**PROJECT SUMMARY**

**OVERVIEW**

Our group aims to develop fundamental research on controll on the morphology of graphitic carbon, and therefore, its properties by the introduction of strain in the form of doping within and between layers of carbon in a graphitic material. It is well known that carbon not only has interesting properties itself but also that these properties depend on its morphology and carbon bonding, i.e. sp2, sp3, or a mixture thereof. These properties enable carbon-based materials to be used in a diverse range of applications, such as energy storage[1]–[7], drug delivery[8], [9], and water purification[10], among others. On the other hand, doping of these nanostructures has shown to improve the properties of their undoped counterpart[11]–[16]. However, the production of these materials faces some challenges that limit their use in commercial applications: large scale production, low costs, and low toxicological risks. In this direction, our group has been able to produce a new hollow tubular morphology of carbon which are not carbon nanotubes (CNT). Its production is based on an atmospheric pressure chemical vapor deposition (APCVD) process developed by Cheng et al. [17]–[23] to produce a pseudo-carbon known as GUITAR (Graphite from the University of Idaho Tar). The advantages of this process are that it allows the production of reasonable quantities of GUITAR or GUITAR based materials in a short amount of time and does not use a metal catalyst. Therefore, preparation time, costs, and toxicological risks are vastly reduced. Additionally, these new structures are interesting in applications such as hydrogen storage, due to the presence of B and its hollow structures.

Different ratios of the boron precursor to the carbon precursor in the APCVD process will produce different types of hollow carbon structures, such as carbon eggs. Since boron bonds form sp3 bonds to carbon, as opposed to sp2 bonds, we hypothesize that we can manipulate the boron concentration to introduce strain and that this strain will drive the growth towards a morphology that minimizes the internal strain. The GUITAR process is extremely versatile and allows tuning the carbon morphology. The project will employ boron and nitrogen dopants as tools to introduce strain, thereby driving the growth towards a specific morphology, i.e. hollow carbon filaments, carbon eggs, or a previously unobserved morphology. In the spirit of manipulating carbon morphologies, the project will also explore the ability of the boron precursor to imprint its conformation on the carbon morphology. Specifically, if we utilize a boron precursor that is used to produce n or p-type semiconductors, will it change the properties of the produced material? What happens to the morphology if we simultaneously dope with boron and nitrogen, where the boron precursor promotes sp3 bonding and nitrogen introduces pentagonal lattice elements into the graphene sheets of the graphite? Assuming they do compete, can we modulate their respective concentrations to create specific carbon morphologies and reproduce our results? Ultimately, this project strives to understand the effects of doping on carbon formation and to manipulate strain to produce carbon materials with properties that lend themselves to technological applications, such as Li batteries, where the morphology of the carbon electrode plays a critical role in battery performance.

**INTELLECTUAL MERIT:** The project proposes to exploit a new way for sculpting the morphology of carbon by controlling the dopant content and therefore the internalized strain within the lattice of the graphitic carbon. We already know that Boron will drastically change the morphology of the GUITAR, but we would like to explore the different morphologies that can be obtained by controlling the amount of B and/or the growth time. Additionally, we will study the effects of Nitrogen doping on the morphology of the GUITAR. We would like to study how the doping will affect the already known electrical properties of the GUITAR. Furthermore, the project will demonstrate that the conformation of the dopant precursor can imprint itself onto the morphology of the carbon produced. In effect, dopants and precursor conformation are tools to manipulate carbon bonding, introduce strain, and create carbon morphologies in a controlled and predictable manner.

**BROADER IMPACTS:** The success of this program will be the ability to produce new morphologies of carbon that are affordable and capable of outperforming existing carbons. These materials are advantageous in the context of catalyst, hydrogen storage, and advanced batteries not only because of their properties but also because these materials can be grown easily and with reduced toxicity since no metal is used for their synthesis. We look for and encourage participation from women, minorities and unrepresented groups throw the OK-LSAMP program and our outreaching activities aim to motivate mainly female students to pursue a career in STEM, particularly in physics.

**Understanding the role of boron on the change of morphology of B-doped GUITAR and its implications in the already known properties of GUITAR**

PROJECT DESCRIPTION

# Introduction

Carbon is an amazing material, where the allotropes have unique properties that allow carbon to be the preferred choice in innumerable applications, such as advanced battery technology [1]–[7]. As an example of this is graphite, one of the materials used for Li-ion batteries, but fast charging can lead to swelling and flaking in graphite[24] or breaking of the graphite particles into smaller particles[25], which diminish its storage capacity or cycle life or lead to catastrophic failure[26], [27]. However, it has also been shown that some of these adverse effects can be alleviated by modifying the morphology of the carbon allotrope[28]–[32] or incorporating carbon and another material into a hybrid structure[33].

The road to the discovery of new forms of carbon is the development of techniques for simultaneously manipulating carbon bonding and the morphology of the structures produced. The pioneers in the field of carbon not only have recognized its versatility but also that controlling its structure and morphology are the keys to unlocking its properties or tailoring it for specific technological applications. All of this drives us to the questions: what if we could completely modify the morphology of a carbon-based material by just introducing a dopant into its synthesis? Will these new materials have novel properties that facilitate new technologies or significantly improve existing technologies?

We already know that doping carbon-based materials with boron (B) enhances a specific property of the material, as compared to the undoped material [11]–[16] but to the best of our knowledge, few studies have mentioned changes in morphology due to doping. In this direction, our group has demonstrated that previously unobserved forms of graphitic carbon can be obtained by manipulating the strain in a form of graphite developed by Cheng et al. [17]–[23], which he has dubbed GUITAR: Graphite from the University of Idaho TAR. The morphology of the structures can be controlled by the ratio of the B precursor to the carbon precursor of the chemical source solution and the growth time.

***The focus of this proposal is NOT to study GUITAR but to borrow the process for producing GUITAR to scientifically explore/utilize dopants as a method for controlling the morphology of the carbon structures and subsequently develop methodologies for producing new morphologies of graphite-based carbon.***

The process for producing GUITAR is an atmospheric pressure chemical vapor deposition (APCVD) process involving the pyrolysis of carbon nucleation. This process allows the production of reasonable quantities of GUITAR or GUITAR based materials in a short amount of time. Additionally, the process facilitates the doping since it is done *in-situ* with no need for a metal catalyst, thus reducing the risk of having materials with toxicological content. Additionally, due to its unique electrochemical properties[17], [19], [34], [35], GUITAR, in comparison to regular graphite, is a more favorable choice in applications such as sensors[22], energy storage and conversion[21], and water purification[10].

