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Relationship between growth rate and lifetime on carbon nanotube synthesis

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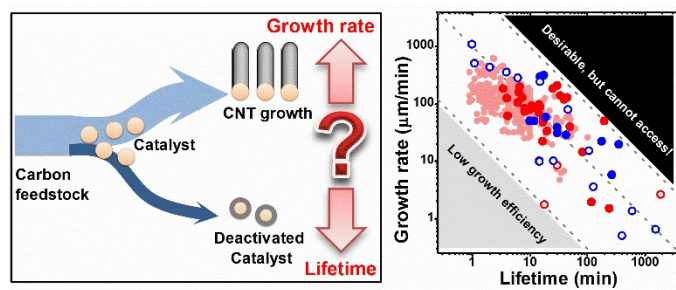
ABSTRACT

We report an inverse relationship between the carbon nanotube (CNT) growth rate and catalyst lifetime by investigating the dependence of growth kinetics for ~330 CNT forests on carbon feedstock, carbon concentration, and growth temperature. We found that increased growth temperature led increased CNT growth rate and shortened catalyst lifetime for all carbon feedstocks, following an inverse relationship of fairly constant maximum height. For increased carbon concentration, the carbon feedstocks fell into two groups where ethylene/butane showed increased/decreased growth rate and decreased/increased lifetime indicating different rate-limiting growth processes. In addition, this inverse relationship held true for different types of CNTs synthesized by varied chemical vapor deposition techniques and continuously spanned 1000-times range in both growth rate and catalyst lifetime, indicating the generality and fundamental nature of this behavior originating from the growth mechanism of CNTs itself. These results suggest it would be fundamentally difficult to achieve a fast growth with long lifetime.

Keywords

Carbon nanotube, growth rate, lifetime, growth kinetics

TOC GRAPHICS



Over the decades the synthesis of carbon nanotubes (CNTs) has continuously improved as exemplified by chirality selective growth, highly efficient synthesis to make highly aligned forest, and semiconductive selective growth, etc.¹⁻⁴ The growth efficiency has been one of the central issues of CNT synthesis because it is the key to achieve industrial scale mass production. To achieve highly efficient synthesis, fast CNT growth rates and long catalyst lifetimes are required. Therefore, significant research has been invested to improve both growth rate and catalyst lifetime, such as tailoring catalyst composition/structure,^{5,6} exploring support layers,^{7,8} modulating growth conditions,⁹⁻¹³ introducing growth enhancers (e.g. water),^{1,14-16} etc.

These efforts have fallen into two main directions to improve growth efficiency: extension of the catalyst lifetime at a slow CNT growth rate or increased CNT growth rate with a short catalyst lifetime. For example, Zhong et al has reported the growth of 0.5 cm single-walled CNT (SWCNT) forest at low growth rate of $\sim 2.6 \mu\text{m}/\text{min}$ for ~ 32 h growth time.⁵ Bronikowski has demonstrated millimeter-scale multi-walled CNTs (MWCNTs) synthesized at a growth rate of $\sim 0.64 \mu\text{m}/\text{min}$ for ~ 26 h.¹³ On the other hand, recently, introduction of growth enhancer (oxygen sources) has shown to significantly improve the growth rate. Patole et al has produced ~ 5.5 mm-tall MWCNT forests at a high growth rate of $\sim 310 \mu\text{m}/\text{min}$ but the growth terminated after ~ 17.8 min.¹⁵ Hasegawa et al has synthesized millimeter-tall SWCNT forest with an average growth rate of $\sim 200 \mu\text{m}/\text{min}$ but also with very short lifetime within ~ 7 min.¹⁶

Generally, there are two dominant competing processes during CNT synthesis (Fig. 1a): CNT growth and catalyst deactivation. The carbon feedstock will affect both processes, because a fraction will contribute to the synthesis, reflecting in growth rate, and the remaining unused fraction will contribute to the deactivation of the catalyst through carbon coating, i.e. catalyst lifetime. Therefore, from this standpoint, the growth rate and lifetime are expected to be

fundamentally inversely related. This point is empirically known as observed by the results mentioned above.^{5,13,15,16} However, the inverse relationship itself has yet to be studied. Therefore, still very important issues remain as open questions, such as generality, dependence on the growth conditions, and growth ambient.

