Reactor Design for Low-Temperature Growth of Vertically Aligned Carbon Nanotubes

A. V. Vasenkov[*], D. Carnahan[**], D. Sengupta[*] and M. Frenklach[***]

[*]CFD Research Corporation, 215 Wynn Drive, Huntsville, AL 35805
[**]NanoLab, Inc., 55 Chapel Street, Newton, MA 02458
[***]Department of Mechanical Engineering,
University of California, Berkeley, CA 94720-1740

ABSTRACT

This paper reports on the design of novel reactor for low-temperature growth of Vertically Aligned Carbon Nanotubes (VACNTs). Two mechanisms for selective heating catalytic nanoparticles were investigated: (i) a heating from exothermic reaction of catalytic oxidation and (ii) an induction heating. The requirements for efficient induction heating catalytic particles of size varying from micron to 100s nanometers are discussed.

Keywords: CNT, low-temperature growth, selective heating nanoparticles, multiscale modeling

1 INTRODUCTION

For many applications, varying from field emitters, tweezers, electrical interconnects, and antennas to thermal management materials, there is a need for well aligned arrays of Carbon Nanotubes (CNTs) that can be patterned both in fields and as single, stand-alone structures. CFDRC and NanoLab has recognized the need for a new, lower temperature synthesis method to produce these arrays. The standard temperature for the growth of Vertically Aligned CNTs (VACNTs) is about 600°C, which can easily damage many materials commonly found in integrated circuits, such as aluminum, photoresists, etc. The high growth temperature is a limitation to designers who seek to create CNT- based devices with lithographically defined features, in low temperature and lower cost materials. If the growth temperature could be reduced at least down to 400°C, the spectrum of applications for in-situ grown VACNTs would be substantially widened.

Recently, we have reported results of feasibility studies for low-temperature growth of CNTs by selective heating catalyst [1, 2]. This paper continues the study of previously reported selective heating catalytic particles and outlines reactor design for low-temperature growth of CNTs.

2 EFFECT OF OXYGEN ON VACNT GROWTH

The CNT growth involves catalytic decomposition of hydrocarbons and carbon incorporation into CNT. The results of computational studies presented in Sec. 4 show that catalytic decomposition of hydrocarbons can efficiently occur even at room temperature. Consequently, high temperature of CNT synthesis is required only for carbon incorporation into CNT. We attempted to reduce this temperature via addition of oxygen to the gaseous feedstock in thermal Chemical Vapor Deposition (CVD) reactor. Results of our previous experiments indicated that heating from exothermic reactions of oxidation can be significant in plasma-enhanced CVD reactor [2]. A series of experiments were conducted and yield data obtained in thermal CVD reactor are summarized in Fig. 1. Results show that at all temperatures, the addition of oxygen reduced the observed yield. At 500ºC, there was essentially no growth for either condition, indicating that the catalyst is not active at this temperature. At 600ºC, the carbon yield from the 20 sccm oxygen test was approximately half of the yield without oxygen. At 700ºC, the yield with oxygen was ~80% of the yield without oxygen. We found that the positive effect of oxygen was an improved morphology of CNTs at temperatures below 700ºC as shown in Fig. 2.
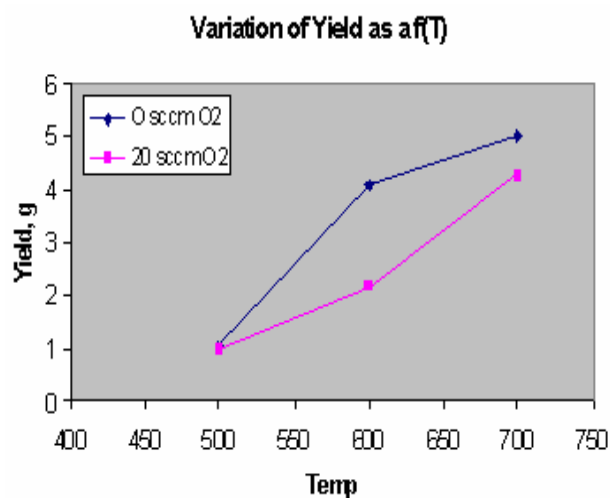

