

Rational Synthesis of Helically Coiled Carbon Nanowires and Nanotubes through the Use of Tin and Indium Catalysts**

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Helically coiled carbon nanotubes (HCNTs) and nanowires (HCNWs) represent novel nanostructural morphology and have technological and scientific significance. Their potential applications^[1] span high frequency electronics,^[2] tactile and magnetic^[3] sensors, and structural foams for cushioning and energy dissipation.^[4,5] It is also interesting to make a connection between the CVD synthesized helical carbon nanostructures to organic forms found in nature, such as DNA and proteins, and indeed, these structures can be used for templates in collagen growth.^[6] It was also suggested that a coil could correspond^[7] to a sequence of alternating metallic/semiconducting junctions, which is very interesting from the point of view of application to nanoelectronic systems.^[8,9]

While several groups have previously reported on the synthesis of coiled nanostructures using chemical vapor deposition (CVD), patterned substrates^[10-16] were always used. While mostly HCNWs are seen, there have also been a few reports on the synthesis of HCNTs.^[17,18] Patterned growth of coiled nanotubes based on using previously aligned straight CNTs as templates was also demonstrated.^[19] It is typically found that such methods, in addition to limiting the amount of material due to the catalyst distribution, is often accompanied by the formation of linear multiwalled nanotubes.^[20] It would be desirable to develop a process that is independent of the underlying substrate, utilizing gas-phase synthesis alone,^[18] with controllable coiling characteristics (i.e., length, pitch etc.). In this paper, we report on a liquid-precursor-based synthesis method which has the additional advantage that either coiled nanotubes or nanowires, with differing electrical and mechanical properties,^[5,8,21] can be fabricated. We provide a rational explanation for the distinct growth modes based on

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[+] Present address: Department of Materials Science and Engineering, Carnegie Mellon University, Pittzburgh, PA 15213, USA. an analysis of the binary equilibrium phase diagrams, where the mutual affinity of secondary catalysts (In/Sn), with the primary catalyst (Fe) in the ferrocene–xylene mixture, promotes nanotube/-wire formation.

Coiled carbon nanostructures have been predicted to be energetically stable,^[22] and various mechanisms have been posited for their formation. While the curvature, in the case of helically coiled single-walled nanotubes could possibly be due to the regular insertion of pentagon-heptagon pairs at the junctions,^[23] it is unclear if a similar mechanism could hold for multiwalled nanotubes and HCNWs. Other formation mechanisms invoke localized stresses and anisotropic rates of carbon deposition^[19,24] on faceted catalyst particles.^[17] However, there is no experimental evidence for the above, as it is seen that helical structure is induced even though catalyst particles are not obviously present in the structure. It is also noted that the above mechanisms cannot be invoked for amorphous carbon nanocoils^[16] and compound (e.g., boron carbide) nanowires.^[13] To provide a comprehensive explanation, we have proposed a thermodynamic model,^[25] where helix/coil formation is explained on the basis of the interactions between specific catalyst particles and the growing nanostructure. We use the degree of wettability of the nanostructure surface by the catalysts as a criterion for coiling. It is seen, through the Young equation, that the wetting angle $\theta \left[= \cos^{-1} \left(\frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}} \right) \right]$ of

liquid metals with graphite surfaces^[26] (where γ_{sv} is the solid/ vapor interfacial energy, γ_{sl} is the solid/liquid interfacial energy, and γ_{lv} the liquid/vapor interfacial energy) is large for the interaction of certain catalysts (e.g., In: 159°, Sn: 156°, Cu: 156°, Ge: 164°, Al: 159°) while smaller for other metal catalysts (e.g., Fe, Co, and Ni, where $\theta < 75^{\circ}$) Consequently, the latter elements have a net attractive interaction with the growing nanostructure (exemplified through the Baker model^[27]) surface while catalysts such as In and Sn, induce a repulsive interaction through non-wetting, and promote nonlinear/coiled growth. The rationale for helix formation can then be understood through a simple model^[25] where the overall growth is analyzed in terms of linear, bend, and twist modes.

