



## Refractory-Metal Diffusion Inhibitors Slow Erosion of Catalytic Metal Particles in the growth of Carbon Nanotubes

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### ABSTRACT

*Catalytic growth of substantial amounts of Carbon Nanotubes (CNTs) to lengths greater than 1 – 2 cm is currently limited by several factors, including especially the deactivation of the catalyst particles due to erosion of catalyst atoms from the catalyst particles at elevated CNT growth temperatures. Inclusion of refractory metals in the CNT growth catalyst has recently been proposed as a method to prevent this catalytic particle erosion and deactivation, allowing the CNT to grow for greater times and reach substantially greater lengths. Here are presented results of recent investigations into this method. The system investigated employs Molybdenum as the erosion inhibitor and Iron as the CNT growth catalyst. Results show that inclusion of Mo leads to substantially longer catalyst particle lifetimes.*

### INTRODUCTION

Carbon nanotubes (CNTs) are of interest for materials applications because of their high tensile strength, high stiffness and outstanding electrical and thermal conductivities [1 – 3]. However, many envisioned bulk applications exploiting these properties for manufacturing [4, 5] will require substantial amounts (kg or more) of CNT whose lengths are comparable to the dimensions of the manufactured items, many cm or more. Thus, much previous research has focused on bulk growth of CNTs to such lengths.

CNTs can be grown using metal-catalyzed Chemical Vapor Deposition (CVD), in which carbonaceous gases flow over nanometer-sized metal catalyst particles of

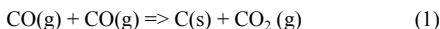
catalytic metals. Under appropriate conditions of temperature, pressure and flow, the gases decompose to release carbon, which forms CNTs by nucleating and growing nanotubes upon the metal particles. CNT growth in such circumstances normally stops after the nanotubes have reached lengths of a few hundred microns or less, making such nanotube unsuitable for many materials applications. As has been discussed previously [6], a primary mechanism of this growth cessation involves Ostwald Ripening [7,8], which causes the metal particles to either erode away or grow too large to support nanotube growth. This erosion and ripening substantially shortens the catalyst particle lifetimes, resulting in much shorter CNT than would otherwise be possible.

Recently, a novel method was proposed to overcome this catalyst particle erosion and ripening by using two component catalysts that combined catalytic metals and high-melting-point refractory metals in a single catalyst material, in which the refractories serve as diffusion inhibitors to prevent the detachment of the catalyst metal atoms from the particles [6]. That study presented results from one such catalyst system, The Re/Mo system, that showed that the diffusions inhibitor (Re) can indeed increase the CNT-growth lifetimes of the catalyst particles. The investigations presented in this paper describe ongoing studies of catalyst/diffusion inhibitor combinations which offer promise for growing high-quality CNTs to long lengths by minimizing erosion of the catalyst particles in this way. In particular, the present study uses iron, a highly catalytic 4<sup>th</sup>-row transition metal, as the catalyst metal in the catalyst/diffusion inhibitor combination. It is anticipated that it will eventually be catalytic metals such as Fe, with their high catalytic activity, that lead to the growth of ultra-long CNTs.

Past research on CNT growth has shown a standard pattern of CNT growth behavior in which the nanotubes grow for a certain time at a rate that is either constant or slowly decreasing, after which CNT growth stops [9 – 22]. Reference 10 gives a simple formulation for this growth: CNTs grow at a constant rate  $\rho$ , for a time  $\tau$ , after which growth stops. The final CNT length, denoted  $\lambda$ , is then the product  $\rho \times \tau$ . The values of  $\rho$ ,  $\tau$ , and  $\lambda$  are dictated by the details of the chemistry involved, and can be measured experimentally. The ultimate goal of this study was to maximize the value of  $\lambda$  by varying experimental parameters to trade-off between the values of  $\rho$  and  $\tau$  to maximize the product  $\rho \times \tau$ . We will adhere to this formulation in our description and interpretation of the studies described here.

## EXPERIMENTAL

The methods of catalyst preparation and CNT growth used in these studies have been described in details elsewhere [6]. Briefly, the CNT growth substrates used were prime-grade Si wafers processed to have the surface composition: Al<sub>2</sub>O<sub>3</sub>(15 nm)/SiO<sub>2</sub>(1 $\mu$ m)/Si. Mixtures of organometallic compounds containing the catalyst and refractory metals of interest were spun onto these substrates, then plasma-oxidized to give thin films (typically 1 – 10 Å) of oxides of the metals. CNTs were grown on these substrates by catalytic CVD in a 1-inch OD quartz reaction tube contained with a tube furnace. Carbon monoxide (CO) was passed over the substrates at elevated temperatures, under which conditions CO reacts to produce elemental carbon upon the catalyst via reaction (1):



This process gave dense forests or mats of CNTs with the nanotubes growing perpendicular to the substrate surface and parallel to each other. The length of the

resulting CNTs was then simply the thickness of the resulting mat, which was measured using Scanning Electron Microscopy (SEM) and, when appropriate, optical microscopy.

