Abstract

Various morphologies of multi-walled carbon nanotubes (MWNTs) are grown catalytically on metal-alloy probes in counterflow diffusion flames using methane as fuel. Carbon nanotube (CNT) properties and morphologies are investigated as functions of local gas-phase temperatures, C-related species concentrations (e.g. C$_2$H$_2$, CO), sampling positions, C$_2$H$_2$ adding to the fuel, and metal-alloy compositions (i.e., Fe, Fe/Cr, Ni/Cu, Ni/Ti, Ni/Cr, Ni/Cr/Fe). MWNTs grow optimally in non-sooty regions of the flames. C$_2$H$_2$ addition is found to promote direct synthesis of vertically well-aligned MWNTs with uniform diameters from Ni/Cr/Fe and Ni/Ti alloys.

Keywords: Carbon nanotube; Materials synthesis; Diffusion flame

1. Introduction

Carbon nanotubes (CNTs) define a new class of engineering materials with remarkable physical and electromagnetic properties. Numerous techniques have been developed for the production of CNTs, including arc discharge [1,2], laser ablation [3], and chemical-vapor deposition (CVD) [4]. However, large-scale applications will require synthetic methods that are continuous and energy efficient. CNTs have been documented in sooting flames [5–18], which possess an intrinsically cheaper source of process heat than any other technique, without the need for expensive starting materials. With combustion synthesis having demonstrated a history of scalability, it is worth investigating the fundamental mechanisms of catalytic CNT formation and growth in well-designed and practical flames, so that process conditions can then be defined that enable high-rate and high-purity synthesis of CNTs with specific characteristics.

Studies of flame synthesis of metal-catalyzed CNT formation can be broadly classified into aerosol catalyst [10–13,18] and supported-substrate methods. With respect to the latter method, as investigated in this work, several researchers [5–9,14–17] have been successful in producing various morphologies of CNTs in flames of different geometries (mainly co-flow) and modes (i.e. pre-mixed and non-premixed). In our setup, transition-metal-alloy substrates are inserted into a diffusion-flame structure to probe for conducive regions of CNT synthesis (see Fig. 1). Under favorable conditions, catalyst nanoparticles are formed, and carbon-based precursor species readily undergo dissociative adsorption and diffuse through the catalyst nanoparticles and grow into CNTs [19], with the nanoparticles either remaining attached to the substrate and situated at the base of the growing CNT or detaching from the probe and situated at its tip.
The present study is motivated by several considerations. First, we note that simple and well-defined flame geometries allow for meaningful comparisons between precise experimental probing and detailed computational simulations, facilitating deduction of fundamental controlling mechanisms. As such we employ the quasi-one-dimensional counterflow diffusion flame. We note that only Merchan-Merchan and co-workers [7,8,20] have utilized this geometry (for oxygen-enriched flames). By determining local in-situ temperature and gas-phase chemical-species concentrations corresponding to given CNT morphologies and growth rates, not only are fundamental mechanisms revealed, but "universal" conditions are also established which should be directly applicable as specific operating conditions for other methods of synthesis. Second, since the hydrocarbon fuel not only provides the source of process heat but also the carbon-based growth reagents to make CNTs, we specifically investigate methane/air systems, thus exploring the possibility of using natural gas in atmospheric air to economically synthesize large quantities of CNTs. Third, we also examine the effects of acetylene addition. Acetylene is often necessary for metal-catalyzed CNT growth since C2 species readily undergo dissociative adsorption. Concurrently, however, the molecular path towards soot formation requires C2 species, most notably acetylene (C2H2), which is essential to the formation of the first aromatic ring, benzene, enabling subsequent polycyclic aromatic hydrocarbon (PAH) growth. PAHs can then form soot particles adulterating the yield. Moreover, PAHs (which are particularly stable thermodynamically and resistant towards catalytic dissociation [10,21]) can be detrimental to CNT growth by deactivating the metal-catalyst species. Fourth, and in line with the previous consideration, in order to achieve high-purity yields, we probe CNT synthesis in soot-free regions of the flow field where C-related species (i.e. CO and C2) concentrations are still high. Since soot formation is a rate process, subject to residence-time considerations, the aerodynamic straining implicit in counterflow diffusion flames becomes advantageous. Because growth from acetylene into a phenyl ring occurs relatively slowly in comparison to ring-growth reactions, it may be possible to produce CNTs in an acetylene-rich flame without a lot of soot byproduct. Finally, we tailor our flames such that the local growth conditions are similar to those that we employed in our previous work [22] on flame synthesis of CNTs on metal alloys in co-flow inverse diffusion flames. Optimal local conditions for

