

E.1. Multiphysics, Multiscale Modeling of CVD-based Carbon Nanotubes Synthesis:

We have previously developed a detailed modeling framework for carbon nanotubes (CNTs) synthesis during Chemical vapor deposition (CVD) process (pls. refer to our activities report during annual year 2005-2006). Based on the constructed flowchart, we are now developing both continuum and noncontinuum level modeling individually as discussed in the following sections. After both modeling regions are completed, they will be fully coupled together to get a detailed CNTs synthesis and their formation based on CVD fabrication process.

Continuum Level Modeling: As the first modeling region, we have placed our boundary conditions on the CVD quartz tube boundaries. We assume that the inlet hydrocarbon gasses are at the ambient temperature. Initial velocities are calculated by setting up the gas flow rates to the desired values. The inside pressure of the CVD quartz tube is considered as ambient pressure. The heating elements in our CVD system are located around the quartz tube which creates a uniform temperature along the quartz tube wall. The produced heat penetrates inside the tube by either convection or radiation from the quartz tube walls which will heat up both hydrocarbon gases and the silicon substrate. We use fully coupled multiphysics technique to calculate gas phase and substrate surface phase reactions, both convection and radiation heat transfers and non-isothermal fluid dynamics to arrive at a clear picture of all the continuum level process inside the CVD quartz tube. The multiphysics modeling is based on the continuity, Navier-Stokes, energy balance, chemical reaction energy and the mass balance equations. In this model, under applied heat, the inserted gases (CH_4 and H_2 gas mixture) decompose into the different components based on 34 reversible reactions. The produced chemical components from gas phase reactions, participate in other chemical reactions near silicon substrate, in which deposited catalyst layer will also involve. A total of 21 surface reactions is considered in our modeling. From the surface phase reactions, carbon and carbon component molecules will be produced which participate in the nanotube ring formation around cobalt nanoparticles. The produced chemical components resulting from inlet gas phase reactions and surface phase chemical reactions that take place near the silicon substrate are shown in Figure 1.

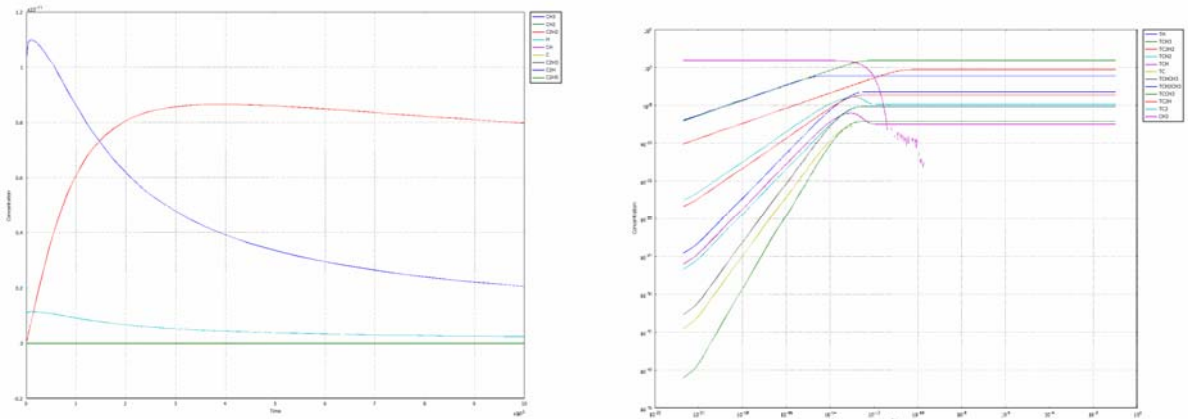


Figure 1: Gas phase (left) and surface phase reactions (right) during CNTs synthesis by CVD process.

In order to study the concentration of the participated gases in CNTs formation during fabrication process by CVD system, the obtained results by the chemical reaction modeling are transferred into the constructed CVD model and fully coupled with the heat transfer and nonisothermal fluid dynamics physical phenomenon that take place inside CVD quartz tube. The surface concentration result from these couplings is depicted in Figure 2.

