Carbon Nanomaterials Deposition in an Alumina Microcombustor

THESIS

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By

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Abstract

Carbon nanomaterials, including few-layered graphene (FLG), are synthesized on nickel and copper wires using boundary layer deposition inside an alumina microcombustor. Previous work in flame synthesis of FLG has utilized impinging jets on flat foils as well as flame doping with hydrogen. It is shown that different carbon structures, including bulk graphite, 5-8 layers of graphene, and carbon nanotubes or fibers, can be synthesized on nickel and copper substrates by adjusting only the flow parameters of a methane/oxygen flame within the microcombustor. In addition, the effect of the boundary layer on carbon formation down the length of the wire substrates is examined.

Previous to the carbon nanomaterial synthesis, the development of the microcombustor platform itself is detailed. Two microcombustor channel geometries, a nested spiral and a Y-design geometry, are characterized across their operational range. In the case of the spiral combustor, Dean Number effects on the stability of an oscillating flame reaction in the curved channels are investigated and correlated to the audible frequency of the reaction.

The Y-design microcombustor is utilized for the carbon nanomaterial synthesis and ultimately 5-8 layers of well-ordered graphene are deposited on copper substrates showing the ability of the microcombustor platform to match other flame synthesis methods in number of layers produced, while improving on the disorder within the layers. Dedication

In memory of my father, Michael E. Kellie.

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Chapter 1: Introduction

Section 1.1: Background and Motivation

Graphene is a one-atom thick layer of carbon. Interest in graphene is high because of unique properties such as its high charge carrier mobility of 15000 cm² V⁻¹ s⁻¹ [1, 2] which make it ideal for use in electronic devices. By comparison, silicon has a charge carrier mobility of 1400 cm²V⁻¹s⁻¹, showing an improvement of over tenfold for graphene films. Additionally, graphene has shown promise as filler for composite materials. When added to a polymer blend at a 20% solids loading by weight, it was observed that the material's flexural modulus increased by over 60% to 3.8 GPa while remaining lightweight [3]. As a pure material, monolayer graphene has been shown to have a Modulus of Elasticity of 1 TPa which more than five times the Modulus for A36 structural steel [4]. As a result, research activity in the area of graphene synthesis has been high and many approaches have been investigated to form graphene films.

One of the easiest and earliest methods is the mechanical exfoliation of graphite for the isolation of graphene flakes [2]. In this method, graphene sheets were isolated by repeatedly peeling flakes from highly oriented pyrolytic graphite. However, mechanical exfoliation is not widely scalable for large-scale commercial device production. Eda *et al.* have shown a pathway to large-area thin films through the reduction of graphene oxide flakes which are separated and controlled through a solution filtering process [5].

Additional approaches have sought to scale the production of graphene and increase both the efficiency of the process as well as its reliability. Previous approaches utilizing chemical vapor deposition (CVD) have been shown to be effective for producing few- and mono-layer graphene films but require large chambers sealed against the outside atmosphere, vacuum levels of 10 millitorr or higher, and multi-step wet chemistry processes [6, 7]. Many different configurations for CVD reactors exist and a variety of gas mixtures are utilized within them, including methane, hydrogen, and even inert gases such as argon. Effects of gas composition, metal substrate type, and deposition temperature conditions have been explored extensively [8, 9]. In a CVD system the deposition of graphene usually takes on the order of several minutes, with 30 minutes as a rule of thumb, which does not account for reactor start-up and shutdown times. Furthermore, these systems require fine control over deposition conditions [6, 10, 11]. Graphitization of silicon carbide has also been explored using processes that anneal the surfaces under high vacuum [12-14]. However, this method suffers from many of the same challenges and limitations as those of CVD.

Alternatively, high throughput methods for faster deposition of graphene have been considered such as the work by Li *et al.* [15] where it was shown that few-layered graphene (FLG) films can be created on nickel foils using a dual-flame alcohol burner in open environments within 30 seconds. However, this dual-flame approach may not scale well nor be efficient due to the large dual flames that must cover the nickel foil to shield the synthesis area from the surrounding atmosphere, as can be seen in their experimental setup in Figure 1.



Figure 1: Experimental setup of Li et al. for dual-flame synthesis of FLG on nickel foils

Furthermore, Li *et al.* did not report the actual number of layers grown in their study. Based on the Raman spectra presented in their paper and comparing to previous reports in literature, it is likely that Li *et al.* had 8 or more layers of FLG, with 10 layers considered to be enough to form bulk graphite. Memon *et al.* have also shown a combustion-based method for FLG film generation on nickel and copper foils utilizing a methane/oxygen flathead burner that operates on a diffusion flame doped with hydrogen [16]. However, their method was similar to the atmospheric pressure CVD reactors with experiments conducted in a closed quartz chamber with slow deposition taking nearly 30 minutes, as shown in Figure 2. Furthermore, Memon *et al.* have used a complex gasmixture with methane, oxygen, and hydrogen which required fine control over the gas composition for 5-8 layer FLG film synthesis. It should be noted that all previous graphene deposition methods, either by CVD or flame synthesis, have utilized the same

flow geometry in which hot gases impinge on a substrate in a stagnation flow configuration.



Graphene on Cu or Ni

Figure 2: Experimental setup for Memon *et al.* which shows a flame impinging on a foil which is characteristic of previous flame synthesis methods

In this thesis, a new platform is reported for synthesis of carbon nanomaterials including few-layered graphene. Several innovations over existing graphene synthesis methods are reported and discussed. An alumina microcombustor, which is a combustion system with sub-millimeter critical dimensions for graphene synthesis, is reported in this work. The data reported here will show that it is also possible to deposit other carbon nanomaterials, including carbon nanotubes, using the microcombustor. However, the main emphasis is on FLG synthesis. The microcombustor uses a methane/oxygen flame, which removes the added complexity of hydrogen or inert gas doping in flame chemistry,

while using the microcombustor's enclosed exhaust channel as the synthesis zone. This allows carbon to be deposited on either nickel or copper wire substrates by the inner flow region in the boundary layer of the flow as it moves along the exhaust channel as seen in Figure 3. Using this flow geometry, the deposition of 5-8 layers of FLG on copper substrates was accomplished in 20 seconds of exposure.



Figure 3: Schematic showing boundary layer development around a wire substrate within the microcombustor channel. The streamlines carry the carbon rich combustion products causing them to deposit on the wire substrate.

Next, a brief discussion of microcombustion systems, commonly referred to as microcombustors, is presented to describe the development of the platform which is applied to FLG synthesis.

Microcombustors, which are combustion systems with a critical channel dimension below 1 mm, are able to generate higher mass and heat transfer fluxes than their macroscale counterparts [17]. Prior to the work of Masel, Shannon, and Prakash in the early 2000s, it was thought that generating stable flames in microchannels was impossible due to the phenomena of thermal and chemical quenching, whereby the flame temperature drops significantly due to excessive heat loss to combustor walls [18] or due to loss of key chemical species from the gas-phase [19].



Figure 4: The Y-design microcombustor operating with a stable non-premixed flame at the stagnation point of the incoming fuel and oxidizer flows.

