

## Controlling the size and the activity of Fe particles for synthesis of carbon nanotubes

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### Abstract

The properties of carbon nanotubes (CNTs) are controlled by their structure and morphology. Therefore, their selective synthesis, using catalytic chemical vapor deposition, requires precise control of a number of parameters including the size and activity of the catalyst nanoparticles. Previously, an environmental scanning transmission electron microscope (ESTEM) has been used to demonstrate that electron beam-induced decomposition (EBID) of Fe containing precursor molecules can be used to selectively deposit Fe catalyst nanoparticles that are active for CNT growth. We have extended these *in situ*

ESTEM observations to further our understanding of the EBID parameters, such as electron beam current, deposition time, and substrate temperature, that control the size and placement of Fe catalyst particles for two precursors, namely diiron nonacarbonyl ( $\text{Fe}_2(\text{CO})_9$ ) and ferrocene ( $\text{Fe}(\text{C}_5\text{H}_5)_2$ ). We found that the diameter of deposited particles increased with increasing deposition time. Electron energy-loss

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spectra, collected during deposition, show the incorporation of C in the Fe particles. The C content decreased as the substrate temperature was increased and was negligible at 100 °C for Fe<sub>2</sub>(CO)<sub>9</sub>. However, C and Fe were co-deposited at all temperatures (up to 450 °C) when Fe(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub> was used as an iron source. After deposition, the substrate was heated to the CNT growth temperature in flowing hydrogen to remove the co-deposited C, which was an important step to activate the deposited Fe catalyst for the growth using acetylene. Our measurements revealed that the Fe nanoparticles fabricated from Fe<sub>2</sub>(CO)<sub>9</sub> had higher activity for CNT growth compared to the ones fabricated using Fe(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>. The deposited particles from Fe(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub> formed a core-shell structure with Fe surrounded by graphitic carbon at 300 °C to 400 °C. We also found that the co-deposited carbon in this case could not be removed by heating in hydrogen. We speculate that the reduced activity is due to the C content in the deposit for the latter.

### Highlights

- We fabricated Fe catalysts for CNT growth using EBID with Fe<sub>2</sub>(CO)<sub>9</sub> and Fe(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>.
- Electron beam location and dwell time controlled catalyst position and diameter.
- Catalysts from Fe<sub>2</sub>(CO)<sub>9</sub> had less carbon than catalysts from Fe(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>.
- More catalysts from Fe<sub>2</sub>(CO)<sub>9</sub> grew nanotubes compared to catalysts from Fe(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>.
- Carbon reduces catalyst activity and must be removed during or post-deposition.

### Keywords

Carbon nanotubes, catalyst activity, electron beam induced deposition, *in situ* electron microscopy, iron catalysts

## 1. Introduction

The wide range of properties of carbon nanotubes (CNTs) is in part dependent on their structural and morphological diversity. Potential applications so far have been hindered by the lack of our ability to synthesize CNTs with same structure and morphology on a large-scale. Moreover, it will be advantageous for some applications, such as field emission displays, for CNT synthesis to be a part of the fabrication process. Large-scale synthesis of CNTs can be achieved by decomposition of a hydrocarbon precursor on a transition metal (Ni, Fe, Co, Mo etc.) catalyst at temperatures above 400 °C. For direct fabrication of CNTs on a device, catalyst particles with controlled diameter and spacing are first deposited on the substrate; then CNTs are synthesized using chemical vapor deposition (CVD) by flowing a hydrocarbon precursor over the heated substrate. The assumption is that the same diameter catalyst particle will result in the formation of CNTs with same diameter and length, and the controlled spacing will reduce the screening of individual nanotube emitters during field emission (Bonard *et al.* 2001, Kim *et al.* 2000) or organize the nanotubes into the desired geometry for nanoelectronics (Baughman *et al.* 2002, Dai 2002, de Jonge and Bonard 2004).

