Selective Matching of Catalyst Element and Carbon Source in Single-Walled Carbon Nanotube Synthesis on Silicon Substrates

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Received: October 7, 2004; In Final Form: November 29, 2004

We have studied the compatibility of various catalysts for ethylene and ethanol chemical vapor deposition (CVD) syntheses of single-walled carbon nanotubes (SWNTs) on Si substrates. A strong selectivity between the catalyst elemental species and carbon source was found; SWNT yield for Fe (Co) catalysts was much higher for ethylene (ethanol) CVD than for ethanol (ethylene) CVD. This strong and completely opposite selectivity implies significantly different SWNT growth mechanisms for ethanol and ethylene CVD on Si substrates.

Introduction

Since their discovery by S. Iijima in 1991,¹ carbon nanotubes, especially SWNTs, have garnered an extremely high level of attention from both the academic and industrial societies due to their fascinating and promising physical and chemical characteristics. Even though it was anticipated that SWNTs would serve as an ideal material for applications spanning electronic devices,^{2–8} high strength composites,⁹ to conductive composites,¹⁰ real products have not yet been realized because of the difficulties surrounding the synthesis of SWNTs. Therefore, it is of critical importance to accumulate knowledge regarding the growth of SWNTs through fundamental research.

The importance of SWNT synthesis on Si substrates by CVD stems from the use of standard lithography for the fabrication of SWNT electronic devices. However, SWNT synthesis is commonly difficult on Si substrates which results in low yields, therefore, improvement in CVD growth is eagerly demanded. In CVD, the catalyst and the carbon source are the two most important factors. On Si substrates, hydrocarbons (methane/ ethylene)^{2,7,8,11-16} and ethanol^{6,17-20} represent two classes of carbon sources where successful SWNT synthesis has been reported by many groups. Additionally, a number of different catalysts have been previously reported using a variety of preparation methods and compositions.^{2,4–8,11–15,17–20} Catalysts have been prepared in the form of thin metal layers,^{6,8,11} thin metal salt layers,^{2,5,7,15,17,18} and nanoparticles,^{4,12-14,19,20} and their composition varied from Fe, Co, to their alloys with Mo. Furthermore, a number of catalyst/carbon source combinations exist. However, a general understanding concerning the compatibility of the catalysts and the carbon sources does not exist because only one, or at the most two, of the combinations have been investigated in each individual research.

Our research is motivated to establish a general understanding of CVD synthesis of SWNTs on Si substrates particularly regarding the compatibility among various catalysts and carbon sources, specifically ethylene and ethanol. We prepared most of the catalysts that had been reported in the past to provide a reasonable SWNT yield and carried out a comparative series of both ethylene and ethanol CVD growths with these catalysts on Si substrates. From our survey, while the catalyst-preparation method proved to be a less significant issue, we discovered a significant importance in the matching of the elemental species of the catalyst and carbon source for high-yield SWNT synthesis. Specifically, Fe (Co) catalysts showed high SWNT yields for ethylene (ethanol) CVD while showing very low yield for ethanol (ethylene) CVD. This strong and completely opposite selectivity implies that the growth mechanism of SWNTs substantially differs for ethanol and ethylene CVD when grown on Si substrates.

Experimental Section

Catalyst Preparation. Fe, Co, and their alloys with Mo are often used as catalysts for SWNT synthesis. We prepared most of the Fe and Co–Mo catalysts (Table 1) that have been previously reported to provide a high yield of SWNT growth in various forms, such as metal thin layers, metal salt layers, and nanoparticles, synthesized by wet chemistry, metal deposition by sputtering and ultrahigh-vacuum e-beam deposition, and the reverse-micelle method, respectively. Each catalyst was synthesized following a recipe adopted from the literature that has been adjusted locally to optimize the SWNT yield.^{2,6,8,11,13,15,17}

Fe Salt. A solution of $Fe(NO_3)_3$ ·9H₂O in isopropyl alcohol with a concentration of 0.25 mM was prepared. Si substrates were dipped into the solution for 10 s and rinsed 10 times in hexane and dried with argon gas.²

