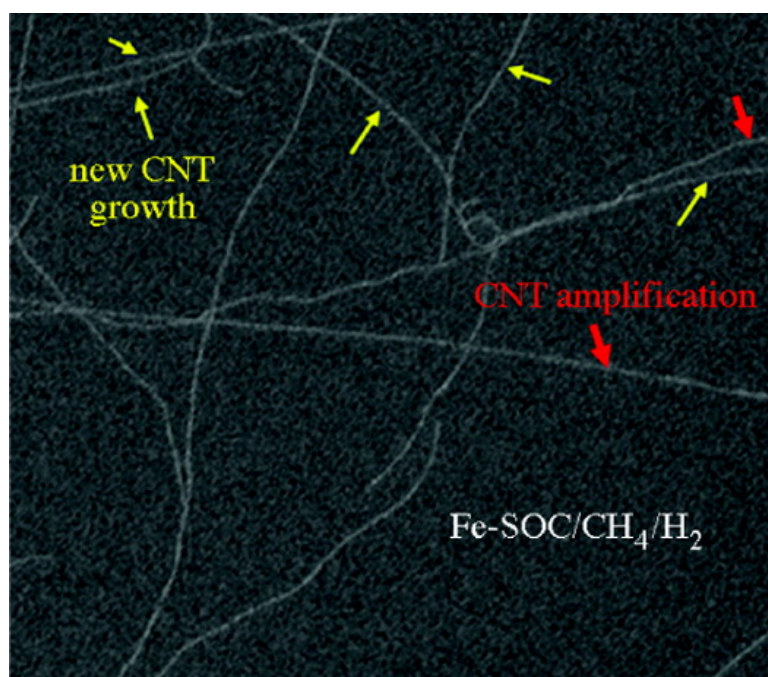


## Growth, New Growth, and Amplification of Carbon Nanotubes as a Function of Catalyst Composition

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## Growth, New Growth, and Amplification of Carbon Nanotubes as a Function of Catalyst Composition

Christopher A. Crouse,<sup>†</sup> Benji Maruyama,<sup>‡</sup> Ramon Colorado Jr.,<sup>†</sup> Tyson Back,<sup>‡</sup> and Andrew R. Barron<sup>\*†</sup>

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**Abstract:** Carbon nanotubes (CNTs) have been grown using Fe, Co, Ni, and Co/Fe spin-on-catalyst (SOC) systems, involving the metal salt dispersed with a spin-on-glass precursor. During initial growth runs (CH<sub>4</sub>/H<sub>2</sub>/900 °C), the CNT yield followed the order Co-SOC > Fe-SOC ≫ Ni-SOC. The Fe catalysts produced the longest nanotubes at the expense of a larger average CNT diameter and broader diameter distribution than the Co-SOC system. A series of Co/Fe-SOCs were prepared where as the atomic percentage of Co is increased nucleation of CNT increases but the CNT length decreases. The linear relationship between the diameter and length of CNTs grown from the Co/Fe-SOC suggests that slow growth is beneficial with respect to control over CNT diameter. After initial CNT growth, the original samples were subjected to additional growth runs. Four individual reactions were observed in the Fe-SOC and binary Co/Fe-SOC: regrowth (amplification), double growth (a second CNT growing from a previously active catalyst), CNT etching, and nucleation from initially inactive catalysts (new growth). CNT etching was observed for the mixed catalyst systems (Co/Fe-SOC) but not for either Fe-SOC or Co-SOC. During the regrowth experiments, CNTs were observed that were not present after the initial growth run (and were not as a result of amplification or double growth). Thus, catalysts, which were initially inactive toward nucleation of CNTs in the original growth run, are capable of becoming activated when placed back into the furnace and submitted to regrowth under identical conditions.

### Introduction

The exact details of the growth mechanism for single walled carbon nanotubes (SWNTs) are open to much debate; however, it is generally agreed that three key mechanistic steps are involved: nucleation, growth, and termination.<sup>1–3</sup> Nucleation is often described as both the formation of a catalyst particle and the initial construction of the carbon framework on which subsequent growth occurs. Nevertheless, in cases where pre-formed catalyst particles are used, it is better to limit the nucleation process to the initiation of the carbon nanotube (CNT) structure (e.g., cap formation and lift-off<sup>4</sup>). During nucleation, gaseous hydrocarbons are adsorbed onto the surface of metal nanoparticle catalysts. Once adsorbed, the C–H bonds disassociate and carbon is dissolved (absorbed) into the metal particle. Precipitation of the carbon, in the form of CNTs, begins once the molten particle becomes saturated with carbon. This is believed to occur first in the form of a fullerene cap. As the cap extends away from the particle, the sidewalls of the CNT

are formed. The continuous addition of carbon to the sidewalls of the nanotube is known as growth. Termination of growth can occur through multiple routes. Ideally, termination would occur when the carbon feedstock is cut off and there is no more carbon present to continue growing the CNTs. Alternatively, the catalyst could become fouled with amorphous carbon on the surface, creating an impermeable barrier between the catalysts and the carbon feedstock resulting in termination. Catalyst poisoning can also occur through the resolidification of the catalyst particle in the form of a carbide or through reactions with the growth substrate (e.g., metal silicide formation).<sup>5</sup>

For a high yield (one nanotube per catalyst particle) of long (high  $M_w$ ) nanotubes to be prepared under any particular growth conditions from a specific catalyst, it is necessary that both nucleation and growth be highly efficient. Setting aside issues of growth rate being limited due to nanotube•••surface interactions<sup>6</sup> or the catalysts effect on the diameter and type (as defined by the SWNT's m,n value) of tube produced,<sup>7,8</sup> the major factor controlling the growth of a carbon nanotube should be the

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“activity” of the catalyst, i.e., its ability to generate the initial cap (nucleation) along with the rate of decomposition of the hydrocarbon feedstock and subsequent C–C bond formation (growth).<sup>9</sup> A variety of transition metal catalysts and alloys have been studied toward nanotube nucleation and growth. The metals most commonly used for SWNT growth are iron, cobalt, nickel, molybdenum, and various bimetallic alloys of these metals.<sup>10</sup> Despite the wide range of catalysts studied, it is difficult to make a comparison of various catalysts under identical growth conditions.