Currently, catalyst particles are synthesized using physical vapor deposition or wet chemical methods. Neither of these techniques provides control over diameter or placement of the catalyst particles. Moreover, not all catalyst particles are active for CNT growth. Electron beam induced deposition (EBID) is a direct-write technique whose versatility in fabricating structures of controlled shapes and sizes has been demonstrated (Furuya 2008, Randolph *et al.* 2006, Utke *et al.* 2008, van Dorp and Hagen 2008). The technique has also been successfully employed to fabricate catalysts for the growth of carbon nanotubes (CNT) (Ervin and Nichols 2009, Lau *et al.* 2002, Mukawa *et al.* 2005, Sharma *et al.* 2009). EBID particles can be fabricated on a substrate in two ways: (1) by rastering the electron beam, or by holding the focused electron probe stationary over a point for desired period. The first method will generate an

area with a large number of catalyst particles but the size distribution is not well controlled (Ervin and Nichols 2009). The second method will result in the formation of single particles whose diameter may depend on the electron dose. The second method has the potential to generate individual deposits with sizes below 10 nm reproducibly (Tanaka *et al.* 2005a, van Dorp *et al.* 2008). However, the relationship between EBID synthesis parameters, chemical composition and morphology of the deposit, and CNT growth is still not well understood.

Particles containing significant amounts of co-deposited carbon have been frequently encountered during EBID fabrication (Botman *et al.* 2009, Crozier and Hagen 2008). Co-deposited carbon typically comes from three sources; (1) hydrocarbon contaminants from the vacuum system, contaminants present on the sample, and/or (3) the precursor itself. It is possible to minimize contributions from the first two sources by baking the TEM chamber and plasma cleaning the sample and the holder (Ketharanathan *et al.* 2006). Tanaka *et al.* (2005b) has demonstrated that in an ultrahigh vacuum transmission electron microscope, with clean substrates and iron pentacarbonyl as a precursor, the amount of carbon in Fe deposits can be reduced substantially at room temperature. In addition, strategies (both during deposition and post-deposition) for reducing the amount of co-deposited C have been developed to improve the performance of EBID-fabricated electrical contacts. For conventional high vacuum systems, substrate heating above 150 °C is typically used to suppress the formation of hydrocarbon contaminants (Crozier and Hagen 2008). Previous work has shown that post-deposition treatment is necessary to activate the catalysts (Ervin and Nichols 2009, Sharma *et al.* 2009). Even so, only some of the fabricated EBID particles were active for CNT growth and it might be due to the co-deposited carbon. Therefore, we need to elucidate the role of carbon in suppressing the activity in order to develop targeted strategies to improve catalyst activity.

We have earlier reported that EBID Fe particles fabricated using diiron nonacarbonyl are catalytically active for CNT growth (Sharma *et al.* 2009). Here we systematically studied the effect of deposition

parameters, electron dose and substrate temperature, on the particle diameter. We have included ferrocene to understand the effect of the nature of the Fe source on EBID parameters. We also followed how carbon incorporation into the deposited particles can affect their catalytic activity for CNT growth. We propose methods to reduce C content during or after deposition that can be used to design active nanoparticles for CNT growth.

## 2. Materials and Methods

The experiments were carried out in a modified FEI Tecnai F20<sup>2</sup> with a differentially pumped environmental cell (Sharma 2005). The microscope is equipped with a 200 kV Schottky field emission source and has a nominal spot size of  $\approx 0.2$  nm in scanning transmission electron microscopy (STEM) mode. The substrates were nominally 50 nm thick perforated SiO<sub>2</sub> membranes that are either fabricated in-house on Mo TEM grids using magnetron sputtering or commercially purchased window grids. The ESTEM column and gas delivery lines were baked and the heating holder (Gatan model 628 Single Tilt Heating Holder and model 652 Double Tilt Heating Holder with a Inconel furnace<sup>2</sup>), hex rings washers, and membrane samples were plasma cleaned prior to the start of experiments to minimize the residual hydrocarbons in the system. Subsequently, the membranes were loaded into the TEM holder and immediately transferred into the TEM. The vapors of the precursors, Fe<sub>2</sub>(CO)<sub>9</sub> or Fe(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>, held at room temperature, were introduced into the ESTEM sample area. Nanoparticles were fabricated in STEM mode by holding a focused beam stationary for fixed time (dwell time) in steady precursor pressure of  $\approx 0.13$  Pa ( $1 \times 10^{-3}$  Torr) for both the Fe<sub>2</sub>(CO)<sub>9</sub> and Fe(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>. Electron dose was varied by changing the dwell time from 5 s to 30 s. The temperature was held constant during deposition and each set of deposition times