Nanoparticles by FeCl₃. Fe-containing nanoparticles were formed by immersing Si substrates into a solution of 10 mL of 0.01 mM FeCl₃•6H₂O(aq), followed by the immediate addition of 100 μ L of 40 mM NH₂OH•HCl(aq). After soaking in the solution for 2 min, the substrate was removed, rinsed with isopropyl alcohol, and dried.¹⁵

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 TABLE 1: Summary of the Compatibility of the Catalyst

 (Element and Preparation Method) and Carbon Sources

 (Ethanol or Ethylene) with the Yield of SWNTs^a

		yields	
catalyst	preparation methods	hydrocarbon CVD	alcohol CVD
$Fe(NO_3)_3^1$ $FeCl_3^{15}$ Fe thin film ⁸ Fe nanoparticles ¹³	Fe Catalysts wet chemistry nanoparticles thin film nanoparticles	0.27 2.28 1.08	
Co–Mo acetates ¹⁷ Co/Mo thin film ⁸ Co-Mo nanoparticles ¹³	Co Catalysts wet chemistry thin film nanoparticles		0.92 0.14 0.31
Fe or Co Cata	alysts with an Al ₂	O3 Underlayer	
Fe/Al ₂ O ₃ thin film	thin film	1086.00	
Co/Al ₂ O ₃ thin film	thin film	0.82	

^{*a*} The yield of SWNTs was analyzed from Raman spectra where it was assumed to be propotional to the ratio of the peak heights of the tangential-mode G band due to SWNTs against the Si Raman peak at 520 cm⁻¹ due to the Si substrate. The value for Fe/Al₂O₃ thin film is very high due to the fact that the laser power was substantically attenuated by the thick SWNT mat.

Fe and Co/Mo Thin Films. An iron thin film of 1-2 nm on a Si wafer was prepared by magnetron sputtering. Similarly, Co/Mo thin films were fabricated by successive sputtering of molybdenum (1-2 nm) and cobalt (1-2 nm).^{6,8,11}

Co–Mo Salt. Molybdenum acetate $((CH_3COO)_2Mo)$ and cobalt acetate $((CH_3COO)_2Co\cdot 4H_2O)$ were dissolved into ethanol by 4 hours of sonication to make a metal acetate solution with a concentration of 0.01 wt %. Si substrates were immersed

into the prepared solution for 10 min. After drying, the substrate was calcined at 400 $^\circ C$ for 5 min in air. 17

Fe and Co–Mo Nanoparticles Synthesized by the Reverse-Micelle Method. Iron chloride, FeCl₃, was dissolved into toluene with a cationic surfactant, didecyldimethylammonium bromide, to prepare the Fe nanoparticles. Similarly, a solution of cobalt chloride hexahydrate (CoCl₂•6H₂O) and molybdenum chloride MoCl₅ was prepared for the Co–Mo nanoparticles. Reduction of the metals was carried out by adding aqueous solution of sodium tetrahydroborate NaBH₄ into each of the Fe and Co–Mo solutions to form colloid of nanoparticles. Finally the prepared nanoparticles were dropped onto the Si substrate and left to dry.¹³

Chemical Vapor Deposition. Ethylene and ethanol CVD syntheses were implemented at specific experimental conditions that were determined from our previous CVD experiments covering a wide range of growth conditions and were very similar to those used previously by other groups to synthesize SWNTs.^{2,14,16,17,19} CVD at these growth conditions produced a fairly good yield of SWNTs for all of the catalysts we had prepared. For ethylene CVD, samples were annealed to 750 °C in Ar and H₂ (total 1000 sccm), and growth was carried out at 750 °C for 2 min with 10 sccm of ethylene.^{2,14,16} For ethanol CVD, samples were annealed to 800 °C in Ar gas with 3% H₂ at 300 Torr, and upon reaching 800 °C, the gas supply was stopped and the furnace was evacuated to 1–2 Torr. Consequently CVD growth was initiated by supplying ethanol vapor from a thermal bath at 10 Torr for 15 min.^{17,19}



Figure 1. AFM images of the SWNTs on Si substrates grown by ethylene CVD with various catalysts: (a) $Fe(NO_3)_3$ salt; (b) nanoparticles by $FeCl_3$; (c) Fe thin film; (d) Co–Mo salt; (e) Co/Mo thin film; (f) Co–Mo nanoparticles synthesized by the reverse-micelle method; (g) Fe nanoparticles synthesized by the reverse-micelle method.