As part of our studies on SWNT growth and amplification, we have observed variations in the relative efficiencies between different catalysts. For preformed catalyst particles, iron catalysts show moderate catalyst yield (i.e., SWNT/catalyst particle ratio  $\leq 50$ ) and good catalyst activity (as measured by the average SWNT length).<sup>6</sup> In contrast, iron–molybdenum alloys are actually a poorly initiating catalyst (catalyst yield  $< 1\%$ ) and show less activity than that of pure iron.<sup>11</sup> When an iron catalyst is attached to a preformed SWNT and the resultant conjugate is exposed to growth conditions, significant growth ( $40\times$  original length) was observed; however, the amplification yield (i.e., number of SWNTs that increased in length) was very low ( $< 1\%$ ).<sup>12</sup> In contrast, the use of Fe/Mo catalysts results in  $> 40\%$  amplification yield, but only a  $3\times$  growth in SWNT length.<sup>13</sup> Thus, while the Fe/Mo catalyst appears to show poorer nucleation and growth rate than an iron catalyst, it shows a better amplification yield (i.e., number of SWNTs that increase in length). A further example of the control over the nucleation and growth steps has been previously demonstrated by Liu and co-workers in which nucleation can be promoted by introducing a short pulse of  $C_2H_6$  prior to the introduction of the main carbon feedstock ( $CH_4$ ). The  $C_2H_6$  has a higher rate of carbon absorption into the nanoparticle than  $CH_4$ , which was used to sustain growth of the carbon nanotubes.<sup>14</sup>

Although the cloning of SWNTs has been demonstrated, it is limited by low yields; therefore, our efforts have been to identify the effects that different catalyst compositions have on the regrowth of SWNTs during the amplification process. In the present study, we have investigated the catalyst yield and activity of Fe, Co, and Ni catalysts for the growth of CNTs. In addition, we have investigated the potential regrowth of CNTs. This was accomplished by using newly grown CNTs with their original catalysts still attached to the end of the tube and then cycling through additional growth cycles in an attempt to reactivate the original catalysts toward desired amplification.

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**Table 1.** Summary of Nanotube Growth Resulting from Various SOC

spin-on-catalyst Co:Fe ratio	surface density (# CNTs $\mu\text{m}^{-2}$ )	CNT diameter (nm)	CNT length ( $\mu\text{m}$ )
0:100	0.2	$5.1 \pm 0.4$	$6.7 \pm 1.0$
20:80	3.2	$3.1 \pm 0.2$	$2.8 \pm 0.5$
50:50	2.5	$2.5 \pm 0.2$	$2.5 \pm 0.4$
80:20	4.4	$2.1 \pm 0.1$	$1.7 \pm 0.3$
100:0	7.9	$1.9 \pm 0.1$	$1.0 \pm 0.1$

This cycling process also allows for the measure of a catalyst’s ability to grow either additional CNTs from previously inactive catalyst particles or grow new CNTs from the same catalyst particle. The results of this study are presented herein with a discussion of the analogy between CNT catalysis and polymerization catalysis.

## Results and Discussion

**Growth of SWNTs from SOC.** To readily compare a range of catalyst compositions, we have employed the spin-on-catalyst (SOC) system for the present study. In the SOC system, a metal salt is dissolved with a spin-on-glass (SOG) precursor.<sup>15</sup> Conversion to metal catalyst nanoparticles imbedded in a silica support is accomplished by heating either prior to growth or during the ramp-up to the SWNT growth temperature ( $900\text{ }^\circ\text{C}$ ) (AFM in Supporting Information). The siloxane matrix simultaneously provides for the controlled formation of catalytic nanoparticles via phase separation and, upon heating, a smooth, continuous film of  $SiO_x$ , which prevents catalyst coarsening, mobility, and agglomeration at growth conditions.

The SOC method originally focused on  $Fe(NO_3)_3 \cdot 9H_2O$  as the catalyst precursor.<sup>15</sup> From this work, it was determined that a Fe-SOC concentration of  $4.0\text{ mg mL}^{-1}$  ( $10\text{ mM}$ ) provided the best results for SWNT growth with an average tube diameter of  $1.88\text{ nm}$  using a mixture of  $CH_4$  and  $H_2$  at  $900\text{ }^\circ\text{C}$ .<sup>16</sup> In the present studies, attempts to use a similar concentration of Fe-SOC resulted in a surface coverage that was too high to allow for observation of regrowth on specific tubes. As a result, we adjusted our optimal concentration for growth to  $5.0\text{ mM}$  ( $2\text{ mg mL}^{-1}$ ), allowing us to observe and track individual tubes. This concentration also allowed for a direct comparison of growth yields with respect to the catalyst used. Carbon nanotubes were observed for each of the SOC used; however, significant differences in yield, diameter, and length were observed for each of the individual catalysts.

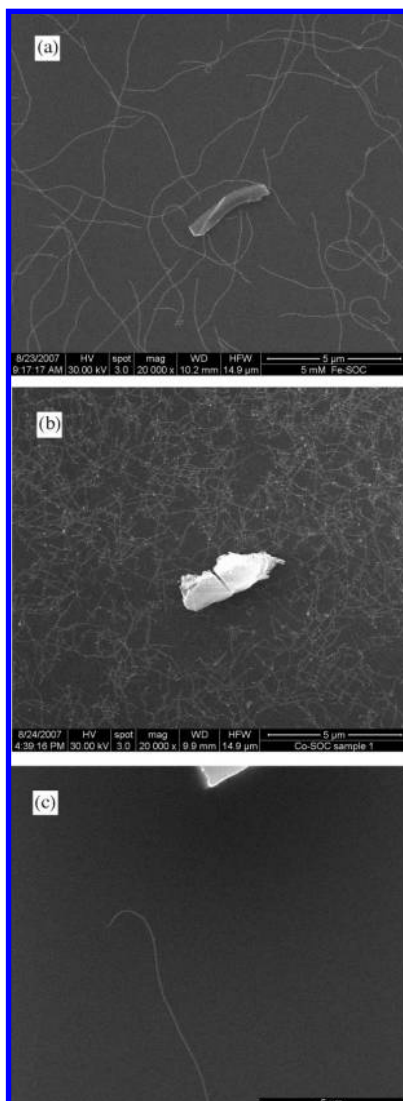
Samples of each SOC were spin coated onto a Si wafer and introduced into a tube furnace at  $900\text{ }^\circ\text{C}$  under a  $CH_4$  and  $H_2$  atmosphere, see the Experimental Section. After removal, AFM and SEM were used to characterize the samples to determine the number of grown CNTs. A summary of CNT growth resulting from various SOC is given in Table 1.

