

Gas-phase production of carbon single-walled nanotubes from carbon monoxide via the HiPco process: A parametric study

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We have demonstrated large-scale production (10 g/day) of high-purity carbon single-walled nanotubes (SWNTs) using a gas-phase chemical-vapor-deposition process we call the HiPco process. SWNTs grow in high-pressure (30–50 atm), high-temperature (900–1100 °C) flowing CO on catalytic clusters of iron. The clusters are formed *in situ*: Fe is added to the gas flow in the form of Fe(CO)₅. Upon heating, the Fe(CO)₅ decomposes and the iron atoms condense into clusters. These clusters serve as catalytic particles upon which SWNT nucleate and grow (in the gas phase) via CO disproportionation: CO+CO⇒CO₂+C(SWNT). SWNT material of up to 97 mol % purity has been produced at rates of up to 450 mg/h. The HiPco process has been studied and optimized with respect to a number of process parameters including temperature, pressure, and catalyst concentration. The behavior of the SWNT yield with respect to various parameters sheds light on the processes that currently limit SWNT production, and suggests ways that the production rate can be increased still further. © 2001 American Vacuum Society. [DOI: 10.1116/1.1380721]

I. INTRODUCTION

Carbon single-walled nanotubes (SWNTs) exhibit many unique and useful physical and chemical properties.¹ Traditional methods for producing macroscopic quantities (mg or more) of SWNTs involve growth from carbon vapor produced either by arc evaporation of metal-doped carbon electrodes^{2–4} or by laser vaporization of metal-doped carbon targets.⁵ SWNTs can also be grown by catalytic decomposition of molecules such as C₂H₄ and CO (Ref. 6) and CH₄ (Ref. 7) on supported metal particles. These methods produce SWNTs in milligram to gram quantities in a few hours. However, many potential applications of SWNTs require kilogram to ton quantities.

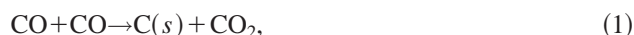
Many groups have investigated gas-phase continuous-flow production of carbon fibers. These studies typically involve passing a mixture of carbon source gas and organometallic catalyst precursor molecules through a heated furnace. The organometallics decompose and react, forming clusters on which carbon fibers nucleate and grow. Endo and co-workers carried out studies of the production of carbon fibers by this method, using mixtures of molecules such as ferrocene and hydrocarbons.⁸ Some of these early studies actually produced small amounts of SWNTs in addition to more plentiful multiwalled carbon nanotubes.^{9–11} Tibbets *et al.* have reported gas-phase synthesis of carbon fibers in heated flowing mixtures of methane or hexane with organometallics such as iron pentacarbonyl [Fe(CO)₅] (Ref. 12) and ferrocene.¹³ Rao and co-workers^{14,15} have investigated the catalytic growth of carbon nanotubes in the gas phase, both by direct pyrolysis of metallocenes and by catalytic decom-

position of hydrocarbons or carbon monoxide in the presence of metallocenes or Fe(CO)₅. Production of SWNTs from mixtures of Fe(CO)₅ with hydrocarbons was reported in some cases.¹⁴ Dresselhaus and co-workers have reported the production of SWNTs in a heated flow of benzene and ferrocene.¹⁶

This group has recently reported initial investigations on the production of SWNTs in high-pressure carbon monoxide.¹⁷ We report here progress in ongoing investigations of this process, in which the catalytic production of SWNTs is induced by the decomposition of Fe(CO)₅ in continuously flowing CO at high pressure and elevated temperature. We designate this method the “HiPco” process (from the words high-pressure CO). Regions of the experimental parameter space in which the HiPco process occurs have been explored, and the production of SWNTs has been studied as a function of temperature, pressure, Fe(CO)₅ concentration, and reactor geometry. The behavior of the SWNT yield with respect to these parameters provides information on the processes that currently limit SWNT production, and suggests ways that the production rate can be increased still further.

II. EXPERIMENT

As reported previously,¹⁷ we have produced SWNTs by flowing CO mixed with a small amount of Fe(CO)₅ through a heated reactor. The products of Fe(CO)₅ thermal decomposition [probably Fe(CO)_n, n=0–4] react to produce iron clusters in the gas phase. These clusters act as nuclei upon which SWNTs nucleate and grow: solid carbon is produced by CO disproportionation (the Boudouard reaction):



which occurs catalytically on the surface of the iron particles.