In the present study, we performed experiments to elucidate the specific role of In and Sn catalysts. A simple two-stage thermal CVD reactor (Fig. 1) is used for synthesizing highpurity HCNTs and HCNWs in bulk. The In and Sn sources (indium isopropoxide and tin isopropoxide, respectively) are individually dissolved in a xylene–ferrocene mixture, which is then continuously injected into the CVD reaction tube at ca.



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Figure 1. Schematic of the two-stage CVD reactor utilized for the HCNT and HCNW synthesis.

1-1.5 mL h⁻¹. Simultaneously, acetylene along with argon carrier gas is passed through the chamber, at atmospheric pressure. Parameters such as the reactor temperature, gas flow rate, relative concentrations of Fe, In, and/or Sn were investigated and adjusted for optimal synthesis. Subsequently, after ca. 1 hour of reaction time, the HCNTs/HCNWs were found to be formed on the bare quartz substrates. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were performed for structural and morphological characterization.

We have, in general, found that indium catalysts promote the growth of coiled nanotubes (Fig. 2) while tin based catalysts catalyze the growth of coiled nanowires (Fig. 3). The above observations can be related to the relative affinity of Sn



Figure 2. Electron microscopy images of HCNTs. a) A typical SEM image of as-grown HCNT array, prepared through the use of In catalyst, subsequent to peeling off from the quartz substrate. b) Highly aligned HCNTs with nearly identical diameter and pitch. c) TEM image. d) High-resolution TEM image of a HCNT.

or In with the primary transition metal catalyst-Fe. It is seen through an elementary analysis of the empirical Hume–Rothery rules^[28] that Fe and Sn form substitutional solid solutions, i.e., due to similar values of the atomic radius (Fe: 0.172 nm, Sn: 0.172 nm) and the higher valence difference. On the other hand there is less tendency for mutual dissolution in a Fe–In mixture, i.e., due to a 16 % atomic radius disparity (Fe: 0.172 nm, In: 0.200 nm) We also analyze these results in the context of the Fe–Sn binary equilibrium phase diagram^[29] where extensive solid solubility

and intermetallic formation is observed in contrast to negligible solubility in the Fe–In case.

Consequently, the formation of bimetallic Fe–Sn phases would then mean less availability of Fe for linear nanotube growth and promote HCNW formation. On the other hand, In is not bound to Fe when the indium isopropoxide is co-introduced with ferrocene and can nucleate carbon nanotubes (i.e., HCNTs)–the In is responsible for the coiling, by the mechanism previously outlined.^[25] One can then a priori predict nanostructure growth through such analyses.

The above mechanisms also enable us to qualitatively explain a few observed anomalies. We have occasionally seen, while investigating the experimental parameter space, that other factors, such as i) the relative concentrations of In or Sn

> compared to Fe and ii) local temperature in the reactor, could also be playing a role. For instance, a larger ratio of In:Fe (In:Fe \geq 3) promotes coiled nanowire growth, while if the ratio of In:Fe concentrations is ≤ 2 , coiled nanotubes are seen. We have also noted that when Sn is used, coiled nanotubes are seen in certain regions of the reactor which could be correlated to increased local temperature. Increasing the concentration of In, relative to Fe, would result in increased Fe-In binding and cause a move away from the tendency to form coiled nanotubes; instead coiled nanowires (HCNWs) would be formed. Increased temperature could enhance diffusion and cause precipitation of the Fe with a tendency for HCNT formation. From this brief glimpse of exciting possibilities, we clearly see much scope for future investigations. Our experimental data is qualitatively well supported by our hypotheses. Quantitative agreement is difficult due to the extremely complex conditions existing in the CVD chamber.

