Synthesis of Carbon Nanotubes and Nanofibers within Flame Environments

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Introduction

Carbon nanotubes and nanofibers are potentially useful in many applications and desirable in large quantities. Their full use requires a bulk method of synthesis. We are pursuing flame synthesis towards this end, as it is already used in the industrial production of nanoscale TiO_2, SiO_2 and carbon black.

Our previous work has shown a strong reactivity difference between Fe and Ni nanoparticles [1-3]. With high selectivity, Ni reacts with CO/C_2H_2 gas mixtures to produce nanofibers; whereas, Fe reacts with CO to produce SWNTs. Coincident with their products, Fe particles react with CO when roughly 1 nm in size; whereas, Ni particles react with CO/C_2H_2 mixtures when approximately 4 nm in size [3]. Both metals were introduced as metal nitrate salts in ethanol solutions at similar concentrations. Both metals have been tested in identical gas compositions and pyrolysis flame environments, as characterized by temperature and gas composition. Therein, the residence times were also the same for catalyst formation and nanotube growth. However, the ethanol/nitrate salt carrier system greatly complicates the chemistry of the growth pyrolysis. To directly study the highly selective reactivities of these different metals, the onset of catalytic activity and the potential associated particle size effects, laser ablation was used to generate the metal nanoparticles. With catalyst particles entering the flame in a reduced and active state, size dependent reactivities of the different metals may be examined. Relative reactivities are no longer obscured by the catalyst buildup/formation within a complex gas environment encountered in previous studies.

Experimental

The metal aerosol was produced by pulsed-laser (a 30 Hz Nd:YAG laser operating at 1064 nm) ablation of a rotating metal target. The laser energy was 300 mJ/pulse, with a beam spot of approximately 300 microns on the target. The target and motor were contained within a stainless steel cell to allow control of the gas environment in which the ablation occurred and the entrainment of the

ablated nanomaterial into the flame environment. The catalyst particles were carried from the cell with He to a tee below the burner. It was mixed with the rest of the gas mixture, $CO/H_2/He/C_2H_2$ as needed, and passed through a centered 3/8 inch tube that terminated level in the sintered metal surface of the water-cooled McKenna burner. All gas flows were controlled independently by mass flow controllers or rotometers.
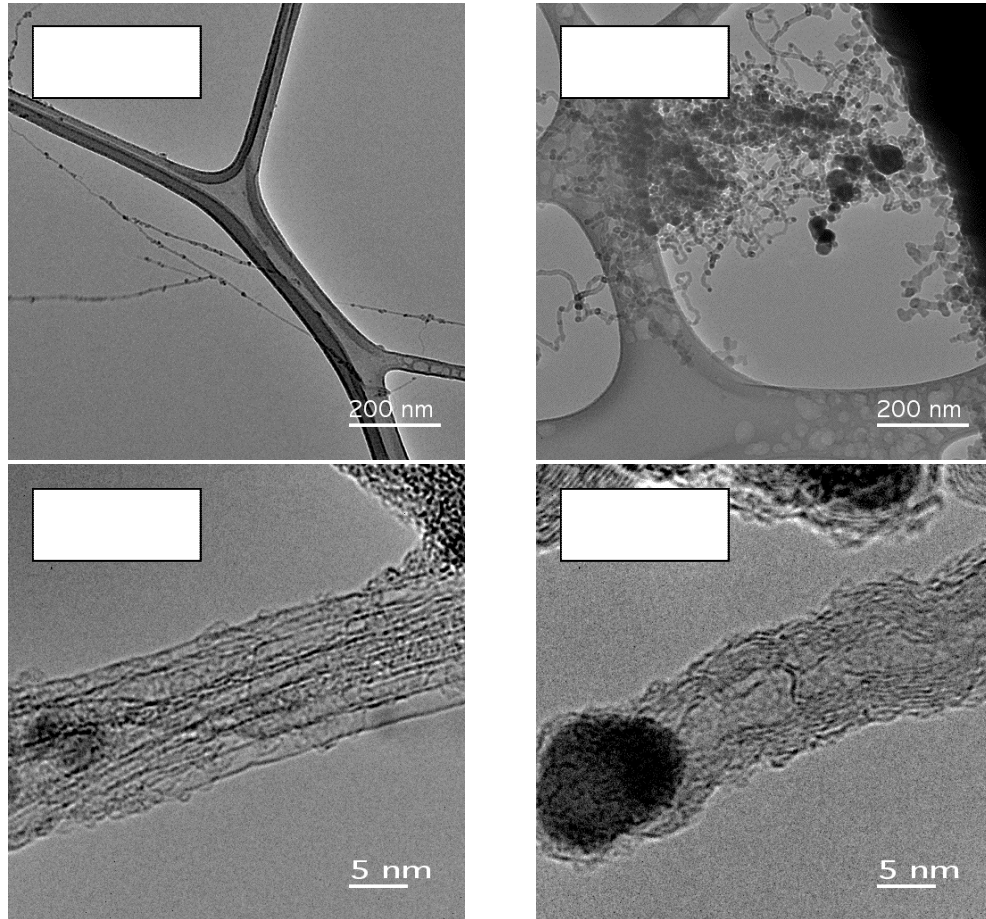