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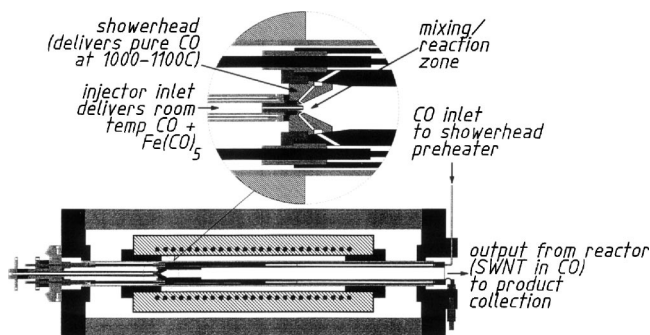


FIG. 1. HiPco reactor, with the mixing/reaction zone shown enlarged.

Figure 1 shows a diagram of our high-pressure reactor. This reactor consists of a 3-in.-diam thin-walled quartz tube surrounded by an electrical heating element, both of which are contained within a thick-walled aluminum cylinder. CO and $\text{Fe}(\text{CO})_5$ flow through the quartz tube. The heating element itself and the space between the quartz tube and the aluminum cylinder's inner wall reside under an atmosphere of argon maintained at slightly higher pressure than that of the CO inside the quartz tube.

Mixtures of $\text{Fe}(\text{CO})_5$ and CO are injected into the reactor through an insulated, air- or water-cooled stainless-steel injector tipped with a copper nozzle. As discussed previously,¹⁷ rapid heating of the CO/ $\text{Fe}(\text{CO})_5$ mixture can enhance the formation of nanotubes. Hence, around the end of the injector was positioned a circle of orifices (the "showerhead"), through which preheated CO was sprayed to mix with and heat the cold flow emerging from the injector nozzle. The showerhead CO preheater consists of a thick-walled graphite tube (1.5 in. i.d., 2.75 in. o.d., 36 in. length), through whose walls have been longitudinally bored six equally spaced 3/8 in. channels. Each of the six channels contains a graphite rod of 1/8 in. diam, which was resistively heated (15–30 Å, 50–200 W per rod) during nanotube production. As shown in Fig. 1, CO for the showerhead was flowed through these channels and was heated by contact with the 1/8 in. graphite rods. The heated CO passes from the 3/8 in. channels into the showerhead orifice circle (also machined from graphite), and passes through the showerhead orifices and into the mixing/reaction zone, as shown. There, it collides and mixes with the cold injector flow emerging from the copper nozzle, which protrudes through the showerhead and into this reaction zone. The temperature of the heated CO passing through the showerhead, T_{SH} , was controlled by varying the current passed through the heating rods, and was measured by thermocouples inserted into thermal wells in the front face of the graphite CO preheater. Note that because the hot showerhead CO mixes with the room-temperature injector flow, the actual reaction temperature will be lower than T_{SH} by a calculable amount.

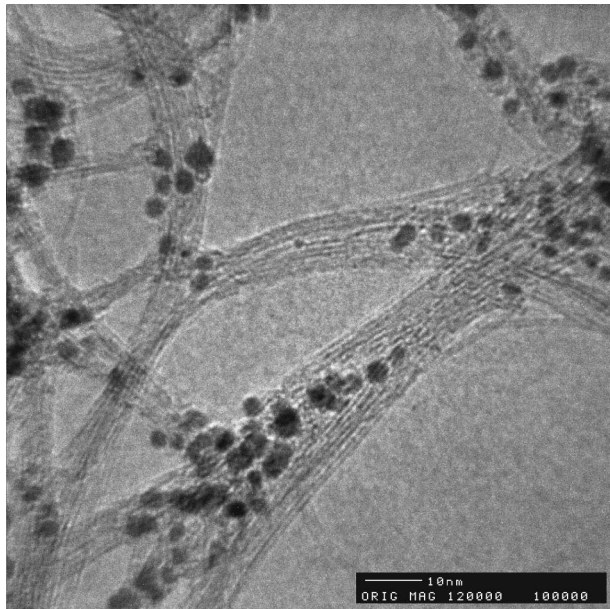
Our highest SWNT production rate was achieved with a showerhead consisting of a circle of orifices distributed equally around a circle, positioned with the orifices about 1 mm away from the injector nozzle, and set at an angle of 30° with respect to the injector flow propagation direction (the

quartz tube axis). The number of orifices in this circle can be varied: we have tried three, six, and eight orifices, all with similar results. It should be noted here that due to the very large number of possible geometries for collision/mixing of gas jets, it is unlikely that our current showerhead/injector geometry represents the best design to accomplish $\text{Fe}(\text{CO})_5$ heating and SWNT formation.