Microcombustors, such as the Y-design combustor shown in Figure 4, have typically been developed with a vision to drive applications similar to macroscale applications of combusting systems. Since wall temperatures may exceed 1000°C in some cases, their primary use to date has been to act as compact heat sources, as has been demonstrated previously by the Prakash group among others. This energy dense heat source has shown potential for many applications in micro-power generation [18, 20, 21], micro-jet thrusters [22, 23] and micro-engines [24]. An example of such a device is the work by Senesky *et al.* to develop a Wankel engine for microelectromechanical systems (MEMS) power shown in Figure 5.



Figure 5: A steel rotor used in a MEMS Wankel engine by Senesky *et al.* to drive a MEMS electrical generator [20].

We developed a potentially new area of applications for microcombustion by exploiting the portability of microcombustor systems, along with their high thermal energy densities [25], for on-demand chemical synthesis of carbon nanomaterials.

Microcombustor operation necessitates the development of high temperatures and sometimes harsh reactants. This prevents the use of many traditional metals, such as steel or aluminum, and excludes the use of high temperature transition metals due to the potential for reaction with oxygen during high temperature operation. Therefore, the construction of these microcombustion systems necessitates the use of ceramic materials to fabricate the microcombustor [17]. Ceramics are desirable for this application due to their chemical inertness, high strength, high temperature tolerance, and dimensional stability through a range of elevated temperatures (usually > 400° C). However, some mechanical properties of ceramics, such as high hardness and brittleness, may limit the geometries achievable with traditional machining and forming methods. These machining and material processing methods add significant stresses to the material which can lead to

cracking or brittle failures. In other cases traditional methods may be technically possible but economically prohibitive, such as in diamond milling or laser cutting of alumina ceramic [26, 27]. In this thesis, microcombustors were fabricated with two different methods: low toxicity gel-casting and computer numerical control (CNC) milling as described in Chapter 2. Of the two methods, the CNC milled devices were used for FLG synthesis due to the speed of the fabrication process which enabled faster iterations during experimentation.

Section 1.2: Organization and Scope of Thesis

This thesis is organized as follows: Chapter 1 (present chapter) begins with a discussion towards the importance of graphene and provides a brief introduction on graphene synthesis. Next, the development of a microcombustion platform is described and contrasted with existing methods to point out the innovations in the present work. In Chapter 2, the two methods for microcombustor fabrication are discussed with details on flame characterization in microchannels to match results to previous reports of microcombustion. The discussions include the characterization of two combustor channel geometries, nested spirals and a three channel Y-design. The effect of the Dean Number on flame propagation in the curved channels of the spiral combustor is presented along with wall temperature and visual flame characterizations. The Y-design combustor, which is ultimately utilized for few-layered graphene synthesis, is characterized with wall temperature measurements across all fuel/oxidizer operation conditions.

Chapter 3 discusses the application of the Y-design combustor for few-layered graphene synthesis on high purity nickel and copper wires. The effect of varied flow equivalency, constant equivalence through a range of flow rates, and the change in carbon structures down the length of the wire substrate are investigated.

Finally, in Chapter 4 conclusions on the use of the microcombustor platform for graphene synthesis are drawn with some suggestions for future work presented.

Chapter 2: Development of Microcombustor Platform

Section 2.1: Fabrication by Gel-Casting

Section 2.1.1: Introduction to Gel-Casting

Gel-casting allows complex ceramic bodies to be fabricated using a facile process [26, 28]. It has shown promise in alleviating ceramic processing issues by allowing the formation of ceramic parts with complex geometries while simultaneously allowing submillimeter critical dimensions [29]. Gel-casting is a process by which an underlying ceramic powder is mixed with a polymer binder and cast in a mold (See Figures 6 and 7 for pictorial descriptions). Upon release from the mold, the desired ceramic structure is achieved. To enhance the density of the ceramic, the molded structure is often fired in a furnace at elevated temperatures (greater than 1100°C) in a standard atmosphere. Previously, many of these gel-casting processes have also utilized toxic materials or binders [26, 29, 30].

Recently, Kellie and Prakash have reported a method to fabricate alumina microchannels with critical dimensions at 200 µm by using a low toxicity gel-casting of alumina ceramic structures for applications in microcombustion [31]. Previous reports by Morissette *et al.* [32, 33] on low-toxicity gel-casting systems with organotitanate coupling agents showed a possible pathway to integrate non-toxic binders in alumina gel-casting.

The microcombustors which are created through gel-casting and utilized in this work contain CR 1 (1.1 μ m) alumina particles. These are coupled with a non-toxic poly vinylalcohol (PVA) binder. A repeatable fabrication process was developed that allows sintered ceramic bodies with solids loading greater than 80% to be produced with minimal variations in final structure from the nominal design. Process parameters were optimized during the fabrication of the microcombustors to develop repeatable results with sub-millimeter critical dimensions while warping and feature defects were minimized.

Section 2.1.2: Methodology¹

CR1 alumina powder (1.1 μ m particle size, Baikalox Corporation) was used and evaluated in the fabrication of ceramic microcombustors. Samples were prepared both with, and without, the use of a dispersant and deflocculant, Darvan (821A, Vanderbilt Corporation, Norwalk, CT).

Figure 7 describes the alumina gel-casting process schematically. Parameters such as drying time, rate of ceramic powder addition, and sintering were changed systematically and their result on the sintered product was examined visually and quantified through mass reduction and size shrinkage.

The initial slurry mix consists of PVA and deionized water (10.7% w/v). In the samples with dispersant, four drops of Darvan were added. The mixture is stirred at 85°C and 700 rpm until the PVA was completely dissolved in the water.

¹ This section includes material reported by Kellie and Prakash in [31].

A total of 33.6% (w/w) alumina powder was added in increments, allowing 10 minutes of mixing between additions to allow the slurry to reach a well-mixed state and prevent aggregation of the alumina particles. This composition then mixed for 24 hours at 85°C with constant stirring at 700 rpm. Next, maleic acid (99%, Sigma-Aldrich, St. Louis, MO) was added to the slurry and stirred for an additional 5 minutes. The maleic acid acts as a heat-activated catalyst for cross-linking the PVA. Note, that while no cross-linker was used in the work reported here, harder polymeric binders can be achieved by adding cross-linking agents. The resulting mixture was poured into a PDMS (polydimethylsiloxane) mold which is generated from a brass master. The brass master mold has channels that are 1.6 mm wide by 0.5 mm deep and was generated by CNC milling operations.

The mixture in the mold, known as the gel-cast, is partially dried in a vacuum to remove air pockets from the slurry. Any air pockets in the ceramic slurry mix can cause the ceramic body to shatter during the sintering process as they expand.



Figure 6: A digital photograph showing alumina slurry as a gel-cast packed into a PDMS mold.

The mold is slowly air dried over approximately 7 days in an open atmosphere. Next, the resulting gel-casted green body is heated on a hotplate at 60°C for 24 hours to dispel any excess solvent or volatile organic matter as per previously reported procedures [17, 34, 35].

Finally, the ceramic green body is sintered in a furnace process at atmospheric pressure to burn out the organic material in the slurry. The result is a fully sintered alumina ceramic body.



Figure 7: Gel-cast process flow chart depicting the essential steps in the fabrication of ceramic microcombustors.

