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The Infinite Possible Growth Ambients that Support Single-Wall Carbon Nanotube Forest Growth

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We report the virtually infinite possible carbon feedstocks which support the highly efficient growth of single-wall carbon nanotubes (SWCNTs) using on the water-assisted chemical vapor deposition method. Our results demonstrate that diverse varieties of carbon feedstocks, in the form of hydrocarbons, spanning saturated rings (e.g. trans-deca-hydronaphthalene), saturated chains (e.g. propane), unsaturated rings (e.g. dicyclopentadiene), and unsaturated chains (e.g. ethylene) could be used as a carbon feedstocks with SWCNT forests with heights exceeding 100 ums. Further, we found that all the resultant SWCNTs possessed similar average diameter indicating that the diameter was mainly determined by the catalyst rather than the carbon feedstock within this synthetic system. A demonstration of the generality was the synthesis of a carbon nanotube forest from a highly unorthodox combination of gases where trans-decahydronaphthalene acted as the carbon feedstock and benzaldehyde acted as the growth enhancer.

The development of scientific research and industrial applications for carbon nanotubes (CNTs) has been primarily limited by its synthesis, and as a result, immense research, encompassing the control of the structure and underlying growth mechanism, has been invested over the past two decades to improve growth control, e.g. efficiency[1–8], crystallinity[9–13], and chirality[14,15]. Apt examples include the water-assisted chemical vapor deposition (CVD) method to improve growth efficiency[2], floating catalyst CVD method to improve crystallinity[11], and catalyst gas pretreatments for metallic selective growth[14,15].

Post-synthetic techniques have also been developed to improve the purity or selectivity of the CNTs. For example, density gradient ultracentrifugation combined with the appropriate surfactant enables effective individualization of single-wall carbon nanotube (SWCNT) for the separation of metallic versus semiconducting SWCNTs as well as the enrichment of a single-chirality, (6,5)[16]. In addition, numerous post-synthetic processes have been developed for the purification of CNTs ranging from chemical oxidation, such as gas phase, liquid phase, and electrochemical oxidation, to physical-based purification, such as filtration, centrifugation, functionalization, and high temperatures annealing and combinations[17–19].

In the synthesis of CNTs by the CVD process, numerous carbon feedstocks have been applied, often in the form of hydrocarbons, such as methane[20,21], acetylene[20,29,30], and ethylene[2,20] and even anthracene[21]. Further, each synthetic method, i.e. thermal CVD, plasma-enhanced CVD, floating catalyst CVD, laser ablation, seemed to show preferences on the carbon feedstock[22–24]. For example, in plasma-enhanced CVD, methane or other low molecular-weight carbon feedstocks are preferred[22], while for floating catalyst CVD, which is carried out at higher temperatures, cyclic aromatic hydrocarbons, *e.g.* toluene, xylene, and benzene are most commonly used due to their high decomposition temperatures[23,24]. For thermal CVD, acetylene and ethylene have become the commonly-used carbon feedstocks due to their high reactivities. However, carbon feedstocks are not limited to the previously listed examples, and some research has even shown that natural derivatives of carbon, such as camphor, or even tire rubber can be used as a carbon feedstock for CNT synthesis[25].

Beyond the ability to support CNT growth, the choice of the carbon feedstock has been reported to have great consequences on the amount of CNTs which can be grown from a catalyst system, ie yield, and, in some growth systems, the structure as well[1–8,20,21,26,27]. For example, a number of reports have demonstrated a clear dependence of the CNT structure on the choice of carbon feedstock and have found clear preferences in forming single-wall carbon nanotube (SWCNT) or multi-walled carbon nanotubes[20,21,26]. Similarly, carbon feedstocks containing

oxygen, such as alcohol, have reported to dramatically increase catalyst efficiency to form SWCNT forests[27], and further, the use of CO enabled the first large scale mass production of SWCNTs[28].

