EPA Presidential Green Chemistry Challenge Awards Program Nomination Package

Project Title:

Improved resource use in carbon nanotube synthesis *via* mechanistic understanding

Nomination Date: December 30, 2011

Primary sponsor: Desirée L. Plata, Ph.D.; Principal Investigator

Contact person:

Desirée L. Plata, Ph.D.
Assistant Professor
Box 90287
Department of Civil and Environmental Engineering
Duke University
Durham NC 27708
T: 919-660-5209
F: 919-660-5219
e-mail: desiree.plata@duke.edu

Contributors:

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Co-authors of the primary discovery and technology development include: Prof. Philip M. Gschwend, Massachusetts Institute of Technology; Dr. Christopher M. Reddy, Woods Hole Oceanographic Institution; and Prof. A. John Hart and Dr. Eric R. Meshot, University of Michigan.

Project Title: Improved resource use in carbon nanotube synthesis *via* mechanistic understanding

Milestones:

Patent Filed. Filing Date: June 17, **2010**; U.S. Patent Application Number: 61/187704; Entitled "Alkyne-assisted carbon nanostructure growth"; Inventors: D.L. Plata, E.R. Meshot, A.J. Hart, C.M. Reddy, and P.M. Gschwend.

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Eligible award category: Academic. The discovery and development were conducted in an academic setting.

EPA award focus area: This technology meets criteria in both focus areas (1) the use of greener synthetic pathways and (2) the use of greener reaction conditions.

United States component: All research was conducted in the United States of America (USA), by citizens of the USA, and it was demonstrated to be successful in the USA. A US-based company recently licensed the technology for use.

Abstract: Carbon nanotube (CNT) production by catalytic chemical vapor deposition (CVD) is increasing globally, with current production rates exceeding 300 tons per year. The current "state-of-the-art" CVD process is inherently energy consumptive and plagued by inefficiency, with less than 3% atom economy. We demonstrated that emissions from ethene- and H_2-fed CVD reactors included over 45 distinct chemicals, including the potent greenhouse gas, methane (up to 1.7% by volume), and toxic and smog-forming compounds, such as benzene and 1,3-butadiene (up to 3600 ppmv), and trace quantities of polycyclic aromatic hydrocarbons. Eliminating thermal treatment may prevent the formation of unwanted by-products, reduce energetic demands, and improve our overall control of the synthesis. However, heating the feedstock gas is necessary for rapid CNT growth, due to the thermal generation of previously unidentified-yet-critical CNT precursor molecules. Using *in situ* CNT height measurements and complimentary gas analysis, we identified thermally generated compounds that were correlated with CNT formation rate (e.g., propyne and but-1-en-3- yne). To demonstrate that these alkynes were responsible for rapid CNT growth, we delivered each chemical along with typical feedstock gases (C_2H_4/H_2), without pre-heating, directly to a locally heated metal catalyst substrate. Using these compound-specific experiments, we demonstrated that many alkynes (e.g., ethyne, propyne, and but-1-en-3-yne; i.e., acetylene, methyl acetylene, and vinyl acetylene, respectively) accelerate CNT formation. This presents a distinct CNT formation mechanism where the chemical precursors may be intact during C-C bond formation, such as in polymerization reactions, challenging the widely

accepted hypothesis that precursors completely dissociate into C (or C_2) units before "precipitating" from the metal. Armed with these mechanistic insights, we were able to form high-purity CNTs rapidly with a 15-fold improvement in yield, a 50% reduction in energetic costs, 20 and 40% reductions in ethene and H_2 starting material requirements, respectively, and order-of-magnitude reductions in unwanted byproduct formation (translating to ton-sized emissions reductions in toxic and smog-forming chemicals and greenhouse gases). In addition to environmental benefits, the reduced starting materials and energetic requirements lower the net cost of the technology without sacrificing product quality, and thus, this patent-pending work has already been licensed by a commercial CNT manufacturer.