In this work, we address these issues and studied the inverse relationship between the CNT growth rate and catalyst lifetime by examining the growth kinetics, i.e. average growth rate and catalyst lifetime, of more than ~330 SWCNT forests for several carbon feedstocks (ethylene, acetylene, butane, and propane), carbon concentrations (0.4-12%), and growth temperatures (725-825 °C). For every case, we found an inverse relationship between the average growth rate and lifetime. We found that for all carbon feedstocks studied, the increase in growth temperature led to an increase in growth rate and shortened lifetime, in a manner following an inverse relation where the maximum height was fairly constant. On the other hand, the carbon feedstocks fell into two groups in regards to their dependence on increased carbon concentration where ethylene/butane showed an increase/decrease in growth rate and a corresponding decrease/increase in lifetime indicating different rate-limiting growth processes. When the results of the literature were included, the inverse relationship continuously spanned 1000-times range in both growth rate and catalyst lifetime, suggesting that this behavior is a very general fundamental phenomenon originating from the growth mechanism of CNTs itself.

To investigate the relationship between the growth rate and lifetime, we created a “growth rate-lifetime map” by plotting the data from growths spanning diverse growth conditions, i.e. several carbon feedstocks, carbon concentrations and growth temperature. To achieve this, a family of SWCNT forests was synthesized from an alumina/Fe catalyst by water-assisted chemical vapor deposition (CVD) implemented with various carbon sources, concentrations and

temperatures, encompassing a wide range of experimental conditions (Fig. 1b). The growth kinetics of each member of family of SWCNT forests was determined from the plot of the height versus time (growth curve) as measured by an *in situ* height monitoring system (Fig. 1c). The lifetime was defined as the time until growth termination, i.e. when the growth stopped. The growth rate was defined as the quotient of the height at termination and the termination time.