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**Fig. 1.** Experimental setup for (a) Flame #1, and (b) Flame #2, with visible orange soot layer. Flame structure for (c) Flame #1, and (d) Flame #2. Thermocouple measurements (TC) assess actual probe temperatures. Strain rate is 20 s⁻¹. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this paper.)
CNT synthesis should be “universal,” as stated in the first consideration, and such comparisons allow for assessment of the role of spatial gradients in temperature and species in affecting CNT morphologies and growth rates.

2. Experiment and computation

The burner configuration, as shown in Figs. 1a and b, consists of two convergent nozzles with a 19-mm exit diameter and 15-mm separation distance. Airflow as oxidizer is issued from the top burner, and nitrogen-diluted fuel flow is issued from the bottom burner, establishing a flat flame in-between. Co-flowing nitrogen eliminates oxidizer entrainment into the flame, extinguishes the outer flame, and minimizes shear instabilities. For the relative concentrations of fuel and oxidizer used in our experiments, the flame is located on the oxidizer side of the stagnation surface. A metal-alloy probe (0.8 mm) is inserted into the hydrocarbon-rich fuel side of the flow field (strategically in the stagnation region to minimize flame perturbation), thereby precipitating CNT growth via carbon migration diffusion through the catalytic nanoparticles extracted from the probe. The resulting flames are monitored by a cathetometer, and flickering of these flames is minimal, with less than ±75 μm of spatial displacement. By mounting the probe to a linear translation stage, CNT growth characteristics are investigated as a function of axial position.

In our study, we examine two specific flame conditions, which we refer to as Flame #1 and Flame #2. Flame #1 is a non-sooty 50% CH4/50% N2-versus-air flame (Fig. 1a). Flame #2 is a 42% CH4/3% C2H2/55% N2-versus-air flame, with a very-thin visible soot layer adjacent to the blue flame chemiluminescence, as shown in Fig. 1b. Note, however, that the probes are inserted into the non-sooty stagnation region for Flame #2. Both flames have the same characteristic peak temperature. Figures 1c and d display their flame structures (along with the regions probed), as predicted computationally using GRI-Mech 1.2 [23] and verified experimentally using spontaneous Raman spectroscopy (SRS) for gas-phase temperatures and major species concentrations (i.e. CH4, C2H2, CO, H2). Temperatures within the flame structure are also measured using a 125 μm Pt/Pt-10% Rh thermocouple (S-type) coated with BeO-Y2O3 to better assess the actual catalytic probe temperatures, which are expected to differ from gas-phase temperatures due to radiative effects and conductive losses along the probe lengths.

Prior to synthesis, all metal-alloy probes are ultrasonically cleaned in ethanol and pretreated with diluted nitric acid to remove natural oxidize layers. Post-synthesis, the surfaces of the probes are imaged directly using field emission scanning electron microscopy (FESEM) to assess CNT morphology. After ultrasonic treatment, high-resolution transmission electron microscopy (HRTEM) characterizes individual CNTs and bundles; XEDS analyzes the included catalyst nanoparticles.