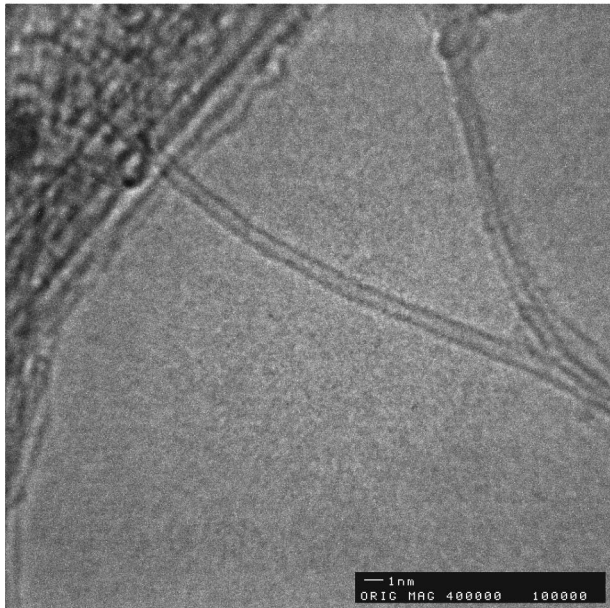
$\text{Fe}(\text{CO})_5$ is introduced into the injector flow by passing a measured fraction of the CO flow through a liquid- $\text{Fe}(\text{CO})_5$ -filled bubbler maintained at room temperature [where the vapor pressure of $\text{Fe}(\text{CO})_5$ is approximately 28 Torr]. Inside the 1.5 in. inner bore of the graphite heater, the CO/ $\text{Fe}(\text{CO})_5$ mixture is rapidly heated and mixed with the showerhead CO: the $\text{Fe}(\text{CO})_5$ decomposes and forms Fe clusters, which spawn and grow SWNTs as discussed above. The SWNTs and iron particles are carried out of the reactor by the hot, dense gas flow, into the product collection apparatus. There, the CO flow passes through a series of filters and cooled surfaces, upon which the SWNTs condense. Once purged of SWNTs the CO gas passes through absorption beds containing NaOH and a molecular sieve (type 3A), which remove the CO_2 product of reaction (1) and H_2O , respectively. The CO is then recirculated back through the gas flow system and reactor using a compressor (Fluitron, Y5-200); our reactor flow system thus constitutes a closed loop through which CO is continuously recycled. The gas flowing in the system can be analyzed with a gas-chromatography/mass spectrometry analysis system (Varian, Saturn 2000), which is used to measure product CO_2 concentration in the reactor exhaust stream, carbonyl concentration in the reactant stream, and concentrations of trace gases such as H_2 .

III. RESULTS

The reaction product is a loose black felt consisting of SWNT ropes interspersed with carbon-overcoated metal particles. This material is analyzed with scanning electron microscopy (SEM), transmission electron microscopy (TEM), and energy-dispersed x-ray (EDX) spectroscopy to determine product morphology and elemental composition. The primary emphasis of the current research has been on optimizing the mass yield of SWNTs per unit time with respect to available experimental variables. The behavior of the SWNT production with respect to such parameters also yields insight into the details of the SWNT production mechanism. Our standard running conditions are 450 psi (30 atm) of CO pressure and 1050 °C reactor (showerhead) temperature. CO is flowed through the showerhead preheater at 8.4 L/min volume flow [250 standard liters per minute (slm) mass flow], while CO containing 0.25 Torr of $\text{Fe}(\text{CO})_5$ vapor is flowed through the injector at 1.4 L/min (42 slm). The total flow of CO through the reactor is thus 9.8 L/min, and the ratio of showerhead flow to injector flow is 6:1. Typical run times are 24–72 h. Under these conditions, our reactor produces SWNT material at a rate of approximately 450 mg/h, or 10.8 g/day.



(a)



(b)

FIG. 2. (a) TEM image of SWNT material produced by the HiPco process. (b) High-resolution TEM image of a single HiPco nanotube.