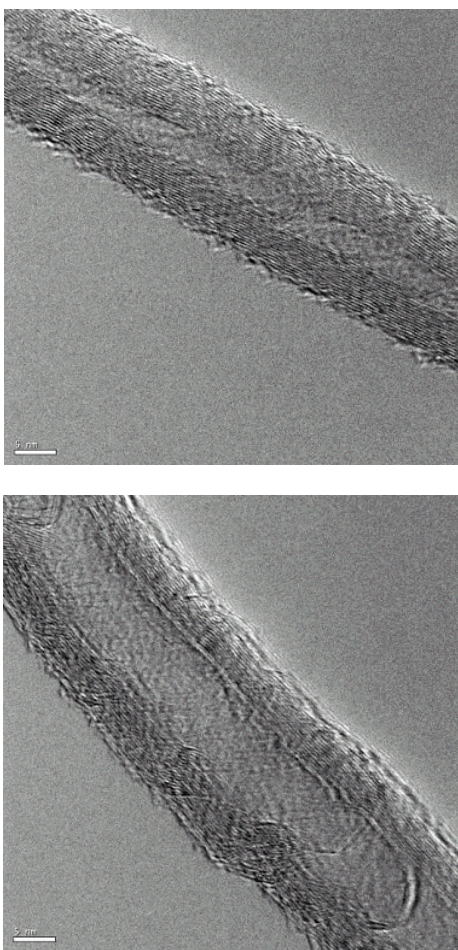Figure 1: The thermal CVD tests of oxygen addition.

Figure 2: Morphology of CNTs grown at 600°C without (top) and with (bottom) gaseous oxygen. The graphitization was improved with the oxygen addition.

3 INDUCTION HEATING NANOPARTICLES

Results of our multi-scale (spanning 100s nm to 10 cm ranges) simulations demonstrated that particles of specific sizes could be efficiently heated within certain ranges of frequency [1]. Particularly, we found for nickel nanoparticles that micron scale particles are heated efficiently by MHz frequency irradiation, but as the particle size is reduced, the optimal frequencies quickly reached the GHz range [1]. Here, we report results of experimental validation of computational trends. In our tests, nanoparticles were prepared using our sphere masking technique. Al particles of various sizes were deposited on a Corning 1737F glass substrate. These substrates were sent to Duke University, where the frequency response of the structures was investigated between 8 and 12 GHz. In these investigations, a microwave waveguide setup was used to analyze absorption of the signal by measuring both the reflected and transmitted power as a function of frequency. The total of these two is constant, and equal to the original transmitted power, unless the substrate is an absorptive. It was found that the substrate was capable of absorbing power through inductive heating of the metal particles as was computationally predicted. In the series of experiments, three sizes of aluminum metal particles were investigated and the smallest of these (590 nm) has a resonant frequency at about 8 GHz range.

Aluminum is not catalytic to CNT growth, but it was useful to show experimentally that the nanoparticles made by sphere masking showed a resonance. Nickel, with its higher resistance and therefore smaller skin depth as was predicted by our calculations, will have a higher frequency than aluminum.