Upon completion of the initial growth runs, Co-SOC was consistently the best system toward the nucleation of growth displaying the overall highest surface density of nanotubes, ca.  $7.9\text{ tubes } \mu\text{m}^{-2}$ . The Fe-SOC was significantly worse at nucleation of CNTs having a lower overall surface density ( $0.2$

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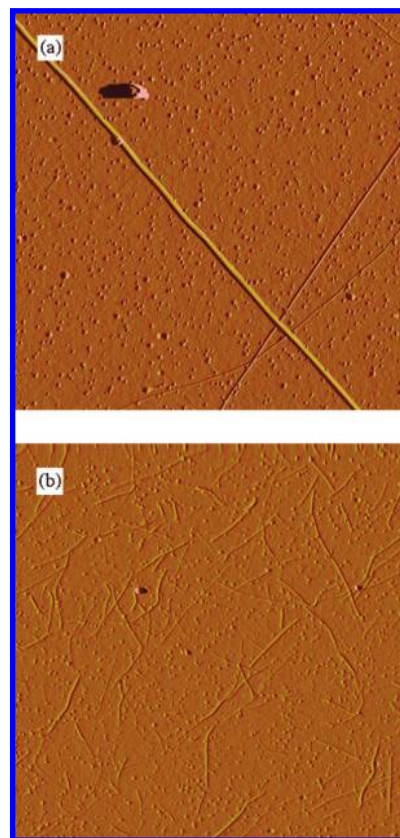




**Figure 1.** SEM images from initial growth of CNTs produced from 5.0 mM (a) Fe-SOC, (b) Co-SOC, and (c) Ni-SOC showing the relative number of tubes and their length distribution.

tubes  $\mu\text{m}^{-2}$ ), and only a single CNT could be found on the Ni-SOC samples.<sup>17</sup> The relative growth density is readily seen from the SEM images (Figure 1). Typical AFM images for the CNTs grown from Fe-SOC and Co-SOC are shown in Figure 2.

Despite the lower surface density (and hence catalyst yield), the Fe catalysts that did nucleate and grow a nanotube were very good at sustaining growth producing the longest nanotubes observed in the three systems ( $l_{\text{ave}} = 7 \mu\text{m}$ ) with some growing longer than  $20 \mu\text{m}$ . The diameter distributions associated with the Fe-SOC system obtained from AFM measurements were very broad ( $d = 1.1\text{--}9.5 \text{ nm}$ ) with an average tube diameter of ca.  $5 \text{ nm}$  (Figure 3a), suggesting that the presence of few-walled and possible small multiwall CNTs ( $d = 14 \text{ nm}$ ) were produced along with SWNTs.<sup>18</sup> The tubes grown from Co-SOC displayed



**Figure 2.** Representative AFM images ( $5 \mu\text{m} \times 5 \mu\text{m}$ ) from initial growth of CNTs produced from 5.0 mM (a) Fe-SOC and (b) Co-SOC showing the typical CNT diameters.

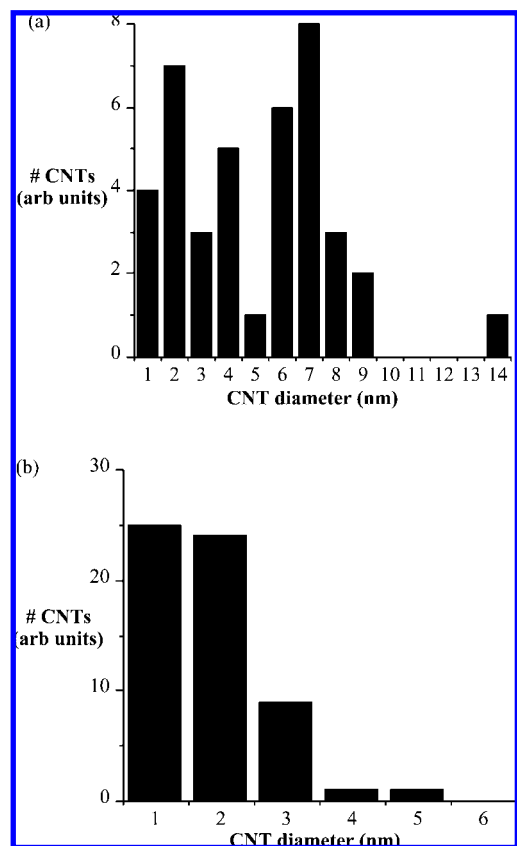
a much smaller average diameter ( $1.9 \text{ nm}$ ) and narrower diameter distribution ( $d = 0.9\text{--}6 \text{ nm}$ ) than those produced in the Fe-SOC system (consistent with the production of predominantly SWNTs); attempts were made to confirm the presence of SWNT radial breathing modes (rbm) in the Raman spectrum, however, fluorescence from the SOG quenched all characteristic CNT peaks. Yet, the overall lengths of the nanotubes produced were typically very short with the vast majority being less than  $2 \mu\text{m}$  in length, and the longest tube found in the Co-SOC system was only  $6 \mu\text{m}$  in length. These results suggest that the Co-SOC appears to be a very good catalyst toward the nucleation of CNT growth; however, its ability to sustain the growth is limited, resulting in shorter tubes.

As previously mentioned, the Ni-SOC system was generally inactive toward CNT nucleation, with only one nanotube being observed throughout all growth runs. The lack of nucleation in the Ni-SOC was rather intriguing due to the common use of Ni as a catalyst for CNT growth in several types of growth conditions. A majority of the samples imaged after growth displayed some deterioration of the SOG-SiO<sub>x</sub> surface, signifying the likelihood of unfavorable reactions between Ni and the SOG, possibly including the formation of nickel silicide. The single nanotube that was found in the Ni-SOC system was rather long ( $9 \mu\text{m}$ ), suggesting that Ni is probably good at sustaining growth; however, we were not able to produce enough tubes to generate any statistical evidence to support this result.

**Growth of CNTs from Mixed Fe/Co-SOC.** It would be desirable to combine the large number of nucleated tubes present in the Co-SOC system and the sustained growth leading to the long tubes displayed in the Fe-SOC system. A series of SOCs

(17) The growth density can be broadly correlated with catalyst yield because the concentration of metal precursor is identical in each SOC sample.

(18) Attempts were made to confirm the presence of SWNTs using Raman spectroscopy; however, fluorescence from the SOG substrate quenched all peaks characteristic with carbon nanotubes.