Three samples (MC 1, MC 2, MC 3, see table 1) were prepared. These contained the same amount of solids at 33.6% loading before sintering and all were sintered as per the temperature profile shown in Figure 8. The solids loading after firing was found to be 80%, which increases due to the loss of the polymer binders and moisture during the furnace process.



Figure 8: The plot shows the temperature-time profile used for sintering the alumina green bodies to achieve the final ceramic structure.

Of the three samples, MC 2 and MC 3 had the dispersant added to evaluate the effect of adding a deflocculant to the alumina slurry. The resulting dried ceramic green body is then removed from the PDMS mold and sintered in a furnace (CM Furnaces, Bloomfield, NJ) in air to 1600°C by using the temperature cycle shown in Figure 8 and developed iteratively depending on the final state (e.g., relative warping, cracking, etc.) of the alumina structure achieved. It was observed that by implementing controlled ramp rates and dwell times the thermal shock to the green body could be minimized.

Section 2.1.3: Microcombustor Development

In this section, data and results from three final microcombustors are presented as a representative discussion.

Table 1: Summary of the Experimental Conditions for Microcombustor Fabrication.

Experiment	Particle Size	Particle Feed Rate	Surfactant
MC 1	CR 1	1.15 g /10 min	No Darvan
MC 2	CR 1	2.3 g / 10 min	Darvan added
MC 3	CR 1	2.3 g / 10 min	Darvan added

Microcombustor 1 (MC1)

Figure 9 shows a both a top and side view of microcombustor 1 (MC1). Note the pitting that occurs in the flat, featureless regions of the ceramic body which are highlighted in the dotted circles in Figure 9.



Figure 9: Top (part A) and side (part B) views of MC 1 showing the pitting on the surface. This sample did not have any surfactant added to prevent alumina particle agglomeration.

Also note the wall cracking in multiple areas along the microcombustor walls. This may be due, in part, to the green body air drying too quickly, which can cause the gel-cast to contract and pull away from the PDMS mold.

In part B of Figure 9 warping in the sintered product can be observed. As sintering occurs, mass exits the alumina green body in the form of water and polymeric binders. Most of this loss is expected to occur through the top of the green body due to its large surface area as the materials burn out. This can cause contraction and warping of the ceramic body.

Microcombustor 2 (MC 2)



Figure 10: Top (part A) and side (part B) views of MC 2 detailing warping and cracking in the sintered combustor body.

Figure 10 shows the effect of halving the amount of slurry used to produce the microcombustor. The amount of warping in the sintered product is larger than that observed in the previous sample (MC 1, Figure 9). Rather than warping only slightly and still maintaining and overall flat profile as before, MC 2 warps to the extent that a curved profile is generated across the top surface, as can be seen clearly in part B of Figure 10. This warping occurred during the sintering of the green body in the furnace. However, note the improvement in surface pitting in comparison to MC 1. This is due to the use of Darvan deflocculant in this sample which helped prevent agglomeration of alumina particles in the slurry mixture.

Microcombustor 3 (MC 3)

In Figure 11 cracking was observed in some areas along the walls of the microcombustor as marked in the figure. These defects were formed, in part, due to a non-uniform drying rate of the green body and show the importance of a controlled drying rate. It is important to note that these cracks and defects in the green body did not propagate or worsen in the final sintered body and do not affect this device's ability to be integrated into an operable microcombustor. Furthermore, MC 3 did not warp during the furnace sintering process and adding the Darvan to the slurry again improved the dispersion of the alumina particles and likely reduced pitting in the sample.



Figure 11: Top view (part A) and side view (part B) of MC 3.



Figure 12: The details of the channel structure of the microcombustor are seen in the SEM images (parts A and B) for the regions marked in the optical image by dotted black lines.



Figure 13: The SEM image shows more details of curved combustor channel. The channel wall smoothness is verified visually. The interior details of the channel walls appear to be no different than the outside surfaces under SEM images.

Figure 12 shows detail of a sintered microcombustor with scanning electron microscope (SEM) images and a digital photograph denoting the specific regions imaged. At the top of the figure in part A the microcombustor wall is detailed. Note that the definition in the walls is clear even at small scales. Part B on the right side of the figure shows a zoomed detail of the mixing zone of the microcombustor. Figure 13 shows more detail of the curved combustor channel and visually verifies the smoothness of the channel wall.

Green Body	Sintered Body	Percent Change	
Dimensions (Top Surface Area)			
55.1 x 55.2 x 4.2 mm	45.3 x 45.2 x 2.0 mm	Loss 32.7% of S.A.	
Mass Change			
15.1 grams	11.3 grams	Loss of 25.3%	

Table 2: Effect of Sintering on the Top Surface Area and Mass of Gel-Cast Bodies

Before sintering, the green body was measured at 55.1 mm x 55.2 mm x 4.2 mm (L x W x T). After sintering the microcombustor was measured and found to be 45.3 mm x 45.2 mm x 2.0 mm (L x W x T). This corresponds to a top surface area loss of 32.7%. Additionally, the green body had a mass of 15.1 g while the sintered product weighed 11.3 g. This corresponds to a weight loss of 25.3% between the green body and sintered product, as shown in Table 2. Therefore, the alumina percentage in the sintered body is 80% by weight. Young *et al.* showed less than 4% binder content by weight [26] while Zhu *et al.* showed approximately 70% alumina content by weight [36], for comparison. Commercially available sintered alumina plates with no features can reach
95-98% alumina content by weight. Therefore, the gel-cast structure reported here can achieve significant alumina loading.

Section 2.1.4: Conclusions on Gel-Casting

Gel-casting of alumina ceramic bodies utilizing low-toxicity binders was examined by changing recipe parameters to examine the effect on green bodies and sintered products. Sintered bodies with solids loadings of greater than 80% were achieved. CR1 (1.1 μ m) alumina powders were utilized to achieve channels with depths on the order of 200 μ m.

Warping of ceramic bodies is a major factor to control in both the air-drying and sintering stages of gel-casting. It was observed that defects in air-dried green bodies such as cracking and pitting do not worsen in the sintered body. While gel-casting is a method that produces near-net shapes, even from green bodies with minor defects, it is more suited to complex parts with 3D features. In addition, for the work conducted here the gel-casting process was found to be too time intensive with each device taking nearly 10 days to prepare. Therefore, for faster iterations on device operations an alternate method for fabricating the microcombustors was explored.

Section 2.2: Fabrication by CNC Milling

In addition to fabrication through the gel-casting process, microcombustors were also produced through the machining of non-sintered alumina bisque (McMaster-Carr #8484K61) with a CNC milling setup. This process eliminated the problem of warping present in gel-casting by machining the spiral and Y-designs directly into the top plane of the bisque, as seen in Figure 14 below. This process produces devices that are 5 cm square with channels that are 1.12 mm x 0.8 mm (LxD) before sintering. Since the CNC mill's tool path is computer guided, the process is repeatable and the channels produced are of high quality and ready to be assembled as operational microcombustors. The machined bisque can be sintered with the same furnace process that was utilized previously for gel-cast devices.

While the simple channel geometry of these microcombustors is well matched by the capabilities of CNC milling the physical limitations of the available tooling diameters cause the resulting channels to be larger than those produced by gel-casting, which can be seen in the comparison section below.