3. Results and discussion

Table 1 summarizes the metal-alloy substrates examined. In general, transition metals (e.g. Ni, Co, and Fe) and their alloys have been used as catalysts for CNT growth. Bimetallic catalysts, such as alloys, are known to increase the yield of CNTs [24]. Alloys show a decrease in their melting temperature and an increase in the carbon solubility as compared to single metals [25]. Since both CO and C2 species can participate in the growth processes of CNTs, we tailor our flames such that there are sufficient concentrations of them in the regions that we probe. Flame #1 and Flame #2 mainly differ by the C2H2 concentrations in the region of interest, as seen in Figs. 1c and d. Since our synthesis process involves both catalyst nanoparticle formation and CNT growth, the temperatures in the probed region must be conducive for nanoparticle nucleation and active catalytic behavior. In this respect, hydrogen presence in the flame structure (see Figs. 1c and d) is very important. Catalyst metal particles can be obtained by selective hydrogen reduction of the alloy, and preliminary results show that hydrogen prolongs the life of the catalysts, perhaps by satisfying unfilled carbon valencies at the precipitating rear facets of the metal catalyst. At the same time, however, there may exist competition between etching of sp2 carbon by H atoms and deposition of sp2 carbon by hydrocarbon intermediates. Consequently, we carefully assess CNT morphologies as functions of local gas-phase temperatures, concentrations of precursor species, and metal-alloy compositions.

Figure 2 compares the morphologies of MWNTs synthesized on different metal alloys in Flame #1 and Flame #2. The Fe/Cr case is not shown in Fig. 2 because no filamentous carbon grows on its surface for the flame conditions.
Fig. 2. Typical FESEM images of MWNTs grown on different catalytic metal-alloy probes for Flame #1 and Flame #2. The axial height $z$ corresponds to distance from the fuel nozzle as shown in Fig. 1.
tested. As can be seen, filamentous carbon grows on 99.5% Fe, and CNTs grow on Ni-included Cr-containing alloys (i.e. Ni/Cr and Ni/Fe/Cr). Although the melting temperature of the Fe/Cr alloy is lower than that of the pure Fe metal, and nanoparticles are readily formed on the probe, Cr presence in the nanoparticles may deactivate or lower the catalytic activities of the Fe. It seems that Ni presence in Cr-containing nanoparticles permits favorable carbon solubility and CNT precipitation at these temperatures. We now examine the CNTs produced in Flame #1 (left-hand column of Fig. 2). For the 99.5% Fe probe, micro- and nano-scale carbon fibers and tubes are produced, as seen in Fig. 2a, which are characterized by various forms along with a large diameter and distribution (50–100 nm). The fibers/tubes tend to be coiled and entangled. Also compared to other metal alloys, CNT yield from the Fe substrate is low. We next consider the three bimetallic Ni-based alloys starting with the lowest melting temperature. The Ni/Cu probe is covered with an entangled mat of CNTs of uniform diameter (≈20 nm), as shown in Fig. 2c. Randomly-directed entangled CNTs cover uniformly the surfaces of both Ni/Ti and Ni/Cr probes, as indicated in Figs. 2e and g. The Ni- and Fe-containing alloy, i.e. Ni/Fe/Cr, allows for entangled growth of CNTs directed outwards from the probe surface with a layer of catalysts at the top of the CNTs. Among the Ni-containing metal alloys, Ni/Fe/Cr and Ni/Cu tend to grow CNTs of smaller diameter (≈10–25 nm), while Ni/Cr and Ni/Ti grow CNTs of relatively larger diameter (≈20–40 nm).

TEM imaging reveals that the CNTs synthesized on the alloys are MWNTs with strong graphitic structure. Figure 3 shows characteristics of the MWNTs produced by the Ni/Cu alloy. Figure 3a presents a low magnification TEM image of bundles of MWNTs, some with catalyst nanoparticles at the tips and some with open tips caused by the removal of catalyst nanoparticles during ultrasonication. Figure 3b displays a HRTEM image of a MWNT with an open tip, where the spacing between the coaxial graphitic cylinders is ≈0.34 nm. Figure 3c shows a 25 nm-diameter MWNT segment with parallel graphite walls enclosing a hollow core.