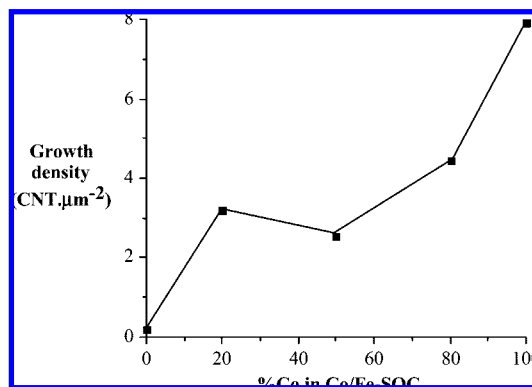


**Figure 3.** Diameter distribution of CNTs grown from (a) Fe-SOC and (b) Co-SOC.

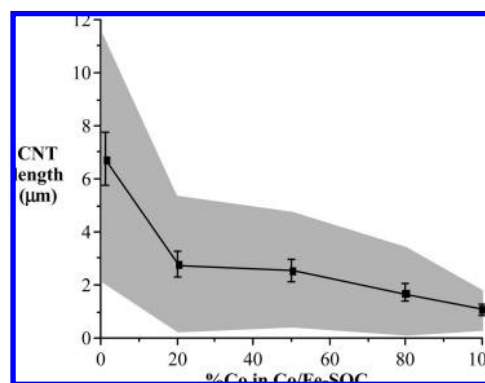
containing binary mixtures of Fe and Co at varying atomic percentages were prepared to determine if the two metals would alloy in the SOC system. If an alloy is formed, then the catalyst yield, as well as the length and diameter of the CNTs produced, should track the composition. If the two metals do not alloy, then a mixture of CNT types (those associated with each catalyst) will be produced.

Binary Co/Fe mixed catalysts (Co/Fe-SOC) were produced with Co:Fe ratios of 20:80, 50:50, and 80:20. A statistical summary of the CNTs grown from the binary Co/Fe catalysts can be found in Table 1 in comparison with the pure archetypes.

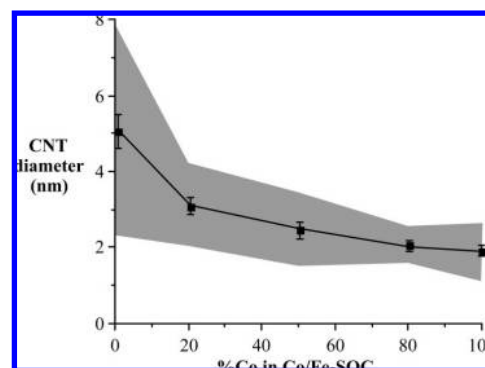
The general trends observed for the nucleation of CNTs from the prepared Co, Fe, and binary CoFe-SOCs demonstrates that as the atomic percentage of Co is increased, the likelihood for nucleation of nanotubes also increases (Figure 4). This increase in nanotube nucleation did come at the expense of nanotube length, which shows a decrease in length with increased Co content in the catalysts (Figure 5). Consistent with the changes in CNT length, the average diameter of the CNTs produced also decreases as the percentage of Co is increased (Figure 6). From the diameter distribution of the CNTs grown from Co/Fe(50:50)-SOC (Figure 7) it is clear that the catalyst does behave as an alloy and not individual components, which would result in a bimodal distribution (as is observed in the Co/Fe(20:80)-SOC, Figure S3a, Supporting Information). Corresponding CNT diameter distributions are observed for Co/Fe(80:20)-SOC and Co/Fe(20:80)-SOC (Supporting Information). There is a linear relationship between the average diameter and average length of CNTs grown from the Co/Fe-SOC (Figure 8), suggesting that under the present conditions slow growth is beneficial with respect to control over CNT diameter.



**Figure 4.** Surface density (catalyst yield) of CNTs ( $\mu\text{m}^{-2}$ ) as a function of percent Co in the Co/Fe-SOC system.



**Figure 5.** Average CNT length ( $\mu\text{m}$ ) as a function of percent Co in the Co/Fe-SOC system. The error in the average is shown, and the shaded area shows the standard deviation.



**Figure 6.** Average CNT diameter (nm) as a function of percent Co in the Co/Fe-SOC system. The error in the average is shown, and the shaded area shows the standard deviation.

**Regrowth of CNTs from SOC.** After initial CNT growth from the SOC was completely analyzed, the original samples were returned to the tube furnace for a second (or third) growth run. During this run, no attempts were made to “activate” the catalysts prior to regrowth, such as additional oxidation or reduction steps; however, it is likely that the catalysts were oxidized when exposed to the atmosphere during the analysis of the initial growth. It was our intention to study the likelihood of regrowth as a function of the catalysts species to determine if any of the SOC combinations exhibited a preferential ability to reactivate and continue the growth of the original CNT (i.e., amplification). This was accomplished by comparing SEM

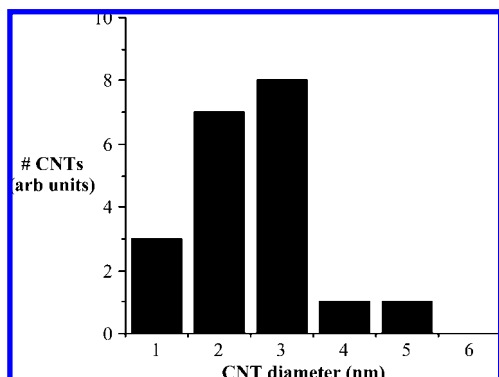


Figure 7. Diameter distribution of CNTs grown from Co/Fe(50:50)-SOC.

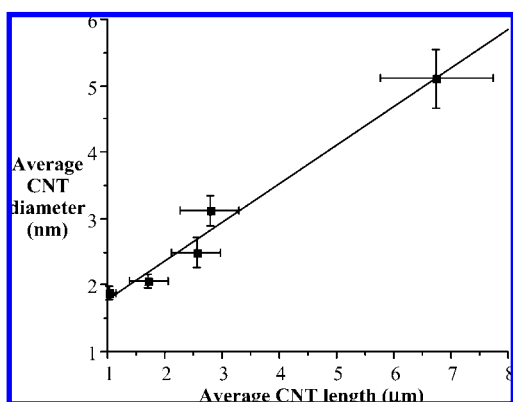


Figure 8. Plot of average diameter (nm) versus average length for CNTs grown from Co/Fe-SOC ( $R^2 = 0.977$ ).