Based on the obtained results, we formulated requirements for induction heating catalyst nanoparticles during VACNT that are very unique. Typically, industrial applications use RF induction heating in the 450 KHz range. For these applications, water-cooled copper coils are used as inductors. For plasma CVD in semiconductor industry, typical supplies are at 13.56 MHz frequency. Our inductive heating concept points in a very rare frequency range. For example, our results indicated that for catalyst particle of 100 nm in size, the most efficient RF heating for CNT growth is near 20 GHz. Smaller catalyst particles are typically required for single-wall VACNT growth. The use of these particles would require even higher frequencies. Based on our discussion with industrial engineers we identified a specific RF source for novel reactor capable of manufacturing VACNTs at low temperature. The assembly and testing of the reactor are in progress.
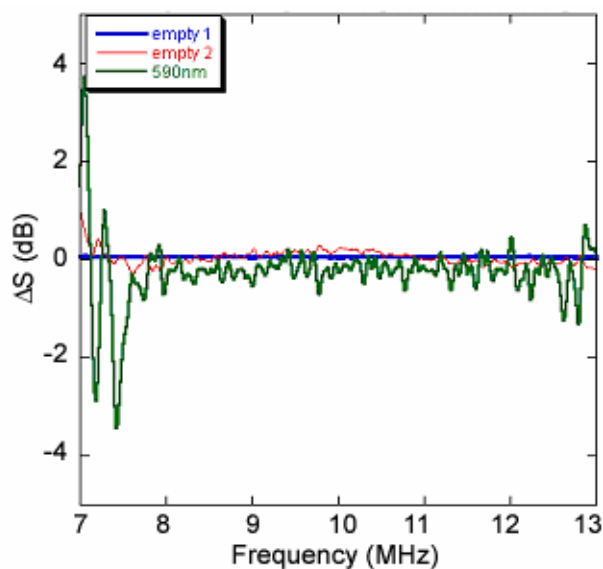

Figure 3: Resonances between 7 and 8 GHZ are clear in the 590 nm aluminum nanoparticles deposited on the glass substrate.

4 ATOMISTIC SIMULATION OF HYDROCARBON DECOMPOSITION

To investigate the effect of temperature on catalytic decomposition of hydrocarbons, we have integrated Molecular Dynamics (MD) code developed by Prof. Frenklach group at UCB [3] with Mopac, a general-purpose semiempirical quantum mechanics package for the study of chemical properties and reactions in gas, solution or solid-state. The integrated multi-scale simulator was used to investigate the dissociation of C_2H_2 on the surface of iron nanoparticle used as a catalyst during the CNT synthesis. This process is known to be a major path for carbon supply during CNT growth [4].
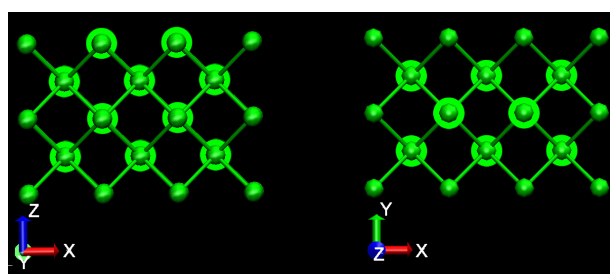

Figure 4: Simulation domain represents a small fraction of the BCC Fe crystal nanoparticle. Large spheres depict quantum atoms.
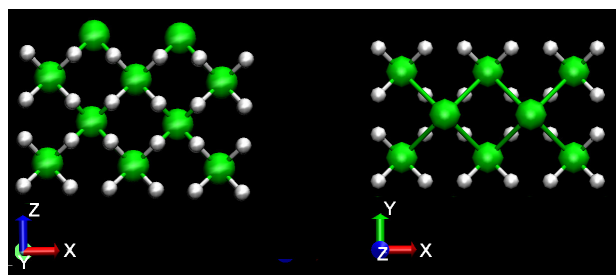

Figure 5: Quantum atoms were passivated with hydrogen at the boundaries for computing semiempirical quantum potential.

Prior to running simulations, we have prepared a simulation domain by truncating the surface of Fe nanoparticle used in CNT growth experiments to a size that is a computationally tractable by the developed multi-scale simulator. The constructed simulation domain, shown in Fig. 4, represents a small fraction of the Body Centered Cubic (BCC) Fe crystal. As a result of the truncation, artificial boundaries with periodic boundary conditions were introduced. Since Mopac 7.2 does not support the calculation of gradients for a 2-dimensional periodic system we considered two groups of atoms as shown in Fig. 4: fixed empirical atoms, located at the bottom and side boundaries, and quantum atoms forming a cluster.