Figure 14: Microcombustor produced by CNC milling geometry into top surface. This microcombustor was then sintered in a furnace process similar to gel-cast devices.

Section 2.3: Comparison of Two Fabrication Methods

Gel-casting and CNC milling fabrication methods each have a number of benefits and draw backs. It can be seen in Table 3 that the two methods each undergo similar amounts of mass and surface area reduction after the sintering process. However, the two key differences between the processes are the processing time required and the geometry to which each method is best applied. In the case of the former, CNC surface milling is superior as it is able to produce up to 9 microcombustors in a repeatable fashion in only 8 hours of processing time. Gel-casting, on the other hand requires up to two weeks of processing time per device and hourly input from the researcher to pack the slurry and monitor air drying progress. Gel-casting of alumina is superior to CNC surface milling when complex, 3D geometries are required. The CNC milling process can only create channel patterns in the surface of the alumina, whereas gel-casting can make any geometry of component from a suitable mold.

Gel-Casting	CNC Surface Milling		
25.3% mass change after sintering	26.5% mass change after sintering		
32.7% top surface area reduction after	12.8% top surface area reduction after		
sintering	sintering		
Two weeks to produce each device	9 devices produced in 8 hours		
Cracking, pitting, warping must be	Channel cracking controlled by tool speed.		
controlled by air drying	Pitting and warping are not concerns.		
Well suited to complex 3D part geometries	Well suited to producing surface patterns,		
from a mold	such as channels.		
Channel dimensions below 1 mm achievable	Only depths below 1mm achievable due to size		
for both width and depth	of available tooling		

Table 3: Comparison Between Gel-Casting and CNC Milling Fabrication Methods

Section 2.4: Assembly and Operation of Microcombustor Devices

Regardless of fabrication method, whether by gel-casting or CNC milling operations, the microcombustors were sealed with a quartz top (Fisher Scientific, #CGQ-0620-07), as well as alumina ceramic tubes (McMaster Carr, #8746K451) which serve as conduits for fuel and oxygen to the microcombustor which are delivered via mass flow controller. All materials were attached using a commercial high temperature adhesive, Ceramabond 671 (Aremco), shown schematically in Figure 15 below.

The quartz window allows visual characterization of the flame behavior and material deposition during combustor operation. Furthermore, external thermocouples were placed on the combustor walls to quantify external wall temperatures during operation.



Figure 15: Microcombustor (A) sealed with quartz glass (B) and with alumina legs attached to transport reactants (C).



Figure 16: Microcombustor running with center flame. Fuel/oxidizer inlets and exhaust outlet shown. Fuel used is methane (99%) and oxidizer is oxygen (99.6%). Combined flows range between 316 and 600 sccm.

The type-K thermocouples (Omega) are in contact with the quartz window along the exhaust channel and are spaced equally along the 2.5 cm length, as seen in Figure 17. The fourth thermocouple is in contact with the bottom of the microcombustor, directly under the center of the microcombustor to read wall temperatures. Convective effects on the thermocouples are minimized through the use of an insulated covering around the wires.



Figure 17: Thermocouple locations on the MC. Thermocouples locations are denoted by red circles and are adhered to the surface of the quartz glass. The fourth thermocouple is located underneath the combustor.

Section 2.5: Visual, Thermal, and Flow Characterization of Spiral Microcombustors

The spiral microcombustor was designed to have the mixed fuel and oxygen ignited at the exhaust port. The flow rates would then be adjusted such that the edge flame would burn up the channel and around the spiral channel into the central mixing area where it would stabilize. As can be seen in Figure 18, adjusting the equivalency to be fuel rich will drive the flame up the straight exhaust channel toward the center of the spiral. However, the third frame of the image shows where the flame progression stalls, at a fuel-to-oxygen equivalency of ~0.93. Continuing to adjust the fuel/oxidizer equivalence ratio upward causes the flame to become unstable and extinguish at a value of 1.82.



Figure 18: Changing flame position in spiral microcombustor as a function of flow rate. Fuel-to-oxygen flow equivalencies from left to right: 0.93, 1.18, 1.79

Previous work by Richecoeur *et al.* has shown that mesoscale combustor flame reactions can become unstable in 4 mm diameter curved channels with Reynolds numbers below 120. This is because the edge flame, which is a reaction that occurs where the laminar fuel and air streamlines meet, can be disrupted by centrifugal velocities or eddies induced by the curved channels [37]. The tendency for disruption may be able to be correlated to a Dean number. The Dean number is a dimensionless number which is the product of the Reynolds number and the square root of the curvature ratio of the channel the fluid is reacting in. Explicitly, the Dean number is given by:

$$De = \frac{\rho VD}{\mu} \left(\frac{D}{2R}\right)^{1/2} \tag{0.0}$$

Where ρ is the density of the fluid, μ is the dynamic viscosity, *V* is the axial velocity, *D* is the hydraulic diameter of the channel, and *R* is the radius of curvature of the channel's path.

Due to the spiral shape of the microcombustor's channels, the radius of curvature of the channel is a function of the position within the channel. That is, the radius of curvature will decrease along the length of the combustor channel from the exhaust toward the mixing zone at the center. This can be seen in Figure 19 below.



Figure 19: Scale plot of the spiral exhaust channel beginning at 0 radians in the center mixing zone and extending to the end of the spiral at 20.24 radians. Used in the determination of the Dean Number as a function of the radius of curvature of the spiral channel.

When examining the fuel-to-air flow equivalency of 1.79, which brings the flame to the start of the spiral as seen in part C of Figure 18 above, it is found that the Dean Number is 14.6, versus the Reynolds number of 80. Therefore, the large radius of curvature has an impact on the flow characteristics, inducing a change of momentum in the fluid and disrupting the fuel/oxygen boundary along which the edge flame reacts. These disruptions still occur even for strictly laminar flow, as seen previously [37], suggesting that small eddies or centrifugal effects induced by the spiral's increasing radius of curvature are able to disrupt the streamline boundary where the flow occurs.



Figure 20: Dean Number as a function of the angle theta of the spiral microcombustor. Angle theta of 0 radians is in the central mixing zone, and angle of 20.4 radians is where the spiral joins the straight exhaust channel and the location at which the Dean Number is 14.6.



Figure 21: Dean Number versus radius of curvature along the spiral channel starting at radius of curvature of 0 at the spiral center.

The edge flames that burn within the spiral microcombustor are an oscillatory reaction; a phenomenon which has been previously observed in other mesoscale and microscale combustors [19, 37]. It has been observed that for the spiral microcombustor an edge flame will form within the reactor at a fuel-to-oxygen equivalence ratio of 0.6. Other equivalencies predominantly produce candle-like flames at the combustor exit with extended operation needed (on the order of several hours) to provide enough heat for sustaining flames in the microchannels. This phenomenon was documented across the entire operable range of the microcombustor, and is similar to observations reported previously for straight microchannels by Miesse [38, 39] and Prakash [19]. However, if the microcombustor is adjusted to an equivalence ratio of 0.6 then an edge flame will be maintained without an exhaust candle-like flame. Table 4 shows that increasing the flow rate, while flow equivalency remains fixed at 0.6, causes the wall temperature on the quartz window above the reaction zone to increase. In each case presented, the edge flame begins after approximately 30 seconds of operation time after the combustor has passed the threshold of 100°C.

