

CARBON NANOTUBE BASED COILS AND HELICES: Thermal effects and Mechanical properties

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Introduction

The synthesis of helical morphologies of nanotubes (NTs) and nanofibers (NFs), through Chemical Vapor Deposition (CVD) techniques, has been widely reported[1] and can be made practical for a wide variety of applications, *e.g.*, nanoscale mechanical springs[2] and electrical inductors[3]. Additionally, nano-coils/-helices could correspond to a sequence of junctions with alternating metallic and semiconducting character[4]. Nanocoil formation 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. 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[5], that could potentially explain coiling. Third, we make specific predictions for the optimal growth of coils, which could be used as a guide for rational synthesis. Then, 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. Finally, the utility of such systems for electronic and mechanical applications will be probed.

Theory

We postulated[6] that the formation of helical nanostructures could be explained by basic thermodynamic principles incorporating minimization of the configurational entropy. For this, we consider energy minimization in nanocoil growth through a simple model. Here, the Gibbs free energy, ΔG , consists of: (a) the elastic energy per unit length (E_c) of the NT/NW. (b) the enthalpy of interaction (ΔH) between the nanocoil and the ambient, and (c) entropy of the system ($\Delta S = \Delta S_c + \Delta S_a$), which includes the contributions from the coiling (ΔS_c) and the ambient (ΔS_a). In this model, coiling or nonlinear growth is favored if the increased elastic energy and the decreased entropy (ΔS_c) is compensated by a decreased energy through coil-ambient interactions and increased ΔS_a , *i.e.*, if $\Delta G [= E_c + \Delta H - T(\Delta S_a + \Delta S_c)] < 0$. We suggest that such conditions can be favored by the use of specific catalyst particles and ambient agitation. For example,

ΔH can be negative if the ambient conditions promote a non-wettability 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[7] or microwave[8] CVD, or use of sublimating compounds[9], can have a similar effect.

It has been observed that the use of certain catalysts (In, Sn or both[10]) 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 $\theta = \cos^{-1} \left(\frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}} \right)$ of liquid metals with graphite

surfaces[11] (γ represents the relative surface energies of the surface (s), liquid (l) metal, and the ambient vapor (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 (as in the Baker model) surface while the former elements, by inducing a repulsive interaction through non-wetting, promote nonlinear growth. This 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. The above model is summarized in Fig. 1, which schematically illustrates ambient conditions in the CVD chamber and shows that the non-wetting In catalyst particles induce coiling/helix formation.

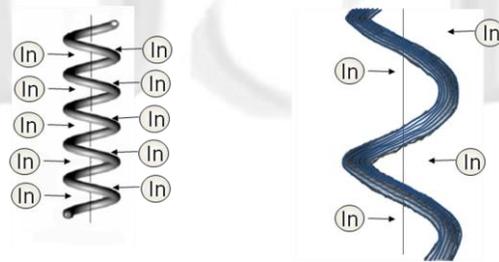


Fig. 1. The non-wetting characteristic of the local Indium catalyst particles on the nano-tube/-fiber (NT/NF) surface is proposed as an underlying mechanism for the evolution of nano-coils/-helices (NC/NH). The concentration of In influences the coil pitch, where (a) a more tightly coiled helix is obtained at larger Indium concentrations, and (b) a helix with larger pitch is seen with smaller ambient Indium.

Experimental

We have verified some of the hypotheses through chemical vapor deposition (CVD) experiments. For the synthesis of the coiled nanotubes (HCNTs), ferrocene and indium isopropoxide are dissolved in xylene, where the ratio of C: Fe: In is maintained at 99:0.25:0.75, injected into a two-stage CVD reactor, along with flowing Ar (~800 sccm) and acetylene (~50 sccm) gases. After ~1 hour run time, the quartz

substrates and the inner walls of the quartz tube inside the furnace are densely coated with soot containing helical CNT arrays. The synthesis conditions for the helical nanofibers are similar to those described for the CNTs except that Sn, in the form of Tin isopropoxide is used and the ratio of C: Fe: Sn is maintained at 99:0.8:0.2. Approximately 50 mg of coiled nanostructures can be prepared in a 1 hr run.