Interactions between empirical atoms and between empirical atoms and quantum cluster were simulated using the empirical Morse potential [5] and interactions of atoms in the quantum cluster were modeled using semiempirical quantum mechanics potential computed by Mopac after each time step in the MD solver [3]. To perform Mopac calculations, the quantum cluster was saturated with "ghost" hydrogen atoms as shown in Fig. 5. The distance between the ghost hydrogen atoms and the quantum cluster was determined by scaling distances between boundary atoms from the quantum and empirical regions [3]. The force matrix computed by Mopac was transferred to MD code. Here, the contributions from the ghost hydrogen atoms were zeroed and empirical atoms with Morse potential were added to quantum atoms.

To validate the developed solver we considered the dissociation of C_2H_2 on the surface of iron catalyst which is known as a major mechanism for carbon supply to growing CNT [4]. In the beginning of simulation, C_2H_2 was introduced 5 Å above the Fe surface as shown in the top panel of Fig. 6 with a velocity directed towards the surface. We found that the dissociation of C_2H_2 involves the formation of C_2H-Fe_n complex (see bottom panel in Fig. 6) due to hydrogen removal reaction:

$$C_2H_2 + Fe_n \rightarrow C_2H\text{-}Fe_n + H\text{-}Fe_n \qquad (R1)$$
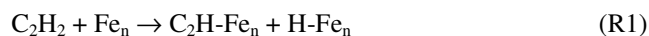
C_2H-Fe_n was not stable and quickly dissociated:

$$C_2H\text{-}Fe_n \rightarrow CH\text{-}Fe_n + C\ Fe_n \qquad (R2)$$

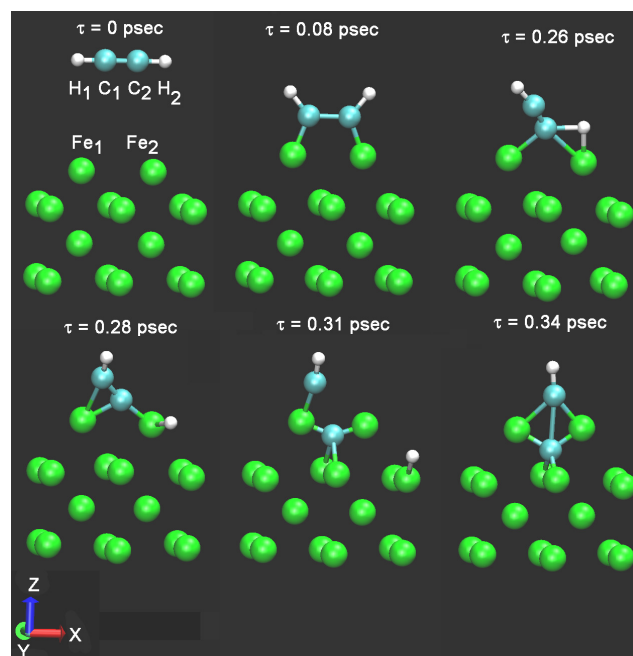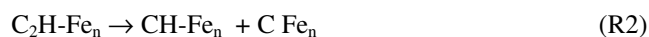Figure 6: Computational results illustrating dissociation of C2H2 on the surface of Fe at 700ºC.
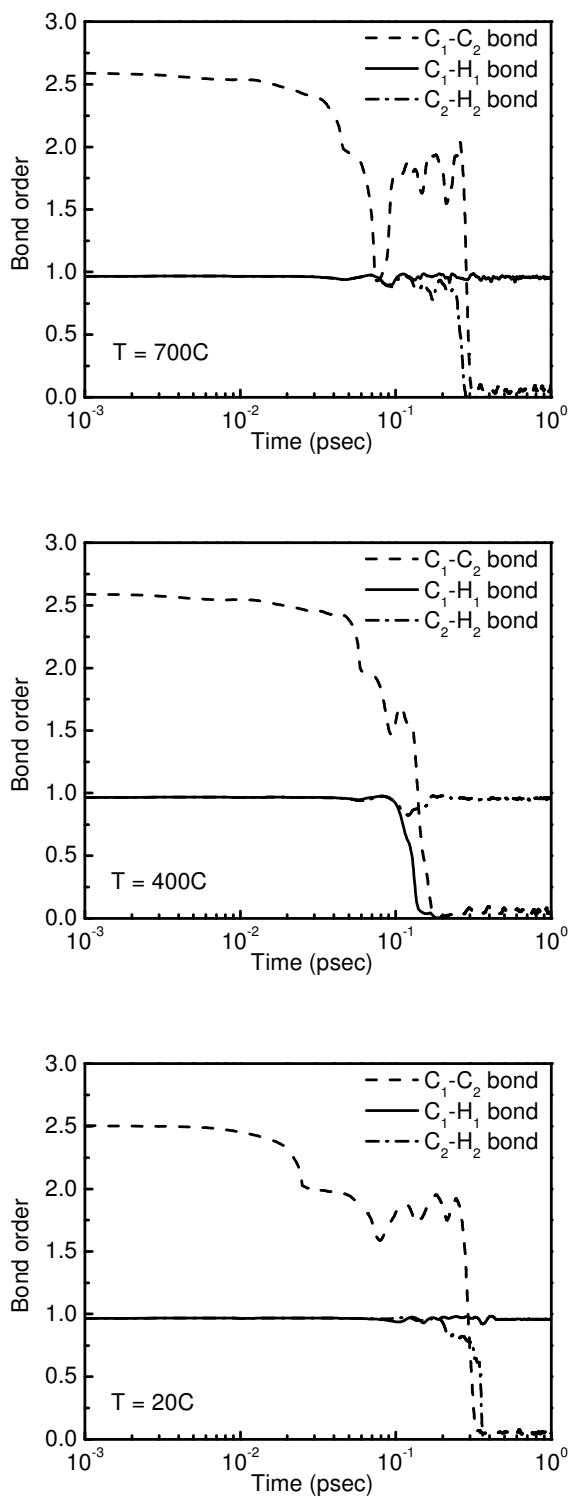
Figure 7: Time-dependent bond order profiles at different temperatures: 700°C (a typical temperature for CNT growth), 400°C (desirable temperature for our CNT experiments), and 20°C (room temperature).