Although many carbon feedstocks have been shown to synthesize CNTs, not many have shown to grow CNTs in high efficiency, where nearly all catalysts are active and produce SWCNTs at a fast rate for an extended time. For SWCNTs grown from catalyst deposited onto a substrate, high efficiency can be observed in the growth of "forests" where the high density CNTs, from high catalyst activity, self-assemble into vertically aligned ensemble. High efficiency is even more obvious with the growth of CNT forests exceeding 100 um to mm-scale meaning that the growth rate was relatively fast with an catalyst lifetime spanning the growth time. In this regard, the variety of carbon feedstocks reported to support the growth of vertically aligned forests have been limited to only a few hydrocarbons that are known to possess high chemical reactivities, i.e. acetylene, ethylene. Acetylene is a widely popular choice for highly efficient SWCNT synthesis because of its high reactivity and is the only reported hydrocarbon to grow SWCNTs efficiently into forests without the use of a "promoting gas/growth enhancer". In fact, previous reports have demonstrated that acetylene exhibited an order of magnitude higher efficiency than other hydrocarbons[29], was the primary component in CNT growth[30], and possessed an exceptionally low activation energy[31].

Through the addition of a proportionately small amount of promoting gas, (growth enhancer), which contains oxygen, the set of useable hydrocarbon feedstocks to support high efficiency CNT growth, and therefore forest, was shown to greatly expand[32]. The first use of growth enhancer, water, used ethylene as the carbon feedstock to synthesize a 2.5 mm high vertically aligned forest in a 10 minutes growth time[2]. Since that report, intense research have been invoked to further expand the gas systems which could support highly efficient CNT growth. For example, it was demonstrated that any molecule that contained oxygen, such as alcohols, ethers, esters, ketones, aldehydes, and even carbon dioxide, could act as a growth enhancer similar to that of water[32]. However, the choice of carbon feedstock was limited to acetylene or ethylene, and it is not still known if other hydrocarbon sources can serve as carbon feedstocks for the highly efficient CNT growth. SWCNT forests are becoming increasingly important because they have been shown to possess advantageous properties, such as high specific surface area, aspect ratio, and extremely high carbon purity and have been used to develop rational applications, such as mechanically durable conductive rubbers[33] and high voltage-power super-capacitors[34]. Moreover, water-assisted CVD technique has now been developed into a pilot production plant, and thus true industrial-scale mass production of SWCNT forests is expected to be realized within a few years, and with it, the simultaneous achievement of mainstream commercial CNT applications.

In this paper, we have studied the adaptability of many carbon feedstocks, in the form of hydrocarbons, for highly efficient SWCNT forest growth with the aid of water as the growth enhancer. We have found that many hydrocarbon sources, spanning saturated rings (e.g. trans-deca-hydronaphthalene), saturated chains (e.g. propane), unsaturated rings (e.g. dicyclopentadiene), and unsaturated chains (e.g. ethylene) could be used as a carbon feedstocks to synthesize SWCNT forests with heights exceeding 100 ums. Interestingly, we found that all the resulting SWCNTs from the various carbon feedstocks were similar in average diameter which meant that the diameter was mainly determined by the catalyst rather than the carbon feedstock for this synthetic system. On the contrary, the carbon feedstocks showed a great influence on the crystallinity of the CNTs where highly active carbon sources were advantageous because only a small input level was required to grow similar yields of CNTs resulting in higher ratios of the graphitic "G-band" to disorder "D-band" by Raman spectroscopy. When our results are combined with previous

other results with growth enhancers[32,35], we propose that there are virtually an infinite number of carbon feedstock-growth enhancer combinations suitable to support SWCNT growth provided that the carbon feedstock does not contain oxygen and a growth enhancer does contain oxygen. This was demonstrated by the synthesis of a CNT forest using a highly unorthodox combination of gases where trans-decahydronaphthalene acted as the carbon feedstock and benzaldehyde acted as the growth enhancer.