Results and Discussion

In addition to the observed coiling, catalyzed by In addition, it was noted that when the In/Fe ratio in the feedstock mixture was large, ≥ 3 , helical CNFs were formed in the majority (Figure 2a), while with a decreased In/Fe ratio, say ≤ 2 , helical CNTs (Figure 2b) with a larger pitch were synthesized. In the latter case, several nanotube structures of smaller diameter are loosely bundled together, possibly due to van der Waals forces.

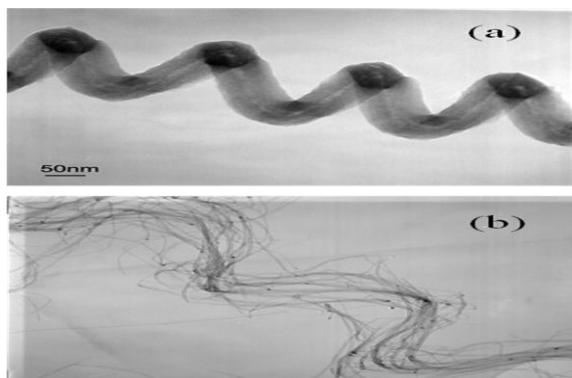


Fig. 2 Electron Microscope micrographs of (a) singly-wound, carbon nanocoil and (b) nanotube (NT) bundles obtained through In and Sn catalyzed CVD processes.

Generally, coiled growth could be obtained when surface energy considerations dominate while linear nanostructures form when elastic energy effects dominate, e.g., a higher degree of twist is seen for a nanofiber compared to a nanotube. The twist has been found to increase with increased nanocoil growth and temperature (Figure 3).

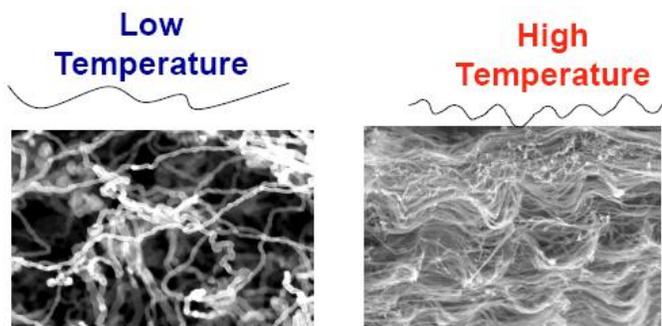


Fig. 3 A transition from linear to coiled nanostructure is seen as the temperature, and hence In concentration, in the CVD chamber is increased.

It would be interesting to speculate a correspondence between the increased surface energy of a nanotube and increased elastic energy, due to tighter coiling, of a nanofiber (Fig. 2a)

In addition to the possible use of these structures as electrical inductors, experiments have been performed in their use for enhanced impact response (Fig.4)

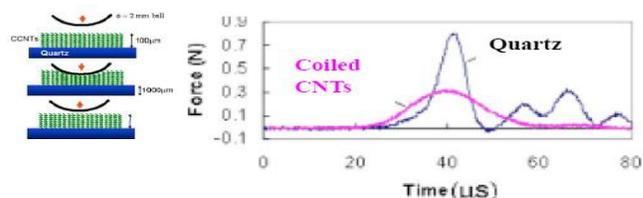


Fig. 4 On impact, coiled carbon nanostructures exhibit a greater damping force compared to quartz substrates

Conclusions

We have postulated a model, based on fundamental thermodynamic criteria, for the growth of helically coiled nanotubes and nanofibers and verified the hypotheses through CVD experiments. The influence of temperature in inducing coiling could be explained by the increased In catalyst concentration. The helical nanotube/nanofiber morphologies present exciting opportunities for novel electronic architectures and for reduced mechanical impact response.

Acknowledgments We appreciate the support from the National Science Foundation (Grant ECS-06-43761)

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