Figure 2. Raman spectra showing the presence of the SWNTs on the Si substrates synthesized by the hydrocarbon CVD with iron catalysts formed from various catalysts: (i) Fe thin film; (ii) nanoparticles by FeCl₃. The laser excitation wavelength was 514.5 nm. The frequency ranges were $1800-100 \text{ cm}^{-1}$ (top) and $350-100 \text{ cm}^{-1}$ (bottom). For the samples where Fe salt and Fe nanopatricles synthesized by the reverse-micelle method were used as the catalyst, the yields of the SWNTs were not sufficient to implement reliable Raman experiments. However, from AFM images, the tube sizes were estimated to be in the range of 1-3 nm; thus we conclude that the synthesized nanotubes are SWNTs.

Results and Discussion

A series of ethylene and ethanol CVD syntheses on Si substrates was carried out at appropriate growth conditions for each of the seven types of catalysts. Figure 1 shows atomic force microscopy (AFM) images of the surface of the as-grown ethylene CVD samples with different catalysts. For Fe salt (Figure 1a), nanoparticles by FeCl₃ (Figure 1c), Fe thin film (Figure 1e), and Fe nanoparticles synthesized by the reversemicelle method (Figure 1g), a high density of nanotubes entangled into a spaghetti-like form was observed. It is worthy to note that in parts c and e of Figure 1, the Si substrates could not be imaged and the nanotubes formed a thick mat (thickness estimated up to 100 nm) covering the entire substrate. The yield of SWNTs reported here is comparable to the highest reported yield of SWNTs synthesized on Si substrates with a hydrocarbon source, a fact that highlights our well-optimized catalyst preparation and CVD growth procedures. In sharp contrast however, for Co-Mo salt (Figure 1b), Co-Mo thin film (Figure 1d), and Co-Mo nanoparticles (Figure 1f) catalysts, the yield of SWNTs was very low, despite the surface being covered with numerous catalysts in the form of nanoparticles whose sizes fall in the range suitable for SWNT growth. As clearly shown later, failure to synthesize nanotubes from these catalysts was due to an extremely strong selectivity of SWNT growth on the combination of the catalyst and carbon source rather than the ability of the catalysts to produce SWNTs.



Figure 3. A TEM image of SWNTs grown by ethylene CVD.

We confirmed that the nanotubes observed in Figure 1 were SWNTs by Raman analysis and transmission electron microscope (TEM) observations. Figure 2 shows a series of Raman (excited by Ar ion laser at 514 nm) spectra of the samples where nanotubes were observed. The radial breathing mode (RBM) peaks that are characteristic to SWNTs were observed in the low-frequency range of 150-260 cm⁻¹, confirming the existence of SWNTs. The diameter of SWNTs was calculated to be in the range of 1.0 to 1.7 nm, from the expression $\omega = 248/d^{21}$, where ω is the RBM frequency (cm⁻¹), and *d* is the diameter of SWNTs (nm). The tangential-mode G band showed narrow, strong peaks in the region of 1590 cm^{-1} . In contrast, the socalled "D band" around 1350 cm⁻¹ related to defects, and the presence of amorphous carbon was small. These results make evident that the nanotubes are well crystallized high-quality SWNTs without an amorphous component. A typical TEM image of the nanotubes from the FeCl₃ catalyst (Figure 1c) is presented in Figure 3. The image clearly shows that essentially all of the nanotubes are long, clean, and high-quality SWNTs. TEM observations of nanotubes grown from other catalysts showed similar results, and no evidence for multiwalled carbon nanotube formation was found, demonstrating that our catalysts and CVD growth were well-suited to selectively grow SWNTs.