Figure 2 shows TEM images of typical SWNT product material. This material consists of ropes of SWNTs interspersed with small (2–5 nm), denser particles or clusters of particles. As discussed in the previous work,¹⁷ the particles in the SEM and TEM images are readily identified as clusters of iron atoms interspersed with the SWNT ropes, presumably the final form of the iron present in the $\text{Fe}(\text{CO})_5$ precursor molecules. Our TEM images suggest, and high-resolution TEM images confirm,¹⁸ that the sidewalls of these SWNTs are essentially free of amorphous-carbon overcoating. This is in contrast to SWNTs produced in the laser vaporization or arc discharge methods, which typically have

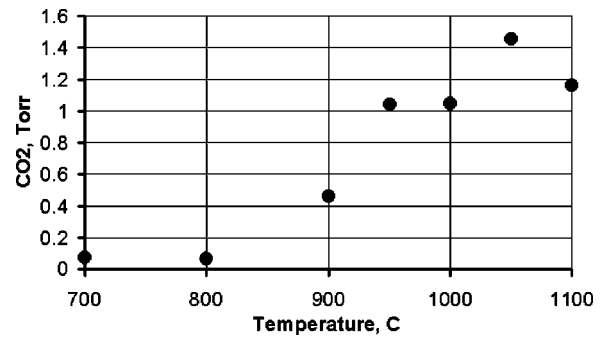


FIG. 3. CO₂ yield vs reactor (showerhead) temperature. Reaction conditions: pressure, 30 atm; showerhead flow, 8.4 L/min (252 slm); injector flow, 1.4 L/min (42 slm); and $\text{Fe}(\text{CO})_5$ concentration (in injector flow), 0.25 Torr.

substantial overcoatings of amorphous carbon that must be removed in subsequent processing steps. EDX spectroscopy shows that the HiPco product typically consists of 97 mol % of carbon and 3 mol % of iron. Because organometallics are used to nucleate the SWNTs produced, there will always be some nonzero density of metal particles in raw HiPco SWNT material, although increased efficiency in SWNT nucleation and/or growth can, in principle, make this concentration arbitrarily small (see the discussion below).

For maximizing SWNT production, it was found that real-time measurement of the concentration of CO₂ in the gas flow exiting the reactor was a valuable tool. By varying experimental parameters while monitoring CO₂ production, it is possible to maximize CO₂ (and, hence, carbon) production with respect to any parameter. The maximum CO₂ production will correspond to the maximum production of nanotubes provided that the carbon product is in the form of nanotubes. This could be confirmed by analyzing (with SEM and TEM) the product from extended runs using the optimized parameters.

SWNT production was studied as a function of reaction temperature. Figure 3 gives the concentrations of CO₂ in the exhaust stream measured for various showerhead temperatures. The production of SWNTs is very small at showerhead temperatures below 800 °C, and appears to turn on between 850 and 900 °C. By 950 °C the production rate is beginning to level out. SWNT production reaches a maximum at 1050 °C, and begins to fall off at higher temperatures.

CO₂ production was also investigated as a function of the concentration of $\text{Fe}(\text{CO})_5$ in the injector gas flow. Figure 4 shows a typical result: the relative concentration of CO₂ produced as $\text{Fe}(\text{CO})_5$ concentration was varied, at a pressure of 45 atm. It was found that CO₂ production first increases approximately linearly with increasing $\text{Fe}(\text{CO})_5$ concentration, but that it eventually levels off. As the $\text{Fe}(\text{CO})_5$ concentration is increased further, the CO₂ production actually decreases, and only increases again at much higher concentrations. This qualitative behavior was observed for all temperature, pressure, gas flow, and heating/mixing conditions investigated, and appears quite general. SEM and TEM analysis of the SWNTs produced at very high $\text{Fe}(\text{CO})_5$ concentrations indicated that a much larger fraction of the

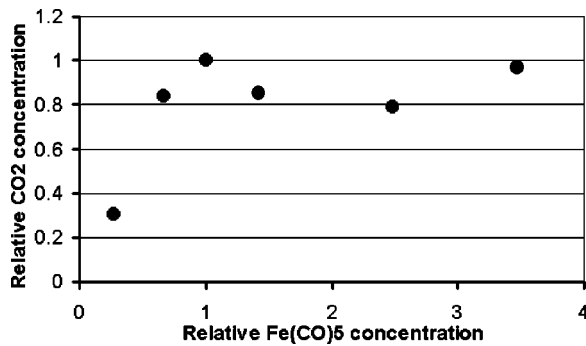


FIG. 4. CO₂ yield vs Fe(CO)₅ concentration in injector flow. Reaction conditions: 45 atm, 1050 °C, 4.2 L/min showerhead flow, and 0.7 L/min injector flow. Values are shown relative to Fe(CO)₅ and CO₂ concentrations at maximum SWNT yield. (0.38 and 1.4 Torr, respectively).