Flow Rate	Temp
(sccm)	(°C)
100-175	193.4
150-262	268.9
200-350	311.1
250-437	315.9
300-525	350.7
350-612	372.9

 Table 4: Maximum Wall Temperatures Above the Reaction Zone Versus Flow Rate at Constant Equivalency

The oscillating nature of the edge flame reaction within the spiral microcombustor produces an audible buzz, similar to previous reports by Prakash *et al.* [19], suggesting that these combustors also exhibit ignition-extinction phenomena. These sound emissions were recorded and their frequency analyzed versus time and temperature. Figure 22 shows the measured frequency versus time for a fuel flow rate of 275 sccm and a fuel-to-air equivalence ratio (ϕ) of 0.6, which yields a stable edge flame.



Figure 22: Frequency of the oscillating edge flame versus time of operation. Frequency becomes steady at 518 hertz.

It can be seen that the frequency of the edge flame oscillation rises as the microcombustor operates. However, the frequency emitted by the microcombustor begins

to stabilize after approximately 200 seconds of operation and reaches a maximum frequency of 518 hertz at 600 seconds of run time. In Figure 23 it can be seen that the temperature and frequency follow a roughly linear trend, suggesting that the frequency of the microcombustor's sonic emissions are correlated to the temperature of the reacting flow.



Figure 23: Frequency of microcombustor oscillating reactions versus operating temperature at flow rate of 275 sccm, ϕ =0.6.

The Strouhal Number is a dimensionless number which describes oscillating flows. The equation for the Strouhal Number can be seen below:

$$St = \frac{fL}{V} \tag{1.2}$$

In this case the Strouhal number depends only on the frequency of the flow since for the flow rate presented, the characteristic length (L) and velocity of flow (V) are constant. The results can be seen in Table 5 below.

Time	Frequency	Temperature	St #
(sec)	(Hz)	(C)	(-)
0	0	33	0
15	311	51	0.056
30	342	79	0.062
45	363	105	0.066
60	379	126	0.069
90	414	144	0.075
95	421	153	0.076
100	427	158	0.077
105	433	159	0.079
130	444	155	0.081
180	479	162	0.087
210	475	166	0.086
270	485	176	0.088
390	499	181	0.090
480	509	209	0.092
570	517	214	0.094

Table 5: Flow Parameters for Spiral Combustor at Flow Rate of 275 sccm, ϕ =0.6

The data reported here agrees with the previous work by Richocheur, Prakash, and Miesse *et al.* for flame structure and dynamics. Therefore, microcombustors produced from either CNC milling or gel-casting match the data previously reported for microcombustors made in sintered alumina and prepared by diamond saw or laser etching.

Section 2.6: Characterization of Y-Design Microcombustors

Wall temperature measurements were also conducted for the Y-design combustors and trends were verified to match previous reports. These data are reported in Appendix A: Y-Design Temperature Plots.



Figure 24: Y-design combustor in operation with a methane/oxygen flame located at the center area where the fuel and oxygen channels converge and mix.

The Y-design microcombustor does not exhibit the same oscillating flow reaction as the spiral combustor. Rather the reaction is a steady flame located at the stagnation point where the methane and oxygen converge and mix, as seen in Figure 24. Because of the simplified flow geometry and flame reaction in this case, the Y-design combustors were utilized exclusively for carbon deposition experiments on both Ni and Cu wires.

Chapter 3: Boundary Layer Deposition of Carbon Materials on Copper and Nickel Wire Substrates

Section 3.1: Introduction to Raman Spectroscopy of Graphene Films

Raman spectroscopy is widely employed for characterization of graphene films and has been used as the primary method of characterization for many previous works. This is because the Raman response for graphite and graphene films has been heavily analyzed and is well understood [9, 40-44]. The method allows the type of carbon synthesized to be determined as well as an estimate to be made about the quality and quantity of the graphene layers present [41]. In this work, Raman spectroscopy is the principle method by which the FLG films are characterized, with visual confirmation made using a scanning electron microscope (SEM). As such, a brief introduction to Raman spectroscopy is presented to understand the basic principle of the instrument's operation.

Raman spectroscopy is a measurement of the wavelength and the intensity of light that has been inelastically scattered from molecules. The light source utilized in this work is a 514 nm argon laser with a grating of 1800 lines/mm, which is the optimum grating to use for the chosen laser wavelength. The vast majority of the light emitted from the laser source (more than 99.99%) undergoes Rayleigh scattering making it useless for characterization purposes [45]. This leaves only a small amount of the laser light to be inelastically scattered and detected by the instrument. The inelastic scattering that occurs can either exhibit a Stokes or an Anti-Stokes frequency, which refer to whether the light's frequency is reduced by the Raman active mode of the sample being characterized or increased by it, respectively [45]. Different molecules have different Raman active modes, giving many materials a distinct "Raman fingerprint" which allows them to be detected and characterized.

The inelastically scattered light is then collected and separated from the Rayleigh scattered light by using notch filters to prevent the latter from overwhelming the small amount of useful signal present. Finally, the shift in frequency is measured and recorded using a detector and appropriate software package.



Figure 25: Raman response of mono-layer graphene from Ferrari *et al.* [41] showing no D peak (~1350 cm⁻¹) and a G peak (~1580 cm⁻¹) intensity approximately one-third that of the 2D peak (~2700 cm⁻¹).

In the area of graphene research, three principle carbon peaks occur: the D peak (~1350 cm⁻¹), the G peak (~1580 cm⁻¹), and the 2D peak (~2700 cm⁻¹). The ratio of the intensities of these peaks have previously been utilized to characterize both the quality of the synthesized films (the ratio of the D peak to G peak intensities) well as estimate the number of layers present (the ratio of the G peak to 2D peak intensities) [16, 41]. For high quality mono- and bi-layer graphene, no D peak is present which suggests very high order and, furthermore, the G to 2D peak intensity ratio (I_G/I_{2D}) is approximately 0.3, as seen in Figure 25 above. As the number of layers present increases, the I_G/I_{2D} ratio increases to greater than 1.0.

Additionally, as disorder within the synthesized layers increases, the D peak becomes pronounced and the I_D/I_G ratio increases. Graphene layers synthesized by CVD have shown I_G/I_{2D} ratios of 0.35 [16], though ratios both higher (more disorder) and lower (less disorder) are reported here.

Section 3.2: Experimental Setup

The carbon source for graphene production is generated by the Y-design microcombustor. As a conceptual framework, the generation of gas-phase species can be considered similar to an atmospheric pressure CVD reactor at elevated temperatures, with the flame zone acting as both the chemical species generator and the heat source. The inlet volumetric fuel and oxidizer ratios were varied between 1.0 and 2.9 by controlling the inlet volumetric flow rate in the 200 – 300 sccm range for fuel (CH₄)and 80 –

400 sccm range for oxidizer (O₂). This range of volumetric flow rates translates to an incoming velocity of 3.7 m/s to 9.9 m/s for CH₄ and 1.5 m/s to 7.4 m/s for O₂.

