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Received June 12, 2009; Revised Manuscript Received July 31, 2009

ABSTRACT

The density of the aligned single-walled carbon nanotubes (SWNTs) grown on quartz substrates is an important factor for the performance of fabricated electronic devices. It was discovered that the addition of a sulfur-containing compound (thiophene) to the reaction mixture improved the density of SWNTs by a factor of 2 or more, from $\sim 2$–$4$ SWNTs/$\mu$m to $6$–$8$ SWNTs/$\mu$m under similar growth conditions. It was also observed that along with the increase in nanotube density, the cleanness of the samples improved as well. These effects were demonstrated over a large range of growth conditions, indicating that the addition sulfur makes the growth processes more favorable for the nucleation and growth of aligned SWNTs.

The impressive electronic properties of single-walled carbon nanotubes (SWNTs) combined with their diverse utility make them a leading material for the development of nanoelectronic devices. As such, having a fundamental understanding of their growth mechanism as well as the ability to control the properties of the as produced SWNT products is paramount to their incorporation into mainstream applications. Some of the most critical properties that need to be controlled for this mainstream application are density, length, and alignment. Recently, significant progress has been made in the ability to control the alignment of SWNTs. As such, perhaps the most significant challenge standing in the way of this mainstream application is the fact that, in a typical chemical vapor deposition (CVD) growth process, mixtures of approximately 1:2 metallic:semiconducting SWNTs are produced. Having such a mixture presents application problems, as most applications require either metallic or semiconducting SWNTs. Recently, our group found a method to selectively produce perfectly aligned samples of almost exclusively semiconducting SWNTs (95–98%). The selective production of these clean, aligned semiconducting samples represented a significant step in the integration of SWNTs into nanoelectronic devices and mainstream technology. However, further investigation into the mechanism of this growth was necessary to fully understand and therefore utilize the factors which lead to this selectivity.

Previous work has demonstrated that sulfur-containing compounds can be used to control the diameter as well as the number of shells of carbon nanotube products. However, perhaps the most investigated effect of sulfur is that sulfur-based growth promoters such as thiophene can be utilized to increase the yield and quality of bulk produced SWNTs, typically by approximately 30%. It is said that sulfur can influence SWNT growth by blocking active sites on the catalyst particle, lowering the melting point of the catalyst, or interacting with the growing nanotube. It has also been suggested that the appropriate amount of sulfur can help prevent the buildup of amorphous carbon and thus the poisoning of the catalyst particles. However, it is still unclear whether these are the factors which contribute to sulfur’s SWNT growth promotion, and which among these possible factors plays the most significant role during growth.

In our previous work, we found that the combination of the appropriate quartz substrate, catalyst size, and amount of MeOH all played significant roles in the selective production of semiconducting SWNTs (s-SWNTs). Notably, we hypothesized that OH radicals from the MeOH selectively etched the metallic nanotubes because of their lower ionization potential. Also, MeOH may raise the carbonization temperature of the system, which may also contribute to the selective production/nucleation of such small diameter s-SWNTs. However, further work was necessary to investigate and clarify these hypotheses. Herein, we analyze the effect of sulfur on the EtOH/MeOH system in order to help
elucidate the mechanism of this selective growth as well as the origin of the sulfur growth promotion.

All samples were grown on 36° Y-cut single crystal quartz substrates and using 1 mM Fe(NO$_3$)$_2$·9(H$_2$O) or FeCl$_3$ and CuCl$_2$ as catalysts. Catalyst solutions were made in 200 proof EtOH and stabilized by poly(vinyl pyrrolidinone) (PVP). The catalyst diameters ranged from approximately 0.7 to 2.5 nm, with an average diameter of 1.6 as determined by atomic force microscopy (AFM). Detailed synthesis procedures have been described previously.$^1$ Briefly, after the catalyst was patterned, the substrates were annealed in air at 750 °C for 5 min and then reduced under H$_2$ at 750 °C for 10 min. After this reduction, samples were raised to 900 °C and grown under EtOH/MeOH/H$_2$ or EtOH/H$_2$ for 15 min and then cooled under H$_2$. Analysis of the as prepared samples was done using scanning electron microscopy (SEM) and AFM. Using a transfer method described elsewhere,$^1$ samples were transferred to Si wafers with a 1 µm SiO$_2$ insulating layer for Raman analysis. Raman was used to analyze the radial breathing mode (RBM) of the dense, aligned samples using a 633 nm laser in order to determine the selectivity of each growth method.