Results

First, we demonstrate that any hydrocarbon source not containing oxygen while containing at least two carbon atoms can be used as a carbon feedstock to synthesize SWCNT forests by water-assisted CVD. Water-assisted CVD (Super-growth CVD) was used to represent CVD methods in general because the use of water (or growth enhancer) broadened the usable feedstock concentrations to allow higher growth yields. It should be noted that for forests, "yield" can be expressed as CNT forest weight per substrate area and is primarily determined by mass density and height. To encompass the broadest set of carbon feedstocks, we classified the carbon feedstocks into four general groups: saturated rings, saturated chains, unsaturated and aromatic rings, and unsaturated chains and chose several from each category (Table 1). Specifically, this included trans-decahydronaphthalene (TDN), methane, propane, butane, n-hexane, dicyclopentadiene, 1,3-butadiene, ethylene, and acetylene. As a result, we implemented growth using a number of uncommon carbon feedstocks. We would like to note that hydrocarbons containing heteroatoms, particularly oxygen, were purposely excluded because our previous studies showed that these sources were not suited for high yield[32]. For all experiments, we used a standard Al_2O_3/Fe catalyst (40 nm/1.5 nm) prepared by sequential sputtering that was well-established to grow SWCNT forests with high yield. All syntheses were performed using a 1″ fully-automated CVD system equipped with an exchange chamber to enable the numerous (~2000) required syntheses with a controlled and stable ambient. The large number of syntheses resulted from the sequential optimization of the growth temperature, carbon feedstock level, and growth enhancer level for each carbon feedstock as described below. As per the standard Super-growth CVD process, SWCNT forests were synthesized with a C_2H_4 carbon feedstock (~100 sccm), water (50 to 500 ppm) growth enhancer, and He as a carrier gas (total flow 1 liter per minute) with a growth time of 10 minutes. The formation of nanoparticles for all cases was performed under the same conditions, He/H_2:1/9 and temperature, 750°C, to eliminate the catalyst formation step as a variable, then the temperature was adjusted to the growth temperature ranging from 725 to 900°C. The growth temperature and water level were optimized at a fixed specific hydrocarbon flow rate (for highly active feedstocks, the flow rates were intentionally lowered). To account for the differences in hydrocarbon reactivities, the carbon

Table 1 | Four categories of the investigated carbon feedstocks

	Ring	Chain
Saturated	trans-decahydronaphthalene (t-DN) : C10H18 t-DN	Methane: CH4 Propane : C3H8 Butane: C4H10 n-Hexane : C6H14 Methane Propane Butane Hexane
Unsaturated	p-Xylene : C8H10 di-cyclo-pentadiene: C10H12 p-Xylene di-cyclo-pentadiene	Acetylene : C2H2 Ethylene : C2H4 1,3-Butadiene : C4H6 Acetylene Ethylene Butadiene

feedstock concentrations (flow rate range) were tuned as to avoid the formation of excessive amounts of soot and tar from the decomposed hydrocarbon while also supporting the highly efficient growth of forests. Therefore, in total about 2000 CVD processes were required. It should be noted that for nearly all carbon feedstocks, particularly highly reactive, when an excessive amount is input, the catalyst will terminate more quickly resulting in lower purities, i.e. higher levels of carbonaceous impurities[36,37]. Among these four groups, the unsaturated chain category exhibited the highest reactivity, so the input levels were lowest.