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<sup>2</sup> *Disclaimer: The full description of the procedures used in this paper requires the identification of certain commercial products and their suppliers. The inclusion of such information should in no way be construed as indicating that such products or suppliers are endorsed by NIST or are recommended by NIST or that they are necessarily the best materials, instruments, software or suppliers for the purposes described.*

was repeated for temperatures ranging from room temperature to 450 °C. The sample temperature was measured by a thermocouple attached to the furnace body. Electron energy loss spectra (EELS) were also collected using a GATAN GIF 2000<sup>2</sup> concurrently with the deposition for chemical analysis of the particles. Annular dark field (ADF) images for were collected immediately after deposition for deposit size measurement at the highest scan rate to minimize additional electron beam induced deposition.

**Comment [RS1]:** Did you not record the images after purging out the precursor and in TEM mode?

Next, the TEM column was used as a flow reactor for carbon nanotube growth. Details of the growth conditions can be found elsewhere (Sharma *et al.* 2009). First, the precursors were evacuated from the TEM column after catalyst fabrication followed by *in situ* heating to 650 °C to 700 °C under 13 Pa of flowing hydrogen (99.999% purity). Subsequently, the samples were held at this temperature while the hydrogen was pumped out of the system. Finally, 1.3 Pa to 2.6 Pa of acetylene (C<sub>2</sub>H<sub>2</sub>, 99.9% purity) was leaked into the sample area at 650 °C to initiate the growth of CNTs. For this part of the experiment, the E-TEM was switched to TEM mode for image acquisition and digital video recording. (???)

### 3. Results

Figure 1a shows the annular dark field (ADF) STEM image of a typical array of Fe deposits fabricated in our experiments. The intensity in an ADF images is proportional to the mass thickness, therefore the deposited particles appear as bright spots in the image. It should be highlighted here that the ADF image is a 2D projection of a 3D object and so it is difficult to accurately define the size of deposits that grow in the electron beam direction. However, the diameter of the deposited particles can be estimated from the width of the image intensity above the background as shown in Figure 1b. An average diameter was then calculated from at least ten particles for each deposition condition. The deposition results for the two precursors were different as explained below.

#### 3.1 Depositions using Diiron Nonacarbonyl (Fe<sub>2</sub>(CO)<sub>9</sub>)

The average measured diameter for deposition times up to 30 s on substrate held at 22 °C, 60 °C, 80 °C and 100 °C in a precursor flow of 0.13 Pa at are given in Figure 2. When the temperature was raised to 120 °C, extensive deposition took place over the entire imaged area, indicating the onset of thermal decomposition of the precursor. Deposit diameters measured from bright field TEM images are similar to that measured from the STEM image and confirm the observed trends. A transition from combined lateral and vertical growth to pre-dominantly vertical growth has been frequently observed in EBID due to changes in the distribution of emitted secondary electrons as the deposit grows (van Dorp and Hagen 2008). In our experiments, this transition was observed when the deposit diameter exceeded  $\approx 10$  nm (Figure 3a). At this point, the increase in the diameter can no longer be used as an indicator for the amount of deposited material because most of the deposited material contributes to the elongation of the particles and their diameter does not change appreciably (Figure 3b). Furthermore, the particles do not exhibit the same vertical growth rates with some particles having much higher growth rates. This anomaly had been previously reported by Hagan, van Dorp and Crozier (2008) for EBID deposits fabricated on SiN and was attributed to charging effects on an insulating support. Therefore, the conditions resulting in vertical growth should not be used for evaluating the effect of deposition time on the diameter.

**Comment [SW2]:** Renu, should I add this or leave it out? Let us talk about it. Last sentence in the paragraph is contradictory

EELS data collected for a single particle at every deposition temperature are shown in Figure 3. C K-edge above the background decreased with temperature and fell below the EELS detection limit at about 80 °C. The amount of carbon content in the deposit was qualitatively estimated from the integrated intensity over a 100 eV window of background subtracted C-K edge (Table 1). This reduction in carbon content corresponded with a decrease in the measured diameters across all deposition times at 100 °C (see Figure 2). This means that a deposition time of 15 s at 100 °C should be sufficient to obtain particles without measurable co-deposited C and vertical growth.