Graphene was deposited on 0.5 mm diameter 99.98% high-purity nickel and copper wires (Alfa Aesar, MA) by inserting wires into the exhaust port of the microcombustor up to the reaction zone. The sample wires were manually cut to 2.75 cm length and then cleaned by rinsing in acetone followed by DI water, IPA, and DI water again. The cleaning process was repeated thrice and the wires were dried using filtered dry air.

The cleaned wires were inserted into the exhaust port of the microcombustor up to the edge of the reaction zone as estimated by visual inspection. Wire placement was then verified visually through the quartz glass top plate. Samples were exposed for varying times, between 5 and 20 seconds, as seen in Figure 26. For fuel-rich conditions, baseline experiments showed that 5 seconds of exposure was sufficient for carbon material deposition. Other researchers have used much longer times, on the order of several minutes [7]; however, the influence of deposition time on graphene film quality is an open question, and is not the subject of this work. After the exposure time, the wires are removed from the combustor.



Figure 26: Schematic showing insertion of sample wires into exhaust (outlet) port of microcombustor (A, B). (C) shows wire inserted 2.5 cm to edge of reaction zone in operating combustor.

Section 3.2: Results and Discussion for Deposition on Nickel Wire Substrates

A broad range of inlet fuel/oxidizer ratios were tested as listed in the experimental methods section. However, only some conditions yielded carbon deposition on the wire. The flow conditions that successfully deposited carbon on the nickel wires are presented in Table 6 below, along with their corresponding maximum wall temperatures which were measured on the quartz window at the reaction zone.

Fuel (sccm)	Oxidizer (sccm)	Equiv. (-)	External Wall Temp (°C)	Re # (-)
236	100	2.4	256.9	39
236	150	1.6	288.7	46
236	167	1.4	261.3	48

Table 6: Maximum Wall Temperatures and Reynolds Numbers for Carbon-Producing Flow Rates on Nickel Wires

As oxygen content in the inlet gas mixture was increased, the nickel wires were found to oxidize and inhibit the deposition of carbon with the 20 second exposure time. The Ni oxidation was evident as nickel oxide peaks were seen at 500 cm⁻¹ and 1500 cm⁻¹ in the Raman spectra. Specifically, as the inlet volumetric fuel-to-air equivalence ratio at the inlet drops below 1.4, the oxide peaks at 500 cm⁻¹ and 1500 cm⁻¹ become dominant in the Raman spectra [46]. Additionally, carbon deposition at an inlet flow equivalence ratio greater than 2.4 yielded no carbon deposition and suggests a cut-off point for carbon producing equivalence ratios on the Ni wire substrates. Longer deposition conditions (>30 s and reaching 5 min) were also tested but yielded deposition of soot as verified by the Raman spectra. An example of soot reported spectra reported previously is shown in Figure 27 and the one for a sample deposition condition at 336 sccm flow and an equivalence of 2.4 for our tests is shown in Figure 28.



Figure 27: Raman spectra for carbon soot showing D peak (~1350 cm⁻¹), G peak (~1580 cm⁻¹), and shouldered 2D peaks at ~2700 cm⁻¹ and 2900 cm⁻¹ from [47].



Figure 28: Raman spectra for carbon soot showing D peak (~1350 cm⁻¹), G peak (~1580 cm⁻¹), and shouldered 2D peaks at ~2700 cm⁻¹ and 2900 cm⁻¹ which matches the result for soot from literature. The peak at ~3200 cm-1 is likely due to water vapor in the air during characterization.

By holding the fuel flow constant and adjusting the oxygen flow, the effect on carbon production at the tip of the nickel wire sample can be observed. In Figure 29 it is seen that as the oxygen flow rate was decreased from 167 sccm to 100 sccm, the 2D carbon peak intensity reduces and the peak becomes wider with the full width half maximum (FWHM) increasing from 100 cm⁻¹ to over 150 cm⁻¹. This trend is summarized in Table 7 where the I_G/I_{2D} ratio, which provides an estimate of the number of layers present [11], goes from 5.6 at an equivalency of 1.4 down to a value of 4.6 at an equivalency of 2.4. Since the I_G/I_{2D} ratio is > 2.4, it is known from previous work [16, 41] that the carbon material is bulk graphite, corresponding to greater than 10 layers of graphene. It is notable that between the two flow rates, the I_G/I_{2D} ratio increases to 7.6, suggesting more layers of graphite deposited at an equivalency of 1.6. Therefore, for

deposition on nickel, the results for all carbon producing flow rates that were tested, bulk graphite was deposited on the Ni wires.

The ratio of the D peak intensity to that of the G peak (I_D/I_G) represents the disorder in the graphite layers [16] and shows that the disorder in the graphite layers are higher than the previously reported flame synthesis result of 0.35 from Memon *et al.* and Li *et al.* The disorder in the layers was visualized in Figure 30, an SEM of the graphite layers on the nickel wire.



Figure 29: Raman results for boundary layer deposition on nickel wires as function of flow parameters 236-100 sccm (F/A = 2.36), 236-150 sccm (F/A = 1.57), and 236-167 (F/A = 1.41). D (\sim 1350 cm⁻¹), G (\sim 1580 cm⁻¹), and 2D (\sim 2700 cm⁻¹) peaks are labeled.

Table 7: Peak Intensity Ratios, Temperature, and Reynolds Number for Carbon Samples on Nickel Wires

Fuel	Oxidizer	Temp	I_D/I_G	I_G/I_{2D}	Re
(sccm)	(sccm)	$(^{\circ}C)$	(-)	(-)	(-)
236	100	256.9	0.8	5.6	39
236	150	288.7	1.1	7.6	46
236	167	261.3	0.8	4.6	48



Figure 30: SEM showing disordered graphite layers on nickel wires deposited at a flow rate of 236 sccm fuel and 150 sccm oxidizer (an inlet equivalence ratio of 1.6).

Section 3.3: Results and Discussion for Deposition on Copper Wire Substrates Section 3.3.1: Constant Flow Equivalency of 2.36 across Multiple Flow Rates

For deposition on copper wires, multiple flow rates at a constant inlet equivalence ratio of 2.4 were initially tried. In essence, this changes the temperature and velocity of the reacting flow while keeping the volumetric ratios of methane fuel, oxygen the same in the inlet to the combustor. In Figure 31 it can be seen that initially a D peak is present, again showing disorder within the layers present. However, as the flow rate is increased from 336 sccm to 672 sccm, the D peak becomes suppressed and is not present by 704 sccm, meaning that the disorder within the layers has improved. In fact, in this work, we report near-perfect order to the graphitic layers as evidenced by an undetectable D peak at

1350 cm⁻¹ The mechanism behind the suppression of the D peak with increasing total flow rate is still under investigation. In contrast to the previous reports for flame synthesis results on copper substrates [16], which report an I_D/I_G ratio of 0.35, the highest flow rate of 531 sccm fuel and 225 sccm oxidizer yielded an I_D/I_G ratio of 0 and is shown in Figure 32, below. This shows an improvement in the disorder present.



Figure 31: Constant flow equivalency of 2.36. Effect of varying flow rate between 236-100, 354-150, and 472-200. D (\sim 1350 cm⁻¹), G (\sim 1580 cm⁻¹), and 2D (\sim 2700 cm⁻¹) peaks are labeled.