As shown in Fig. 1, we showed that we could grow SWCNT forests with heights far exceeding 100 um from all the carbon feedstocks with the exception of methane. Acteylene showed the highest reactivity, ie. highest yield with lowest input level, but generally, the yields could be increased to the level of acetylene by increasing the input level for all varieties of hydrocarbon-based carbon feedstocks. These results clearly show that a wide range of hydrocarbons can be used as the carbon feedstock with the use of a growth enhancer. We would like to note that we could even grow CNT forests from hydrocarbon sources, such as dicyclopentadiene which is a large molecule containing over 10 carbon atoms. Recent carbon nanotube studies have shown that CNTs precipitate from carbon pairs at the catalyst, which may explain why acetylene has been shown be the primary component for CNT growth[30]. This mechanism may explain why methane was not suitable for highly efficient growth within this growth system. In general, these results showed that essentially any carbon feedstock containing at least two carbon atoms could be used to grow SWCNT forest with high yield.

We analyzed all the grown SWCNT forests from Fig. 1 and found that the SWCNTs were of similar quality and structure. SWCNT selectivity was characterized by transmission electron microscope (TEM) observation. The average and distribution of diameter for the SWCNT forests was analyzed by both the conversion of the S_{11} absorbance band location (measured by Fourier Transform Infrared (FT-IR) spectroscopy) to diameter by the "Kataura plot"[28] and transmission electron microscope (TEM) observation (Supporting information). We found that each of the forests were primarily SWCNTs (>90%) with small variance which we suspect resulted from the elevated growth temperatures. Interestingly, we found that the average diameter for the SWCNTs grown from different carbon

feedstocks fell within a very similar range from 2.5 to 3.1 nm (Table 2). Each of the distributions was fairly wide ranging from ~1 nm to above 4 nm. Both the FTIR data and TEM data agree on the similarity of the average diameters; however, slight variation is observed in the FTIR, which only detects SWCNTs, in the cases where double-walled CNTs were detected by TEM. In addition, the bulk forest densities as measured by the quotient of the mass and volume fell within a small range between 0.028 to 0.046 g/cm³. We would like to note that forests grow by our standard Super-growth technique using ethylene and water possesses an average diameter of ~3.0 nm and forest mass density of ~0.04 g/cm³. These results demonstrate that we could grow SWCNTs using a wide range of carbon feedstocks, and regardless of the carbon feedstock, the size and density was determined by the catalyst system. These results imply that when properly tuned, the catalyst activity can be increased to a value similar to that of ethylene which was reported as 84%[38]. This would mean that nearly all the catalyst can be activated. Raman spectroscopy characterization of the radial breathing mode (RBM) profiles showed very similar RBM profiles with 130, 165, and 230 [cm⁻¹] for all carbon feedstocks (Fig. 2). This is in agreement that CNTs are SWCNTs and similar average diameter. TEM observation, supported these results by confirming that the forests, grown from all carbon feedstocks, were primary composed of SWCNTs and with similar diameter (Fig. 3). We do note a difference in the RBM profile for xylene which we attribute to the higher required process temperature.