### 3.2 Depositions using Ferrocene ( $\text{Fe}(\text{C}_5\text{H}_5)_2$ )

For ferrocene, depositions were carried out with a precursor pressure of  $\approx 0.13$  Pa at the following temperatures; 22 °C, 100 °C, 150 °C, 300 °C and 450 °C. The average deposit diameter as a function of deposition time and temperature is given in Figure 5. The deposit diameter generally increased with time but decreased with increasing temperature. The EELS data collected at different temperatures is shown in Figure 6. The carbon content, as estimated from the C K-edge (described above) in the particles drops between the 22 °C and 150°C but did not change appreciably between the 300 °C and 450 °C depositions. Table 1 compares the typical values for the ratio of Fe  $L_{2,3}$  edge intensity (100 eV window) to C K-edge intensity (100 eV window) for diiron nonacarbonyl and ferrocene. We can infer from these results that  $\text{Fe}(\text{C}_5\text{H}_5)_2$  introduced more co-deposited carbon than the typical deposit from diiron nonacarbonyl.

A marked change in deposit morphology at 300 °C and 400 °C was also observed. Bright field TEM images of the deposits fabricated at 150 °C, 300 °C and 450 °C are shown in Figure 5. The morphology of the deposits fabricated at 22 °C, 100 °C and 150 °C was similar and the intensity distribution within the particles was homogeneous (Figure 6a). However, the image intensities distribution in the deposits changed to core-shell morphology at 300°C (Figure 6b) and remained the same at 450°C (Figure 6c). As the intensities in a bright-field image do not provide definitive information about the composition, the deposits were further analyzed using ADF imaging and spatially resolved EELS. In an ADF image, the intensities are proportional to the atomic number (Pennycook 1992). Therefore the lighter contrast in the core compared to the shell can be interpreted as Fe and C rich regions respectively (Figure 7a). An increase in the Fe  $L_{2,3}$ -edge and decrease in C K-edge in the center of the particle, as observed in the spatially resolved EELS data, further confirmed (Figure 7b) the formation of a Fe-C core shell morphology. The size of the core increased from 3 nm to 4 nm at 300 °C to 4 nm to 5 nm at 450 °C. Additional smaller particles were also observed in the vicinity of the EBID particles at 450 °C



(representative particles are highlighted with a white square in Figure 7c) indicating that this temperature is close to the thermal decomposition temperature of the precursor.

### 3.3 Carbon Nanotube Growth

We followed the same procedure for *in situ* CNT growth as describe earlier for the deposits from  $\text{Fe}_2(\text{CO})_9$ . (Sharma *et al.* 2009) The deposits from the two different sources,  $\text{Fe}_2(\text{CO})_9$  and  $\text{Fe}(\text{C}_5\text{H}_5)_2$ , responded differently to the high temperature (650 °C) pre-treatment in 13 Pa of flowing hydrogen. After the heating in  $\text{H}_2$ , particles without distinguishable amorphous carbon shell were visible on the substrate surface, even for the low-temperature deposits from  $\text{Fe}_2(\text{CO})_9$  (Figure 9a). On the other hand, the deposits fabricated using  $\text{Fe}(\text{C}_5\text{H}_5)_2$  showed a change in morphology for the deposits fabricated at 22 °C, 100 °C and 150 °C (Figure 9b and 9c), whereas those fabricated at 300 °C and 450 °C retained the core-shell morphology (Figure 9d). For the three lower temperature depositions, the initially homogeneous deposits phase separated into distinct nanometer sized particles embedded within an amorphous carbon matrix as shown in Figure 7b and 7c. The presence of carbon after heat pre-treatment in hydrogen was further confirmed by the EELS data. In addition, a number of small particles (4 nm to 8 nm in diameter) which were not present previously in the as-deposited images, appeared in the vicinity of the EBID particles deposited at lower temperatures (< 300 °C) after the heat treatment (Figure 9b). The likely source of these deposits could be the thermal decomposition of adsorbed residual of  $\text{Fe}(\text{C}_5\text{H}_5)_2$  on the substrate. Parasitic deposition by primary electrons forward scattered by the growing deposit (Zhang *et al.* 2006) could also take place and would explain the higher density of particles around the EBID deposits. Similar particles formation was negligible for deposits using  $\text{Fe}_2(\text{CO})_9$ .