Nominated Technology Description

In spite of broad industrial development and significant research efforts over 20 years[1], surprisingly little is known about the formation mechanism of carbon nanotubes (CNTs)[2]. Synthetic efficiencies still do not exceed 3% (g_{CNT} per $g_{Cfeedstock}$)[3], and we showed that undesirable by-products (toxic, smog-forming, and/or greenhouse chemicals) are formed during CNT production via catalytic chemical vapor deposition (CVD) of ethylene[4], a common route for high-volume manufacture. Ignorance of chemical formation mechanisms of CNTs (1) limits true nanometer-scale control of CNT structure (e.g., chirality and defect density), (2) precludes advances in carbon-conversion and energy efficiency, and (3) threatens the ultimate success of the CNT-based product market due to potential environmental and public health threats.

We aimed to surmount these limitations by simultaneous optimization of cost, performance, and environmental objectives through an improved mechanistic understanding of CNT formation. In general, CNT growth by CVD involves the introduction of a gaseous carbon precursor (e.g., C_2H_4 or CH_3CH_2OH) to a heated (e.g., 450-1300°C) reaction zone that contains a free-floating or substrate-supported "catalyst." The "catalyst" is typically a transition metal or oxide nanoparticle that is thought to mediate the reaction, although true catalytic activity was not previously demonstrated. While the current understanding is limited with respect to chemical details[2] the prevailing thought is that the carbon-containing precursor adsorbs onto, and then dissociates at, the catalyst. Initially, a closed carbon network forms the CNT "cap", and then carbon adds to the growing lattice by continual dissociation at, diffusion into or over, and precipitation from the catalyst (similar to the "vapor-liquid-solid" or VLS model)[2].

As a result of the focus on precipitation from the catalyst, few studies evaluated the role of gas-phase reactions in CVD reactors. However, these gas-phase reactions play a critical role in CNT growth; we demonstrated that independently heating the carbonaceous feedstock prior to impingement on a metal catalyst accelerates CNT formation by up to a factor of 20[5]. The thermal pre-treatment step generates a suite of volatile organic compounds (VOCs)[4], some of which may be responsible for enhanced CNT formation[4] while others may diminish CNT quality[5] and present environmental and public health risks[4]. Here, we identified the critical CNT precursors and selectively delivered those compounds, rather than relying on thermal generation to provide the necessary reactants within a complex mixture of chemicals. Direct delivery of critical precursor molecule(s) and avoidance of thermal treatment of the feedstock gas (1) eliminated an energetically expensive component of the process[6], (2) improved the precursor-to-CNT mass conversion efficiency over 10-fold, and (3) reduced the formation of un-intended by-products and environmentally damaging materials by orders of magnitude.

Identification of thermally generated CNT precursor molecules. Using an atmospheric-pressure, cold-walled CVD reactor[5] (Figure 1), we independently controlled the temperatures of the feedstock and catalyst in order to decouple the effect of each on the gas composition. The C_2H_4/H_2 growth mixture was heated to various "pre-heat" temperatures, T_p (860-1040^oC), and then cooled to room temperature prior to impingement on a substrate-affixed, locally-heated metal catalyst (1 nm Fe/ 10 nm Al_2O_3/ 675 um Si). Simultaneously, we monitored the composition of gases evolved from the pre-heater by *ex situ* gas analysis[4], as well as the *in situ* CNT growth rate by monitoring the height evolution of a vertically aligned CNT "forest" using a laser displacement sensor[5]. As pre-heat temperature increased, there were strong linear correlations between the growth rate and the partial pressures of methane, benzene, and vinyl acetylene (but-1-en-3-yne); each with a correlation coefficient (R^2) of 0.99 (n = 4).

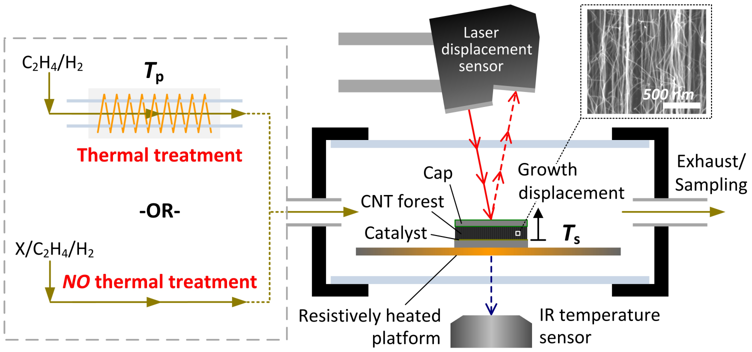


Figure 1. Cold-wall CVD reactor with decoupled thermal control over feedstock and catalyst. Feedstock gases were delivered in one of two modes: (1) with thermal treatment (C_2H_4 and H_2 only) or (2) without thermal treatment (C_2H_4 and H_2 and a test gas, "X"). The height of the growing CNT forest was monitored with a laser displacement sensor.