While the average size of the CNT forest being similar, the crystallinity based on the G-band (1590 cm⁻¹) to D-band (1340 cm⁻¹) (G/D-ratio) intensity ratios as measured by Raman spectroscopy varied from 5.7 to 15 among the different carbon feedstocks. This result must be treated with great care as the input level varied among carbon feedstocks and could influence the G/D-ratio. In order to understand this phenomenon more clearly, we plotted the yield versus carbon feedstock concentration (as defined as the number of carbon atoms per time), and both the carbon feedstock concentration and forest yield (as defined previously as the mass of the forest per substrate area) versus G/D-ratio. First, we could clearly see that the effect of carbon feedstock concentration on both the G/D and the yield (Fig. 4 a, b). However, clear opposing trends emerged as function of the carbon feedstock concentration where the G/D-ratio
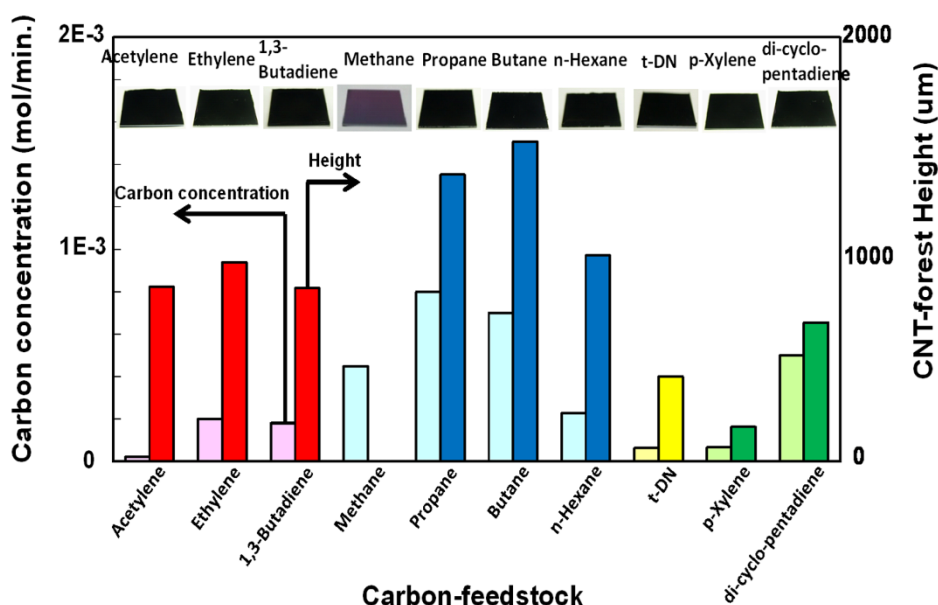

Figure 1 | Carbon nanotube synthesis with carbon feedstock concentration and CNT forest from each of the ten feedstocks. (inset: Digital images of the individual CNT forests).

C-source		C	H/C	Yield (mg/cm2)	Height (um)	G/D	Density (g/cm3)	Diameter (nm)
Acetylene	H–C≡C–H	2	1.0	3.23	823	10.8	0.039	3.1
Ethylene		2	2.0	3.09	938	12.4	0.033	3.0
1,3-Butadiene		4	1.5	3.29	817	15	0.040	2.5
Propane		3	2.7	4.67	1352	5.4	0.035	2.8
Butane		4	2.5	4.98	1508	7.8	0.033	2.9
n-Hexane		6	2.3	2.75	971	6.2	0.028	3.0
t-DN		10	1.8	1.36	400	15.2	0.034	2.8
p-Xylene		8	1.25	0.76	163	5.7	0.046	-
di-cyclo-pentadiene		10	1.2	2.03	655	14.0	0.031	-

Table 2 | Characterization comparison table for the investigated carbon feedstocks

decreased while the yield increased. Therefore, when the G/D-ratio was plotted versus yield, we again observed an inverse relationship (Fig. 4c). In general, this opposing trend is in agreement with previous reports regarding the relation of G/D-ratio and yield[13]. One can conclude from these results that a carbon feedstock with high reactivity requires less input to synthesize a determined amount of CNTs which can result in higher G/D-ratios.