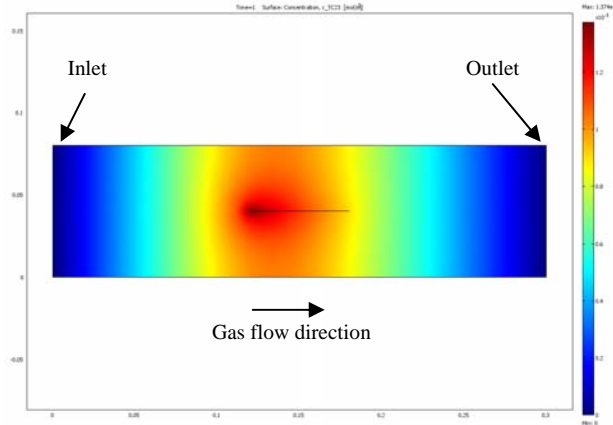


Figure 2: CVD system surface component concentration near silicon substrate.

From Figure 2, it can be observed that the highest concentration of surface chemical components occurs near the tip edge (the silicon edge which is closer to CVD inlet) of silicon substrate and the minimum amount of concentration is observed at the tail edge of the substrate. Therefore, it is expected that the growth rate of the CNTs at the tip edge possesses a higher value compared to fabricated CNTs located at the tail edge. We will be using similar model to extend our surface concentrations investigation for different amounts of inlet gas flow rates.

Molecular Level Modeling: Following our presented noncontinuum framework modeling, molecular dynamics technique is utilized to investigate carbon molecules diffusivity into iron oxide nanoparticles such as FeO and Fe_2O_3 . Such nanoparticles can be used during carbon nanotube (CNT) synthesis process in a chemical vapor deposition (CVD) system. Several simulations are conducted in the atmospheric pressure condition and for different temperatures ranging from 500 to 1100 °C, which is common range for multi-walled and single-walled CNT (MWCNT and SWCNT) fabrication. As shown in Figure 3, four separate amorphous cells are constructed for investigating the diffusivity of carbon molecules.

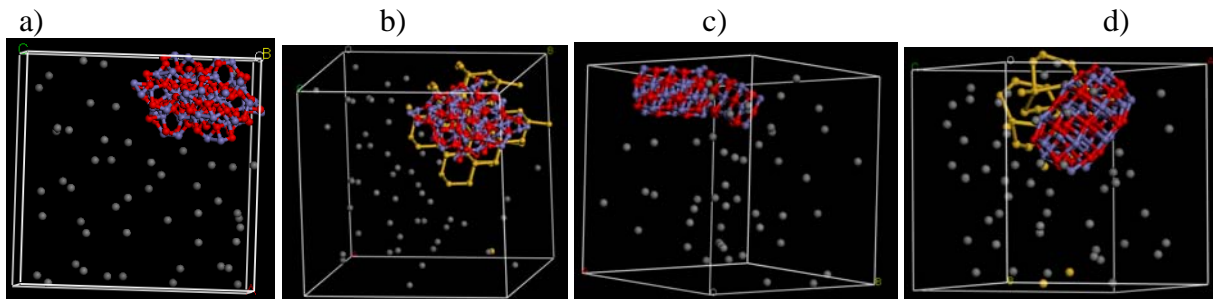


Figure 3: MD-based simulated cells containing carbon molecules and; a) Fe_2O_3 , b) Fe_2O_3 with silicon, c) FeO and d) FeO with silicon

For each case, NPT (pressure constant-temperature constant) simulation is performed initially that the molecular system approaches to its equilibrium condition. Total simulation time is set to 500,000 femtosecond (fs) with 0.5 fs time step size (hence, 1,000,000 total simulation steps) for approaching to an acceptable accuracy. In the second step, since there is no sudden pressure or temperature change during soaking time of CNTs fabrication by CVD system and in order to get more accurate results without any perturbation by pressure and temperature adjustments, the simulation method is switched to NVE process by considering volume and energy as constant values. During NVE simulation, standard Newton

equation without any temperature and pressure control is used. In this case, the simulations are conducted for 15,000 fs with 0.5 fs time step size (hence, 30,000 total simulation steps). During NVE process, all the simulation data such as atoms coordinate and velocity for further analysis were saved after each 250 simulation steps. The obtained data from NVE simulation were later used to calculate mean square displacement (MSD) diagram for each simulated case as shown in Figures 4 and 5.