Figure 1. TEM images of Fe-catalyzed SWNTs using a CO/C_2H_2 gas mixture. Both individual and bundled SWNTs were produced, though bundles were much more prevalent. Figure 2. TEM images of Ni-catalyzed nanofibers using a CO/C_2H_2 gas mixture. Catalyst particles are evident at the tips of the nanofibers (a). The irregularities in the graphene sheet (b) cause undulations throughout the fiber (b).

The surrounding burner was operated using a rich premix of acetylene and air to create the desired reaction temperature. Fuel-air equivalence ratios were 1.5 to 1.55, produced using an acetylene flow rate of 1.5 slpm and an airflow rate ranging from 11.3 to 11.5 slpm. A 3 inch long, 1 inch OD quartz chimney served to stabilize the post-combustion flame gases against buoyancy-induced flicker and guided the metal aerosol and associated reaction gases as a laminar flow. Samples of the metal-catalyzed products were collected by thermophoretic

sampling directly upon lacey TEM grids above the chimney for analysis. Upon introduction of either Fe or Ni into the flame gases, a central red-orange core appeared within the gas flow through the chimney. With either catalyst, yellow emission, associated with C_2 Swan-band emission from burning carbon, was observed in the flame brush as the post-flame and entrained reaction gases mixed with ambient air. The carbon in this instance was in the form of the SWNTs or nanofibers as verified by TEM. Removing the catalyst caused the yellow and red orange emissions to fade and disappear.

Results and Discussion

Fe reacted in both the CO and CO/C_2H_2-based gas mixtures, producing SWNTs (Figure 1). In contrast, Ni was only reactive with the CO/C_2H_2 gas mixture, producing nanofibers (Figure 2). The need for C_2H_2 and CO for the Ni particles to be catalytically active leads naturally to the question; which gas is supplying the carbon? It is possible that both gases contribute and that the more reactive acetylene accelerates the rate of carbon supply sufficiently (due to its higher reactivity) to drive the carbon diffusion through the catalyst particle to supply the growing nanofiber. In this case, one might expect to observe some, although fewer and shorter, nanofibers using only C_2H_2. Alternately, C_2H_2 may be the sole source of carbon to the nanofiber. In this case, the catalyzed nanofibers would appear in roughly equivalent amounts and lengths using only C_2H_2. Finally, there could be synergism between coadsorbates of C_2H_2 and CO in that they assist in the other specie's dissociative adsorption. In this case, without CO, no nanofibers would grow.
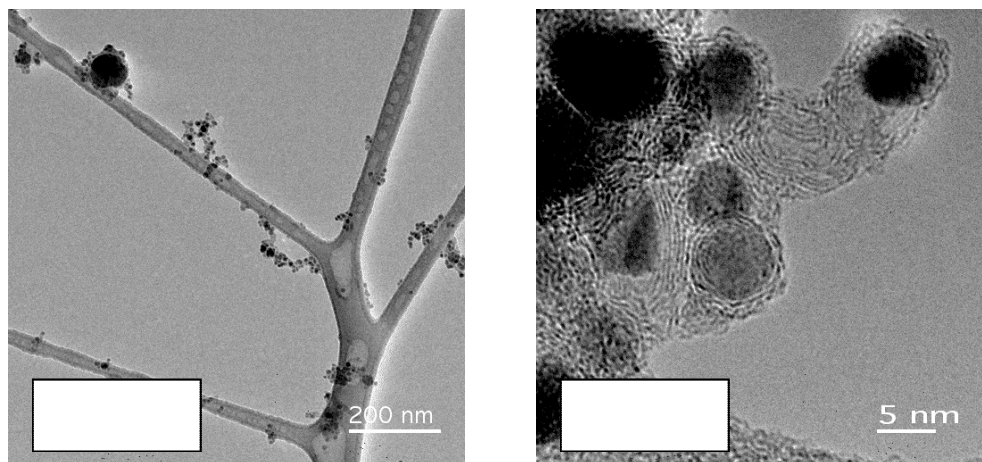