Discussion

Our results, herein, demonstrated that highly efficient growth of SWCNTs could be achieved through a wide range of growth ambients. The growth mechanism of highly efficient SWCNT growth is based on the concept that the very small concentration of growth enhancer removes the carbonaceous coating of the catalyst to maintain catalyst activity. Based on this mechanism, it has been proposed that many growth enhancers, (alcohols (ethanol), ethers (tetrahydrofuran), esters (methylbenzoate), aldehydes (benzoaldehyde), ketones (acetone), a native oxide of carbon (CO_2)) could be used to grow SWCNTs forests with acetylene and ethylene[32]. Now, in this work we have shown that we could grow SWCNT forests with diverse carbon feedstocks spanning saturated chains, saturated rings, unsaturated chains, and unsaturated rings. When these two results are combined, it means that nearly infinite growth ambients exist that can produce CNTs. The
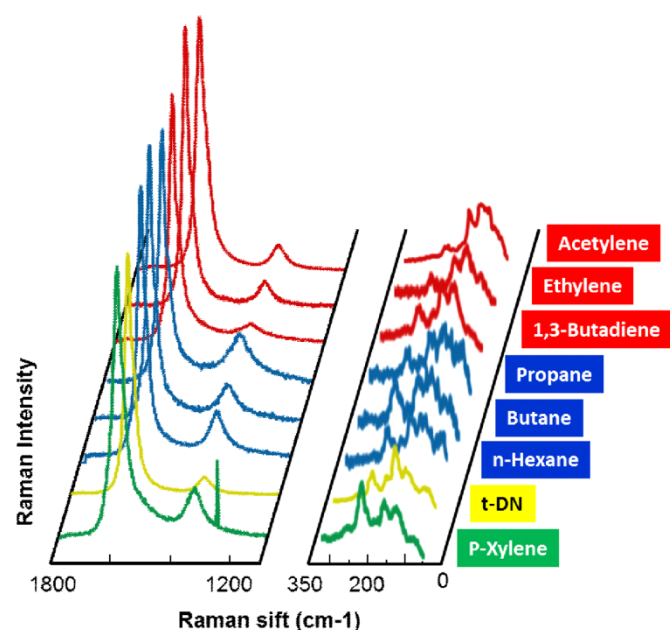

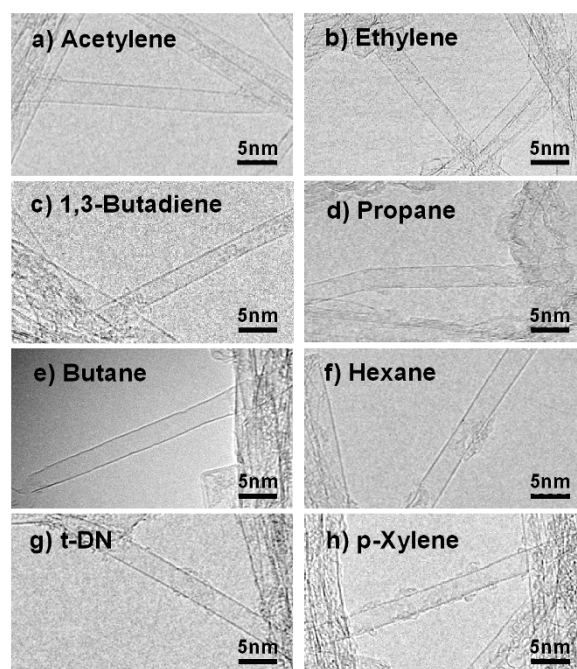Figure 2 | **Raman spectra of the SWCNTs grown from the various carbon feedstocks.**