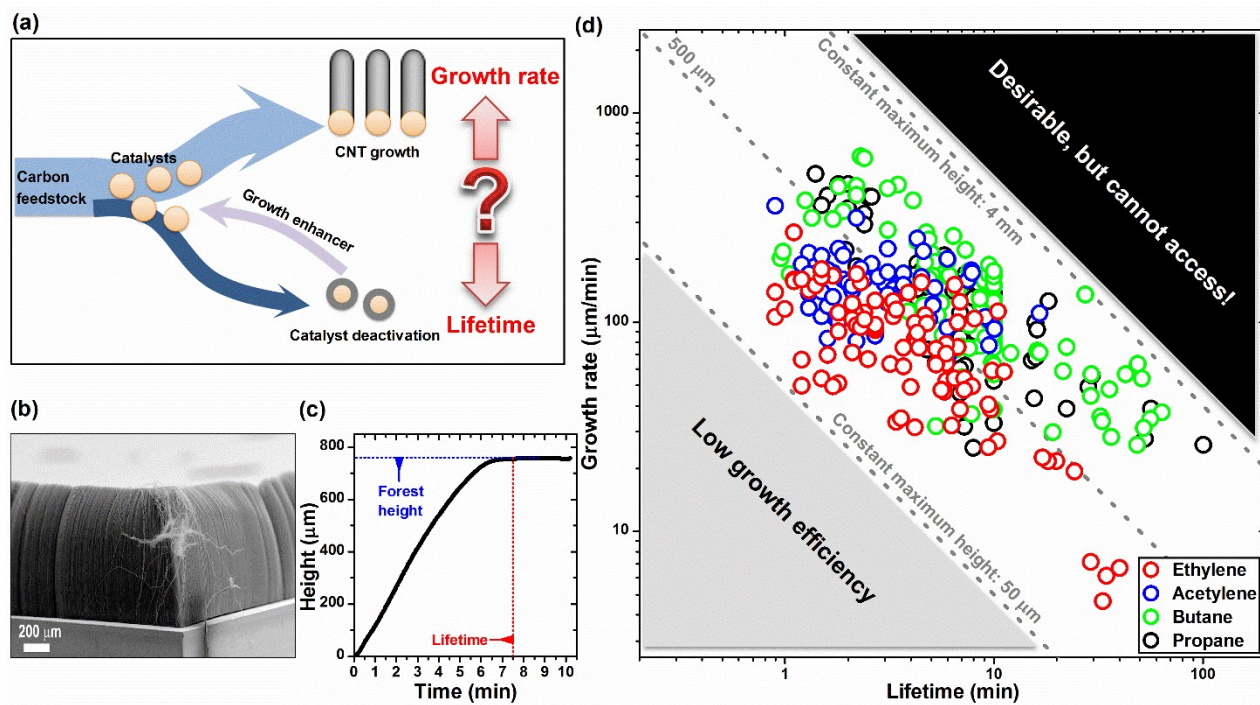


Fig. 1 (a) Schematic demonstrating the two dominant competing processes during CNT synthesis: CNT growth and catalyst deactivation. (b) Scanning electron microscopy image of a typical SWCNT forest. (c) Growth curve (height versus time) measured by an *in situ* height monitoring system. (d) “Growth rate-lifetime map” demonstrating an inverse relationship for various experimental conditions.

We observed several important points from the “growth rate-lifetime map” (Fig. 1d). First, all the data points were constrained in a linear region, demonstrating there is an inverse relation

between the growth rate and lifetime. Second, this inverse relationship was general and independent on the carbon feedstock. Third, the maximum height of forest, which is the product of average growth rate and lifetime and reflected by the dotted lines, could be achieved either with high growth rate (but short lifetime) or with low growth rate (but long lifetime). Fourth, there were two regions that we could not access. The bottom-left corner represents low growth efficiency and was not the target of this work. The upper-right corner shows the high growth rate and long lifetime, which is highly desirable but we could not access because of the inverse relationship.

To investigate the generality of the inverse relationship, we expanded the map (Fig. 1d) to include results from the literature. The average growth rate and lifetime from 23 published reports were plotted in two panels, one overlapped with our results (Fig. 2a) and one with only the references (Fig. 2b).^{5,10,11,13-32} When the literature results were combined with our results, the map clearly showed an inverse relationship regardless of the CNT synthesis method. In addition, the inverse relationship continuously spanned a 1000-times range in both growth rate and catalyst lifetime, meaning that this relationship holds true across at least three-orders of magnitude difference. These results clearly demonstrate the generality of the inverse relationship between growth rate and lifetime. For SWCNTs, it seems to be important to have a growth enhancer to achieve a very fast growth and high growth efficiency. When water was not used, the growth rate decreases dramatically. However, a highly efficient growth is possible if given a long time. The influence of a growth enhancer (e.g. water) is less pronounced for MWCNT synthesis, although the use of water does show an increase in growth rate and lifetime.