Accelerated CNT growth by direct delivery of key precursors without heating feedstock gases. To demonstrate that small alkynes ($C_{n\leq4}$) were responsible for the accelerated CNT growth, we delivered each candidate precursor molecule to a heated metal catalyst without thermal treatment of the feedstock gas (i.e., mode 2 in Figure 1). To simulate the growth environment that would be generated by the pre-heater, but without the convolution of the more than 40 thermally generated compounds[6], we administered trace amounts of the test gas (e.g., < 1% by vol), along with a supply of ethylene (18.7 % by vol) and hydrogen (51.3 % by vol, balance He), to the heated metal catalyst. When equal partial pressures (9.8×10^{-3} atm) of each test gas were delivered, acetylene and methyl acetylene enhanced the growth rate of CNTs beyond rates achieved with thermal pre-treatment (Figure 2a). Due to concentration limitations, vinyl acetylene was tested at a lower partial pressure (3.0×10^{-3} atm), yet still exhibited a growth enhancement, supporting the universal reactivity of small alkynes towards CNT formation.

For completion, benzene was delivered to the catalyst as a test gas (at 3.3×10^{-4} atm, within the range expected from thermal generation), but it did not enhance CNT formation (Figure 2b). Similarly, relevant concentrations of methane did not promote CNT formation rates. Thus, while methane and benzene were both correlated with growth rate, they did not enhance CNT growth at the catalyst. We conclude they where synthesized in concert or sequence with another critical component[7].

To insure that the observed rate enhancements were not merely the result of differences in carbon mass (e.g., methane's low molar mass relative to alkynes), we delivered each test precursor at a constant mass. These tests[8] indicate the accelerating effects of alkynes on CNT growth are not simply due to their relative carbon contents; but rather, they are intimately related to chemical structures, suggesting that alkynes are intact during synthesis and do not dissociate, as previously supposed.

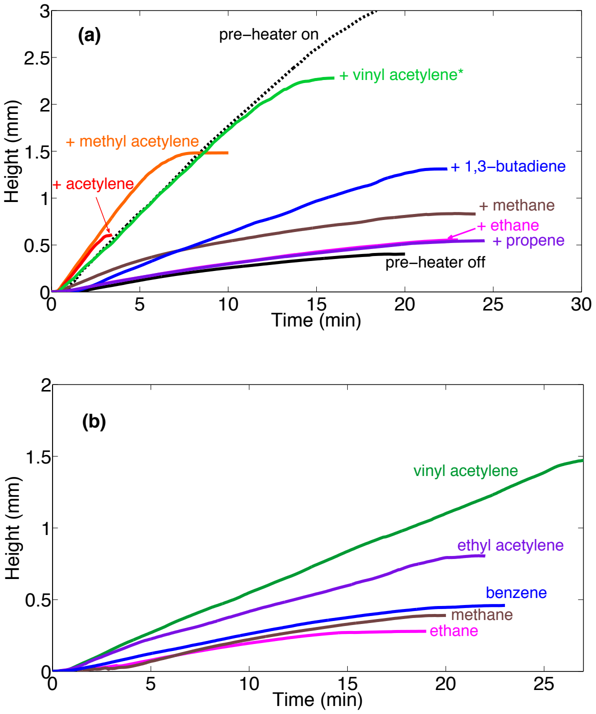


Figure 2. Effects of precursor chemical structure on CNT growth kinetics. In all experiments, standard growth gasses (C_2H_4/H_2 = 120/310 standard cubic centimeters per minute) were delivered without pre-heating in addition to either (1) no test gas ("pre-heater off") or (2) a test gas (e.g., methyl acetylene or methane). To provide a reference for typical growth conditions, a "pre-heater on" case (where only C_2H_4 and H_2 are delivered) is also shown. (a) Test gases were delivered at equal partial pressures (9.8×10^{-3} atm), except for vinyl acetylene, which was more dilute (3.0×10^{-3} atm). All alkynes significantly accelerated growth compared to when they were not delivered (pre-heater off case). (b)Test gases were then delivered at lower partial pressures (3.3×10^{-4} atm), which was necessitated due to thermodynamic limits on the vapor pressure of benzene