Figure 3 | **Transmission electron microscopy images of the eight carbon sources.** (a) acetylene, (b) ethylene, (c) 1,3-butadiene, (d) propane, (e) butane, (f) n-hexane, (g) *trans*-decahydronaphthalene (t-DN), (h) *para*-xylene (p-xylene).
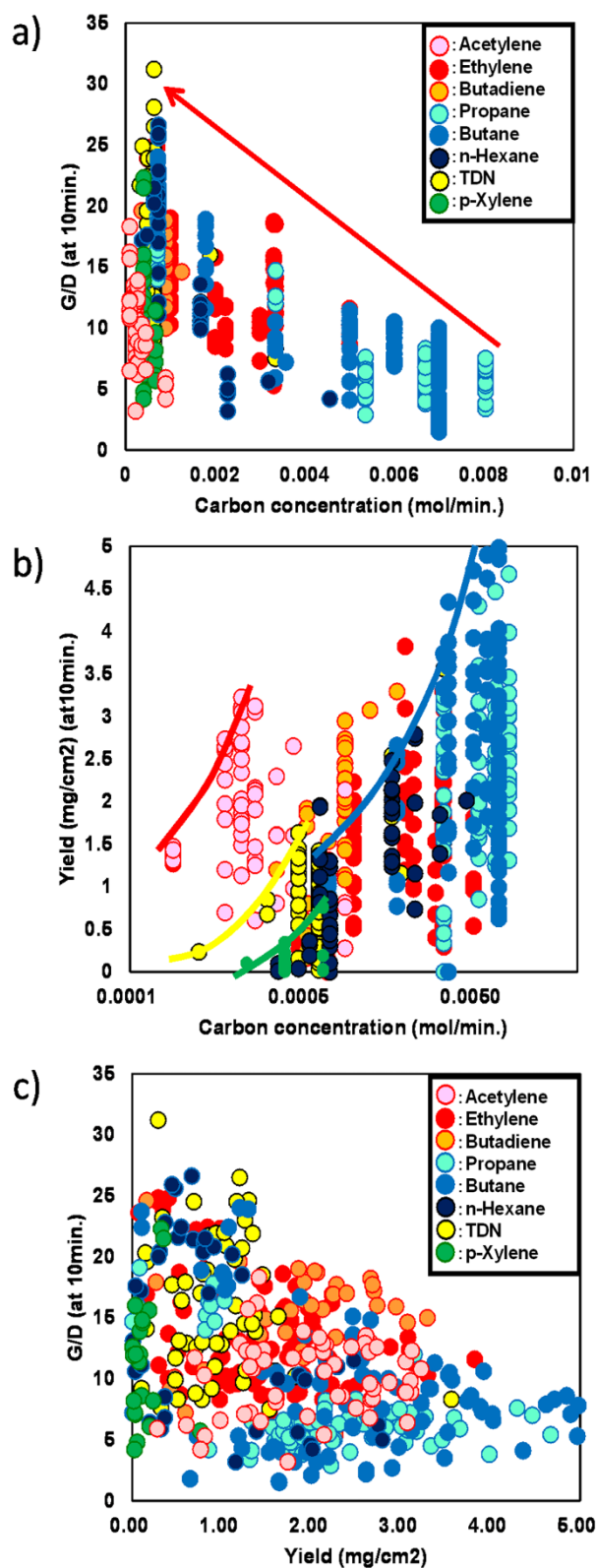
Figure 4 | Comparisons of the SWCNT structure. (a) Raman G/D-ratio as a function of carbon feedstock concentration. (b) SWCNT yield as a function of carbon feedstock concentration. (c) Raman G/D-ratio as a function of SWCNT yield.

basic guidelines are 1) carbon source does not contain oxygen, and 2) a growth enhancer must contain oxygen. It is important to tune the growth enhancer concentration which is far below (∼1/1000) that of the carbon feedstock. Finally, to test the generality of this

proposal, we synthesized a CNT forest from a highly unorthodox combination of gas sources: trans-decahydronaphthalene (TDN) and benzaldehyde (BA). Here, TDN does not contain oxygen and thus acts as the carbon source while BA contains oxygen and acts as the growth enhancer, so the concentration of BA was ∼1/1500 the level of TDN. Despite being unusual for CNT synthesis supported gases, the remaining growth conditions, such as temperature, flow rates, etc were similar to the standard process (750C, 1000 sccm, etc). In fact, the synthesis of this forests to support this proposal required only two CVD processes to adjust the relative level of TDN to BA. It should be noted that CNT forests could not be grown by the individual gases alone. It should be noted that this forest was synthesized as a demonstration of generality that the number of possible growth ambients was nearly infinite, the growth conditions were not optimized, so the sample was characterized. We do know that from the characterization of TDN with water case that the average diameter (∼2.8 nm) and SWCNT selectivity (∼93%) were similar to that of ethylene and water. With the exception of the effect of the growth enhancer on the CNT structure[35], we would expect that a similar average diameter and selectivity in this case. This result is in perfect agreement with our proposed model clearly demonstrating that CNTs could be grown from unlimited possibilities for future CNT growth studies.

