic free energy\textsuperscript{30} ($F_{\text{elastic}}$, where $F_{\text{elastic}}$ is related to

$$\int dV [(K_1(\nabla n)^2 + K_2[n_x(\nabla n_x)]^2 + K_3(n \cdot (\nabla \mathbf{n}))^2],$$

and $K_1$, $K_2$, and $K_3$ are the elastic constants, corresponding to the different modes of growth.

As we have previously postulated that the avoidance of the growing NT/NF with specific catalyst particles is responsible for promoting nonlinear growth, a chemical potential term, $F_{\text{chem}}$ proportional to

$$\Gamma \int dV[n \cdot (\nabla \mathbf{n}) + n_x(\nabla n_x)]$$

is also added to determine the overall energy of the system, where $\Gamma$ is related to the NT/NF interactions with the ambient.

After solving the above equations self-consistently, we arrive at the following solutions for the components of the direction vector $\mathbf{n}(n_x, n_y, n_z)$ as

$$n_x = A \cos^2(\pi t), \quad n_y = A \sin^2(\pi t), \quad n_z = A t,$$

where $t$ is a parameter proportional to $\Gamma/(K_2 + K_3)$ and dictates the magnitude of twist. Interestingly, and in accord with experiment, the growth as described in Eq. (6) corresponds to coiled/helical growth.

We gain insight from the proposed model in that we learn that a variety of factors including the surface energy and the elastic constants, manifested through enthalpy and entropy considerations, influence nonlinear nanostructure growth. Generally, coiled growth can be obtained when surface energy considerations are important while linear nanostructures form when elastic effects dominate. One also observes a higher degree of twist for a nanofiber compared to a nanotube. The magnitude of the twist has been found to increase with increased nanocoil growth and temperature (Fig. 3). It would be interesting to speculate a correspondence between the increased surface energy of a nanotube (due to the inner core) and the increased elastic energy, due to tighter coiling, of a nanofiber.
V. CONCLUSIONS

In this article, we have proposed a plausible model for coiling in nanostructure growth motivated by both energy and entropic principles, that for a given volume of material, the helical form occupies the least amount of space. To compensate for the close packing of the helices, the entropy of the ambient should increase which in turn is facilitated by nonwetting catalyst particles or induced by catalyst/ambient agitation in CVD growth. A more sophisticated model for the evolution from linear to helical forms, based on the spirit of the Zimm-Bragg partition function formulation can also be constructed. However, this would necessitate knowledge of the nucleation and growth parameter values for a growing nanostructure, which is presently not available.

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