The effects of C2H2 addition to the fuel on CNT growth are displayed in the right-hand column of Fig. 2, corresponding to Flame #2. As can be seen in Fig. 1d, C2H2 mole fraction at the probe location is about six times higher for Flame #2 than Flame #1, while gas-phase temperature and CO mole fraction remain about the same. The amount of C2H2 addition was determined by matching the local gas-phase probe conditions (i.e. temperature, C2H2, CO, H2) for Flame #2 to that measured (through SRS) for optimal CNT growth in our previous work [22] which used a co-flow inverse diffusion flame that resulted in vertically well-aligned CNTs for the Ni/Cr/Fe probe. Parenthetically, we note that due to the geometry differences, it was difficult to match the actual probe temperature, which was about 100 °C higher for the counterflow diffusion flame than for the co-flow inverse flame, due to less conductive losses along the length of the probe. Nonetheless, vertically well-aligned CNTs normal to the Ni/Cr/Fe alloy surface (Fig. 2j) are obtained, showing that local conditions for CNT growth and morphology can be translated between different configurations of synthesis. C2H2 addition affects the morphology significantly for the Ni/Cr/Fe alloy, by aligning the CNTs. For the other metal alloys, the effects are more subtle, with close examination revealing that the characteristic diameters may be a bit smaller and the overall yield a bit higher, as shown in Fig. 2, due to the increase of C-related species concentrations.

C2H2 addition is found to significantly affect the floating potential, as induced by flame-gen-

Fig. 3. TEM images of MWNTs grown on Ni/Cu probe inserted at z = 6.2 mm in Flame #1. (a) Low magnification TEM image shows MWNTs of different diameters ≈10–25 nm. Inset shows a highly-bent CNT. Arrows show included catalyst nanoparticles. (b) HRTEM image of a MWNT open tip showing graphitic rings, with a hollow core, as indicated by the arrow. (c) HRTEM image of graphitic wall layers of a MWNT with a hollow core, as indicated by the arrow.
erated ions and electrons, on the Ni/Cr/Fe probe. For Flame #1, the floating potential is \(-2\) mV, while for Flame #2, it is \(-14\) mV. The floating potential for our previous co-flow study [22] was \(-24\) mV; the difference in induced voltages may be due to differences in ion deposition rates from different probe temperatures. Nevertheless, our previous study [22] and others [7] have shown that such electric potentials can significantly affect CNT alignment. Although applied potentials as small as a few tens of millivolts can develop an electric field exceeding 1000 V/cm at the characteristic nanotube diameter [7], perhaps causing alignment, we do not observe alignment in the other metal alloys, even under applied voltage bias. As such, the density of catalytic nanoparticles formed is likely the key parameter, which allows for neighboring CNTs to provide vertical support for each other so that orderly growth perpendicular to the substrate occurs. Carbide-induced break-up of the alloy surface to form catalyst nanoparticles responsible for CNT growth may be affected by C2 transport to the surface, as reflected by the induced voltage. XEDS of a single catalyst nanoparticle at the tip of a CNT grown from a Ni/Cr/Fe probe reveals that both Fe and Ni are present. Re-inspecting the FESEM image of Fig. 2j, it seems that a layer of densely-packed nanoparticles of Ni-Fe-Cr composition is uniformly lifted off the surface of the probe, catalyzing aligned nanotube growth. Interestingly, the Ni/Cr/Fe alloy is more favorable for aligned-CNT growth than is Ni/Cr (Fig. 2g and h) or Fe/Cr (which does not catalyze CNT growth at all). As such, it is possible that Ni is the active catalyst in this nanoparticle, and the presence of Fe in the alloy solution alters mixture properties such that closely-packed nanoparticle nucleation is possible. This hypothesis seems plausible given the observation that the nanoparticles at the tips of the CNTs are often larger in diameter than the CNTs themselves. Nonetheless, more study is needed.