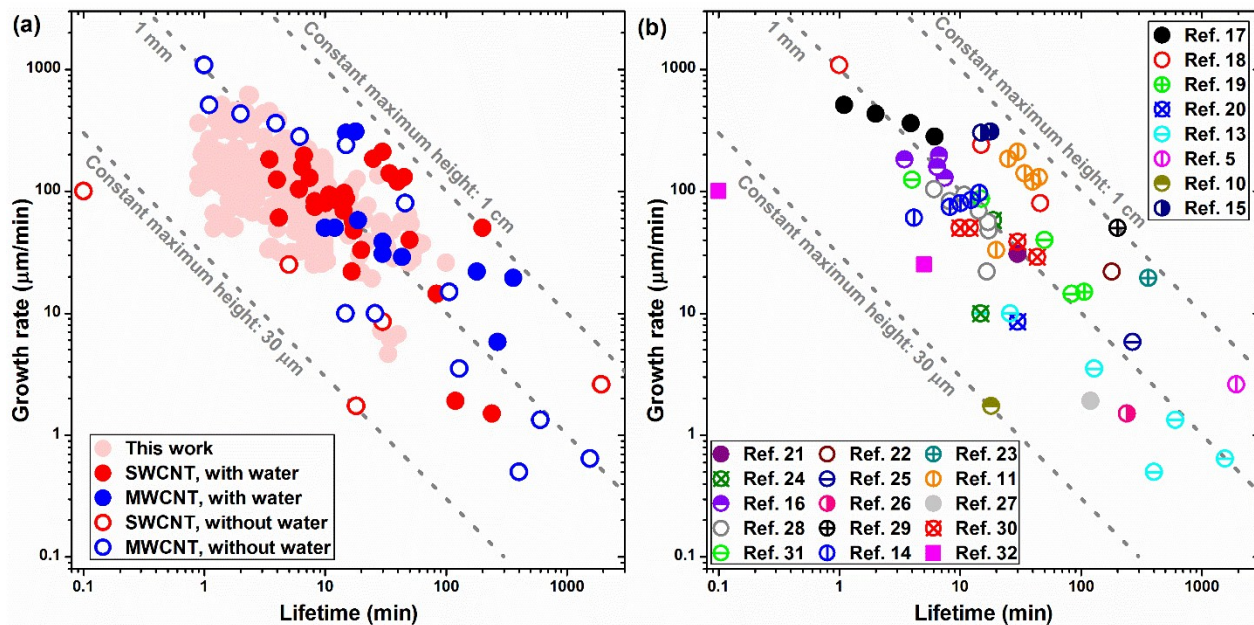


Fig. 2 Generality of the inverse relationship between growth rate and lifetime: (a) overlapping with our results, and (b) with only the references.

We would like to note that we focused on the growth temperature range of 725-825 °C in this work because most reported efficient growths of CNT forests occurred within this range. In order to further extend our comparison, we included the CNT synthesis results from reports above and below our current process temperatures.³²⁻³⁸ For low temperature syntheses, ~510 to ~450 °C, the growth rates were exceptionally slow ~0.15 to ~0.1 μm/min, but there was no information regarding the catalyst lifetime and could not be included into the figure.³⁶⁻³⁸ From Fig. 2b (Square), we observe the following: First, these additional points exhibit the same inverse relationship between growth rate and lifetime. Second, these additional points all tend to be located along the slower growth rate-shorter catalyst lifetime domain (bottom-left corner) because the growth efficiency of CNT forests is usually very low at these extreme conditions. Third, as the process temperature was increased, the growth rates increased moderately, and their lifetimes

decreased. Specifically, as the growth temperature increased from ~ 750 to ~ 1000 °C, the growth rate increased from ~ 25 to ~ 100 $\mu\text{m}/\text{min}$ but the lifetime decreased from ~ 5 to ~ 0.1 min.³²

We further studied the dependence of the inverse relationship on experimental conditions, such as carbon feedstock, carbon concentration, and growth temperature. First, we plotted the dependence of the growth rate versus lifetime on the process temperature at a fixed carbon concentration for four carbon feedstocks: ethylene, acetylene, butane and propane (Fig. 3a). All four carbon feedstocks showed the inverse relationship between growth rate and lifetime. In addition, all four carbon feedstocks exhibited the same dependence on process temperature, where increased temperature showed increased growth rate and decreased lifetime. This result is expected because both the CNT growth process and the catalyst deactivation process are accelerated which would lead to faster growth rates and shorter lifetimes. Furthermore, the trends for each carbon source were roughly parallel to the dotted lines, which indicates slope of constant maximum forest height (a product of the growth rate and lifetime). This means that the growth reaches the same maximum height regardless of the temperature within this range. It further indicates that we can reach the same maximum height by both a slow growth with a long lifetime and a fast growth with a short lifetime. Moreover, this is evidence that the catalysts consume a specific number of carbon feedstock before they deactivate, which is in accordance with catalyst deactivation process as described in Fig. 1a, *i.e.* catalyst deactivation by carbon coating.