We are proposing to design the morphology and properties of GUITAR through the introduction of dopants. In support of this hypothesis, consider the work of Yudasaka et al. [36] who found that the inclusion of nitrogen into carbon nanotubes produced helical carbon nanotubes, where they attribute the helical morphology to the formation of pentagons within graphene sheets at the location of the N dopants. They went on to propose that the distortion of the C6 ring morphology introduced strain, where the carbon nanotubes minimized the strain by coiling. However, helical nanotubes have also been observed in the absence of N doping [37], [38], and indicates that other mechanisms may be at play. A calculation by Miyamoto et al. found the sp3 orbital of N dopants is more stable if the graphene sheet is curved [39]. This suggests that dopants with sp3 character can drive a morphological change in graphitic carbon since they facilitate the crosslinking between layers and therefore introduce strain in the lattice. Furthermore, the induced curvature is accompanied by a metallic or semiconducting state depending on the pitch of the helix [40], i.e. one can dictate the properties of carbon through judicious control of its morphology.

We propose to investigate the effects of boron/nitrogen doping and boron/nitrogen co-doping on the structure and properties of the GUITAR

The goals of this project are:

1. Determine the mechanism whereby the boron dopant is incorporated into the carbon lattice.
2. Determine how the source of the precursor will affect the carbon structures and if the conformation of the B and N precursors imprint themselves on the carbon morphology.
3. Produce protocols for producing graphitic carbon with new predetermined morphologies.
4. Determine the effects of the doping/morphology of graphite on surface chemistry and electronic properties.

While the methodology for growing carbon is by no means new, the utilization of dopants at the atomic-molecular scale to control nanoscale morphology is a novel approach to sculpturing carbon to produce properties that meet a specific technological application. Manipulating materials growth at the atomic-molecular level addresses the primary directive of Solid-State and Materials Chemistry of NSF-DMR.

# Background and Preliminary Data

## The GUITAR Process



Figure . (a) A picture of a self-supporting GUITAR film and (b) an SEM image of the edge of the GUITAR film.

The GUITAR carbon process is an atmospheric pressure chemical vapor deposition (APCVD) process developed by Prof. Frank Cheng in the Department of Chemistry at the University of Idaho [17]–[23]. The process involves the pyrolysis of virtually any material with a large molar fraction of carbon in the presence of sulfur. It can be performed in an open-air crucible or the more controlled conditions of a tube furnace. If one begins with a hydrocarbon, such as cyclohexanol, the growth temperature is > 800 oC. The advantage of using a low melting temperature organic compound is that the sulfur can be suspended in the solvent to create a solution that can be bubbled into a tube furnace using N2 as the carrier gas. The process produces a metallic black conformal film (Fig. 1(a)). The film coats any surface in the presence of the vapor. The cross-sectional view of GUITAR in Fig. 1(b) reveals a flake-like morphology. GUITAR exfoliates like graphite, but not into single layers of graphene.



Figure . (a) Raman and (b) XPS C 1s spectra of GUITAR.

Spectroscopically, GUITAR is very similar to other forms of graphitic carbon. Displayed in Figure 2(a) is a typical Raman spectrum of GUITAR [41]. The Raman spectrum consists of almost equally weighted D and G bands of carbon (ID/IG = 0.91), indicative of sp3 and sp2 bonding, respectively, and consistent with graphite [42]. The corresponding XPS spectrum of the C 1s core level state in Fig. 2(b) is also typical of graphite, where the peak at ~284 eV is assigned to sp2 C-bonding and higher binding energy features are assigned to sp3 C-bonding and possible surface contamination H or O). It is important to note that sulfur is not present in GUITAR, which suggests that it acts as a promoter of carbon nucleation or surfactant (see surfactant mediated epitaxial growth [43]). The former is the more likely scenario given the stability of benzo-thiophene complexes [44]. Note also that sulfur is used in the vulcanization of rubber [45], [46]. While the goal of this work is not to study GUITAR, the mechanism by which GUITAR forms will be paramount to the project.

## Preliminary Data on boron doping of GUITAR

Displayed in Fig. 3 is a schematic representation of the morphology of the GUITAR coating that consists of overlapping carbon onions. As the process progresses, the surface of the carbon onions seeds new carbon onions, thereby, building the GUITAR layer by layer of carbon onions upon another. Cermignani et al. [47] reported on carbon onion growth, but only with B-doping, With just benzene as the carbon source, where smooth films were produced when B was absent. This suggests that in their process, boron doping introduced a new carbon morphology. It would appear that sulfur produces the same effect in the GUITAR process. We further speculate that the flakey nature of the edge of GUITAR in Fig. 1(b) are mesoscopic flakes comprised of carbon onions, although this still needs to be verified. The curved nature of the carbon onions is indicative of internal strain and it drives this morphology. The morphology of carbon-based materials is susceptible to the inclusion of non-carbon atoms. The GUITAR process and the process developed by Cermignani et al. [47] are remarkably similar, where they used benzene as the carbon source, sans sulfur, and He as the carrier gas. They used boron trichloride to produce the cone-like growth displayed in Fig.4(a). An AFM map of the surface of undoped GUITAR is displayed in Fig. 4(b) to compare to the work by Cermignani et al. [47]. The morphologies are identical, except for the feature sizes, which are approximately 750 nm for the B-doped films, as compared to 200 nm for GUITAR.



Figure . A schematic representation of the GUITAR coating composed of carbon onion structures.

The transformation of the smooth morphology of their undoped carbon films to a cone-like morphology with B-doping, in conjunction with the morphology of GUITAR films that uses sulfur, indicates that additives to the APCVD process, regardless of whether they are incorporated into the carbon, influences the carbon morphology. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images of a nanostructure coated with GUITAR are displayed in Fig. 5 [34], where the same lumpy morphology is observed as in the AFM image (Fig. 4(b)). The TEM micrographs in Fig. 5(c,d) definitively show that GUITAR is formed by layers of carbon onions [48].



Figure . (a) A SEM of the surface morphology of B-doped carbon films (Cermagnani et al.) and (b) an AFM map of the surface of undoped GUITAR.