Thermal requirements drastically reduced. In our system, the thermal generation of critical precursors accounts for roughly 55% of the total energy budget of the synthesis. Thus, direct delivery of appropriate precursors in place of *in situ* thermal generation could slash energentic requirements to less than half their original value. Further, fewer thermal by-products and closer-to-ambient reaction conditions could lead to enhanced control over the synthesis, not to mention reduced environmental and public health impact. To be thorough, we are in the process of conducting a full life-cycle analysis to ensure that the carbon and/or energy footprint of the upstream fabrication of the alkyne precursor(s) does not outweigh the energetic and carbon benefits they confer during CNT production.

Reduced by-product formation without sacrificing CNT growth. In the typical CVD approach, where feedstock gases are heated, many volatile organic compounds are generated by the thermal treatment of ethylene and hydrogen (Figure 3a), including methane (a potent greenhouse gas), benzene, and 1,3-butadiene (hazardous air pollutants regulated by the Environmental Protection Agency (EPA)). Omitting thermal pre-treatment reduces the abundance of all VOCs (except ethane) by more than an order of magnitude (Figure 3a), and several compounds, including benzene, were not formed in detectable quantities (<0.1 ppmv)[8]. Thus, CNT production techniques that reduce the energy delivered to the feedstock gas offer substantial reductions in unnecessary emissions. Compared to pre-heating, methyl and vinyl acetylene-assisted growth reduced methane formation by about a factor of 30; thereby limiting potential greenhouse gas emissions; reduced 1,3-butadiene formation 60-fold; and benzene formation was effectively eliminated (below detection; <0.1 ppmv), greatly reducing risk to public health.

VOCs are the most abundant components of the CVD effluent, but several toxic PAHs are also formed and emitted[4]. Eliminating thermal treatment of the feedstock gases reduced the total PAH load by an order of magnitude (Figure 3b). Naphthalene, fluoranthene, and pyrene were most sensitive to this change, reduced by 20-, 60-, and 40-fold, respectively[8].