Surprisingly, vastly different trends were observed for ethanol CVD on Si substrates. Figure 4 shows a set of AFM images of the surface of as-grown ethanol CVD samples with the different catalysts. While a strong selectivity was found again, this time, the behavior was completely reversed in terms of the activity of the catalysts when compared to ethylene CVD. For Co-Mo salt (Figure 1b), Co-Mo thin film (Figure 1d), and Co-Mo nanoparticles (Figure 1f) catalysts, a high density of nanotubes entangled into spaghetti forms was observed, but for Fe salt (Figure 1a), nanoparticles by FeCl₃ (Figure 1c), Fe thin film (Figure 1e), and Fe nanoparticles synthesized by the reversemicelle method (Figure 1g), the yield of SWNTs was very low. In parts b and d of Figure 1, nanotube yields were very high and the Si substrates cannot be imaged, indicating that the catalyst preparation and CVD growth procedures were well optimized. We confirmed that the nanotubes in Figure 4 are high-quality SWNTs by Raman analysis and TEM observations. No evidence for multiwalled carbon nanotubes formation was found by TEM observations, and Raman spectra showed RBM peaks at 150-190 cm⁻¹, confirming that the nanotubes are SWNTs (Figure 5).

The results are summarized in Table 1 where the catalyst element, preparation method, and carbon source are listed with their associated SWNT yields. The yield of the SWNTs was



Figure 4. AFM images of the SWNTs on the Si substrates grown by ethanol CVD with various catalysts: (a) $Fe(NO_3)_3$ salt; (b) nanoparticles by $FeCl_3$; (c) Fe thin film; (d) Co–Mo salt; (e) Co/Mo thin film; (f) Co–Mo nanoparticles synthesized by the reverse-micelle method; (g) Fe nanoparticles synthesized by the reverse-micelle method.

approximated to be propotional to the ratio of the tangentialmode G band peak heights from SWNTs and the Si Raman peak at 520 cm⁻¹ from the Si substrate. This method cannot be regarded as an accurate quantitative analysis because a thick SWNT mat would attenuate the incident laser energy on the Si substrate and other graphitic carbon materials can also contribute to the G-band; however, we assume that it provides a reasonable first-order approximation of the yield of SWNTs on Si substrates. From Table 1, it is clear that there exists a strong selectivity between the combination of the atomic species of the catalyst and carbon source. Matching of the catalyst element and carbon source was found to be of extreme importance, while the catalyst-preparation method proved to be a less significant issue. Fe catalysts produced a high yield of SWNTs growth for ethylene CVD, while the yield was very low for ethanol CVD. Interestingly, for Co catalysts, the selectivity was completely reversed where the SWNT yield was high for ethanol CVD but very low for ethylene CVD. This strong and completly reversed selectivity involving the catalytic element and carbon source observed on SWNT synthesis implies that the SWNT growth mechanism is considerably different for ethylene and ethanol CVD.

We reached this conclusion regarding selectivity through a wide range of CVD experiments of which Figures 1-5 are only a part. The results of the whole body of experiments are divided into two aspects: (1) elemental composition of the catalyst and (2) CVD growth conditions. The catalysts used in experiments of Figures 1-5 were made of Fe and Co-Mo, compositions of catalysts that are most commonly used in SWNTs syntheses. We have also prepared and tested several Fe-Mo and Co

catalysts (e.g., Fe–Mo nanoparticles, Fe–Mo salt, Co thin film, and Co nanoparticles). Generally speaking, for both Fe and Co, alloying with Mo increased the SWNT yield; however, this did not change the selectivity.