The initial results presented herein were the unexpected outcomes of our attempts to modify the GUITAR process to produce boron carbide. Displayed in Fig. 6 are images of the first samples we produced when the boron precursor was co-introduced during GUITAR deposition. Instead of growing a film comprised of carbon onions, filamentary structures were formed. The dimensions of these new hollow carbon filaments (HCF) far exceed those reported for large diameter carbon nanotubes (CNT) [49]–[52] or multiwalled CNT (MWCNT) [53]–[56], and they do not exhibit the bamboo-like structure characteristic of MWCNT. Therefore, ***these new structures cannot be categorized as carbon nanotubes! Additionally, a catalyst was not used, either.*** Figure 6(a) shows a cluster of the HCF that projects from the substrate surface. The wall thicknesses are in the range of 50-100 nm, where the thickness of the wall of the HCF in Fig. 6(b) is 99 nm. Notice that the end of the HCF in the center of Fig. 6(a) has nearly closed. We believe that the tendency of the HCF to close is due to the presence of internalized stress. Furthermore, we believe the hexagonal geometry at the end of HCF in Fig. 6(c) is also due to these internal stresses, which causes buckling of the wall. Besides, we believe that the buckling signifies the beginning of the transition to a closed-end.



Figure . (a) SEM image of a nanostructure coated with GUITAR, (b) and TEM of the structure in (a) and (c,d) high resolution TEM images of showing the carbon morphology.



Figure . SEM images of hollow carbon filaments formed when a boron precursor is introduced into the GUITAR APCVD process. Panel (a) shows a cluster of the structures, (b) is a close up of the end of a filament, where the wall thickness is ~100 nm and (c) shows the distortion of the end of the structure as is begins to close.

TEM micrographs of the HCF in Fig. 7 reveal a layered but disordered graphitic structure, verifying that they are not carbon nanotubes. Based on the similarities of these TEM images to that of the carbon onions in Fig. 5(d), we have developed the hypothesis that B doping introduces stresses that cause the curvature of the onions to be concave rather than convex relative to the substrate upon which they grow. We further hypothesize that the stress is due to the increase of crosslinking between layers facilitated by the increase of sp3 carbon bonds[14], [57]. This out of plane stress will consequently invert the curvature of the onions making the growth directed away from the surface. The effect of boron-induced stress in the graphite sheets and between them is one of the fundamental questions we will explore in this project.



Figure . TEM images of (a) the end of a HCF and (b) of the wall structure.

We have spectroscopically analyzed the chemical composition of the HCF by FTIR and X-ray photoelectron spectroscopy (XPS). We identified both B-C modes and B-O modes in the FTIR spectra, where oxygen may be bonded to boron (O-B-O) incorporated into the graphite or boron at the surface of the HCF. At this time, the FTIR analysis is incomplete and needs to be examined in greater detail as part of the proposed research project. We conclusively identify boron in the HCF with XPS. Displayed in Figure 8 are spectra of the B 1s core level state for boron-doped carbons [47], [58] (Figure 8 a-b), and our HCF (Figure 8c). Cermignani et al. [47] assigned a B 1s binding energy of ~192.5 eV to B-C bonding (Fig. 8(a)), while Sheng et al. [58] assigned it to B-O bonding (Fig. 8(b)). The binding energy of the HCF B 1s core level state is 192 eV (Fig. 8(c)). The conflicting assignments make it impossible to identify with confidence the origin of the bonding of boron in HCF. Furthermore, our preliminary XPS analysis only provides information to a depth of 10 nm into the HCF and additional mapping of boron and oxygen in the interior would be beneficial to our understanding. Further XPS analysis is needed to determine the bonding of B in HCF and it is another topic of investigation of the project.

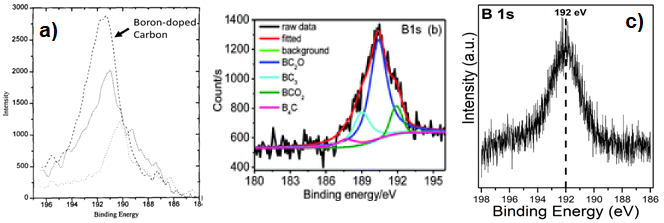


Figure . Figure 8. XPS spectra of the B 1s core level state of boron-doped (a) carbon (Cermignani et al.), (b) graphene (Sheng et al.) and (c) HCF.



Figure . SEM images of (a) the base of a HCF and (b) a top-down view inside an HCF at the early stage of formation. Panel (c) is a schematic representation of the proposed growth of HCF.

The tubular morphology of the HCF by itself is interesting, particularly since they are not carbon nanotubes and a metal catalyst isn’t used, there is much richer materials research to be obtained from studying this system. Consider the initial stage of a HCF formation, as the one shown in Fig. 9(a). The HCF consists of a large base that tapers down, at which point believe that the hollow growth begins. Support for this proposed model of the growth is in the form of the SEM image in Fig. 9(b), where you are looking down into a short HCF. We see what appears to be the walls continuing to grow around a ‘seed’ in the center (highlighted in blue) that has stopped growing. We believe that the terminated seed in the center forms because the boron-induced stress creates a small radius of curvature and the inner layers of the HCF to close in upon themselves. However, for the outer layers, the stress is insufficient to produce sufficient curvature, causing the outer layers to delaminate from the inner layers and they continue to grow in the form of a hollow tube. A schematic representation of the initial stage of growth of the HCF is displayed in Fig. 9(c). We hypothesize that the magnitude of the stress in GUITAR is a function of the boron doping concentration and growth time and this stress can be harnessed to produce a carbon morphology (shape) of one’s choosing. This is another area of investigation of this project.

We have performed preliminary experiments to support our hypothesis. We produced an ensemble of different carbon morphologies by varying the concentration of boron precursor in the cyclohexanol solution, where a few examples of these morphologies are displayed in Fig. 10. Reducing the boron precursor mass ratio in the cyclohexanol solution reduced the HCF diameter and the wall thickness (Fig. 10(a)). The HCF in Fig. 10(a) has a wall thickness of 34 nm, as compared to 99 nm for HCF in Fig. 6(b). Further reduction of the boron precursor concentration produces closed, thin-walled, carbon eggs (Fig. 10(b-d)). Notice that the carbon eggs have burst because the interior continued to grow even after their ends were closed. The material growing inside appears to be thin veil-like sheets of carbon that fold back upon themselves. The continued formation of material within the carbon eggs suggests gases diffuse through the walls to the interior. This diffusion of gases is an important phenomenon that will be explored in this project. The ability of material to diffuse through the walls may be advantageous in the context of catalyst, hydrogen storage, and advanced batteries, where one wants a specific element, such as Li ions, to collect within the interior [59]–[61] while blocking other from entering.



Figure . SEM images of HCF as a function of B-doping: (a) smaller diameter, thin walled, HCF, (b) thin walled carbon eggs that have burst due to continued growth in the interior, (c) a freestanding HCF showing the central core, and (d) another carbon egg that have burst due to continued growth in the interior, (c) a freestanding HCF showing the central core, and (d) another carbon egg that has burst.