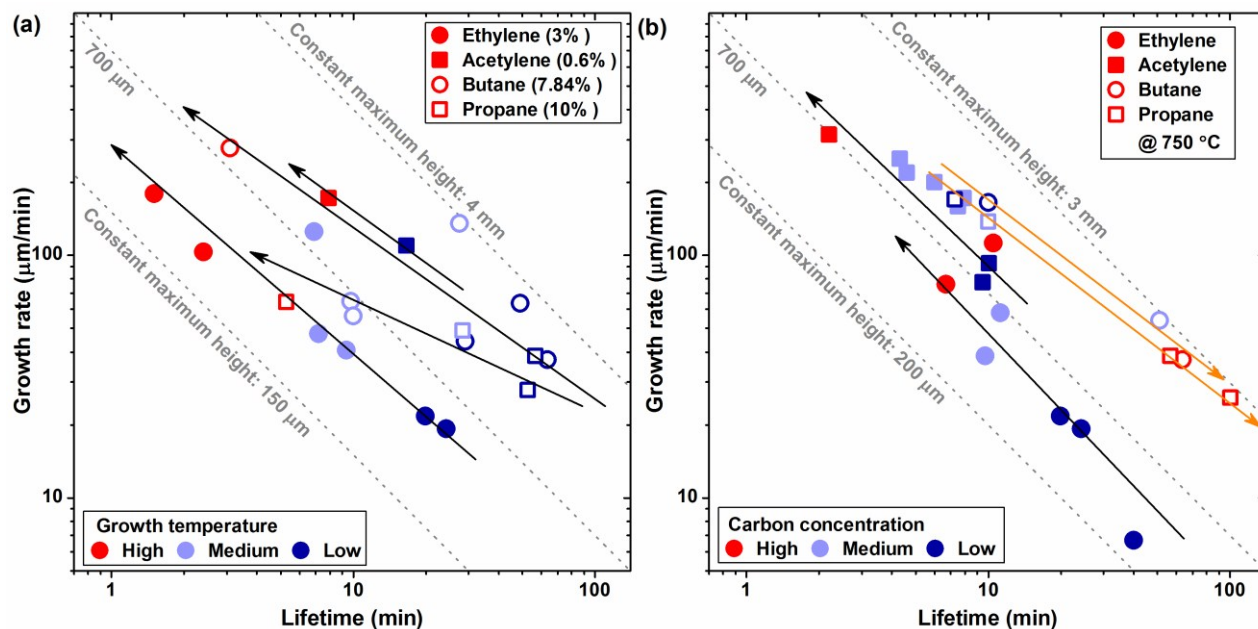


Fig. 3 Dependence of the inverse relationship (a) on growth temperature at a fixed carbon concentration, and (b) on carbon concentration at a fixed growth temperature of 750 °C for every carbon feedstock.

Second, we plotted the dependence of the growth rate versus lifetime on the carbon concentration at a fixed temperature for the four carbon feedstocks (Fig. 3b). All four carbon feedstocks exhibited the inverse relationship between growth rate and lifetime. However, we observed differences in the dependence on the growth rates and lifetimes between the different carbon feedstocks. As the concentration of the unsaturated carbon feedstocks, ethylene and acetylene, increased, the growth rates increased with a corresponding decrease in lifetime. Ethylene and acetylene differed only by the range of growth rates and lifetimes. In contrast, as the concentration of the saturated carbon feedstocks, butane and propane, increased, the growth rates decreased and lifetimes increased.

The difference between the carbon feedstocks was further investigated. To this end, we calculated the activation energies as a function of carbon concentration from Arrhenius plots of the

temperature dependence on the average growth rate (Fig. 4a, 4b). At low ethylene concentration, the activation energy was ~ 2.8 eV, which is in agreement with values reported in the literature (Fig. 4c).^{11,32,39,40} However, we found that the activation energy of ethylene decreased as the carbon concentration increased. At a concentration of $\sim 10\%$, the activation energy decreased to $\sim 1/3$, which was ~ 1.0 eV. This value is close to the activation energy of carbon bulk diffusion in Fe catalyst (1.0-1.7 eV).^{41,42} In contrast, for butane, the activation energy was fairly constant or slightly increased.