Typically, to promote bulk SWNTs growth, a thiophene concentration in the carbon precursor between 0.5 and 5 wt % is often used with Fe catalysts. However, it was found that in surface growth, the best enhancement was observed at much lower concentrations, specifically from 0.01 to 0.1 wt %. Also, these enhancements were seen at different concentrations depending on the type and size of catalyst as well as the source gases. When EtOH/MeOH mixtures were used, density enhancements of up to a factor of 2 were seen at 0.075–0.1 wt % thiophene in EtOH for Cu catalyst (Figure 1) and as low as 0.03–0.05 wt % for Fe catalyst (Figure 2) as determined by SEM and AFM. The difference in these optimum conditions is likely a result of their differing catalytic activities. However obvious density and length enhancements can be seen at thiophene concentrations as low as 0.01 and 0.03 wt % (Figures S1–S3 in Supporting Information). In both cases, the density of aligned nanotubes was improved from ∼2–4 SWNTs/µm to at least 6–8 SWNTs/µm by the addition of the appropriate amount of thiophene (Figure 3, panels C and D). These nanotubes were perfectly aligned and of high quality, with no noticeable amorphous carbon contamination; however, this enhancement was also evident in the catalyst regions as shown in parts A and B of Figure 3. Additionally, the aligned nanotubes were noticeably long, mostly stopping only when encountering a physical barrier on the surface (Figure S4, panels A and C in Supporting Information). When only EtOH was used as the carbon source, the improvement was demonstrated at much lower thiophene concentrations (0.005–0.01 wt % in EtOH). The enhancement was also less dramatic, displaying only approximately a 30–50% density increase. Most nanotubes were very short and all samples without thiophene were dirty as indicated by AFM and SEM (Figure S5 and

![Figure 1](image1.png)

**Figure 1.** Samples grown on quartz using Cu as catalyst and EtOH–MeOH mixtures as carbon feeding gases. Each sample was grown with (A) 0, (B) 0.01, (C) 0.03, (D)0.05, (E) 0.075, and (F) 0.1 wt % thiophene. A factor of 2 density enhancement was demonstrated over this range, giving an average nanotube density of 2–4 nanotubes/µm and 6–8 nanotubes/µm without and with thiophene respectively. (The scale bar in all pictures is 10 µm.)

![Figure 2](image2.png)

**Figure 2.** Samples grown on quartz using Fe as catalyst and EtOH–MeOH mixtures as carbon feeding gases. Each sample was grown with (A) 0, (B) 0.01, (C) 0.03, and (D) 0.05 wt % thiophene. A factor of 2 density enhancement was demonstrated over this range, giving an average nanotube density of 2–4 nanotubes/µm and 6–8 nanotubes/µm without and with thiophene respectively. (The scale bar in all pictures is 10 µm.)
Although the addition of thiophene helped to clean samples produced using EtOH, they were still noticeably dirtier than those produced with EtOH and MeOH, and the density of longer nanotubes was still lower. However, it was obvious from these results that adding the optimal amount of thiophene can improve the density of aligned surface grown SWNTs. It should be noted that, as with the enhancement of bulk samples, adding more thiophene than the optimal amount causes a dramatic decrease in the density of SWNT products (Figure S4 in Supporting Information). To our knowledge, this is the first time a sulfur source has been used to demonstrate such a density enhancement for surface grown SWNTs.