# Research Plan



Figure . A schematic of the hollow carbon filament (HCF) chemical vapor deposition system (APCVD).

Displayed in Figure 11 is a schematic representation of the HCF atmospheric pressure chemical vapor deposition (APCVD) system that will be used to grow all of the materials in this project. The system consists of a tube furnace capable of reaching at least 900 oC, a quartz tube that serves as the reactor, a hot plate/stirrer for heating and mixing the precursors, and a bubbler. Vapor is delivered to the furnace by metered bubbling of N2 into a single solution of the boron precursor/sulfur/cyclohexanol. The system is efficient and easily maintained. The system is housed in a fume hood that carries the exhaust products away.

The following is the list of scientific questions we propose to answer, i.e., the research topics that we are targeting with this project:

1. Determine the mechanism whereby boron dopant is incorporated into the carbon lattice.

* Is oxygen important to the process?
* If oxygen is important, are boron-oxygen complexes formed in the HCF?
* Will using an oxygen-free carbon source, such as hexane, impact HCF formation, and if so, how?
* Do we need sulfur or is boron sufficient?
* If we do need sulfur, is there an S-B interaction and does it facilitate B inclusion?

1. Determine how the source of the precursor will affect the carbon structures and if the conformation of the B and N precursors imprint themselves on the carbon morphology.

* Will the boron source impact the carbon morphology? If yes, is this because other elements of the precursor are carried along with boron and subsequently incorporated into the carbon?
* Does nitrogen introduce different strain in the lattice and therefore produce different structures?
* If nitrogen produces new structures, how are combinations of dopants incorporated into the graphitic form of carbon?
* Can we utilize the boron precursor as a way to co-dope carbon with other elements, such as nitrogen?
* What happens to the carbon morphology is we co-introduce a second dopant precursor, such as ammonia?
* Can we sculpt the carbon morphology by carefully controlling the dopant content?
* Does the source of carbon affect the formed morphology?

1. Produce protocols for producing graphitic carbon with new predetermined morphologies.

* How will heating and cooling times affect the morphology of graphite?
* Does the flow of the precursors determine the thickness of the walls of the HCF?
* How dopant content and growth time influence the thickness of the HCF walls?
* Does wall thickness dictate the length of the HCF before they close? If so, is this a measure of dopant content?
* How does the mechanism differ from other processes for producing carbon?

1. Determine the effects of the morphology of graphite on surface chemistry and electronic properties.

* Does boron doping reduce carbon oxidation?
* How does doping modify the electrical properties of the undoped carbon?
* If the source of boron is important, will it also impact the electrical properties of the materials?
* Is it possible to obtain n-type or p-type materials depending on the source of the boron used in the precursor?

## Determine the mechanism whereby boron dopant is incorporated into the carbon lattice.

One first step in determining how boron is incorporated into the carbon lattice is by determining the chemical composition of the boron in the doped samples. For this aim, spectroscopic analysis and nuclear magnetic resonance (NMR) will be performed. The spectroscopic techniques we will use are Raman, Fourier-Transform infrared spectroscopy (FTIR), and X-ray photoelectron spectroscopy (XPS). Raman and FTIR spectroscopies allow us to identify the dipole and non-dipole vibrational modes, respectively. Particularly, Raman is of interest since it has been shown that changes on the Raman spectra provide a measure of local strain in graphite and graphite related materials[62], [63], therefore by looking at changes in the graphitic bands of our materials, it will be possible to compare the differences in stress as a function of boron doping.

Displayed in Fig. 12 is the preliminary Raman spectrum of HCF (red). Upon comparing the Raman spectrum for HCF in Fig. 12 to that of GUITAR in Fig. 2 (black in figure 12), we see that the G band is at a lower energy shift. The G band is assigned to in-plane stretching of the sp2 C-C bonds and the lower energy shift is due to a decrease in C-C bond stiffness caused by tensile strain [63], [64]. The G band in HCF is also broader indicative of the tensile strain being heterogeneous. Additionally, we observe that the sp2/sp3 (D/G) ratio increases from 0.91 to 0.97 from GUITAR to HCF. We hypothesize that this ratio will correlate with the wall thickness and with the length of the HCF, where the concentration of B doping increases the concentration of sp3 bonding that distorts the graphene lattice and that this reduces the size of the graphite domains through mutual sp3 crosslinking. Therefore, we can track strain within the HCF or any new morphology by tracking the shift of the peak position of the G band as a function of boron concentration. Ultimately, the D/G ratio as a function of boron doping, in conjunction with the carbon morphology, will enable us to model the strain and determine how it drives the carbon morphology.

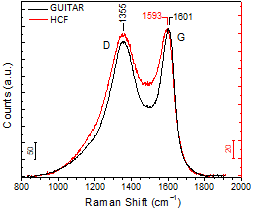


Figure . Raman spectra of GUITAR (black) and HCF (red).

FTIR spectra of HCF will allow us to identify the inclusion of H and O. Our preliminary FTIR data has been difficult to interpret because of the richness of the spectra. There are indications that C-B bonds, similar to boron carbide, are present in HCF, but the lack of consistency of the data makes this identification difficult. Our goal is to determine if oxygen is incorporated into the HCF and if its bonding is C-O, B-O, or C-B-O. The FTIR data of HCF grown with a low ratio of the boron precursor to cyclohexanol suggests the presence of B-O bonding, which is not present in carbon grown with higher boron precursor to cyclohexanol ratios. To address the question of oxygen inclusion, we will switch to hexane, an oxygen-free carbon source. We anticipate that this will reduce the HCF oxygen content and we will be able to determine if oxygen influences the morphology. Additionally, we would like to use oxygen as the carrier gas to see the impact of an oxide environment on the morphology of the carbon. Oxygen usually facilities the introduction of defects into a graphite structure, additionally it will add a dipole-dipole interaction between the basal planes that could become dominant over the Van der Waals forces.

We will acquire complementary Raman spectra to determine if reducing/increasing the oxygen content affects the D/G ratio and, subsequently, the strain. We will also employ FTIR to determine if there are trace amounts of sulfur incorporated into the HCF. We will use FTIR to quantify how much and if it is affected by the concentration of boron incorporated into the HCF and/or the ratio of boron precursor to carbon source. The FTIR spectra of the HCF and literature reports of the FTIR signature of sulfur oxide [65]–[67] suggest that the inclusion of sulfur is in the form of S-O bonding. However, once again, the complexity of the preliminary FTIR data makes it difficult to make a conclusive identification. Further FTIR studies will shed valuable light on the presence of sulfur and if it affects the HCF morphology. Note that there are indications that HCF grow without using sulfur. If possible, we will be able to eliminate sulfur inclusion and any ambiguity about its influence on HCF formation and any new morphologies we observe.