Figure 3. TEM images of Ni-catalyzed nanofibers using the C_2H_2 (as the only carbon source) gas mixture. In general the nanofibers were shorter than when using the CO/C_2H_2 gas mixture, the catalyst particles were smaller and the nanofibers exhibited a more chaotic internal structure.

To distinguish between these cases as outlined above, CO was replaced with an equal flow of He, leaving C_2H_2, the only carbon source gas, at the same

concentration. As shown in Figure 3, Ni-catalyzed nanofibers, but their growth was stunted relative to those obtained with the CO/C_2H_2 mixture. Moreover, the nanofibers and catalyst particles are encapsulated in amorphous carbon. Despite the same C_2H_2 concentration as before, the rate of carbon deposition has apparently increased in comparison to the CO/C_2H_2 gas mixture. This data rules out active synergism of enhanced dissociative adsorption between CO and C_2H_2 and independent carbon supply by both gases. Rather, it suggests that C_2H_2 serves as the main carbon supply for Ni-catalyzed nanofibers. The stunted growth and early encapsulation of the Ni catalyst particles suggests that CO restricts the rate of carbon supply. Its adsorption and associated slower reactivity restricts the rate of C_2H_2 adsorption (by site blockage), and hence, slows the rate of carbon supply. This then balances the rate of carbon supply to the catalyst particle by dissociative adsorption with its rate of uptake by the combined processes of solvation into, diffusion through and precipitation from the catalyst particle. This balance is clearly manifested by the extended lengths and unencapsulated Ni particles observed when using the CO/C_2H_2 mixture, as shown in Figure 2. Finally, it is interesting to note that the Ni particles in the gas mixture containing only C_2H_2 were on average somewhat smaller than the Ni particles in the combined CO/C_2H_2 gas mixture. This is consistent with their premature deactivation. These results demonstrate the selective reactivity of Ni towards C_2H_2.

On the basis of bulk crystal studies, Fe is considered to be more reactive than Ni [4]. Clearly, it achieves an earlier onset of reactivity, as only the very smallest Fe particles catalyze nanotubes, in this case SWNTs. Therein, Fe might be expected to readily react with C_2H_2, particularly since it reacts with CO. One might even predict that CO, as a less reactive carbon source could yet play a similar role in restricting the rate of carbon supply through C_2H_2 dissociative adsorption, as it does with Ni. With CO replaced by a balance of He, the gas mixture containing C_2H_2, as the only carbon source, was tested using Fe. No SWNTs were catalyzed. Only metal catalyst particles were observed. Using the CO/C_2H_2 gas mixture, no definitive increase in SWNT yield was observed. While there may be some synergism between these reactant gases, the absence of an increase in SWNT yield suggests that any synergism is marginal at best. These results demonstrate the selective reactivity of Fe towards CO.