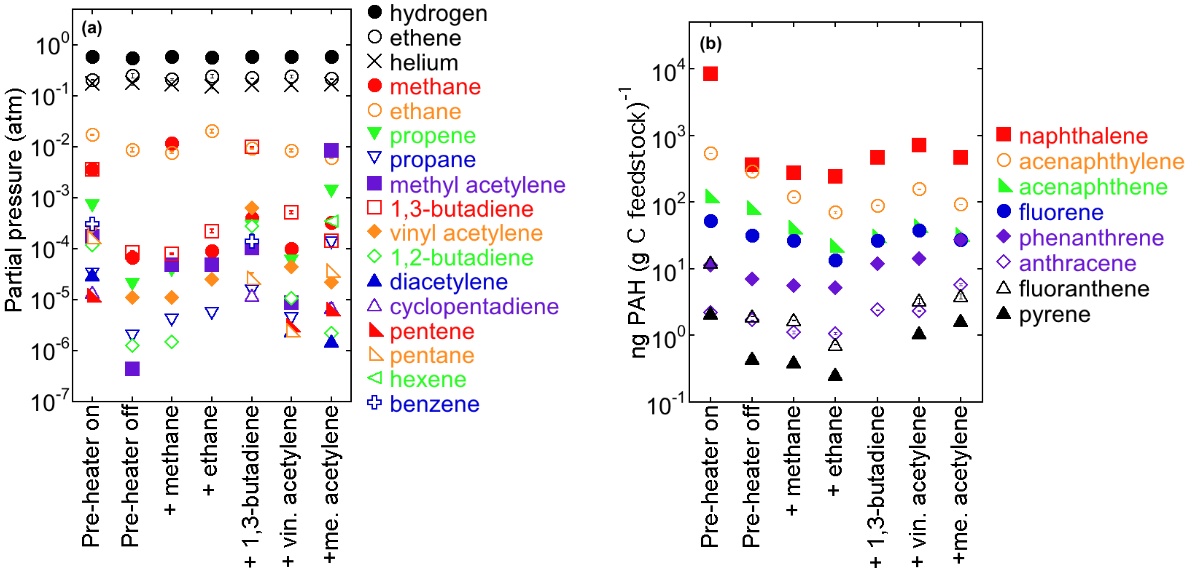


Figure 3. Eliminating thermal pre-treatment of feedstock gases reduced (a) VOC and (b) PAH formation. Labels shown on the abscissa indicate the identity of the test gas and correspond to the growth curves shown in Figure 2a. "Me. acetylene" and "vin. acetylene" are methyl and vinyl acetylene, respectively. In the "pre-heater on" and "pre-heater off" case, no test gas was added to the typical feedstock gas ($C_2H_4/H_2/He = 120/310/174$ sccm). Error bars represent one standard deviation on multiple measurements and invisible error bars are smaller than the symbol. (a) VOC concentrations are reported as partial pressure. (b) PAH abundance was integrated throughout the CNT growth, and so, concentrations are reported relative to total g C delivered. Tabulated values provided in Plata *et al.*[8].

Increased carbon conversion to high-purity CNTs. Augmenting growth with trace amounts of alkynes offered substantial improvements in carbon conversion efficiency (g CNT per g C feedstock x 100%, normalized to catalyst mass). Acetylene- or methyl acetylene-assisted growth improved C conversion by factors of 14 and 15 (1.2×10^5 and 1.3×10^5 % g catalyst^{-1}), respectively, exceeding the efficiencies that were achieved with thermal treatment approaches (8.2×10^4 % g catalyst^{-1}). In addition, dosing unheated feedstock with trace quantities of vinyl acetylene growth offered a 7.5-fold improvement in C conversion (6.4×10^4 % g catalyst^{-1}). In contrast, methane, ethane, and 1,3-butadiene did little to enhance CNT formation beyond what is achieved without pre-heating, further demonstrating that these compounds are not critical reactants for nanotube growth[8].

CNT yields have also been reported in terms of "catalyst efficiency" (g CNT per g catalyst), which does not account for carbon precursor mass. The highest observed efficiencies are for water- and ethanol-assisted CVD (10^{-1} to 10^4 g CNT per g catalyst)[22,23]. Here, without the use of oxidative etchants or thermal treatments, we observed catalyst efficiencies up to 1.1 x 10^3. Thus, while we have made no efforts to optimize our synthesis for catalyst efficiency, we are within the range of the state-of-the-art. With further efforts directly aimed at improving catalyst efficiencies, we may see dramatic improvements beyond what has been possible in CNT synthesis to date.

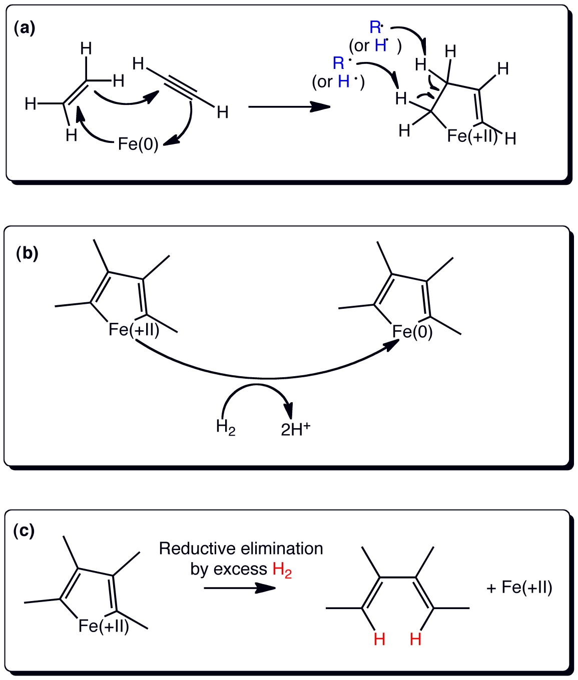
Lastly, and notably, CNT purity (% CNT) was maintained in spite of eliminating thermal treatment of the feedstock. Vinyl acetylene-, methyl acetylene-, and acetylene-assisted growths produced materials with CNT purities of more than 84%, as in the traditional, energy intensive synthetic approach.