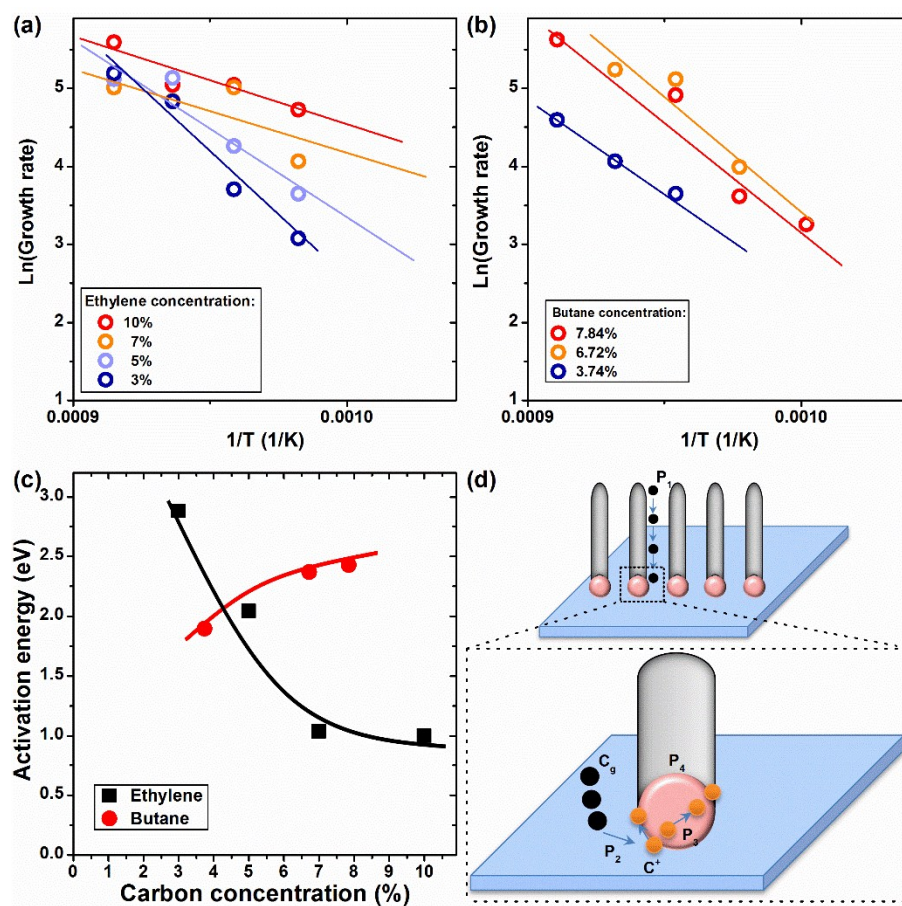


Fig. 4 Arrhenius plots of the temperature dependence on the average growth rate for (a) ethylene and (b) butane. (c) Calculated activation energy as a function of carbon concentration. (d) Schematics of the processes of CNT growth.

These results suggest that ethylene and butane have a different rate-limiting process in CNT growth (Fig. 4d). The process of CNT growth can be described as: 1) carbon feedstock (C_g) diffusion from forest top to catalyst site (P1); 2) carbon feedstock (C_g) dissociation, adsorption into catalyst (P2), which requires energy; 3) carbon (C^+) bulk and/or surface diffusion (P3), which also requires energy; 4) CNT precipitation from the catalyst (P4). Based on the calculated concentration dependence of the activation energy for ethylene, we believe that the rate-limiting process shifts from gas dissociation/adsorption to bulk diffusion of carbon due to the similarity in activation energies (P2→P3). In contrast, for butane, the dependence of the activation energy on the carbon concentration implies that the rate-limiting process does not change significantly and remains as gas dissociation/adsorption (P2).

We recognize that acetylene has been reported as the key growth species for a large range of CVD processes leading to CNT forest growth, including plasma-assisted and cold-wall CVD, alcohol, ethylene, and butane in hot-wall CVD.^{6,26,43,44} Therefore, we suspect that the ease of conversion to acetylene, as well as the unused components, also contributes to the growth rates. To fully understand the fundamental chemical reaction(s) involved, future investigations such as molecular dynamic simulations, *in situ* growth species diagnosis, etc. would be required. We hope this work will invoke this future study.

Conclusions

To summarize, we investigate the relationship between average growth rate and lifetime for over 330 SWCNT forests synthesized from several carbon feedstocks, carbon concentrations, and growth temperatures, always finding an inverse relationship between the CNT growth rate and catalyst lifetime. Moreover, this inverse relationship held true for different types of CNTs synthesized by varied CVD techniques and continuously spanned 1000-times ranged in both

growth rate and catalyst lifetime, suggesting that this behavior is a very general fundamental phenomenon originating from the growth mechanism of CNTs itself. These results suggest it would be fundamentally difficult to achieve a fast growth with long lifetime.

Experimental Methods

Catalyst preparation: A catalyst system of Al₂O₃ (~40 nm)/Fe (~1.8 nm) was prepared by sputtering as it is our well established standard catalyst to grow SWCNT forests with high efficiency.

CNT synthesis: All the syntheses were performed in a 1 in. fully automated CVD system equipped with a telecentric optical system for *in situ* height measurement.⁴⁵ Specifically, SWCNTs were synthesized with different carbon feedstock (ethylene: 1-12%, acetylene: 0.4-2%, butane: 3.74-7.84%, and propane 5-12%), water (20-900 ppm) as growth enhancer, and He as the carrier gas, at the growth temperature ranging 725-825 °C.

ASSOCIATED CONTENT

Notes

Conflict of Interest: The authors declare no competing financial interest.

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