Notably, in either the CO or CO/C_2H_2 gas mixture, Fe does not catalyze MWNTs or nanofibers. Catalysis of either would require larger Fe particles, which are supplied by the *ex situ* laser ablation process. If the larger particles were active towards MWNT or nanofiber synthesis, then these products would be expected, given similar temperature and residence time scales as for Ni. The absence of such products suggests a decline in reactivity with increasing particle size, in contrast to Ni.

The laser ablation method used for catalyst generation produces a distribution of particle sizes prior to interaction with the flame generated gases and

temperature. Only selected sizes of Ni and Fe nanoparticles react to form nanofibers and nanotubes. The only other particles that were collected were very large. The initial broad distribution of particles underwent a change in the flame environment in which only active-sized nanoparticles were protected by catalyzed growth. Other particles must have been sintered into active-sized particles or into large clumps, which were only limited in size by time of coalescence and sintering.

If the electronic properties of a metal nanoparticle resembles those of the individual element, given the finite size and high surface area, then based on energetics associated with its outer electron configuration, $[Ar]5s^2 3d^6$, Fe atoms can achieve a stable half filled d-shell by loss of electron density such as by donation of electron density to an adsorbate, e.g. CO. In contrast, acceptance of electron density might be expected to be energetically unfavorable, given the increase in energy associated with pairing electron density within the d-shell orbitals. Therein, Fe would be expected to be unreactive towards C_2H_2.

The situation for Ni is exactly opposite. Under the same assumption, it would be energetically favorable for Ni to accept electron density to achieve a more stable, filled d shell, namely $[Ar]5s^2 3d^{10}$. Therein, Ni would be expected to be highly reactive towards adsorbates, which donate electron density, e.g. C_2H_2. Correspondingly, Ni would be unreactive towards adsorbates that accepted (withdrew) electron density from the metal nanoparticle, e.g. CO. This exceedingly simple explanation neglects several factors.

By a similar experiment where targets of the same metals were ablated just above the burner surface so that the nanoparticle plume mixed with the flame and added gases, the time of SWNT and nanofiber growth is conservatively placed at 100 ms. Using the flame temperature along the axial streamline, buoyant acceleration within the flame was found. Knowing the height at which successful products were sampled, the time of growth was determined [5].

Conclusions

The higher activity of Fe compared to Ni is illustrated by the requirement of fewer atoms forming a catalyst particle to initiate catalysis, which in turn provides an appropriate sizing to catalyze SWNTs. This greater reactivity is manifested in its activity towards dissociative adsorption of CO, compared to the more reactive C_2H_2. Fe is very selective, reacting with CO and not C_2H_2. In contrast, Ni nanoparticles must reach a much larger size to attain catalytic activity. Its lower reactivity is observed as these larger Ni particles only react with C_2H_2 and produce nanofibers. Therein its selectivity is manifested by its preferential reactivity towards C_2H_2 and not CO.

Results are interpreted on the basis of the dissociative adsorption mechanisms of CO and C_2H_2 and the electronic properties of the metal nanoparticles. By

considering the reactivities of the metal nanoparticles as reflecting that of the elemental atoms, the selective reactivities of Fe towards CO and Ni towards C_2H_2 may be understood based on energetic considerations associated with the metal surface atom's d-shell orbital electron density.

References

[1] Vander Wal RL. Flame synthesis of Ni catalyzed nanofibers. Carbon 2002: 2101-2107.

[2] Vander Wal RL. Fe-catalyze single-walled carbon nanotube synthesis within a flame environment. Combustion and Flame 2002: 37-47.

[3] Vander Wal RL, Hall LJ. Flame synthesis of Fe catalyzed single-walled carbon nanotubes and Ni catalyzed nanofibers: growth mechanisms and consequences. Chemical Physics Letters 2001: 178-184.

[4] Kim CM, Knight C, Somorjai GA. Building of complex catalysts on single crystal surfaces. In Dwyer DJ, Hoffman FM, editors. Surface science of catalysis: in situ probes and reaction kinetics. Washington DC: American Chemical Society, 1992: 108-129.

[5] Vander Wal RL, Berger GM, Ticich TM. Carbon nanotube synthesis in a flame using laser ablation for in situ catalyst generation. Applied Physics A 2003:885-889.