carbon was present as amorphous carbon or as graphitic, fullerene-like partial shells associated with the larger metal particles, rather than as additional SWNTs. Thus, it appears that the production of SWNTs is optimum at the initial maximum in the curve of CO₂ vs Fe(CO)₅; excess iron over this maximum does not give more SWNTs, but instead appears to retard the growth of SWNTs [the decrease in CO₂ as Fe(CO)₅ is increased], and eventually gives much carbon in undesirable forms at very high concentrations.

SWNT production was also studied as a function of reaction pressure. At any given pressure, the curve of CO₂ produced versus Fe(CO)₅ input has qualitatively the same appearance as that shown in Fig. 4. The maximum CO₂ in the curve of CO₂ vs Fe(CO)₅, and the level of Fe(CO)₅ needed to produce that level of CO₂, were found to increase as pressure was increased up to the maximum pressure investigated, 45 atm. These results are shown in Fig. 5 (normalized to our ‘standard’ running condition, 30 atm). Both maximum CO₂ and maximum Fe(CO)₅ were observed to be approximately linear in CO pressure.

It has been suggested that the addition of H₂ can accelerate reaction (1).¹⁹ We found that small amounts of H₂, 10–30 Torr in 30 atm of CO, gave no effect, while larger amounts, 100–360 Torr, reduced the rate of nanotube pro-

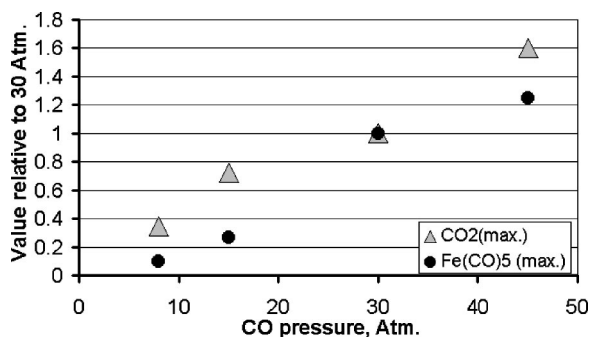


FIG. 5. Maximum CO₂ produced, and concentration of Fe(CO)₅ that produces maximum CO₂ vs CO pressure. Values are shown relative to Fe(CO)₅ and CO₂ concentrations at maximum SWNT yield at 30 atm (0.3 and 1 Torr, respectively).

duction. While still preliminary, our results to date suggest that the HiPco process works best using pure CO as the reactant gas.

IV. DISCUSSION

Carbon SWNTs have been observed to nucleate and grow from small metal clusters on supported catalysts.⁶ We propose that gas-phase nucleation and growth of SWNTs occur in the HiPco process by an analogous mechanism: the iron carbonyl molecules decompose at high temperature to release their Fe atoms, which cluster together to form small catalytic particles from which SWNTs nucleate and grow, all in the gas phase.

Gas-phase iron pentacarbonyl decomposes rapidly above 300 °C.²⁰ Reaction (1) occurs at a significant rate only at temperatures above 500 °C.²¹ Thus, the rate at which the gas mixture is heated through the temperature range of 300–500 °C will be important in determining the outcome of this process. If this rate is too slow, the clusters may grow too big to nucleate nanotubes. Instead, they would simply overcoat with carbon.⁶ On the other hand, the per-atom binding energy for small iron clusters (2–10 atoms) is typically 1.5–2.5 eV, much less than the bulk value of 4.28 eV.²² At temperatures where SWNT formation occurs, such small clusters would tend to evaporate quickly. Thus, heating the gas mixture too quickly might curtail the formation of SWNTs.