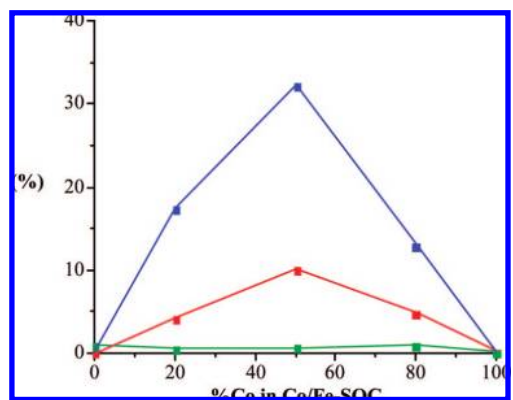


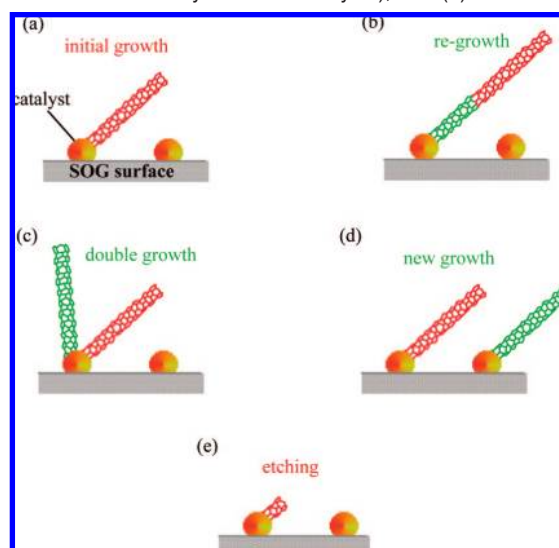
Figure 9. Plot of percentage (of the original CNTs from the first growth run) of CNT that are amplified (green ■), partially etched (red ■), or totally etched (blue ■) during the second growth run.

images of the same area that were obtained after the first growth run and those obtained after the regrowth.

Four individual reactions were observed during the regrowth experiments in the Fe-SOC and binary Co/Fe-SOC systems; these include: regrowth (amplification), double growth (a second CNT growing from a previously active catalyst), CNT etching, and nucleation from initially inactive catalysts (new growth). Each of these processes is pictorially described in Scheme 1.

The Co-SOC system did not display any amplification when exposed to a second growth run under the described conditions. In contrast, all of the Fe containing SOC's showed nanotube amplification (Figure 9) albeit at a low level: ca. 1% of the original CNTs. Figure 10 shows an example of nanotube

Scheme 1. Schematic Representations of (a) Initial Growth, (b) Regrowth (Amplification), (c) Double Growth, (d) New Growth (Nucleation from Initially Inactive Catalysts), and (e) CNT Etching<sup>a</sup>



<sup>a</sup> Red CNT represents material grown during first growth run, green CNT represents new material formed during subsequent growth runs.

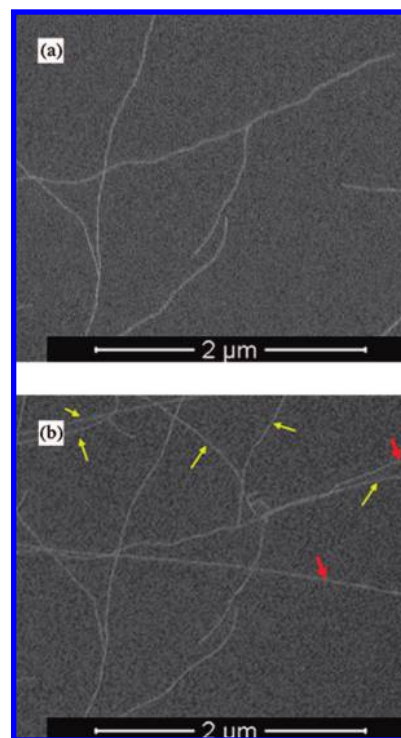
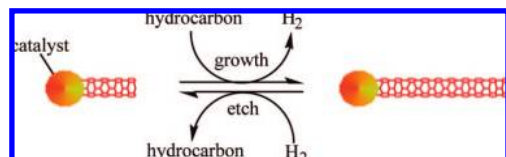


Figure 10. SEM images (a) after initial growth and (b) after a second growth reaction, displaying CNT amplification (red arrows) in the Fe-SOC system. Yellow arrows indicate new CNTs grown from previously inactive catalyst.

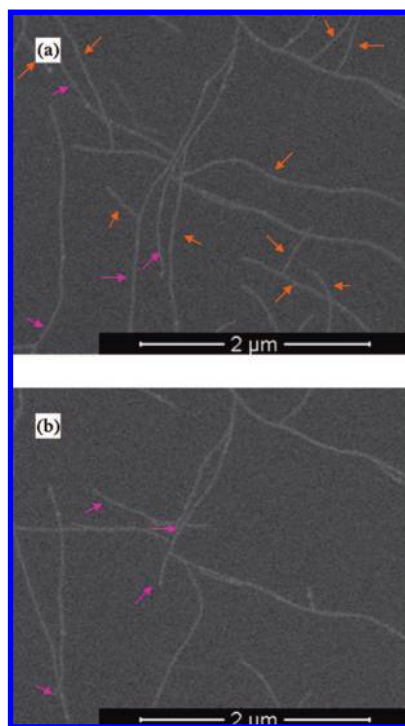
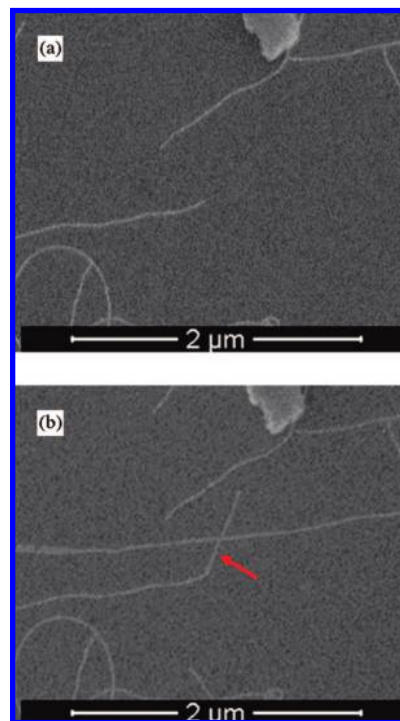
amplification in the Fe-SOC system. It is unclear, due to the inability to determine tube diameters from SEM measurements, as to whether or not the initial diameter (and hence chirality) is maintained for the newly grown portion of the CNT; however, our prior results with Fe catalyzed amplification suggest that CNT diameter is maintained.<sup>12</sup> Nanotube amplification is believed to occur when the original catalysts remain attached to the end of a CNT. Upon re-exposure to the growth gas ( $\text{CH}_4/\text{H}_2$ ), the catalysts become reactivated and continue



**Scheme 2.** Schematic Representation of the Relationship between CNT Growth and Etch-Back

the growth of the original tube (Scheme 1b). The inactivity of the Co-SOC catalyst suggest that reactivation of the catalyst does not occur under the conditions employed ( $\text{CH}_4/\text{H}_2$  @ 900 °C). However, a small fraction of Fe is sufficient to allow the catalyst to be active upon the second growth run.