In summary, we have expanded the opportunities for highly efficient SWCNT synthesis where in place of conventional hydrocarbon feedstocks, such as acetylene and ethylene, we demonstrated that diverse varieties of hydrocarbon-based carbon feedstocks (saturated rings, saturated chains, unsaturated and aromatic rings, and unsaturated chains) can produce SWCNT forests. We believe that this expansion is important to the community because these results support the mass production of SWCNT from more economical carbon feedstocks and CNT forest growth from unusual carbon feedstocks. Among the observed structural property variations, our results show that the average diameter and forest density were mainly determined by the catalyst while the yield was determined by the growth ambient, i.e. carbon feedstock. Through this work, we demonstrated that essentially an infinite number of growth gas combinations (carbon feedstock and growth enhancer) could support CNT growth provided they follow the simple rules where the carbon source contains no oxygen and the growth enhancer contains oxygen. It would be very interesting subject to investigate what combination would be most efficient or what combination would produce the highest quality.

Methods

SWCNT synthesis. We used a standard Al_2O_3/Fe catalyst (40 nm/1.5 nm) prepared by sputtering that was well-established to grow SWCNT forests with high yield. All syntheses were performed using a 1″ fully-automated CVD system equipped with an exchange chamber to enable the numerous (∼2000) required syntheses with a controlled and stable ambient. In the standard Super-growth process, SWCNT forests were synthesized with a C_2H_4 carbon feedstock (∼25 sccm), water (50 to 500 ppm) growth enhancer, and He as a carrier gas (total flow: 500 sccm) with a growth time of 10 minutes. Formation of nanoparticles for all cases was performed at the same conditions, He/H_2:1/9 and temperature, 750°C to eliminate the catalyst formation step as a variable, then the temperature was adjusted to the growth temperature ranging from 725 to 900°C. The growth temperature and water level were optimized at a fixed specific hydrocarbon flow rate (for highly active feedstocks, the flow rate was intentionally lowered). Carbon feedstock purities: ethylene: 99.999%; acetylene (10% diluted with He): C2H2: 99.99%, He: 99.999%; 1,3-Butadiene: 99%; Propane: 99.99%; n-Butane: 99.95%; n-Hexane: 96%; t-DN: 99%; *p*-xylene: 98%.

Liquid carbon feedstock injection. The liquid carbon sources were introduced using a syringe pump set-up with a capillary (100 um: ID) input port. The line was preheated before injecting into the growth ambient to ensure vaporization of the liquid source occurred prior to the growth ambient.

Calculation of carbon input level. For gas sources, the carbon input rate was calculated from the direct conversion of the gas flow rate [sccm] to [mole/min] as displayed below:

$$Eth. Concentration[mol/\min] = flowrate[sccm] \cdot \left(\frac{1L}{1000cm^3}\right) \cdot \left(\frac{P}{R \cdot T}\right) \cdot \left(\frac{2molcarbon}{1mol.ethylene}\right)$$

where P is the pressure (1 atm), R is the gas constant (0.082 L/atm.mol.K), T is temperature in Kelvin (300 K).

For liquid sources, the carbon input rate was calculated by converting the liquid injection rate [ul/min] to [mol/min] as follows:

Carbon concentration (mol/min.) = Liquid source input rate (μl/min)*(1 mL/ 1000 uL)*liquid density (g/ml)*(1/Molar mass (g/mol))*number of carbon atoms per molecule

Raman spectroscopy. Raman spectroscopic characterization was performed using a Thermo-Electron Raman Spectrometer with an excitation wavelength of 532 nm and a macroscopic sampling diameter of 0.3 mm.

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Author contributions

K.H., D.F., H.K. conceived and designed the experiment and co-wrote the paper, H.K. and J.G. performed the experiments, S.Y. and S.S. contributed to material preparation, M.Y. advised the study.

Additional information

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