Reactions (R1) and (R2) were investigated at three different temperatures: 700°C (a typical temperature for CNT growth), 400°C (desirable temperature for our CNT experiments), and 20°C (room temperature). Time-dependent bond order profiles for the cases with different temperatures are given in Fig. 7. At the beginning of simulations, when C_2H_2 was 5 Å above the Fe surface, C-C bond order was slightly less than 3 due to the strain resulting from Fe cluster. For $t < 3 \times 10^{-2}$ psec, C-C bond order slowly decreased with time at all temperatures. We observed a sharp minimum for C-C bond order at about 0.08 psec (see Fig. 6 for corresponding space configuration). This minimum resulted in braking C-C bond at T= 400°C. C-C bond at 700°C and 20°C recovered from the minimum at 0.08 psec and was broken at the later time. C-H bond always preceded braking C-C bond. The obtained results demonstrated that breaking C-C bond during interaction of C_2H_2 molecule with Fe cluster can happen even at room temperature. Consequently, carbon supply for growing CNT can be successfully generated even at room temperature.

The further work is in progress. For example, we plan to investigate how the presence of oxygen affects the catalytic decomposition of hydrocarbons (C_2H_2, CH_4 etc.).

5 CONCLUSIONS

We obtained mixed experimental results for reducing growth temperature of VACNTs using oxygen in CVD reactor. Oxygen improved the morphology of CNTs, but diminished the yield of CNTs. The combined experimental and theoretical results demonstrated that 100s nm scale metal particles are heated efficiently by GHz frequency irradiation. The results of atomistic simulations showed that decomposition of hydrocarbons can efficiently occur on the surface of catalyst even at room temperature. The assembly and testing of the reactor for low-temperature VACNTs are in progress.

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