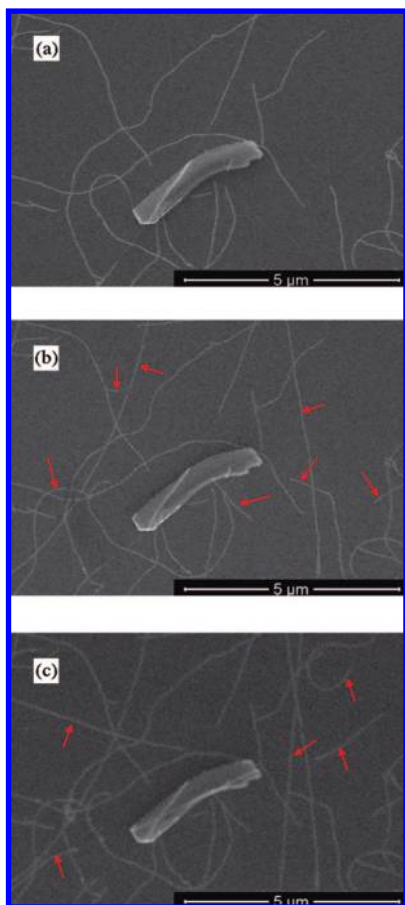
Nanotube etching and growth are at equilibrium during the growth process (Scheme 2); however, under ideal growth conditions, nanotube growth is favored and hydrogen is only present to keep the catalyst particle in a reduced state and to prevent or inhibit fowling of the particle by amorphous carbon. Etching may be considered as the reaction of dissolved or absorbed carbon on the catalyst surface with hydrogen to generate a hydrocarbon. No etching was observed for either Fe-SOC or Co-SOC; however, under the present conditions ( $\text{CH}_4 = \text{H}_2 = 225$  sccm), there is significant etch-back of the CNTs for the mixed catalyst systems (Co/Fe-SOC). Examples of nanotube etching in the CoFe(50:50)-SOC system are found in Figure 11. As may be seen from Figure 11, some CNTs are only partially etched whereas other are etched completely. The relative amount of each remains essentially constant irrespective of the catalyst composition (Figure 9), suggesting that the difference between partial and complete etching is possibly a function of the length of the original CNT and the reaction conditions and not a particular type of CNT per se. The ability of the catalyst to etch is highly dependent on the composition of the catalyst. The Co/Fe(50:50)-SOC system exhibited the

**Figure 11.** SEM images (a) after initial growth and (b) after a second growth reaction, displaying CNT both partial etch-back (purple arrows) and complete etch-back (orange arrows) in the Co/Fe(50:50)-SOC system.**Figure 12.** SEM images (a) after initial growth and (b) after a second growth reaction for the FeSOC system, showing the presence of double growth where a second CNT (red arrow) appears to grow from the same catalyst as another CNT.

highest percentage of completely etched and partially etched nanotubes for any of the catalysts studied, Figure 9. Although etch-back of the CNTs is clearly counterproductive to the overall goal of SWNT amplification, this result does show promise. First, the ability of a catalyst to etch a CNT is dependent on its physical attachment to the CNT, i.e., the same requirement of amplification. Second, given the equilibrium relationship between growth and etching (Scheme 2), we propose that the investigation of alternative conditions could result in a switch from etch-back to amplification. Lastly, if we assume that the “activity” of a catalyst to perform either etching or growth reactions is related, then the use of alloy catalysts (rather than pure Fe) would provide a higher yield of amplification. This has already been observed in our Fe<sup>12</sup> and Fe/Mo<sup>13</sup> systems.

One argument against the concept of “amplification” arises if the catalyst in a CNT-catalyst conjugate does not continue the growth of the original CNT seed but instead grows a new CNT; then, the goal of controlled CNT type (diameter and chirality) will fail. We have previously observed no evidence for “double growth” (Scheme 1c) in our amplification studies; however, a few examples of double growth were observed for Fe-SOC. Double growth is a process that occurs when the catalyst from which an original CNT was grown either separates from that tube or is not capable of amplifying the growth of that tube but instead nucleates the growth of a second tube. Typically, for our system, it has been observed that the newly grown CNTs often grow at a much different angle from the original tube, clearly distinguishing it from amplification. An example of double growth is shown in Figure 12. Although we cannot rule out that the new growth is due to a defect (bend) in the CNT,<sup>19,20</sup> we see no incidents of such defects during normal

(19) Charlier, J.-C. *Acc. Chem. Res.* **2002**, *35*, 1063.

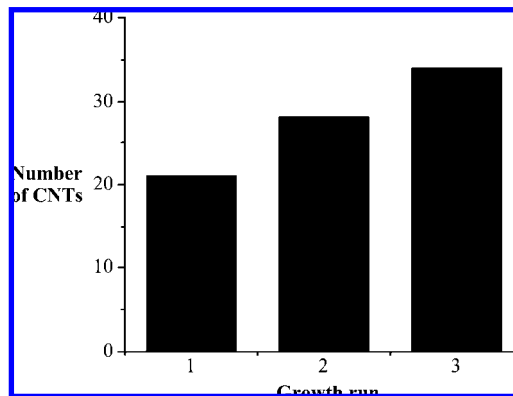


**Figure 13.** SEM images of nascent nucleated growth (red arrows) observed for Fe-SOC during (b) first and (c) second regrowth, as compared to the initial growth (a).

growth. With regard to CNT amplification, double growth is counterproductive, because there is no driving force for the second CNT to have the same chirality (diameter) as the original CNT. Fortunately, we have only observed a few examples of double growth, and it is possible that it is the result of either the catalyst particle separating from the CNT or surface forces inhibiting the further growth of the original CNT.<sup>6</sup>

**Growth of CNTs from Previously Inactive Catalyst.** Perhaps the most intriguing observation made during the regrowth experiments with the Fe-SOC and CoFe-SOC systems was the presence of CNTs after regrowth that were not present after the initial growth run (and were not as a result of amplification or double growth). These observations suggest that catalysts, which were initially inactive toward nucleation of nanotubes in the original growth run, are capable of becoming activated toward nucleation and growth when placed back into the furnace and submitted to regrowth under identical conditions. This observation was reproducible for all Fe-containing catalyst samples, with new nanotubes being seen after each subsequent growth run.

