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## Microplasma synthesis of metal nanoparticles for gas-phase studies of catalyzed carbon nanotube growth

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Catalytic properties of metal nanoparticles toward gas-phase carbon nanotube (CNT) growth are presented. Narrow dispersions of iron (Fe) and nickel (Ni) nanoparticles are prepared in a direct current microplasma reactor and subsequently introduced with acetylene ( $C_2H_2$ ) and hydrogen ( $H_2$ ) into a heated flow furnace to catalyze CNT growth. Aerosol size classification and high-resolution transmission electron microscopy show that CNT growth occurs on Ni particles at lower temperatures than that for similarly produced Fe nanoparticles. Activation energies of 117 and 73 kJ/mol are found for Fe and Ni catalyst particles, respectively, suggesting that CNT growth occurs by carbon surface diffusion. © 2007 American Institute of Physics. [DOI: 10.1063/1.2786835]

The unique physical and chemical properties of carbon nanotubes (CNTs) are defined by their atomic structure. Carbon nanostructures are commonly synthesized using transition metal nanoparticles as catalysts.<sup>1,2</sup> The structure of CNTs has been found to be determined by the size and chemical composition of the metal catalysts.<sup>3,4</sup> However, at present, the diameter, length, and chirality of CNTs have not been controlled sufficiently in a single process due to incomplete understanding of the role of the catalyst in nanotube nucleation and growth. In conventional thermal and plasmaenhanced chemical vapor deposition (CVD) processes, CNT growth is performed on a substrate making it difficult to separately control the properties of catalytic particles.<sup>5</sup> In addition, CNT nucleation and growth are difficult to monitor *in situ* which necessitate postgrowth characterization.<sup>6,7</sup> Recently, CNTs have been synthesized in a flowing gas stream using metal particles that catalyze decomposition of carbon precursors in a substrate-free reactor.<sup>8,9</sup> Elimination of the substrate offers the advantage of revealing the true catalytic properties of metal nanoparticles toward CNT nucleation and growth. Gas-phase synthesis of CNTs can be coupled with aerosol instrumentation to monitor growth in real time.<sup>10,11</sup> Therefore, kinetic studies of CNT growth can be easily performed giving valuable insight into the growth mechanism on various catalysts.<sup>12</sup>

In this letter, we report on a synthesis route based on a microplasma reactor that produces metal particles less than 3 nm in diameter for catalyzed, gas-phase CNT growth. Previous reports of CNT growth using aerosol catalyst particles have suffered from broad size distributions which required size selection.<sup>12,13</sup> Microplasmas are miniaturized glow discharges that contain energetic electrons which permit nonthermal decomposition of gaseous precursors to nucleate particles. Because of the small spatial scale of the reaction zone, narrowly dispersed nanoparticles are produced in a single step.<sup>14</sup> We have extended this gas-phase process to the preparation of iron (Fe) and nickel (Ni) catalyst particles from ferrocene and nickelocene, respectively. CNT growth is achieved by adding acetylene  $(C_2H_2)$  and hydrogen  $(H_2)$ gases to the particle-laden flow in a tubular flow furnace. Aerosol instrumentation is used for in situ measurement of CNTs, allowing the length of CNTs to be obtained directly. The temperature dependence of CNT growth rate shows that the activation energies for Fe and Ni particles are 117 and 73 kJ/mol, respectively, which are significantly lower than values associated with other thermal-CVD processes.<sup>7,15,16</sup>

The experimental setup schematically illustrated in Fig. 1 consisted of a microplasma reactor for synthesis of metal catalyst particles, tubular flow furnace for CNT growth, and aerosol size classifier. Metal nanoparticles were grown in a direct current (dc), atmospheric-pressure microplasma reactor. The microplasma was formed in a flow geometry using a stainless-steel capillary tube [180  $\mu$ m inside diameter (i.d.)] as the cathode and a stainless-steel mesh as the anode.<sup>17</sup> The electrodes were separated by a gap of 2 mm and pressure sealed inside a quartz tube. To nucleate metal particles, either ferrocene or nickelocene vapor was introduced into the reactor by subliming the solid powder at room temperature in an argon flow. Typical discharge voltages and currents used were 320 V and 3 mA, respectively, for ferrocene and 380 V and 4 mA, for nickelocene. The particle size and distribution of metal catalysts were determined by aerosol size classification using a cylindrical differential mobility analyzer (DMA) (model 3080N, TSI, Inc.) and ultrafine condensation particle counter (CPC) (model 3776, TSI, Inc.). Details of this particle sizing method have been described elsewhere.<sup>18</sup> To prevent aggregation, size distributions of the metal particles were determined immediately downstream from the microplasma reactor. For both precursors, the mean particle size and standard deviation of the distribution increased with concentration. Here, we present size distributions of Fe and Ni particles acquired with the DMA-



FIG. 1. Schematic diagram of microplasma reactor and tubular flow furnace used for catalytic, gas-phase growth of carbon nanotubes. As-grown nano-structures are continuously monitored by a DMA and CPC.