The specific CVD growth conditions for Figures 1-5 were carefully chosen based on preliminary CVD experiments results covering a wide range of growth conditions. For ethylene CVD, the growth temperature was varied from 700 to 800 °C, growth time was varied from a few seconds to 30 min, ethylene flow rate was varied from 0.5 to 100 sccm, hydrogen concentration was varied from 20% to 100%, and He was used as the carrier gas. For ethanol CVD, the growth temperature was varied from 700 to 900 °C, growth time was varied from 2 to 60 min, the growth pressure was varied from 5 to 30 Torr, and the H₂ concentration was varied 3 to 6%. Among the growths conducted on this wide range of experimental conditions, the specific growth conditions of Figures 1-5 showed fairly good, if not the best, yield of SWNTs for all of the catalysts we have prepared. If carefully tuned, the best growth conditions differ with each catalyst. Nonetheless, as long as the same carbon source is used, the optimized growth conditions for each different catalyst seems to fall into a similar range of experimental conditions.

By a change of the catalyst–substrate interaction, it might be possible to relax the strong selectivity of the catalyst and carbon source on Si substrates and grow SWNTs. Some recent research^{11,22,23} has pointed out that SWNT growth can be significantly improved by placing a thin intermediate layer (Al₂O₃, Ti) between the catalyst and Si substrates. To investigate how this factor influences the selectivity, Fe and Co metal thin



Figure 5. Raman spectra showing the presence of the SWNTs on the Si substrates synthesized by ethanol CVD with Co–Mo catalysts of various forms: (i) Co–Mo salt; (ii) Co/Mo thin film; (iii) Co–Mo nanoparticles. The laser excitation wavelength was 514.5 nm. The frequency ranges were 1800–100 cm⁻¹ (top) and 350–100 cm⁻¹ (bottom).

film catalysts with thin Al_2O_3 (10 nm) layers underneath were fabricated on Si, and ethylene CVD was performed. The doublelayered catalyst was fabricated by standard magnetron sputtering where Al_2O_3 was first deposited from a Al_2O_3 sputter target followed by Fe deposition. Interestingly, high yields of SWNTs could be grown with ethylene even with Co catalysts (Figure 6b and Table 1) with the Al_2O_3 intermediate layer underneath the catalyst. It is worthy to note that growth with Fe catalysts (Figure 6a and Table 1) with an Al_2O_3 sublayer showed a even higher yield growth. It is reported that the Al_2O_3 thin layer promotes the formation of sufficiently small catalyst particles that are able to catalyzes SWNT growth and also inhibit further coalescence of the catalysts, ^{22,24} In addition, the Al_2O_3 thin layer could keep the catalysts from interacting from the silica surface or change the atomic strain of the intermediate layer.

From experiments alone, it is difficult to understand why such a strong selectivity exists between the catalyst and carbon source. To understand the mechanism of the selectivity, it is crucial to simultaneously observe the atomic structure of the catalysts and SWNTs and obtain information about their interface. Currently such a work is in progress.

In conclusion, we have investigated the matching of various catalysts and two representive carbon sources (ethylene and ethanol) for SWNT CVD on Si substrates. We found an extremely strong selectivity; Fe (Co) catalysts showed high SWNT yields for ethylene (ethanol) CVD while producing very low SWNT yields for ethanol (ethylene) CVD. The method by which the catalyst was synthesized proved to be less of a factor. The observed strong and completely reversed selectivity suggests that ethanol and ethylene CVD have a significantly different growth mechanism of SWNTs on Si substrates. Our results



Figure 6. AFM images showing SWNTs grown by catalysts prepared on Si substrate with an Al_2O_3 underlayer: (a) SiO_2 (500 nm)/ Al_2O_3 (10 nm)/Fe (1 nm); (b) SiO_2 (500 nm)/ Al_2O_3 (10 nm)/Co (1 nm). In both cases, the yields of SWNTs were high. However, the yield was much higher when Fe was used as the catalyst than when Co was used. This point could be easily confirmed by the color of the sample; the sample with Fe catalysts became totally black, while the color of the sample with Co catalyst remained similar to that of the Si wafer.

clearly demonstrate that it is of critical importance to choose the appropriate combination of substrate, catalyst, and carbon source for efficient SWNTs synthesis.

Acknowledgment. This work was supported by the New Energy and Industrial Technology Development Organization (NEDO) as a part of the Nano Carbon Technology (NCT) project.

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