The CNT-growth catalyst chosen for investigation was iron, while Molybdenum was chosen as the diffusion inhibitor metal due its high melting point relative to that of iron (2623 °C for Mo vs. 1538 °C for Fe). Growth rates, times and final lengths of the nanotubes were determined as a function of the amounts of Mo and Fe in the catalyst.

## RESULTS

Catalyst films of Fe/Mo metal were prepared on the substrates described above, with varying amounts of Fe catalyst and Mo diffusion inhibitor. As reported previously, pure Mo metal does give some CNT growth from CO, although substantially less than that given by Fe under most conditions [11, 23]. Importantly, catalyst films of pure Fe gave no CNT growth under these conditions: some Mo admixture was necessary for Fe-containing catalysts to produce nanotube growth. Catalysts containing both Fe and Mo produced dense mats of parallel CNTs under these growth condition. A typical results is shown in Figure 1.

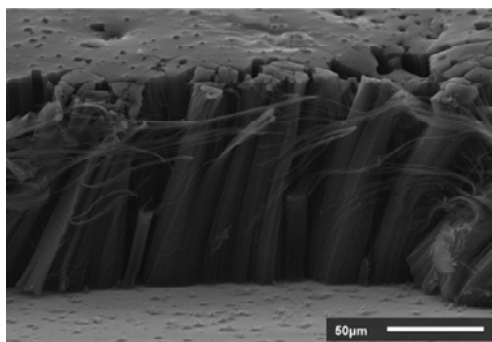


Figure 1. SEM image of dense mat of parallel CNTs grown from a Mo/Fe catalyst on  $\text{Al}_2\text{O}_3(15 \text{ nm})/\text{SiO}_2(1 \mu\text{m})/\text{Si}$  substrate. CNT growth conditions: Catalyst metals, Mo(6Å)/Fe(2Å); Carbon source gas, CO at 8 Atm (6080 Torr) pressure; Temperature, 1000 °C; Growth time, 12 hours.

The optimized CNT growth parameters used for this study were:  $T = 1000 \text{ }^\circ\text{C}$ ;  $P = 8 \text{ Atm}$  (6080 Torr) of CO, the highest pressure at which our apparatus could be safely operated; and flow rate = 45 sccm of CO, giving a gas flow velocity of 0.033 cm/sec.

Detailed study of CNT growth was carried out for a set of catalysts with varying Fe/Mo ratio. For each catalyst, growth runs with various growth time were carried out, with maximum growth time of 24 hours for all Fe/Mo catalyst combinations investigated. In most cases, resulting CNT length increased with increasing growth time, ultimately slowing and stopping as time continued to increase. One set of results is shown in the SEM images in figure 2. These images show CNTs grown from a Mo/Fe catalyst for times up to 24 hours. CNT length increases rapidly with time initially, but the rate of lengthening decreases at greater times. All iron-containing catalysts behaved

in this way, with initial substantial growth rate, which gradually decreased to zero with time. On the other hand, catalyst composed of pure Mo gave CNTs which continued to grow at a constant (though smaller) rate, even for growth times up to 24 hours. It should also be noted that *pure Fe catalyst gave no CNT growth under these conditions*: the presence of Mo was required to produce CNT under these conditions. Figure 3 shows the results of such series of growth runs for every catalyst combination investigated.

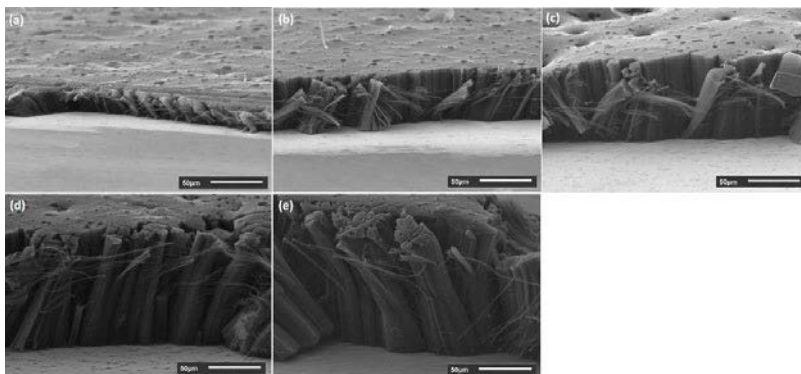


Figure 2. SEM images of CNT mats grown for various times. CNT growth conditions: Catalyst, Mo(6Å)/Fe(2Å); Carbon source gas, CO, 8 Atm; Temperature, 1000 °C; Growth times: a) 1 hr.; b) 3 hr.; c) 6 hr.; d) 12 hr.; e) 24 hr.