XPS is also an excellent tool for further characterizing the HCF. It is important to note that we have not observed sulfur in the XPS spectra of GUITAR [17], [19], [20] or HCF. All this tells us is that if sulfur is present, it is below 1%. Consequently, XPS analysis will be restricted to the C 1s, B 1s, O 1s, and N 1s core level states, and the S states if observed. Nitrogen is a planned co-dopant we will discuss shortly. We will use XPS analysis and subsequent peak deconvolution of the C 1s core level state to identify changes in the sp2 bonding as a function of boron and nitrogen doping. In addition, we will monitor the B and N 1s core level states, where we anticipate changes in their binding energy with stoichiometric and morphological changes. We plan to perform *in situ* and *ex-situ* hydrogen reduction experiments in conjunction with XPS characterization to ascertain if oxygen is bound to the surface or incorporated into the HCF. More specifically, whether oxygen is bond to boron. High-temperature hydrogen reduction is an excellent way to reduce accessible oxygen (surface bound) by reacting it with hydrogen to form H2O, which evaporates. We have used *in situ* and *ex-situ* hydrogen reduction to reduce metal oxides to metals for catalysis studies [68]. Our XPS system is equipped with a sample heater capable of sustaining temperatures as high as 700 oC and leak valves for introducing hydrogen for *in situ* hydrogen reduction. For *ex-situ* reduction, we will expose the HCF to 10 Torr of hydrogen in a vacuum chamber equipped with a load lock system that allows us to isolate the reduced sample *in vacuo* and transfer it to the load lock system on the XPS system, thereby ensuring that the sample isn’t exposed to atmosphere. We can return the sample back to the hydrogen reduction chamber in the same manner and continue to expose it to hydrogen. If oxygen is only present on the surface of the HCF, the O 1s core level will diminish in intensity with hydrogen reduction and eventually disappear. Alternatively, if oxygen is present at the surface and incorporated into the HCF, we should see the intensity of the O 1s decrease, but not disappear completely. Lastly, subsurface incorporation of oxygen will not be responsive to hydrogen reduction and minimally reduce the intensity of the O 1s core level state, if at all. Determining if oxygen is incorporated into the HCF when grown with cyclohexanol and eliminated when grown with hexane, while simultaneously observing differences in HCF morphology, will determine if the 192 eV binding energy of the B 1s core level state is due B-O or B-C bonding.

In addition to using XPS to identify the bonding of boron in HCF, we will use NMR spectroscopy. 10B has a spin 3/2 with a quadrupole moment, while 11B is spin 3 with a smaller quadrupole moment. We can purchase boron precursors produced with 11B, which will produce sharper NMR peaks than 10B. NMR spectra for HCF as a function of 11B concentration will be acquired and compared to NMR spectra of boron carbide [69]–[71]. Lee et al. [70] used this approach for B-doped graphite to follow the evolution of boron bonding as a function of boron concentration, where they successfully observed the formation of boron carbide at domain edges of graphite. We anticipate that changes in the boron concentrations incorporated in the HCF will manifest themselves in the NMR spectra and correlates with morphological changes. These experiments will be conducted in the OSU-Chemistry NMR center.

The role of sulfur in HCF formation needs clarification, as well as determining if is it is critical to the process. We believe this needs to be inspected at the molecular level, i.e. through bonding of C, B, and S. Boron carbide is the prototypical boron-carbon material [72]–[77], where bonding is via sp3 hybridization. This is in contrast to sulfur-carbon complexes that can form sp2 bonds and favor planar morphologies [44] [78]. This raises the following question; can we incorporate boron into a material that favors sp2 bonding? If so, one option is through the formation of boron sulfide (B2S3) at the edges of the graphite domains, which is the proposed bonding site of sulfur in graphene [79]. Boron sulfide is a planar molecule and readily be incorporated at edge sites of graphite domains. We propose to determine the role of sulfur in the HCF process by only using the boron precursor and the carbon source, sans sulfur. Assuming we are successful, we will compare the concentrations of boron in HCF with and without sulfur by XPS analysis, as well as compare their morphologies. For example, boron incorporation without sulfur may lead to a higher density of sp3 bonding in the HCF, which will increase internal strain, thereby facilitating the closure of their ends and the formation of carbon eggs, as opposed to the longer structures with tapered ends. If we successfully grow HCF without sulfur, we will conduct the same experiments using cyclohexanol (contains oxygen) and hexane (only C and H) to understand the role of oxygen on HCF formation.

## Determine how the source of the precursor will affect the carbon structures and if the conformation of the B and N precursors imprint themselves on the carbon morphology.

This component of the project relies heavily on electron microscopy to examine the initial phases of HCF formation and structural factors driving the formation of HCF, as well as other carbon morphologies, as a function of doping. It would be a game changer in carbon manufacturing if one could imprint the molecular conformation of the boron precursor into the GUITAR process as a method for predetermining and controlling the carbon morphology. To this point, we have only investigated one boron precursor with a three-dimensional conformation. However, there is a vast array of boron precursors at our disposal. One option is to use different polytypes of boron precursors. It has been shown that using two different isomers of closo-dicarbadodecaborane can result in forming either n-type or p-type semiconductors[80]–[82]. Therefore, the carbon placement within the icosahedral cage seems to play a significant role in the electrical properties of the formed boron carbide, thus we would like to perform a comparative study of the effects of these polytypes for C2B10 on the HCF morphology. Another option for the boron precursor is boric acid (H3BO3). This is soluble in alcohols, melts at 170 oC, and can be introduced into the reactor with a bubbler. The same is true for metaboric acid (HBO2). Because the boron acids contain oxygen, additional analysis of the role of oxygen on the HCF morphology is in order. In terms of an oxygen-free precursor, decaborane (B10H14) is an excellent open cage molecule that sublimes at low temperatures, where cage morphology may favor sp3 bonding. We will utilize these families of boron precursors in this study. We will conduct the same set of experiments in section **a)** to correlate the HCF morphology with the ratio of D/G bonding of carbon. The results from **a)** will also help us to better understand if the changes in morphology due to boron source are due to oxygen or other elements being incorporated into the carbon along with boron.