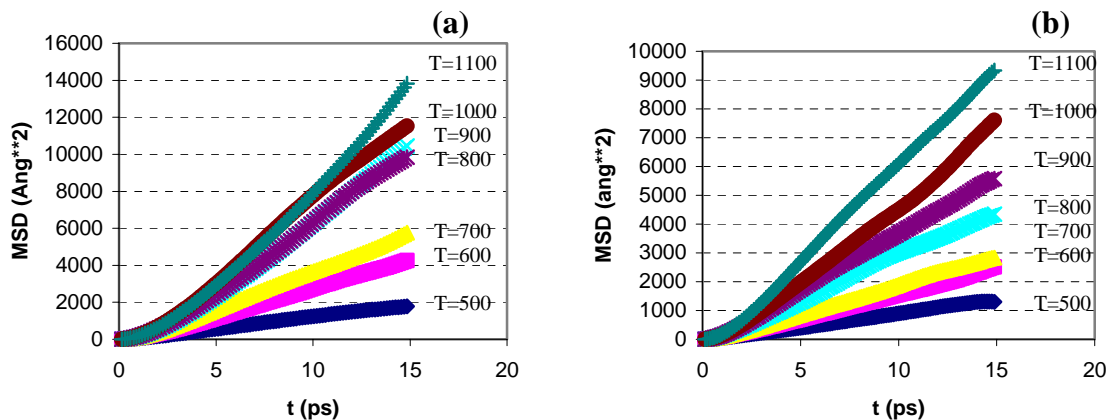


Figure 4: MSD diagrams comparison for; a) Fe_2O_3 nanoparticle and, b) Fe_2O_3 nanoparticle with Si substrate for temperature ranging from $T=500$ to 1100 °C.

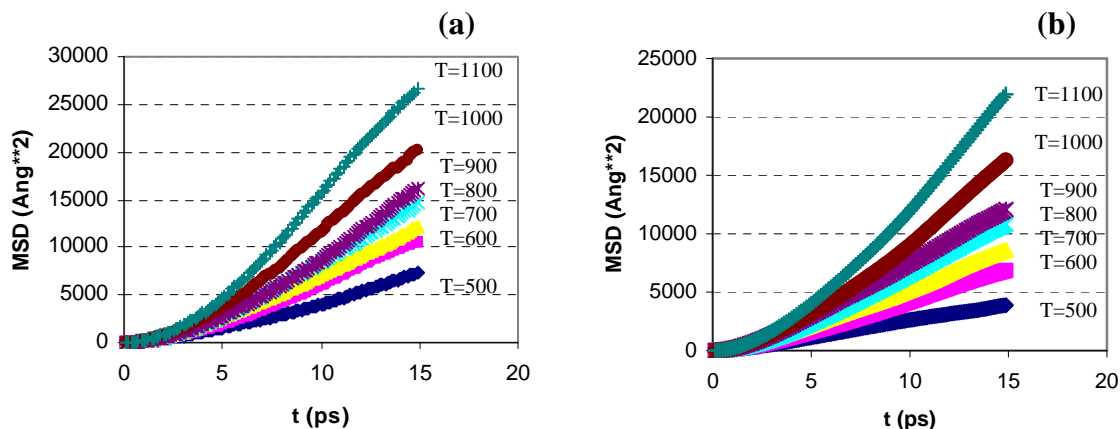


Figure 5: MSD diagrams comparison for; a) FeO nanoparticle and, b) FeO nanoparticle with Si substrate for temperature ranging from $T=500$ to 1100 °C.

From these plots, it can be concluded that as the temperature increases, the slope of the MSD diagram also increases accordingly. Using the slope of MSD diagrams, the diffusivity of each simulation case can be plotted. Figure 6 shows the carbon molecules diffusivity into nanoparticles (blue line), while yellow line presents the diffusivity when silicon substrate is added to the metal nanoparticle.