Another important issue is the mechanism by which nanotube growth ceases. The particles in the product material are 3–5 nm in diameter, substantially larger than SWNT diameters (~1 nm), suggesting that the particles continue to grow even after nucleating a tube. The additional accreting iron atoms could come from several sources: direct gas-phase collisions with other Fe atoms, Fe clusters, or Fe(CO)₅ molecules (by adsorption/decomposition), or by adsorption of Fe atoms, clusters or adsorption/decomposition of Fe(CO)₅ molecules onto the growing nanotube followed by iron atom diffusion to the particle at the end. As a catalytic particle grows larger, more and more catalytically active surface area is created, and eventually a graphitic shell or other structures not associated with the growing nanotube will begin to form on the particle. Eventually the particle will become covered with carbon, preventing the diffusion of additional CO to the particle’s surface and terminating further nanotube growth. Another potential contributing factor to cessation of growth of a nanotube is evaporation of its attached cluster. As discussed above, small iron clusters (fewer than 10 atoms) will tend to evaporate quickly at temperatures where SWNT growth is rapid. The cessation of growth of the nucleated nanotubes would thus derive from a combination of these two effects: some nanotubes would stop growing when their attached catalyst particle evaporates or grows too small, some would stop when their catalyst cluster grows too large.

Our observed temperature dependence of SWNT production is consistent with this picture. Both the decomposition of Fe(CO)₅ and the rate of reaction (1) to form carbon become appreciable only at high temperatures, so one expects that the SWNT production rate will initially increase as the

temperature is increased. At temperatures above 1050 °C the SWNT production rate begins to decline. Apparently, at higher temperatures the rate of evaporation of small, active catalytic clusters is fast enough that growth of SWNTs is strongly curtailed, overcoming gains in growth arising from faster Fe(CO)₅ decomposition and a greater rate for reaction (1).

SWNT yield as a function of Fe(CO)₅ concentration can also be understood in terms of our model of SWNT growth. At low concentrations of iron, accretion of Fe onto already growing nanotubes is slow enough that the faster death of growing nanotubes is more than offset by the nucleation of additional nanotubes, as Fe concentration increases. The addition of more iron thus results simply in the formation of proportionally more nanotubes. As Fe(CO)₅ concentration is increased further, we see a slowing down in the rate of SWNT formation increase, and at sufficiently high concentrations the differential SWNT yield can actually be negative. This behavior could indicate a concentration regime in which diminished nanotube production due to Fe accretion onto growing nanotubes exceeds increased production from formation of additional catalytic particles. Above a critical “turnover” Fe(CO)₅ concentration, the rate of Fe accretion becomes large enough, and the resultant shortening of a nanotube’s growth time severe enough, that the overall yield of SWNTs decreases with increasing Fe(CO)₅ concentration. Eventually, at very high iron concentrations, the yield of carbon turns around and begins increasing again, but as mentioned, the extra carbon is in forms other than nanotubes.

This behavior is qualitatively independent of pressure. Quantitatively, we observe that the turnover concentration increases as pressure increases. Higher CO pressure may simply cause a greater SWNT growth rate from a catalytic cluster, allowing the SWNT to grow longer before its attached particle is deactivated. Alternately, higher CO pressure may give a higher nucleation rate of nanotubes from very small clusters, so that more small clusters nucleate nanotubes and fewer collide with and adsorb onto previously nucleated tubes.

Our results suggest that limits on SWNT production arise primarily from inactivation of Fe catalyst particles once they become too large. One way to circumvent this problem would be to provide for the rapid sequestering of all Fe atoms into clusters. This could be done by providing a “nucleating agent” in addition to the iron, which would rapidly absorb Fe atoms. Examples of such agents are atoms of heavier metals such as molybdenum, ruthenium, and tungsten [which could be introduced in the form of their respective volatile carbonyls along with Fe(CO)₅]. These elements all have much higher binding energies with Fe than do Fe atoms with each other,²³ and also have high catalytic activity for reaction (1).²⁴ In addition, the current setup provides for Fe cluster formation and SWNT nucleation and growth all in the same region of space, at the same temperature. This is clearly nonoptimal, since temperatures suitable for nanotube growth are too high for rapid, efficient iron cluster formation. This problem could be solved with a multiple-temperature-

zone showerhead/injector mixing region. All of these schemes are being investigated in ongoing studies in our laboratory.

V. CONCLUSIONS

We have demonstrated bulk production of SWNTs in the gas phase by the HiPCO process. This process has been investigated with respect to process parameters including temperature, CO pressure, and catalyst concentration. Our current production apparatus can produce nanotubes at rates up to 0.45 g/h, or 10.8 g per day. The main limit on nanotube production appears to be cessation of growth due to accretion of Fe atoms onto growing nanotubes. Several schemes to overcome this limitation are currently under investigation.

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