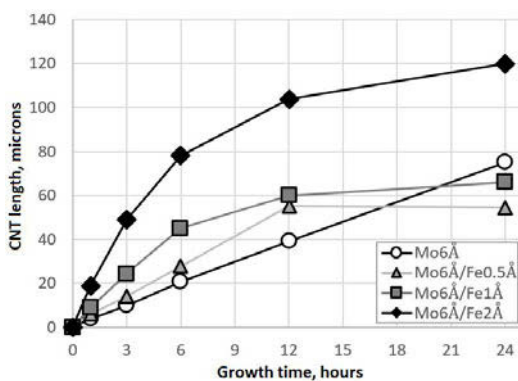


Figure 3. CNT length resulting from Mo/Fe catalyst, as a function of Mo/Fe ratio, for various growth times. CNT growth conditions: Carbon source gas, CO, 8 Atm; Temperature, 1000 °C; Growth times: 1 - 24 hours, as indicated.

## DISCUSSION

Figure 3 displays the length of the CNTs grown vs growth time for catalysts with four different ratios of Fe to Mo. For all Fe/Mo mixed metal catalysts, the growth rate is substantial initially, then decreases with increasing time, eventually reaching zero (cessation of CNT growth). The maximum length achieved is seen to vary depending on Fe content of the catalyst.

Interpretation of these results is simplified by using the formulation and expression for CNT growth given in reference 10: CNTs grow with approximately constant growth rate  $\rho$  for a time interval  $\tau$ , with final length  $\lambda$  given by  $\rho \times \tau$ . If the initial growth rate  $\rho$  (in  $\mu\text{m/hr.}$ ) is taken to be the amount of growth seen in the first hour, then  $\rho$  for each catalyst is simply the length of the CNTs after one hour of growth. This initial growth rate  $\rho$  is plotted vs catalyst Fe content in Figure 4. We see that  $\rho$  is a strongly increasing function of Fe content throughout the range of catalyst compositions investigated.

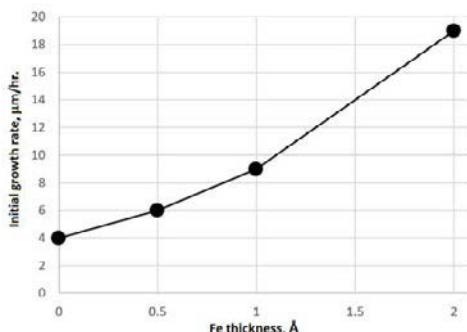


Figure 4. Initial growth rate of CNTs. Conditions used for CNT growth: Catalyst: Mo(6Å) combined with Fe catalyst of thickness as shown; Carbon source gas: CO, 8 Atm (6080 Torr); Temperature: 1000 °C; Growth time: 1 hour.

The time-dependent process of growth cessation can best be visualized by normalizing the length-vs-time growth curve for each catalyst by its initial growth rate, i.e., by dividing the length reached at each time point by the length of the first hour's growth for that catalyst. This will produce curves of CNT length vs time for each catalyst, with the CNT length for each catalyst given in units of the initial CNT growth during the first hour. The resulting growth curves are plotted in figure 5.

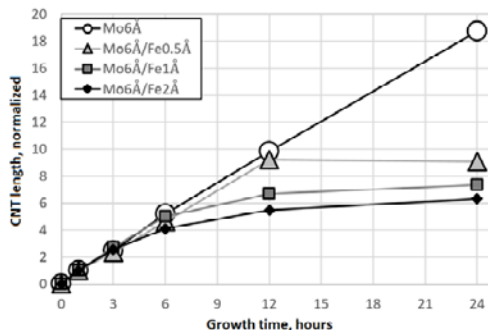


Figure 5. Length of CNTs (given in units of the initial observed growth rate) vs time, for various Mo/Fe catalyst combinations. Mo/Fe thickness is as shown; Growth time: 1 - 24 hours.