Particularly interesting CNT-growth morphology is manifested by the Ni/Ti alloy under Flame #2 conditions. Although the majority of the surface of the probe is covered with entangled CNTs as shown in Fig. 2f, selected areas display high growth rates of well-aligned MWNTs with much smaller diameter.

Fig. 4. FESEM of well-aligned MWNTs grown on Ni/Ti probe inserted at \(z = 6.2\) mm in Flame #2. (a) Low magnification, and (b) high magnification of vertically well-aligned MWNTs of \(\sim 10\) nm diameter. (c) Bundles of well-aligned MWNTs. (d) Bundled “walls” of well-aligned MWNTs.
(\sim 10\,\text{nm}), as shown in Fig. 4. These MWNTs are very densely packed, much more so than those grown from the Ni/Cr/Fe alloy (Fig. 2). For a 10-minute growth duration, the MWNTs are about 20\,\mu\text{m} in length. As shown in Figs. 4c and d, these MWNTs are often found in bundles held tightly together by Van der Waals forces. These different morphologies of CNTs appear to sprout out of fissures on the substrate surface. In hydrocarbon-rich flames, carbide-induced breakup of the alloy surface can occur along grain boundaries and other faults due to volumetric lattice mismatch between the carbide and surrounding metal [26]. As such, non-homogeneities in the grain structure and crystallinity of the metal-alloy probe formed by the die during the drawing process may allow for densely-packed nucleation of nanoparticles in these selective sites. Additional study is needed.

The large characteristic thermal and chemical gradients characterizing our flames are especially advantageous for determining CNT growth conditions in that a large parameter space of conditions can be investigated within a single flame. Metal alloys are tested at different axial locations \( z \) in Flame #1 and Flame #2. In both flames, no filamentous carbon (only amorphous carbon) deposits above \( z = 6.6\,\text{mm} \), corresponding to the fuel side where the local gas-phase temperature is 1350\,\text{K}, despite increasing concentrations of CO and C\(_2\)H\(_2\). This is likely due to deactivation of the catalyst at higher temperatures. Figure 5 shows FESEM images of MWNTs grown on Ni/Cr probes inserted at three different axial locations (near the stagnation point) in the two flames, respectively, where the gas-phase temperatures range from 1300 to 1000\,\text{K} with decreasing axial height. As can be seen in Figs. 5a-c for Flame #1 and Figs. 5d-f for Flame #2, there appear to be very-slight decreases in CNT diameters, but obvious decreases in yields and lengths. The catalyst nanoparticles are active at these temperatures, and the increase in CNT diameter with axial height may be attributable to continued nanoparticle growth with increasing temperature (see Fig. 1c and d). The decrease in CNT yield with decreasing axial height is attributable to reduced rates of catalytic nanoparticle formation at lower temperatures. Below \( z = 5.8\,\text{mm} \) in Flame #1 and Flame #2, where the local gas-phase temperatures are \sim 950\,\text{K}, CNTs are no longer observed, despite sufficient concentrations of CO for both flames and sufficient concentrations of C\(_2\)H\(_2\) for Flame #2. This corresponds to lack of nanoparticle formation at these temperatures. Note from Figs. 1a and b that probe temperatures and gas-phase temperatures are approximately the same in the region of CNT formation. Similar trends are found for the other metal-alloy compositions.