The activation of new catalyst particles that showed no initial activity is not limited to the first regrowth after characterization, but as may be seen from Figure 13, even a further fraction of catalysts are activated after the second characterization/growth cycle. The number of new CNTs grown with each successive



**Figure 14.** Number of CNTs grown per unit area as a function of repeated growth runs for Fe-SOC.

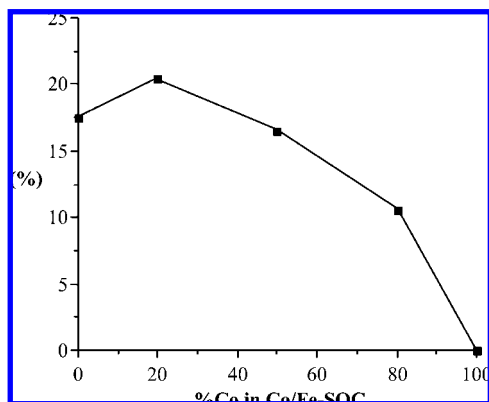
cycle appears to represent a fraction of the “inactive” SOC present after each growth run (Figure 14).

In the SOC system, it is believed that generally only a small portion of the metal catalysts remains active toward growth due to the majority of the particle reacting with the SOG to form various metal silicides.<sup>15</sup> It has been suggested that the formation of carbon crust around a metal catalyst may be responsible for removing as an active catalyst. The more carbon dissolved in the metal, the higher the potential rate of delivery to the surface and the potential for crust formation. Carbon is much more soluble in Fe than Co, thus making Co the better initiating catalysts and allowing for the potential crust formation. However, CoC is a more stable than FeC, but both still have positive heats of formation, and the presence of carbon in either metal should actually lower the melting point of the catalysts and make them better catalysts. Although we cannot rule out alternative explanations, we propose that in our system the SOC forms particles of various sizes and that some of these catalyst particles become “poisoned” resulting in the formation of carbide or a carbon shell. During the exposure of the samples to the atmosphere for sample characterization, the reduced Fe present in the system will become oxidized. This may be beneficial if the catalysts that were not initially active toward CNT growth were coated in an amorphous carbon shell, because oxidation would likely cause that shell to break open due to the increase in volume of the particle caused by the oxidation. With the shell thus cracked, then the potential for that particle to nucleate and grow a CNT becomes increased because it will be exposed to a suitable growth environment for a second attempt at growth. If the particle initially became poisoned through the formation of carbide, then it is likely that the carbide will be reduced under growth temperatures with the presence of hydrogen as a reducing agent.<sup>5</sup> Alternatively, the initial inactive particles could be covered with a thin SiO<sub>x</sub> layer that is desorbed from the surface when ramped up to regrowth temperatures. Either of these explanations gives the particle a second chance at nucleation and growth. Each successive removal and reintroduction into the growth chamber offers additional SOC the opportunity to be “activated”. Our observation that just because a catalyst is poisoned once does not mean it remains in this state is in agreement with the proposal of Jiang et al., that catalyst poisoning can be overcome through subsequent processing.<sup>5</sup>

As with the amplification studies, it is clear that the likelihood for nucleation of new tubes from initially inactive catalysts decreases as the percentage of cobalt in the system increases (Figure 15). This is as expected given that no additional growth

(20) Suenaga, K.; Wakabayashi, H.; Koshino, M.; Sato, Y.; Urita, K.; Iijima, S. *Nat. Nanotech.* **2007**, *2*, 358.





**Figure 15.** Plot of new CNT growth (as a percentage of the number of CNTs from the initial growth run) after regrowth as a function of cobalt concentration in Co/Fe-SOC.

occurs for Co-SOC suggesting that all the catalyst particles are “active” during their first exposure to the growth gas. On the basis of the SEM images, it does not appear that the etched tubes were responsible for the nucleation and growth of new nanotubes. In particular, new growth is observed for the Fe-SOC in the absence of any etching reactions. Thus, etching of CNTs and nucleation from initially inactive catalysts are separate events occurring simultaneously during the regrowth process for the Co/Fe-SOCs.

## Conclusions

The overall reaction for the synthesis of a CNT from a hydrocarbon precursor involves two groups of reactions: first, the decomposition of the hydrocarbon precursor to carbon and hydrogen (or hydrogen containing side products), and second the growth of the CNT from the catalyst surface. The mechanism for the former series of reactions is clearly related to the hydrocarbon decomposition on a wide range of metal surfaces as well as chemical vapor deposition of carbon and carbides. In contrast, the mechanistic steps of this latter reaction (i.e., growth of CNTs from the metal catalyst particle) can be likened to polymerization catalysis.

The polymerization of an organic monomer proceeds via three general reaction steps: initiation, propagation, and termination. These have their analogs in CNT growth: nucleation, growth, and termination. With respect to CNT growth, termination is ordinarily assumed to be due to catalyst poisoning, even though alternative processes are possible. We note that because catalyst poisoning can occur prior to any growth, we will, herein, differentiate between the two processes, i.e., “catalyst poisoning” occurs prior to growth resulting in no CNT being formed, whereas “CNT termination” applies to the session of growth by any mechanism. The control of the relative rates of initiation, propagation, and termination for any polymerization catalytic process is important in defining the molecular weight, molecular weight distribution (polydispersity), and structure of the polymer. For example, a catalyst where initiation is faster than propagation will have a narrow molecular weight distribution. On the basis of this analogy, we can suggest a comparison of Fe-SOC with Co-SOC.