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FIG. 2. (Color online) Temperature-dependent aerosol size distributions of carbon nanostructures grown on (a) Fe and (b) Ni catalyst particles. Lognormal distribution fits are shown. The insets show the size distributions of the nanoparticles (NPs) synthesized in the microplasma reactor (experimental conditions: 10 SCCM (SCCM denotes cubic centimeter per minute at STP) ferrocene+90 SCCM Ar for Fe NPs and 20 SCCM nickelocene +80 SCCM Ar for Ni NPs).

CPC system at a fixed precursor concentration [see insets of Figs. 2(a) and 2(b), respectively]. Experimental data was fitted to a log-normal distribution in order to obtain the geometric mean particle diameter  $(D_g)$  and standard deviation  $(\sigma_g)$ . As-grown Fe and Ni particles were found to have a  $D_g$  of 2.87 and 3.11 nm, respectively, with a  $\sigma_g$  of 1.12 and 1.16, respectively. The observed  $\sigma_g$  values reflect a much narrower distribution than measured by other aerosol methods without size selection.<sup>19</sup>

The metal nanoparticles generated in the microplasma reactor were rapidly introduced into a tubular furnace with  $C_2H_2$  and  $H_2$  to synthesize CNTs. The CNTs were activated and grown to a well-defined length by controlling the temperature and residence time in the tube furnace (1.8 cm i.d.  $\times 30$  cm length). For all experiments discussed here, the residence time was fixed at 30 s. CNT growth was continuously monitored at the exit of the furnace as a function of temperature with the DMA-CPC system. At 400 °C, no appreciable change was observed in the particle size distribution for Fe particles from that of unreacted Fe. In comparison, at the same temperature, the size distribution for Ni particles exhibited a shift from a mean mobility diameters of 3.11 to 5.35 nm, indicating that carbon deposition was occurring [see Fig. 2(b)]. As the furnace temperature was



FIG. 3. HRTEM images of carbon nanostructures grown in a tube furnace on (a) Fe particles at 500 °C, (b) Fe particles at 600 °C, (c) Ni particles at 500 °C, and (d) Ni particles at 600 °C (experimental conditions: 0.5 SCCM  $C_2H_2$ +50 SCCM  $H_2$ ).

further increased, the mean mobility diameters increased significantly for both Fe and Ne catalyst particles [see Figs. 2(a)and 2(b), indicating the onset of CNT growth. Comparing the size distribution of Fe- and Ni-catalyzed growths at 600 °C, we found that the particle counts were much higher for Ni than for Fe, implying that Ni nanoparticles catalyze a larger number of CNTs. Between 400 and 700 C, no particle counts were observed when the plasma or metallocene flow was shut off, confirming that the metal particles produced in the microplasma reactor catalyzed CNT growth. However, above 700 °C, counts were observed in the absence of nanoparticles. This is consistent with previous studies which have reported that self-pyrolysis of C<sub>2</sub>H<sub>2</sub> occurs at these temperatures leading to nucleation of carbon nanoparticles.<sup>12</sup> Therefore, below 700 °C, the size distributions are representative of catalytic decomposition and allow kinetic studies of CNT growth to be performed.