Finally, since the axial gradients are large in our flames, we assess the effects of probe diameter on CNT growth. Two different diameters (0.5 and 0.8\,\text{mm}) of Fe and Ni/Ti probes are compared. The results show no discernable differences in characteristics of as-grown MWNTs, and we conclude that for the characteristic probe diameters employed in this work, the CNT morphologies and characteristics obtained correlate well with absolute local conditions.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure5.png}
\caption{FESEM images of MWNTs grown on Ni/Cr probes inserted at different axial locations \( z \), near the stagnation plane for Flame #1 and Flame #2. Insets show interesting structures.}
\end{figure}
4. Concluding remarks

In the present investigation, we have successfully grown CNTs on various catalytic metal alloys in non-sooting methane/air counterflow diffusion flames. Alloy composition strongly affects CNT morphology, along with gas-phase temperature and local C\textsubscript{2}H\textsubscript{2} concentration. Vertically-well-aligned MWNTs are synthesized on Ni/Cr/Fe (\textasciitilde 20 nm diameter) and Ni/Ti (\textasciitilde 10 nm diameter), when there is sufficient C\textsubscript{2}H\textsubscript{2} concentration. Notably, C\textsubscript{2}H\textsubscript{2} addition affects the potential induced on the substrate. We also observed some special structured CNTs such as coiled and highly-bent CNTs, as seen in the insets of the figures. Comparisons with our previous work using co-flow flames evince that local conditions for CNT growth and morphology can be translated between different configurations of synthesis.

Acknowledgments

We extend our thanks to Prof. Frederic Cosandey for his help with HRTEM and FESEM and to Prof. Yiguang Ju of Princeton University for his help with the computations. Funding from the National Science Foundation (NSF-CTS-0213929, NSF-CTS-0522556) and the Rutgers University Academic Excellence Fund supported this work.

References


Comments

Kozo Saito, University of Kentucky, USA. In your presentation, you mentioned flame synthesis is more favored for large production than CVD. However, the currently operated CVD already produced over 100 tons/year in 2005 [1]. What data do you use to justify your remarks made in your introduction?

Reference


Reply. Flame synthesis is promising for large-scale applications due to its scalability, configurationally versatility, and efficiency (i.e., providing both heat source and reagent). Furthermore, flame synthesis allows for the growth of CNTs over large areas (and at atmospheric pressure), which is especially challenging for other methods, such as CVD.

Z.A. Mansurov, Al-Farabi Kazakh National University, Kazakhstan. What is the form of your catalytic probes—rod or plate, and the time of exposition? What is your opinion why Ni/Cr/Fe is more effective than pure Fe?

Reply. The catalytic probes are rods, with diameters ranging from 0.5 to 1 mm. The exposition time in the flame structure is 10 min. The results indicate that the
Ni/Cr/Fe probe is more effective than the Fe probe at producing high densities of well-aligned CNTs only for the specific conditions tested. Given that the examined characteristic gas-phase temperature is ~1250 K, the lower melting point of the alloy (1623 K versus 1808 K for Fe) plays a role by allowing for increased carbon solubility. However, as discussed in the paper, catalytic nanoparticle formation is likely the key parameter, which is highly dependent on various alloy properties, as well as carbide-induced breakup of the probe surface. Additional study is needed.

William H. Green, MIT, USA. How does the morphology depend on the radial position of the catalytic probe?

Reply: The counterflow flame is employed due to its ideal, quasi-one-dimensionality. Experimentally, of course, there are radial variations. However, for our flames, measured gas-phase properties and resulting CNT morphologies were uniform and constant within a few millimeters of the axial centerline. All of our studies, as well as modeling, are directed at the axial centerline, so that reasonably representative growth can be correlated to local conditions at specific vertical positions.

Randy L. Vander Wal, NCSER at NASA-Glenn, USA. Please note that all of our flames were non-sooting, i.e., the only solid carbon that was formed were catalyzed CNTs. The formation of catalyst particles by reliance upon a carbide induced breakup process of the metal probe would seem to complicate interpretation of the results. For different metal alloys, such a process could lead to differently sized catalyst particles and even change their chemical composition relative to that of the nominal bulk material. Would you please comment?

Reply: Absolutely. This aspect of catalytic nanoparticle formation is discussed somewhat in the paper; however, much more study is needed. This is an excellent point.