Given a theoretically constant rate of growth, if all catalysts nucleate at the same time, the CNTs grown should be of comparable length. This is not observed, suggesting that for Fe-SOC the rate of nucleation is slow. Thus, if we ignore catalyst poisoning, the rate of nucleation is less than the rate of

growth for Fe-SOC. The observation (see above) that iron catalysts inactive on the first growth run may be subsequently activated suggests that the rate of catalyst poisoning is about equal to the rate of nucleation. A different picture arises for Co-SOC. Here the narrow length distribution (c.f., narrow molecular weight distribution for a polymer) and high catalyst yield suggest that (1) the rate of catalyst poisoning is much less than the rate of nucleation and (2) rate of nucleation is greater than the rate of growth. In each case, the question of the rates of termination are complicated by the myriad routes and the potential CNT•••surface forces that may inhibit growth.<sup>6</sup> The activity of the alloy catalysts (Co/Fe-SOC) suggests that the relative rates of each of the basic reaction steps can be controlled by the composition of the catalyst. We are continuing our investigation of catalyst composition as a route to controlling CNT growth. In particular, the important observation is that etching is highly efficient for alloyed catalyst but not the individual component catalysts.

For the growth of CNTs, it is proposed that catalysts in the range of 1–100 nm are sufficient; however, to specifically target the growth of SWNTs, the catalyst needs to only be composed of 20–2500 metal atoms (i.e., 1–5 nm).<sup>21</sup> Within this range, the size of the catalyst particle has been proposed to have an effect on the diameter of the tube produced.<sup>7,8</sup> Although evidence for this postulate was limited, it has been an attractive research goal that specific catalysts can be designed to provide a specific *n,m* SWNT or at least a limited range of SWNT types. We have previously shown that for Fe catalysts single walled carbon nanotubes (SWNTs) can be grown from large catalyst particles countering the concept that catalyst size controls CNT diameter. The present study of Co/Fe-SOC system suggests that growth rate is actually a better control over CNT diameter.<sup>6</sup> The formation of the smallest cap from the catalyst surface (i.e., half of a C<sub>60</sub>) should lead to the smallest SWNT diameter. This will only occur if the delivery of carbon to the SWNT/catalyst interface is slower or equal to the rate of the cap lift-off. If the rate of carbon diffusion/delivery is greater than the rate of cap lift-off, then the cap will increase in size forming a larger diameter CNT. The smallest diameter CNTs will be produced by a lower rate of C–C bond formation (a function of the carbon concentration in the catalyst). Under the growth conditions, it is difficult to estimate the exact carbon concentration in either Fe-SOC or Co-SOC; however, on the basis of the relative phase diagrams for metal-carbide formation, we estimate that the carbon concentration should be lower in Co-SOC than in Fe-SOC simply due to the much lower carbon solubility at growth temperatures. Given the high catalyst yield of Co-SOC, we can conclude that cap formation and lift-off are facile reactions; this assumption in combination with the lower carbon solubility is in agreement with our proposal for the conditions suitable for smaller diameter CNT growth. Thus, an ideal catalyst (and growth conditions) for the growth of only the smallest CNTs would be a catalyst with low carbon solubility, but rapid and efficient cap formation and lift-off. This may be accomplished either through the right growth conditions or the choice of catalyst. We are continuing our studies in this area.

## Experimental

Accuglass T1–11 Spin-on-glass (Honeywell), Fe(NO<sub>3</sub>)<sub>3</sub>•9H<sub>2</sub>O, Ni(NO<sub>3</sub>)<sub>2</sub>•6H<sub>2</sub>O, and Co(NO<sub>3</sub>)<sub>2</sub>•6H<sub>2</sub>O (Sigma-Aldrich) were used as purchased. SEM images were obtained on an FEI Quanta 400

(21) Ding, F.; Rosén, A.; Bolton, K. *J. Chem. Phys.* **2004**, *121*, 2775.

high-resolution field emission environmental SEM operating in high vacuum mode at 30 kV. Samples were prepared by mounting the spin-on-catalyst (SOC) coated silicon wafers onto an aluminum SEM stub with carbon tape. Images acquired before and after regrowth were obtained by selecting a specific position or feature on the silicon wafer and then returning to that same position after regrowth. AFM measurements were obtained on a Digital Instruments NanoScope IIIa scanning probe microscope operating in tapping mode. A RTESP type Nanoprobe SPM Tip with a drive frequency of 300 kHz was used. Images were obtained at a scan frequency of 1.5 Hz and 512 samples/line. Images were taken directly from the surface of the SOC coated silicon wafer.

**Preparation of SOC.** Spin-on-catalyst (SOC) solutions were prepared by dissolving the metal nitrate salts into the Accuglass T1-11 spin-on-glass (SOG) SiO<sub>2</sub> preceramic polymer and diluting to 5.0 mM total metal concentration with SOG. The alcohol/acetone solvent in the SOG allows for complete dissolution of the metal nitrate salts. In a typical preparation, a 5.0 mM Fe-SOC solution was prepared by dissolving Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (50.0 mg, 0.062 mmol) into SOG solution (25 mL). All SOC solutions were stored at or below 4 °C to prevent curing of the SOG.

**Carbon Nanotube Growth.** Samples for the growth of carbon nanotubes were prepared by spin coating (2000 rpm; 40 s) two drops of SOC solutions onto RCA cleaned [30% H<sub>2</sub>O<sub>2</sub> (10 mL), 28% NH<sub>4</sub>OH (10 mL), and deionized H<sub>2</sub>O (50 mL)] n-type silicon wafer cut into 1 cm<sup>2</sup> pieces. The coated wafers were placed into a

quartz boat and inserted into a Lindberg Blue Minimite tube furnace fitted with a 1 inch quartz tube and plumbed with UHP gases. Flow rates were maintained at 500 sccm for Ar and 225 sccm for both CH<sub>4</sub> and H<sub>2</sub>. The tube was purged with argon as the furnace was heated to 900 °C over a period of 30 min. Upon reaching the temperature, growth was initiated by introducing H<sub>2</sub> and CH<sub>4</sub> and Ar flow was stopped. Growth conditions were maintained for 15 min, after which Ar was turned back on and CH<sub>4</sub> and H<sub>2</sub> were turned off. The furnace was allowed to cool to room temperature. Subsequent growth runs used toward the regrowth of nanotubes were performed as described above by reintroducing the original sample back into the tube furnace.

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**Supporting Information Available:** Full description of the material. Length distribution, SEM images, AFM images, diameter distributions for CNTs grown using Co/Fe-SOC. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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