After CNT growth in the ESTEM at 650 °C with 1.3 Pa to 2.6 of  $\text{C}_2\text{H}_2$ , we find that the EBID catalyst particles fabricated from  $\text{Fe}_2(\text{CO})_9$  (Figure 10a) had grown multi-walled CNTs whereas most of the EBID catalysts particles from  $\text{Fe}(\text{C}_5\text{H}_5)_2$  (Figure 10b) remained encapsulated in carbon and did not grow any

CNTs. Moreover, some of the particles formed by thermal decomposition during pre-treatment were active for CNT nucleation and growth. In fact, almost all the CNT growth we had seen from  $\text{Fe}(\text{C}_5\text{H}_5)_2$  depositions were due to the thermally deposited particles. This is illustrated in Figure 10c where both the EBID and thermally deposited particles can be seen but most of the CNT growth was from thermally deposited particles while the EBID particles remained within the carbon matrix and were inactive. These CNTs from the thermally deposited particles generally had fewer walls and smaller diameters compared to the multi-walled CNTs from the  $\text{Fe}_2(\text{CO})_9$  depositions. Sometimes, single walled CNTs were also observed. Finally, all the CNTs observed in our *in situ* studies grew via root growth.

#### 4. Discussion.

Our results demonstrate that for both precursors, the size and placement of the particles can be controlled in a straightforward manner using EBID. The placement and the deposit diameter could be controlled by the electron beam position and deposition time, respectively. Furthermore, raising the substrate temperature resulted in lower carbon content in the deposits from both the precursors. However, the intensity of the C-K edge in the energy-loss spectra was significantly lower for the deposit from the diiron nonacarbonyl compared to the ones from the ferrocene, indicating higher carbon incorporation for the latter. A simple explanation of the difference could be that the C to Fe ratio in  $\text{Fe}(\text{C}_5\text{H}_5)_2$  (10 to 1) is higher than in  $\text{Fe}_2(\text{CO})_9$  (9 to 2). However, the C content in the latter reduced to negligible levels at 80 °C, but it remained significant for the former at all temperatures. Therefore, the difference in the C content in deposits from two precursors may be better explained on the basis of the difference in their decomposition products. The amount of co-deposited carbon can be influenced by ligand chemistry. Wnuk *et al.* (2011) recently compared the decomposition products of five precursors with different ligands using mass spectrometry. They found that methane was released for precursors containing the methyl ligand, whereas precursors with large ligands like cyclopentadienyl and methylcyclopentadienyl did not result in methane as dissociation product. Therefore we can expect the dissociation product for the

two precursors to be different. Precursors from the carbonyl family were expected to introduce minimal carbon into the deposit since the ligand would be released as CO which can be easily pumped away by the vacuum system. Tanaka *et al.* 2005b had showed that for iron pentacarbonyl, the amount of carbon from the dissociation of CO is very small and incorporated carbon is mainly due to hydrocarbon contamination from the vacuum system and substrate. It was also shown that decomposition of Fe(CO)<sub>5</sub> by low energy electrons can proceed autocatalytically after the loss of the first ligand, which leads to rapid removal of the remaining ligands (Kunz and Mayer 1987, Kunz and Mayer 1988 ). We expect Fe<sub>2</sub>(CO)<sub>9</sub> to behave in a similar manner. It is also conceivable that CO may be also oxidized by the residual oxygen and water vapor partial pressure in the TEM column instead of dissociating into C and oxygen as vacuum levels in our ETEM have been observed to have enough oxygen partial pressure to re-oxidize reduced ceria at lower temperature. (add Crozier et al).

Comment [SW3]: Keep or remove?

In contrast, the dissociation of precursors containing cyclopentadienyl ligands, such as Fe(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>, does not result in volatile hydrocarbon products as highlighted earlier (Wnuk *et al.* (2011)). The hydrocarbon product may further dissociate to produce a carbon deposit, especially in the presence of the Fe catalyst particle; a reaction similar to that for CNT formation. Furthermore, the presence of metal particles had been found substantially lower the graphitization temperature of carbon (Yudasaka 1998). Figure 7c indicates that some graphitization may have taken place for the 450 °C deposits. It is well known that the catalytic activity of metal particles for CNT growth stops when the particles become completely engulfed by carbon/graphitic shells. Therefore, co-deposited carbon can adversely affect the CNT growth; it should be either avoided during EBID or removed after EBID.