The morphology of carbon nanostructures produced by microplasma synthesis of metal catalysts and free-flow CNT growth was analyzed by high-resolution transmission electron microscopy (HRTEM). Thin films of material were collected for 1 h by depositing the aerosol onto carbon-coated copper grids using an electrostatic precipitator (ESP) (model 3089, TSI, Inc.). HRTEM microcharacterization was performed with a Philips Tecnai F30 operated at 300 kV. Figure 3 shows TEM images of carbon nanostructures grown using Fe and Ni particles at two different temperatures. At a growth temperature of 500 °C, the Fe particles appear to be coated by onionlike graphitic layers [see Fig. 3(a)]. The inner and outer diameters of coated particles are 2 and 5 nm, respectively, with a narrow size distribution which is consistent with obtained DMA size distributions [see inset of Fig. 2(a)]. The observed carbon structures bear similarity to in situ TEM observations<sup>20</sup> and molecular dynamic simulations<sup>21</sup> of CNTs produced catalytically at low temperatures, which have shown that graphitic encapsulation of Fe nanoparticles occurs when the growth temperature is between 227 and 527 °C. At 600 °C, Fe particles were found to catalyze CNT growth [see Fig. 3(b)]. HRTEM shows that the CNTs are highly crystalline and multiwalled with an outer diameter of 10 nm [see Fig. 3(b)]. In Figs. 3(c) and 3(d), TEM images of CNTs grown at 500 and 600 °C using Ni catalysts are given that show multiwalled nanotubes are grown at both low and

This



FIG. 4. Arrhenius plots for growth rates of CNTs on Fe and Ni catalyst particles.

high temperatures. The TEM analysis verifies that Nicatalyzed CNT growth occurred at lower temperatures than in the case of Fe-catalyzed growth, which is in accordance with our aerosol measurements.

Kinetic parameters for CNT growth are obtained from DMA-CPC analysis. Briefly, aerosol size classification separates nanomaterials based on their electrical mobility in a carrier gas, which corresponds to their projected area. Thus, the length of CNTs can be calculated from  $L_t = \pi D_A^2 / 4D_t$ where  $L_t$  is the CNT length,  $D_t$  is the CNT diameter, and  $D_A$ is the projected area diameter.<sup>12</sup> We have assumed that the projected area diameter of the nanotubes is equal to their mobility diameter for the lengths produced by our process.<sup>22</sup> The average CNT diameter is approximated to be 10 nm as inferred from HRTEM analysis. The overall growth rates of CNTs using Fe and Ni particles are then estimated from the mean mobility diameter, residence time, and  $C_2H_2$  partial pressure. To extract kinetic parameters, we have chosen the temperature range of 475-600 °C where CNTs were found to grow from in situ aerosol measurements and HRTEM analysis. Figure 4 compares the growth rate as a function of reciprocal temperature for Fe and Ni nanoparticles. From the slope, the activation energies for CNT growth with Fe and Ni particles are estimated to be 117 and 73 kJ/mol, respectively. The activation energy for Ni-catalyzed CNTs is close to that found in a previous study on gas-phase CNT growth where the metal catalysts were 15 nm in diameter.<sup>12</sup> These results indicate that the activation energy for catalytic, gas-phase CNT growth may be independent of particle size, but a strong function of catalyst material.

Although there have been few reports of free-flow CNT synthesis, the catalytic properties of Fe and Ni nanoparticles have been previously studied for CNT growth on substrates. For thermal CVD at temperatures above 700 °C, the activation energies for CNT growth on Fe and Ni catalysts have been found to be comparable to the diffusion energy of carbon in the respective bulk metals.<sup>23,24</sup> However, since the bulk diffusion rates of carbon in Fe and Ni are relatively similar, the activation energies for CNT growth on the catalyst materials only differ slightly.<sup>16</sup> Experiments at lower temperatures with plasma-enhanced CVD ( $<500 \circ C$ ) have found that the activation energy for CNT growth on Ni catalysts is much lower than that for Fe.<sup>25</sup> Overall, our activation energies are significantly lower than values associated with thermal growth, but higher than plasma-enhanced CVD. This is commensurate with the intermediate temperature range of our study where both bulk and surface diffusion are known to contribute to CNT growth.<sup>26</sup> While the lower activation energies observed here compared to thermal CVD could also be due to the absence of mass-transfer effects,<sup>12</sup> the gasphase process should be identical for both Fe and Ni particles. Because of the lower temperatures used here than the other thermal-CVD processes and the large difference in activation energies for Fe and Ni particles, we suggest that surface diffusion of carbon is responsible for the material dependent catalytic properties.

In summary, we have demonstrated the controlled synthesis of Fe and Ni catalyst particles by an atmosphericpressure, dc microplasma for gas-phase growth of CNTs. Our study shows that Ni particles allow the growth of CNTs at lower temperature than Fe where surface diffusion is the rate-limiting step. The synthesis methodology is also applicable to studies of alloyed, nontransition metal,<sup>27</sup> and semiconductor<sup>28</sup> catalysts for CNT synthesis.

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