Figure 32: Lorentzian curve fit for 531-255 (F/A = 2.36) shown separately for detail. D peak (~1350 cm⁻¹) is not present, suggesting well ordered FLG. The ratio of I_G/I_{2D} shows that approximately 5-8 layers of FLG are present.

Table 8 details the ratios between the D and G peak intensities (I_D/I_G) as well as the ratios between the G and 2D peak intensities (I_G/I_{2D}). It can be seen that above the initial flow rate, the D peak is no longer present, showing that the disorder within the graphene layers is very low. This improves upon the results previously reported for flame synthesis on copper, which showed an I_D/I_G ratio of nearly 0.4. The I_G/I_{2D} shows that by increasing the flows, and with it the temperature of the reaction, the number of layers of graphene is reduced. This takes the result from highly ordered bulk graphite at 236-100 sccm and 354-150 sccm to approximately 5-8 layers of well-ordered graphene at 531-225 sccm. These results are comparable with those presented previously for flame synthesis on copper by Memon *et al.* however the full width half maximum of the 2D peak is approximately 150 cm⁻¹, which is higher than that reported previously[16, 41, 42].

Fuel	Oxidizer	I_D/I_G	I_G/I_{2D}	Re
(sccm)	(sccm)	(-)	(-)	(-)
236	100	0.5	7.1	39
354	150	N/A	4.6	59
472	200	N/A	3.2	79
531	225	N/A	2.2	89

Table 8: Peak Intensity Ratios, Wall Temperature, and Reynolds Number for Fixed Equivalency of 2.4 on Copper

Section 3.3.2: Constant Fuel Flow of 531 sccm with Varied Oxidizer

These results suggested that flow rates around 531-225 sccm should be examined. Figure 33 shows that even small changes in the oxidizer content of the reaction cause significant changes in the carbon structures deposited. By adjusting the oxidizer flow up to 230 sccm (F/A = 2.31) the 2D peak is suppressed, suggesting that highly ordered pyrolyzed graphite layers are the result. This result is confirmed by SEM analysis in Figure 34, however it is also seen that carbon nanotubes or fibers are protruding from the surface. These structures were observed across the wire at only this flow equivalency and detail can be seen in Figure 35 below. Analysis of these structures is on-going at beyond the FLG synthesis focus of this work.

Adjusting the oxidizer flow down to 220 sccm (making the flow equivalence more fuel rich) creates disorder in the layers deposited and gives the I_D/I_G ratio of 0.43, which is high compared to previous results on copper.

By adjusting the oxidizer flow down again to 215 sccm increases the disorder in the layers deposited and gives the I_D/I_G ratio of 0.5, which is also high compared to our

previous carbon results on copper. However, the trend of a shrinking D peak with increasing oxidizer is present, while the presence of the 2D is only strongly evident at an equivalence of 2.36 (F=531 sccm, Ox=225 sccm). Table 9 shows the peak intensity ratios for each of the flow rates for comparison.



Figure 33: Effect of carbon signal for F=531 sccm and varying oxidizer to 215 sccm (F/A = 2.46), 200 sccm (F/A = 2.31), 225 sccm (F/A = 2.36), and 230 sccm (F/A = 2.31). D (\sim 1350 cm⁻¹), G (\sim 1580 cm⁻¹), and 2D (\sim 2700 cm⁻¹) peaks are labeled.

Table 9: Peak Intensity Ratios, Wall Temperature, and Reynolds Number Fixed Fuel Flow of 531 sccm on Copper

Fuel	Oxidizer	I_D/I_G	I_G/I_{2D}	Re
(sccm)	(sccm)	(-)	(-)	(-)
531	215	0.5	14.2	87
531	220	0.43	N/A	88
531	225	N/A	2.2	89
531	230	N/A	N/A	90



Figure 34: SEM image for flow rate 531-230 sccm (F/A = 2.31) showing bulk graphite layers with carbon nanotubes or nanofibers extruding from the surface.



Figure 35: SEM image showing detail of either carbon nanotubes or nanofibers protruding from layers of disordered pyrolyzed graphite.

Section 3.3.3: Carbon Structure Evolution down Length of Copper Wire

Carbon deposition also changes as it is deposited down the length of the wire, which is shown for a fuel-to-air flow inlet equivalence ratio of 2.4 and combined flow rate of 756 sccm. In Figure 36, it is seen that the carbon forms are predominately highly ordered pyrolytic graphite down the wire, with the exception of around 40 microns from the tip where FLG is present. Additionally, the carbon signal stops beyond 200 microns on the wire. This shows that the type of carbon deposited varies with respect to the distance down the wire's length for a constant flow rate on a single wire substrate.

The type of carbon synthesized and the distance down the wire it is deposited are related to the boundary layer created as the reacting flow interacts with the wire in the channel. The boundary layer thickness steadily increases down the wire, eventually becoming large enough within the microchannel to be considered fully developed. Note, estimates of boundary layer thickness in a microchannel with reacting flows is a research problem in itself likely requiring extensive numerical modeling. In this thesis, a flat plate solution is implemented by assuming the reaction is at 600 °C with gas properties for methane and oxygen used at that temperature. The mixed gas properties, such as density and viscosity, are determined for the particular flow equivalence being examined. Therefore, we have a first-order approximation to the boundary layer thickness which can be seen in Table 10. However, the main point is that the flow regime is viscous flow with deposition being governed by the reaction-diffusion-convection model within this viscous flow regime.



Figure 36: Carbon signal evolution down length of wire at F=531, Ox=225, mass equivalency of 2.4. Shows no disorder present (no D peak) along length from tip to 200 microns distance where carbon signal ends. 2D peak is present only around 40 μm.

Distance Down Wire	Boundary Layer Thickness
(µm)	(μm)
0	0
40	21.2
80	42.4
100	52.9
200	105.9

Table 10: Boundary Layer down Length of Copper Wire at Flow of 756 sccm and $\phi = 2.4$ with Re = 89

Another example, at a flow rate of 805 sccm and an equivalence of 1.4, is shown to demonstrate the change in the three principle carbon peaks (D, G, and 2D) down the length of the wire. As can be seen in Figure 37 below, the carbon structures are disordered graphite at the tip of the wire (a distance of 0 microns) and two significant trends can be observed. First, the I_D/I_G ratio decreases down the length of the wire, as can be seen along with the first-order boundary layer solution in Table 11 below.

The improving disorder of carbon structures down the wire may be related to the increasingly dominant boundary layer, as explained previously. Furthermore, it should be noted that as the flow moves from the flame to the exhaust it undergoes convective cooling. This cooling is supported by the temperature data recorded on the external wall, which shows that near the exhaust the wall temperature is on the order of 100 °C.

The second trend to note is that 2D peak becomes suppressed down the length of the wire,. This shows that the boundary layer flow remains rich with carbon radicals up to 5 mm down the length of the wire and is still able to deposit them onto the surface.



Figure 37: Carbon signal evolution down length of wire at F=354, Ox=251, mass equivalency of 1.18. Shows improving disorder (reduced D peak) down length from tip to 5000 microns distance while 2D peak becomes suppressed.