The effect of thiophene can be seen to manifest itself in the diameter distribution of the as produced nanotubes. This is particularly evident in the Raman spectra of these samples (Figure S4 in Supporting Information). Although the addition of thiophene helped to clean samples produced using EtOH, they were still noticeably dirtier than those produced with EtOH and MeOH, and the density of longer nanotubes was still lower. However, it was obvious from these results that adding the optimal amount of thiophene can improve the density of aligned surface grown SWNTs. It should be noted that, as with the enhancement of bulk samples, adding more thiophene than the optimal amount causes a dramatic decrease in the density of SWNT products (Figure S4 in Supporting Information). To our knowledge, this is the first time a sulfur source has been used to demonstrate such a density enhancement for surface grown SWNTs.

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the sulfur interacts with the growing nanotubes, it will also interact with the catalyst to prevent poisoning, as previously claimed.\textsuperscript{12} If this interaction occurs, the smaller catalyst particles that may have previously been poisoned would be kept active by the sulfur. This would help explain the broadening of the nanotube diameter range observed here. The broadening occurs on the lower end of the diameter range, indicating the presence of small diameter metallic nanotubes. Either because of catalyst poisoning or because of the etching of the small diameter nanotubes by OH radicals, these small diameter metallic nanotubes are not seen without the presence of thiophene. Second, if thiophene interacts with catalyst nanoparticles to decrease the etching point of the catalyst, this may offset the increase in the carbonization temperature caused by the MeOH. This would result in more catalyst particles being active for nanotube nucleation. As a result, this eutectic point lowering would expand the window of the viable catalyst particles, which would result in a broadening of the diameter distribution. Lastly, thiophene may interact with the MeOH during growth, preventing it from contributing to the reaction of the EtOH and the catalyst particle. However, if this was the case, the density, quality, and length of samples with MeOH and thiophene would likely match up well with samples produced using only EtOH, which they do not. Samples produced with just EtOH are, on average, denser but dirtier and shorter than those produced here using EtOH, MeOH, and thiophene (Figure S5 and S6 in Supporting Information). Therefore, the most probable explanation is that sulfur does help prevent the selective etching of metallic SWNTs and that perhaps it also helps prevent the poisoning of the catalyst particles. The sulfur may still effect the eutectic point of the catalyst particles as well.

As a corollary, these results and analysis help to support our hypothesis that MeOH selectively etches the metallic SWNTs during growth. By determining that the most likely effect of sulfur is to interact with the catalytic nanoparticle and growing nanotubes, it is reasonable to conclude that the interaction of MeOH during growth must be with one of or both of these factors. The broadening of the nanotube diameter range occurs to incorporate smaller diameter metallic nanotubes, which are less stable than larger diameter nanotubes. Therefore, because they are less stable, they would be more likely to be etched than would nanotubes with larger diameters. This fact supports our hypothesis that the primary role of MeOH is to selectively etch the less stable metallic nanotubes.

Through this work, we have successfully demonstrated the density enhancement of perfectly aligned SWNTs on quartz substrates using thiophene. To our knowledge, this is the first example of a sulfur-based growth promoter being utilized on surface-grown nanotube samples. With SEM and AFM, it was evident that a factor of 2 density increase of these high-quality, long, aligned SWNTs grown from EtOH/MeOH mixtures was achievable. Although less dramatic, a 30–50\% increase of nanotube density was demonstrated when only EtOH was used as the carbon feeding gas. Theses nanotubes were also shorter and of poorer quality than those produced using EtOH and MeOH as determined by SEM and AFM. By utilizing theories discussed in previous work done on bulk nanotube growth using sulfur based components, we were able to further support our previous hypothesis that the role of MeOH in the selective production of s-SWNTs was to selectively etch the less stable metallic SWNTs. Also, these results help to further clarify the role of sulfur during the growth of SWNTs, indicating that it helps to stabilize the growing nanotubes as well as prevent catalyst poisoning.

Acknowledgment. The work is supported by funds from DOE(DE-FC36-05GO15103) and ONR (N00014-09-1-0163). Also, the Shared Materials Instrument Facility is gratefully acknowledged for its support.

Supporting Information Available: Further experimental details and methods, as well as supportive SEM and AFM data. This material is available free of charge via the Internet at http://pubs.acs.org.

References