We recognize that different precursors where the principle element is not boron may be used. Doping with different sources of nitrogen is important to further understand the role of doping in the GUITAR structure and properties. If it is changes in strain into the graphitic layer or between layers that drive the HCF structure, then having an element with a slightly different atomic size to that of carbon may induce different structures. If it is size related, boron has a higher atomic radius compared to carbon, but nitrogen has a smaller radius, therefore they will distort the graphitic layer in different ways. Additionally, N doping favors the formation of sp2 bonds instead of sp3 bonds. On other hand, it has been shown that doping with B and N will result in opposite charge carrier type (p-type or n-type). Therefore, we would like to explore the differences in electrical properties as will be explained later.

We investigate the viability of using co-doping HCF to sculpt the carbon morphology, i.e. long hollow filaments, carbon eggs, etc. For this project, we propose to co-dope with boron and nitrogen. The first approach is to introduce the dopants with separate precursors. We will utilize our proprietary boron precursor (to be revealed in the initial HCF publication) and ammonia (NH3), where we will dope with just ammonia as a control. In terms of identifying whether the conformation of the dopant can affect HCF, we will also nitrogen dope using pyridine (C5H5N), which already has the hexagonal morphology of graphene. Introducing the nitrogen dopant separately allows us a higher degree of control, such that we can modify the ratio to control the HCF morphology. Nitrogen doping will introduce pentagonal bonding into the graphene lattice, which will produce lattice strain, thereby affecting the HCF morphology. We are interested in identifying the effects of stress on boron sp3 bonding, i.e. does a secondary stress promote sp3 bonding in the HCF, and if so, does this affect its morphology? Do we obtain new morphologies that we have not as yet observed? Can we use the concentration of the dopant as a morphological design parameter? We are also interested to determine if the dopants compete adversely with one another. In other words, can we counter their effects on HCF morphology by controlling the ratio of the concentrations of nitrogen to boron (N/B ratio)? Lastly, for this component of the project, we will determine if sulfur is still necessary, and if not, how does its exclusion affect dopant concentrations or the ratio thereof. Once again, we will perform the same measurements outlined in section **a)** for these co-doped materials.

An alternative to co-doping with two separate precursors is to use a single precursor, where the caveat is whether the precursor fragments and incorporation of the co-dopants are independent of one another or if the precursor remains intact and whether the more easily incorporated dopant can drag the other dopant along for incorporation. This is a difficult proposition given that HCF are grown at ~900 oC. However, we believe that decomposition can be avoided by using borazane (([B](https://en.wikipedia.org/wiki/Boron" \o "Boron)[H](https://en.wikipedia.org/wiki/Hydrogen))3([N](https://en.wikipedia.org/wiki/Nitrogen)[H](https://en.wikipedia.org/wiki/Hydrogen))3), available from Gelest. It decomposes at temperatures above 1000 oC [83], making it an excellent candidate for this study. A pyrolysis study of borazane by Frueh et al. [83] determined that it decomposes into polyiminoborane, as well as forms borazine above 130 oC, where both compounds are capable of being harvested for incorporation. Vapor phase reactions with the carbon precursor and sulfur cannot be excluded and will be considered in the evaluation of co-doping with a single precursor. Given that borazane is borane and ammonia, it should be equivalent to co-doping with a 1:1 ratio of ammonia borane.

## Produce protocols for producing graphitic carbon with new predetermined morphologies.

HCF formation is catalyst-free, which is extremely unusual. There are a few reports of metal-free growth of carbon nanotubes (CNT), where they were grown on Si or SiO2/Si substrates and nucleate from surface scratches [84]–[86]. However, the reduction of SiO2 by hydrogen produces Si nanoparticles, which act as a catalyst even though they are not metallic. In these cases, the CNT grow up from the catalyst at the surface, as opposed to the bottom of the catalyst, thereby lifting the catalyst off the surface. While these processes are metal catalyst-free, they are still catalytically grown. We are aware of one report where a carbon seed served as the point of nucleation [87]. We too have observed nucleation at scratches, but also in what appears to be the vapor phase. The red arrows in Fig. 6 identify small, quickly closing, carbon structures that appear to grow from the sidewalls of the HCF, much the same way CNT nucleate from a carbon substrate [87].

As of now, we have not examined the initial phase of HCF formation. We postulate that it begins with the formation of an upward curved graphitic onion. We plan to use high-resolution scanning electron microscopy to verify this hypothesis. Specifically, we will perform a series of brief HCF growth experiments that terminate at different points in the early formation of HCF. Our goals are to determine the size of the initial graphite platelets that form the foundation of the HCF and measure their thickness as a function of boron doping (similarly with nitrogen doping and co-doping). This will allow us to correlate morphology with the D/G bonding ratio obtained from the Raman studies in **a)**. An alternative approach to short growths is to abrade the surface after a regular growth cycle and look for the remnants of the bases of the HCF. Either approach will enable us to verify our model in Fig. 9(c) of HCF formation. Besides, it will enable us to verify our hypothesis that the concentration of the boron dopant produces strain and the degree of strain dictates the curvature of the HCF during the initial stages of growth. Specifically, a higher concentration of boron produces the carbon eggs, which correlates with the wall thickness of the structures.

We plan to use transmission electron microscopy (TEM) to quantify the nanomorphology of the carbon structures, perform dopant mapping, measure wall thicknesses as a function of doping, and determine the structure of the veil-like carbon sheets that form inside the carbon egg structures. In contrast to MWCNT, we do not observe a pristine layer structure for the HCF. This is because of the crossover of graphite layers of the graphitic structure. Displayed in Figure 13 is as an expanded view of a section of the TEM image of a HCF in Fig. 7(a) that has been filtered in Photoshop to find edges. While it is not as clear in this document as it is in Photoshop, the filtering algorithm nicely identifies bifurcations, crossovers, and terminations of graphene layers in the HCF. We hypothesize that statistical analysis of the number of bifurcations, crossovers, etc., correlates with the ratio of D/G bonding. We will use this methodology to statistically analyze the different morphologies produced and correlate them with the results of the spectroscopic studies in **a)** and the doping dependent experiments in **b)**. We will also analyze TEM electron diffraction patterns and rings as another method for correlating disorder within the structures. We will also employ energy dispersive spectroscopy (EDS) mode of the TEM to map the distribution of dopants (B, N) within the HCF. We recognize that this may be unsuccessful given that EDS has difficulty distinguishing the light elements like B, C, and N from one another. At a minimum, we will attempt to correlate the concentration of dopants with the location of bifurcations, crossovers, etc. If successful, it should be possible to map strain within the structures and correlate this with the morphology.