Figure 5 shows that, for each Fe/Mo catalyst, the growth rate remains approximately constant for a certain time, then the growth slows and stops. Furthermore, it is clear from figure 5 that the growth slowdown begins sooner for catalysts containing a larger percent of iron, so that the Mo(6Å)/Fe(2Å) curve lies entirely under the Mo(6Å)/Fe(1Å) curve, which lies under the Mo(6Å)/Fe(0.5Å) curve. Again using the formulation of reference 10, the growth time  $\tau$  for each catalyst can be determined from the observed maximum length  $\lambda$  and initial growth rate  $\rho$ , simply as  $\tau = \lambda/\rho$ . Table I lists the values of  $\rho$ ,  $\lambda$ , and  $\tau$  for each Fe/Mo catalyst investigated.

TABLE I. CNTs' initial growth rate  $\rho$ , final length  $\lambda$ , and growth time  $\tau$ , for all studied CNT growth catalysts.

Catalyst:	Mo(6Å)	Mo(6Å)/Fe(0.5Å)	Mo(6Å)/Fe(1Å)	Mo(6Å)/Fe(2Å)
$\rho$ , $\mu\text{m/hr}$	4	6	9	19
$\lambda$ , $\mu\text{m}$	> 75	55	66	120
$\tau$ , hr	> 24	9.2	7.3	6.3

Of particular importance here is the behavior of the growth time as the percent composition of Fe is increased. Table I shows a monotonic decrease in growth time (catalyst lifetime) as the Fe content is increased, or, equivalently, a monotonic increase in lifetime with increasing fraction of Mo relative to Fe. This is just what the proposed model would predict: as the fraction of inhibitor (Mo) increases, the catalyst atoms (Fe) are held in place more strongly and show less tendency to diffuse away from the catalyst particle, resulting in greater catalyst particle lifetimes (larger  $\tau$ ). At the same time, including more diffusion inhibitor in place of catalyst decreases the overall catalytic activity of the catalyst, resulting in slower growth rate. For the particular system studied, the increase in growth time given increasing Mo content is not enough to compensate for the decrease in growth rate, so that the CNT with greatest lengths ( $\lambda = \rho \times \tau$ ) are given by the catalysts with greatest Fe content. Nevertheless, the effect is clear: inclusion of the Mo diffusion inhibitor results in longer catalyst lifetimes, and this lifetime continues to increase as the fraction of diffusion inhibitor in the catalyst increases.

As discussed above, the Mo diffusion inhibitor also acts as a CNT growth catalyst on its own. Comparison of CNT growth from pure Mo vs mixed Fe/Mo catalysts shows that the growth rate from pure Mo catalyst is substantially less, however the growth time appears substantially longer. Indeed, no significant change in rate of CNT growth from Mo catalysts is observed even out to the longest growth times investigated: the growth time  $\tau$  for Mo catalysts must be substantially greater than 24 hours at 1000 °C. This result is also in agreement with the proposed model, as Mo catalyst atoms would be expected to be even more strongly bound than Fe atoms given the refractory nature of Mo.

It should be noted that inhibition of catalyst particle erosion and by Mo inclusion has been inferred from the extended growth lifetimes, rather than observed directly. High-resolution imaging of the catalyst particles themselves by HRSEM, atomic-force microscopy (AFM) or transmission electron microscopy (TEM), would allow direct observation of this effect, for example by providing particle size distributions vs time for various catalyst compositions. Such a high-resolution study of the catalyst particles is certainly important and is planned as part of future, ongoing work in these investigations.

In addition, CO is not particularly efficient at producing CNT material. To achieve CNTs with lengths of cm or longer, it is anticipated that a more reactive gas system will be needed. Future studies will investigate alternate carbon source gases such as alcohols and hydrocarbons. It is also of interest whether other combinations of refractory/catalytic metals could result in CNT growth exceeding that of Mo/Fe. Preliminary investigations have begun on several different such combinations, including Mo/Co, Mo/Ni, Re/Fe, Re/Co, W/Fe, and W/Co. All of these catalysts showed substantial CNT growth rates (several microns/hour or more) under the conditions reported here for Mo/Fe. Future studies will investigate the lifetimes of catalysts with these compositions, as well as maximum CNT length achievable. The ultimate goal of this work is to produce CNTs with lengths of many cm or more.

## CONCLUSIONS

These results give further evidence that high-melting-point diffusion-inhibitor metals can extend the lifetimes of particles of catalytic metals in the growth of CNT, in particular in a case where the catalytic metal is a high-activity 4<sup>th</sup>-row transition metal, iron. It is hoped that planned continuations of these studies will allow growth of longer CNTs still, ultimately enabling production of CNTs many cm or more in length.

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