Next, we consider the effectiveness of the hydrogen treatment for removing carbon or graphite from the surface of the catalysts. McKee (1974) had shown that the gasification of graphite in hydrogen could take place above 600 °C for iron, cobalt and nickel catalysts but the reaction rate was the lowest at this temperature range. He also reported that the rate could be enhanced by the presence of water vapor. This

means that the rate for gasifying graphite would be relatively low at our experimental temperatures. This is reflected in the depositions at 300 °C and 450 °C where the pre-existing carbon shells were not removed during heating in H<sub>2</sub>. The remaining carbon would be essentially a physical barrier between the encapsulated catalysts and the C<sub>2</sub>H<sub>2</sub> used for CNT synthesis. On the other hand, for the nanocomposite morphology, the carbon is amorphous and the kinetics for the gasification of amorphous C may be faster than that for the graphite. This would expose some particles that are near the surface of the low temperature deposit and lead to the few observed CNTs from the EBID catalyst particles. Nonetheless, it is clear that the hydrogen treatment did not remove sufficient carbon from the catalyst particles deposited from ferrocene.

There are post-deposition treatment strategies that are more effective than H<sub>2</sub> such as using water vapor or oxygen. However, our preliminary results with oxygen ( $\approx 13$  Pa of oxygen at  $\approx 400$  °C) showed that as the encapsulating carbon was removed, both EBID deposits and thermally decomposed particles became mobile and coalesced. The incorporated carbon might have played a role in immobilizing the deposits and this coalescence is not desirable if the objective is to maintain the small catalyst sizes (Crozier and Hagen 2008). Mukawa *et al.* (2005) also found that iron particles embedded in their fabricated carbon nanopillars can become mobile at 800 °C and eroded through graphite until they reached the surface of the nanopillars. These particles grew nanotubes when ethanol was introduced as a precursor gas.

Finally, we highlight that while the Fe(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>, EBID particles were not active in CNT formation, the particles formed by the thermal decomposition of residual adsorbed precursor molecules were active for both multi-walled and single walled CNT (Figure 10b-c). However, these particles have the same drawback as synthesized using other techniques such as physical vapor deposition, i.e. their size and placement cannot be controlled. Therefore, precursors such as Fe<sub>2</sub>(CO)<sub>9</sub> should be employed to minimize the carbon incorporation in the EBID particle.

## 5. Conclusions

We have shown that EBID can be an effective way to fabricate catalysts for CNT growth. The placement of the catalyst particles is controlled by the position of the electron beam, the diameter by the deposition time and the composition by the choice of the precursor. Between the two precursors used,  $\text{Fe}_2(\text{CO})_9$  and  $\text{Fe}(\text{C}_5\text{H}_5)_2$ , the latter introduced more carbon into the deposit. We also found that more CNTs grew from the catalyst particles fabricated from  $\text{Fe}_2(\text{CO})_9$  compared to those fabricated from  $\text{Fe}(\text{C}_5\text{H}_5)_2$ , which meant that catalyst activity is correlated to carbon content. The carbon content in the deposit can be reduced by substrate heating during deposition or by post-deposition processing. The deposits from  $\text{Fe}_2(\text{CO})_9$  showed no carbon edge in the EELS spectra when the substrate temperature was raised to  $\approx 100$  °C. However, even at the highest temperature of 450 °C, carbon was detected in the deposits from  $\text{Fe}(\text{C}_5\text{H}_5)_2$ . Furthermore, these deposits formed a stable Fe-C core-shell structure above 300 °C. The carbon content could also be reduced by heating the deposits in hydrogen after deposition. The deposits fabricated from  $\text{Fe}_2(\text{CO})_9$  formed catalyst particles with the lowest carbon content. The deposits fabricated using  $\text{Fe}(\text{C}_5\text{H}_5)_2$  at between 22 °C to 150 °C, phase separated and formed a nanocomposite consisting of distinct particles dispersed within amorphous carbon. The hydrogen treatment also failed to remove the co-deposited carbon from the core-shell structures. We propose that the activity was reduced because remaining carbon formed a physical barrier that prevented the catalyst from interacting with the acetylene. Lastly, we observe that particles formed from thermal decomposition of  $\text{Fe}(\text{C}_5\text{H}_5)_2$  were also active for CNT growth, but they nucleated randomly and did not have the placement and size control of EBID fabricated particles. Therefore, precursors similar to  $\text{Fe}_2(\text{CO})_9$  would be the preferred precursor for fabricating catalyst using EBID.