Figure . . An expanded section of the TEM of a HCF in Fig. 7(a) that has been filtered in Photoshop using the find edges.

To tune the process and get better information about the growth, we plan to study how variations of certain synthesis parameters will affect the HCF morphology. For these studies, we will keep the carbon and boron precursors constant to obtain the HCF morphology, and vary only parameters related to the CVD process such as the heating and cooling times/rates, the flow of the precursors, and the growth time.

It has been shown that cooling times influence the dendrite arm spacing of gray cast iron, the thickness of some graphite plates, as well as the flake formation [88], [89]. With different cooling/heating rates carbon will segregate differently from the surface of the substrate and therefore it could allow incorporation of vacancy-impurities. We hypothesize that it will result mainly in different thicknesses of the HCF walls. On the other hand, a variation on the precursor flow will affect the convection currents inside the furnace, and therefore increasing precursor flow will alter the interface dynamics/energy and may accelerate the growth, but having high flow rates could result in a precursor that acts as an etching agent as well and therefore it will terminate the growth [90]. Modifying synthesis parameters will help us not only better understand the growth process but also to look for a low cost synthesis approach that can be tailored to the material’s application.

The last ‘design’ parameter is the choice and properties of the substrate upon which the HCF are grown. Rather than using the substrate as a template like Cu for graphene, we will use carbon substrates as a template to preferentially favor sp3 or sp2 bonding at the initial phase of HCF formation. We would be adopting the technique outlined in Ref. [87], but expand it to use amorphous carbon (sp2/sp3), HOPG (primarily sp2), graphene on Cu foil (sp2), and CVD diamond thin membranes (sp3). For example, the sp3 of the diamond membrane may produce more bonds to the carbon seed, thereby overpowering the internal strain and inhibiting HCF formation. Alternatively, diamond may increase the diameter of the graphite seed, thereby reducing the curvature of the carbon seed and produce large diameter HCF. This is schematically represented in Figure 14. If this proves to be the case, the diameter of the HCF as a function of doping can be used to estimate the internal strain within the HCF. With sp3 bonding of amorphous carbon, we can expect significantly more crosslinking of the seed (carbon onion) of the HCF to form bonds with the substrate relative to diamond. These bonds will counter the internal strain of the seed, thereby reducing the angle of curvature of the seed. Alternatively, with HOPG or graphene, the sp2 bonding of the substrate will produce weaker adhesion of the seed to the substrate, thereby enabling the strain in the seed to produce a larger curvature of the seed. We hypothesize that the initial curvature of the graphitic seed dictates the overall diameter of the HCF, thereby producing different carbon morphologies.



Figure . A schematic representation of how the surface bonding of the substrate can affect the curvature of the HCF during the initial stage of formation.

## Determine the effects of the doping/morphology of graphite on surface chemistry and electronic properties.

As mentioned before, we plan on using different characterization techniques to categorize and better understand the role of doping on the morphology of graphite carbon. But, not only changes in morphology are of interest. We would like to explore how different morphologies or doping content may affect the chemical and electrical properties of the graphite carbon.

In the past, we have used silica nanosprings (NS) as nanostructured supports for catalysis due to their high surface area and high thermal stability[68], [91]–[94]. Due to the high surface area of the HCF, we plan on performing similar studies and compare the results to those with silica NS. Graphite materials have attracted attention in catalysis because they are eco-friendly and are easy to grow compared to conventional metal catalysts. The goal here is to find materials with better catalytic performance and therefore high catalytic efficiency that are not metal-based.

Another question we would like to answer is if these new structures are good for hydrogen storage. We believe that the hollow nature of the HCF allows hydrogen to absorb due to its large surface area and the accessibility of the said surface. It has already been demonstrated that B doping of graphite dramatically increases hydrogen absorption[95], but the hollow nature of BOD-carbon allows hydrogen to absorb into the inner and outer walls, thereby increasing absorption/desorption rates and capacity. Testing materials with different morphologies will help us to demonstrate this hypothesis. Additionally, depending on the B concentration, H will absorb preferentially near B atoms and promote the formation of H clusters[96]. Thus, controlling B content will allow us to tune the H absorption of this material. For this goal, photoemission spectroscopies (PES) measurements will be performed. Surface adsorption can be detected by looking at changes in the electronic structure of the material after being exposed to different doses of Hydrogen[97], [98]. We plan to compare adsorption at room and low temperature.

Lastly, electronic measurements and Hall effect measurements are needed to better understand the doping effects on the properties of the graphitic carbon. As mentioned before, it has been shown that doping graphitic based materials with N or B will result in n-type or p-type [14], [99]–[101], similarly using different isomers of closo-dicarbadodecaborane[80]–[82]. Therefore, hall effect and current-voltage (IV) measurements are needed to characterize these materials. These results will be compared to changes to the fermi level of the samples measured by ultraviolet photoelectron spectroscopy (UPS). All of these measurements along with the results from **a)** and **b)** will give us enough information to not only understand the role of doping on the morphological changes of the graphite materials but also tailor it to design new forms of carbon with specific attributes tailored to the desired application.

# Project Management

The PI, Dr. David McIlroy, is a physicist with an extensive background in materials development, characterization, and applications. His work has primarily been in the area of 1D nanostructures (boron carbide, silica carbide, gallium nitride, silica, etc.), surface science, catalysis, and sensors. In addition, he has worked with carbon-based materials, such as boron carbide and GUITAR (which he helped to develop). He has managed numerous large research grants from the NSF, DoD, and the W.M. Keck Foundation. In addition to Dr. McIlroy, the research team will consist of a research specialist, a graduate student, and an undergraduate. The research specialist will oversee day-to-day supervision of graduate and undergraduate students. We have weekly group meetings and Dr. McIlroy regularly works alongside the students.

While for the most part, the different components of the project will run in parallel, the boron doping of HCF experiments (boron concentration, boron precursor dependent morphologies (imprinting), etc.) and the role of sulfur are priorities of the first year of the project. Based on the outcomes of these experiments, the second year priorities are co-doping with boron and carbon and identifying the effects of strain on HCF morphology. During the third year, the impact of substrate morphology on HCF will be the top priority.