Ethylene as a co-reactant and hydrogen's effect on catalyst lifetime. To explore the role of H_2 and C_2H_4 in CNT synthesis, we varied the concentration of each independently while fixing acetylene (which, incidentally, is the least expensive of the tested alkynes and a likely target for use on the industrial scale). Consequently, we identified the minimal H_2 and C_2H_4 quantities needed to obtain rapid CNT formation so as to minimize feedstock costs and waste.

As C_2H_4 abundance was reduced, there was a decrease in CNT growth rate[8]. This is consistent with ethylene being a key reactant *in concert with* the alkyne in the CNT formation reaction (Scheme 1a). Note that (1) this co-polymerization proceeds *via* a heterocycle that lends itself to a growing CNT lattice, and (2) the catalyst is oxidized and must be reduced before a subsequent bond-building step can occur. If reduction is required to maintain catalyst activity, the partial pressure of H_2 (pH_2) should have a significant impact on the catalyst lifetime. Indeed, at low pH_2 (<0.31 atm), there was a sharp decrease in the catalyst lifetime, consistent with hydrogen's role as a sustained source of electrons necessary to re-reduce the catalyst after it has been oxidized during bond formation (Scheme 1b). While a minimum amount of hydrogen was necessary to sustain catalyst activity, excess pH_2 reduced the catalyst lifetime. In polyethylene polymerization, an abrupt increase in pH_2 can terminate chain propagation by adding H_2 to the metal catalyst, blocking monomer addition (i.e., Scheme 1c). As such, pH_2 is often used to control the ultimate length of the polymer. Alternatively, termination events could be induced via protonation by water to yield a reductive coupling product (e.g., adding H to the CNT and cleaving the metal-CNT bond), and recent observations of water-induced cleavage of CNT-catalyst contact support this mechanism for termination.

While both ethylene and hydrogen are necessary for efficient CNT growth, we could reduce the delivery rate of each by 20 and 40%, respectively, without sacrificing CNT growth rate, catalyst lifetime, or yield. By delivering the necessary precursors directly, rather than relying on thermal treatment to generate trace quantities of the desired reactant(s), lower quantities of starting materials may be used. Such dramatic reduction in the requisite starting materials' masses will not only reduce waste due to high-volume CNT production, but also translate to cost savings for manufacturers (i.e., incentive to adopt this environmentally conscientious technology).

Scope of problem and comparison to other efforts to address concerns. Global CNT production by CVD is on the order of 300 tons annually. If efficiencies are 3%, then emissions of VOCs due to CNT synthesis could exceed 10,000 tons yr^{-1} today and will rapidly expand with the development of the CNT-based product market (see Plata et al. and references therein for compound-specific emissions quantities and market estimates[4,8]). Currently, the only other "green engineering" efforts include flaming effluents to CO_2 (which only displaces the concern from one of toxicity to one of greenhouse gas impact), reusing effluents for additional CNT production *if and only if* there is demand for more than one batch reaction per day (which is rare), and particle filtration (to minimize CNT or soot particle release potential). Such post-production treatments do not meet the EPA's criteria for Green Chemistry. Here, we provide chemical mechanistic details that were previously absent. Using this knowledge, we proactively design a process where critical alkyne precursors are identified and delivered directly rather than being generated thermally. This offers >50% reduction in energy, 20-40% reduction in feedstock requirement, orders-of-magnitude greenhouse gas and toxic emissions reductions, and >10-fold yield (atom economy) enhancement, all while maintaining product quality and reducing cost[8].



Scheme 1. Chemical effects of ethylene and hydrogen during acetylene-assisted CNT growth. Ethylene may co-react with acetylene to form a metallacycle intermediate (a). Hydrogen may play a dual role regulating the catalyst lifetime, where low partial pressures of H_2 limit catalyst turnover (b) and high partial pressures of H_2 terminate "chain" propagation (c).

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