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## Figure Captions

Figure 1. Annular dark field STEM image showing an array of Fe deposits fabricated using EBID (precursor: ferrocene) (left) and the line profile for a single deposit (right). The arrows indicate where the diameter measurement was made.

Figure 2. Deposit diameter as a function of deposition time at 22 °C, 60 °C, 80 °C and 100 °C using diiron nonacarbonyl at 0.13 Pa.

Figure 3. Bright field TEM images of Fe deposits fabricated using diiron nonacarbonyl where (a) is in combined lateral and vertical growth regime and (b) is in mainly vertical growth regime.

Figure 4. Normalized EELS spectra for the depositions at 22°C, 60 °C, 80 °C and 100 °C showing the C K-edge and Fe L<sub>2,3</sub> edges. The deposition time was 30 s. Note the disappearance of C K-edge at 80 °C

Figure 5. Deposit diameter as a function of deposition time at 22 °C, 100 °C, 150 °C, 300 °C and 450 °C using ferrocene at 0.13 Pa.

Figure 6. Normalized EELS spectra for the depositions at 22°C, 150 °C, 300 °C and 450 °C showing the C K-edge and Fe L<sub>2,3</sub> edges. Note that C K-edge is present in all spectra.

Figure 7. Bright field TEM images of as-deposited Fe particles fabricated using ferrocene showing the change in morphology from homogeneous at (a) 150 °C to a 'core-shell' at (b) 300 °C and (c) 450 °C. Insert in (c) shows a higher magnification image of the particle highlighted with a black square. Representative particles from thermal decomposition are highlighted with a white square.

Figure 8. (a) Annular dark-field STEM image of the particles deposited at 300 °C from ferrocene showing a core-shell distribution of image intensities. (b) The intensity of background subtracted Fe L<sub>2,3</sub>-edge, in the energy-loss spectra collected with 2.6 nm spatial resolution along the line marked across one of the particles, was highest in the center of the particle, whereas the intensity of the C K-edge dipped in the same region.

Figure 9. Bright field TEM images the samples after hydrogen treatment for (a) diiron nonacarbonyl, 22 °C, 15s deposition. (b) ferrocene, 22 °C, 15s deposition (c) ferrocene, 22 °C, 30s deposition (d) ferrocene, 450 °C, 30s deposition. No encapsulating carbon can be seen for diiron nonacarbonyl deposition whereas a carbon shell (has a lighter contrast compared to the SiO<sub>2</sub> support) surrounds the catalyst particles for ferrocene depositions (enclosed in circle in (b)). The deposit in (c) extends into the vacuum, further illustrating the embedded particles. Representative particles from thermal decomposition are marked by white arrows in (b). For the 450 °C deposition, the carbon shell appears to be graphitic. A magnified imaged of the layered structure of the carbon shell is given in the insert.

Figure 10. Bright field TEM images of the samples after exposure to  $\approx 2$  Pa of C<sub>2</sub>H<sub>2</sub> at 650 °C with deposits from (a) diiron nonacarbonyl and (b) ferrocene. CNTs grew from EBID particles for diiron nonacarbonyl and from the thermally decomposed particles for ferrocene as confirmed by the (c) higher magnification image of the highlighted area in (b). CNTs that grew from thermally decomposed particles are marked by arrows. Positions of EBID deposits are enclosed in circles for both samples.

## Tables

Table 1. Fe L<sub>2,3</sub> Edge Intensity to C K Edge Intensity from EELS for depositions using diiron nanocarbonyl (left) and ferrocene (right) respectively. Standard deviations are given in parentheses.

Diiron Nonacarbonyl		Ferrocene	
Deposition Temperature (°C)	Fe/C	Deposition Temperature (°C)	Fe/C
22	0.6 (0.18)	22	0.01 (0.005)
60	0.5 (0.14)	100	0.05 (0.005)
80	- <sup>3</sup>	150	0.05(0.004)
100	- <sup>3</sup>	300	0.06 (0.007)
		450	0.08 (0.014)

<sup>3</sup>The carbon edge falls below the detection limit of EELS and a ratio cannot be calculated. However, it does indicate a decrease in carbon content.



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