# Graduate and Undergraduate Education

This project will provide young scientists with a broader scope of training and infuse them with a culture of interdisciplinary training. The graduate students on the project will work on materials preparation, measurement, and modeling. In today’s scientific landscape, a young scientist needs to have a much larger toolbox to be successful. Combining experimental and modeling expertise will produce scientists with the skills to tackle all aspects of a project. This gives them a much deeper understanding of the problem and better problem-solving skills. The graduate students will also serve as the point of contact for the undergraduates that will work on the project. Both will learn how to work as a team and how to be effective communicators. Also, they will learn project management skills. As we well know, scientists are project managers, yet we don’t emphasize this skill to students. We will emphasize this in weekly group meetings. We will coordinate graduate student recruitment through the OSU’s Student Services unit, the College of Graduate Studies, and the Oklahoma Louis Stokes Alliance for Minority Participation (OK-LSAMP) program. We will also consult applicable searchable databases (e.g. American Physical Society Reach Program, for example) of talented, economically disadvantaged, and underrepresented students interested in graduate school, and the Ronald McNair Scholars online database. Besides, the department provides travel funds to students to attend scientific meetings sponsored by NSHP and Women in Physics.

***Undergraduate Research:*** We will also encourage undergraduate involvement in the project through senior projects and directed studies. These students will be involved in Think Tank (discussed below), where they will learn communication skills. In addition, we have an active NSF-REU program that has successfully recruited students of Hispanic and Native American origins. Students in the REU program will be allowed to work on this project. Besides, Dr. McIlroy’s undergraduates (OSU and REU) are trained to run the university’s electron microscopes. It is a resume builder and breeds confidence and excitement.

***Graduate Research:*** The graduate student on the project will be exposed to a variety of interdisciplinary activities, be through a collaboration with research that utilizes Raman to visiting a lab to perform a measurement. The student will have the opportunity to assist in other projects. While this project will be their primary focus, in our lab we assist one another on projects and therefore learn about the other research. For example, the student on this project will provide GUITAR and HCF samples to research collaborators that are working on applications, such as Li-ion batteries. Furthermore, they will learn to produce materials, characterize them with a variety of spectroscopic and microscopic tools, and develop their writing skills by preparing manuscripts. For example, all of his students are trained to run the university’s electron microscopes and XRD system. Dr. McIlroy’s approach to graduate training has led to a nearly 100% employment of graduate from his group in their chosen postgraduate profession (faculty, national lab researcher, the private sector, etc.)

# Outreach

***K-12 engagement:*** Our plan is to combine K-12 engagement with communicating science through the development of a capstone course. Located an hour south of the OSU campus is the Science Museum Oklahoma (https://www.sciencemuseumok.org/), where the CEO and president, Ms. Sherry Marshall, is an OSU Physics alumnus. Ms. Marshall runs an amazing museum with tons of interactive exhibits. The scope and degree of interactive science activities they have developed fits well with my philosophy of hands-on learning. SMO will assist us with training undergraduate and graduate physics students to be effective communicators of science. Ms. Marshall and her staff will hold a one-day training session, followed by two ½ day sessions, with our students. The training will encompass:

* + Explore the different approaches to learning
  + The role of inquiry in science communication
  + Facilitating effective learning exercises with young students - the right tools at the right time
  + Developing age-appropriate science activities that are fun, engaging, as well as meet state and national educational standards

After the morning training, our students will venture out into the museum, where they practice what they learned by working on the day’s activity in the museum’s Tinkering Garage. Also, they can participate in school holiday activities, such as Tinkerfest, Chemistry Day, and Space Day. I have a vision for a Think-Tank on the OSU campus. Think-Tank will be a half-day activity open to 4th, 5th, and 6th-grade kids. In advance, we will give them a Think-Tank topic, such as ‘How to make an artificial brain?’ We will break the kids into groups overseen by our students, where they will discuss the topic, have some hands-on activities, followed by brainstorming, and then the groups will present their ideas to the other groups. I led a similar outreach activity at Pacific Northwest Laboratories some years back. This leads us to communicating science and a capstone course. Because our physics majors will go out into the world, they effectively communicate their research to a non-scientific audience. I argue that if you can explain science to a kid, you can explain it to anyone. I propose to develop a Communicating Physics Capstone course that will be offered in the Fall, where physics majors are trained to lead Think Tank sessions held in the Spring. Note that participation will be open to graduate students and the postdocs in the department.

# Dissemination of Results:

Educational and research findings will be disseminated in peer-reviewed journals, through presentations/posters at conferences, and on campus activities. We will have biweekly meetings to update the team on progress and research outcomes.

# Report on prior NSF Support (N/A)

# Broader Impacts:

Carbon is known for its great properties and use in a variety of applications. However, carbon materials alone cannot solve every problem, superior carbon will facilitate new technology that is otherwise unattainable.The success of this program will be the ability to produce new morphologies of carbon that are affordable and capable of outperforming existing carbons. These materials will be advantageous in the context of catalyst, hydrogen storage, and advanced batteries not only because of their properties but also because these materials can be grown easily and with reduced toxicity since no metal is used for their synthesis.

For the catalyst application we are looking to keep our collaboration with the University of Idaho through the department of Forest, Rangeland and Fire Sciences. While for advanced batteries applications we would like to start a collaboration with the Materials Sciences and Engineering Department at OSU. Our group will be providing samples and they will use these for testing. The results of these testings along with the information gather though characterization will help us to improve our materials and to provide insight in the development of new technologies. The results of this collaborative work will be presented in meetings and interdisciplinary conferences and activities where diversity is a priority, as for example the APS Conference for Undergraduate Women in Physics.

Since we are looking for participation from women, minorities and unrepresented groups throw the OK-LSAMP program, the undergraduate student from any of these groups will gain research experiences and hands on exposure to different characterization techniques and adcanced materials that make her/him be competitive in the STEM workforce and/or to go to graduate school.

Finally, our outreaching activities aim to motivate mainly female students to pursue a career in STEM, particularly in physics as well as help K-12 teachers to take this new knowledge and love to physics back to the classrooms, to inspire students and show them the different applications that physics could have.

# Intellectual Merit:

The project proposes to exploit a new way for sculpting the morphology of carbon by controlling the dopant content and therefore the internalized strain within the lattice of the graphitic carbon. We already know that Boron will drastically change the morphology of the GUITAR, but we would like to explore the different morphologies that can be obtained by controlling the amount of B and/or the growth time. Additionally, we will study the effects of Nitrogen doping on the morphology of the GUITAR. We would like to study how the doping will affect the already known electrical properties of the GUITAR. Furthermore, the project will demonstrate that the conformation of the dopant precursor can imprint itself onto the morphology of the carbon produced. In effect, dopants and precursor conformation are tools to manipulate carbon bonding, introduce strain, and create carbon morphologies in a controlled and predictable manner.