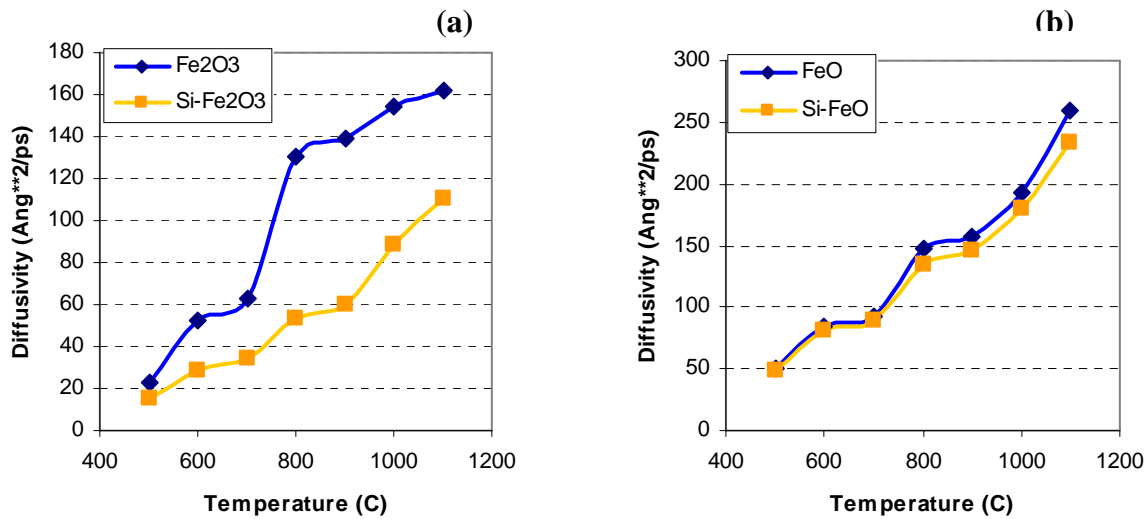


Figure 6: Carbon diffusivity diagram for; a) Fe_2O_3 nanoparticle (dark line), Fe_2O_3 with Si substrate (light line) and b) FeO nanoparticle (dark line), FeO with Si substrate (light line).

In the diffusivity diagrams, three distinctive regions were observed as the simulation temperature varies. Comparing with the results from CNTs synthesis by CVD system, it was later revealed that these regions correspond to the following CNTs fabrication temperature limits:

1. *MWCNT synthesis region:* After initial increase, a reduction in diffusivity rate was observed. This region is located in the temperature limits required for MWCNT synthesis.
2. *Transition region:* As the temperature increases, a considerable increase in diffusivity rate was observed. Compared with the results from experiments, it reveals that this region corresponds to the transition part where MWCNT, SWCNT or the combination of both configurations can be achieved.
3. *SWCNT synthesis region:* By further temperature increase, the diffusivity rate decreases again which is within the temperature limits of SWCNT fabrication.

Also, silicon molecular structure was added to the simulated nanoparticles. The comparison results show a decrease in carbon diffusivity from the simulation case without silicon substrate. This decrease is more distinctive in higher temperatures. Also, it was observed that the effect of silicon on FeO is less than Fe_2O_3 nanoparticle.

This subtask has resulted in the following publications during this report period.

1. **Hosseini, M. R.** and Jalili, N., “Towards Multiphysics, Multiscale Modeling and Control of Nanotube-based Piezoelectric Materials”, *Proceedings of 2006 NSF Design, Service, and Manufacturing Grantees and Research Conference*, St. Louis, Missouri (July 2006).
2. **Hosseini, M. R.** and Jalili, N., “Investigation of Carbon Diffusivity into the Nanoparticles During CVD Nanotube Fabrication Process by Molecular Dynamics Technique”, *Proceedings of 2006 ASME International Mechanical Engineering Congress & Exposition*, Chicago, IL (November 2006)
3. **Hosseini, M.R.** and Jalili, N., “Multiphysics, Multiscale Modeling of Carbon Nanotube Synthesis Process by Chemical Vapor Deposition”, *Proceedings of 2007 ASME International Mechanical Engineering Congress & Exposition*, Seattle, WA (November 2007).