Distance Down Wire	I _D /I _G	I_G/I_{2D}	Boundary Layer Thickness
(µm)	(-)	(-)	(µm)
0	0.72	8.93	0
100	0.62	7.67	58.7
500	0.57	N/A	293.3
1000	0.48	11.01	586.6
5000	0.37	N/A	2933.3

Table 11: Peak Intensity Ratios and Boundary Layer Thickness down Length of Copper Wire with Re = 72

Chapter 4: Conclusions and Future Work

Section 4.1: Conclusions on Microcombustor Platform Development and Application to Carbon Nanomaterial Synthesis

It has been shown that carbon structures, including few-layered graphene, can be flame synthesized on both copper wire substrates using boundary layer deposition, in contrast to the impinging jet used previously. This result was accomplished using an alumina microcombustor whose development and characterization were investigated for two channel geometries and across multiple flow rates. In addition, formation of carbon fibers and/or nanotubes was also observed. Nickel wires showed deposition of bulk graphite for all conditions tested.

On nickel, the carbon synthesis result was always greater than 10 layers of disordered graphene, which is considered bulk graphite. On copper wire substrates, it was shown that 5 - 8 layers of graphene could be synthesized at a flow rate of 531-225 sccm. This estimate comes from a ratio of I_G/I_{2D} of 2.2 which matches with literature. Furthermore, the disorder in these graphene layers was improved upon over previously reported flame synthesis work and for some cases the presence of the D peak was removed altogether. In conclusion, this alumina microcombustor platform is well-suited to carbon structure synthesis and is able to produce a variety of carbon structures, including highly ordered few-layer graphene, by adjusting only the inlet equivalence ratio or the total flow rate of the incoming gases.

Section 4.2: Suggested Future Work on Boundary Layer Deposition

Future work should continue to optimize the microcombustor platform to attempt to synthesize mono- and bi-layer graphene films and successfully transfer synthesized films to new substrates for characterization and basic device fabrication. For the former, work should center about increasing the temperature of the microcombustor during operation and continuing the investigation around flow equivalencies of 2.4. In regards to the latter it is suggested to use a polymer as an interstitial transfer material such as PDMS, as previously reported in other synthesis work, to remove films from the wires to deposit them onto new substrates for analysis.

Appendix A: Y-Design Temperature Plots

The Y-design microcombustor was characterized with temperature measurements only as it does not burn in the same oscillatory manner the spiral combustor does. Rather, it is a steady edge flame located in the center of the combustor at the convergence of the fuel and oxygen channels. Therefore, the Y-design combustor was characterized with thermocouples placed along the length of the exhaust channel and spaced evenly. This information is matched with the graphene data so that the temperature of the system during carbon deposition is understood.



Figure 38: Maximum wall temperature as recorded on the quartz window directly above the reaction area. It is observed that the maximum temperature is achieved at a mass equivalency of approximately 1.75

Figure 38 shows a maximum operation temperature of 295.47°C for the Y-design combustor at a mass flow equivalency of 1.75. The combustor was run with an insulated foam body around it to minimize convective heat transfer effects. The combustors were also run for 45 minutes and the maximum temperatures presented are measured on top of the quartz window at the center of the combustor directly above the reaction flame.

Theoretical flow data was also calculated for the Y-design combustor to understand the flow regimes within it. As can be seen in Table 12, the Reynolds Numbers vary between 35.58 and 68.80 over the operational range of the Y-design combustor. This makes the flow within the combustor laminar, as is expected for a microchannel device.

Methane	Oxygen	F/A Equiv	Re #
(sccm)	(sccm)	(-)	(-)
200	100	2.0	35
210	167	1.3	45
215	167	1.3	46
225	100	2.3	38
225	167	1.3	47
236	100	2.4	39
236	167	1.4	48
236	236	1.0	57
282	200	1.4	57
300	185	1.6	57
300	200	1.5	59
300	300	1.0	72
300	325	0.9	76
300	350	0.9	79
300	375	0.8	82
300	400	0.8	85
350	200	1.8	65
350	225	1.6	68

Table 12: Reynolds number of flow in the Y-design combustor as a function of flow rate
Appendix B: MatLab Script for Frequency Analysis of Spiral Microcombustor

```
MatLab Function "positiveFFT.m"
```

```
function [X,freq]=positiveFFT(x,Fs)
N=length(x); %get the number of points
k=0:N-1; %create a vector from 0 to N-1
T=N/Fs; %get the frequency interval
freq=k/T; %create the frequency range
X=fft(x)/N; % normalize the data
%only want the first half of the FFT, since it is redundant
cutOff = ceil(N/2);
%take only the first half of the spectrum
X = X(1:cutOff);
freq = freq(1:cutOff);
end
```

MatLab Script "wav gather.m"

```
% WAV GATHER.M gathers does spectral analysis on data from a pre-made
.wav
% file. The file must be located in the root folder with this script.
Also
% the function positiveFFT.m must be located in the root folder as
well, as
% it is called. That function chops the freq data and only returns the
% positive results to avoid symmetry.
% It will display the dominant frequency afterward.
% YOU MUST SPECIFY THE NAME OF THE .WAV FILE IN LINE 15
close all
clear;
clc;
%% DATA IMPORTATION
[yarray, Fs] = wavread('Spiral-100-175-Edge.wav');
Ts = 1/Fs; %sample time interval
t = 0:Ts:1-Ts; %sampling period
n = length(t); %number of samples
y = yarray(:,1)'; %makes a (1,n) array
```

```
% %plot the imported sound wave vs. time
% figure(1) %Creates a new figure
% plot time=0:Ts:Ts*(length(y)-1);
% plot(plot time,y);
% xlabel('Time [s]')
% ylabel('Amp')
% title('Imported Sound Data')
% grid
%% DATA CROPPING
% This works for my homemade .wav file but not for the 440hz test tone
Т
% downloaded. How odd. Leaving it in for now.
disp('What time [s] should the analysis start at?');
start time=input('Start analysis at: ');
disp('What time [s] should the analysis end at?');
end time=input('End analysis at: ');
N1 = round(start time*Fs);
N2 = round(end time*Fs);
yold=y;
% %The old way!! This causes it to re-read the data...slow and lame
% [yarray, Fs] = wavread('mid a.wav', [N1 N2]);
% y = yarray(:,1)'; %makes a (1,n) array
8 8---
% The new way! This redefines y vector for just the chunk we want
y=zeros(1,length(N2-N1));
for i=0:(N2-N1);
    y(i+1) = yold(N1+i);
end
% %replot the cropped sound data for confirmation
% figure(2)
% plot(y);
% title('Cropped Data For Analysis');
%% SPECTRAL ANALYSIS
%Call the custom function, finds/fits FFT
[YfreqDomain, frequencyRange] = positiveFFT(y,Fs);
% %Plot Frequency Data
% figure(3) %New figure
% stem(frequencyRange,abs(YfreqDomain)); %abs value of data for
magnitude
% xlabel('Freq (Hz)')
% ylabel('Power')
% title('Frequency Plot of Cropped Data')
% axis([200 600 0 max(y)]);
% grid
```

```
%Determination of dominant frequency
[ma, pa] = max(abs(YfreqDomain));
dom_freq=frequencyRange(1,pa);
disp('The dominant frequency was found to be at');
disp(dom freq);
```

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