> HCNTs were formed in self-aligned arrays on quartz substrates. We could peel off the HCNTs from the substrates (Fig. 2a), which could then be assembled onto a substrate of choice. A closer examination reveals the uniformity of the coiling and pitch (Fig. 2b) through the length of the HCNT.



Figure 3. Electron microscopy images of HCNWs. a) SEM image for asprepared HCNWs through Sn catalyst mediated synthesis. b) A representative SEM image illustrating coiled nanowires of differing diameter and pitch. c) TEM image of an individual HCNW, illustrating the position of a Fe–Sn nanoparticle, at the tip.

Fe, and Sn (Fig. 4). Preliminary Cliff–Lorimer analysis revealed an Fe:Sn ratio of 4:1, consistent with the atomic ratios of the elements in the chemical precursors (Fe:Sn = 0.78:0.22)– see also the Experimental section.

We have demonstrated the rational synthesis of helically coiled nanotubes and nanowires through the use of In and Sn catalysts, respectively, in a floating-catalyst-based CVD process, using unpatterned quartz substrates. Coiled nanotubes (HCNTs) exhibited uniform diameters and pitch, and could be readily peeled off for transfer onto other substrates. On the other hand, coiled nanowires (HCNWs) are randomly aligned and widely distributed in geometry. While a model based on the mutual solubility of Fe with Sn and In, and catalyst-growing nanostructure interactions,^[25] could explain our observations qualitatively, the specific effect of the catalyst in CVD processes^[30] needs further investigation. We hope that our study provides motivation for continued investigation on the scientific and technological aspects of helical nanostructures.

Experimental

For the synthesis of the coiled nanotubes (HCNTs), ferrocene and indium isopropoxide were dissolved in xylene, where the ratio of C:Fe:In was maintained at 99:0.25:0.75. The mixture was immediately injected into a two-stage CVD reactor using a syringe pump at an injection rate of 1.5 mL h⁻¹. The two stages in our CVD reactor–the preheater and the furnace–were maintained at 200 and 700 °C, respectively (Fig. 1). The injected mixture was vaporized in the preheater and carried into the furnace by flowing Ar (ca. 800 sccm) and acety-lene (ca. 50 sccm) gases. After ca. 1 h run time, the quartz substrates and the inner walls of the quartz tube inside the furnace were densely coated with soot-containing HCNT arrays.

The synthesis conditions for the HCNWs were similar to those described for the HCNTs except that Sn, in the form of tin isopropoxide, was used, the ratio of C:Fe:Sn was maintained at 99:0.8:0.2, and a slower injection rate (ca. 1 mL h^{-1}) was used. Approximately 50 mg of these coiled nanostructures could be prepared in a 1 h run.

TEM imaging revealed that the HCNT array comprises subsidiary helical nanotube structure, of smaller diameter (Fig. 2c). The constituent tube diameters were quite uniform in the 15–25 nm range, with a pitch of ca.1 μ m.

Unlike the HCNTs, the HCNWs were found to be randomly oriented on the substrates. Figure 3a illustrates the general appearance of transferred HCNWs. A broader diameter distribution, in the 10–100 nm range, was observed. In several HCNWs, catalyst nanoparticles were discerned at the tips (Fig. 3c). This observation further lends credence to our hypotheses of the compound forming tendency in a Fe–Sn catalyst mixture. It was noted that In catalyst particles were never found in HCNT synthesis. The tip particle was characterized through energy dispersive spectroscopy (EDS), in the TEM, where elemental mapping revealed C,



Figure 4. EDS mapping of the a) HCNW and the tip nanoparticle, shows the elemental distribution of b) C, c) Fe, and d) Sn.



ADVANCED MATERIALS

The as-prepared HCNTs and HCNWs were pure with very little presence of amorphous carbon nanoparticles. SEM (Haitachi S-4800, 20 KV) and TEM (Hitachi HD-2000, 200 KV) were used to explore the structure and morphology of the as-grown HCNTs and HCNWs.

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