

The Discovery and Characterization  
of the Carbon Allotrope  
GUITAR

A Thesis  
Presented in Partial Fulfillment of the Requirements for  
the  
Degree of Master of Science  
with a  
Major in Chemistry  
in the  
College of Graduate Studies  
University of Idaho  
by  
Jeremy D. Foutch

Major Professor: I. Francis Cheng, Ph.D.  
Committee Members: Dean Edwards, Ph.D.; Peter B. Allen, Ph.D.  
Department Administrator: Ray Von Wandruska, Ph.D.

December 2016

## AUTHORIZATION TO SUBMIT THESIS

This thesis of Jeremy D. Foutch, submitted for the degree of Master of Science with a Major in Chemistry and titled “The Discovery and Characterization of the Carbon Allotrope GUITAR,” has been reviewed in final form. Permission, as indicated by the signatures and dates below, is now granted to submit final copies to the College of Graduate Studies for approval.

Major Professor: \_\_\_\_\_ Date: \_\_\_\_\_  
I. Francis Cheng, Ph.D.

Committee Members: \_\_\_\_\_ Date: \_\_\_\_\_  
Dean Edwards, Ph.D.

\_\_\_\_\_ Date: \_\_\_\_\_  
Peter B. Allen, Ph.D.

Department  
Administrator: \_\_\_\_\_ Date: \_\_\_\_\_  
Ray Von Wandruska, Ph.D.

## ABSTRACT

GUITAR (**G**raphene from the **U**niversity of **I**daho **T**hermolyzed **A**sphalt **R**eaction) was first observed as a silvery deposit on the inside of a porcelain crucible after the pyrolysis of oil shale during a routine metals analysis. After initial characterization by optical and electron microscopies it was thought to be multi-layered graphene or graphene paper. Raman spectrographic analysis indicated that it was a nano-crystalline graphite or graphene. Electrochemical characterization showed three significant differences from graphene or graphite; (1) There is lack of electrolyte intercalation through basal plane and edge planes of GUITAR, (2) there is fast heterogenous electron transfer at both the basal plane as well as the edge plane and (3) the hydrogen overpotential is much higher. In this work, GUITAR was subjected to a battery of techniques to more fully characterize its composition, morphology, and structure. Based on the results obtained, it is proposed that GUITAR is a highly noble, porous material, consisting of nanometer-sized grains of two-dimensional graphene-like layers, which are interconnected by three-dimensional diamond-like “defects.” This unique structure begins to give some explanation as to why GUITAR displays many of the useful and superior qualities of both graphene and diamond.

## ACKNOWLEDGMENTS

I wish to express sincere appreciation to Dr. I. Francis Cheng for his excellent tutelage, and continued friendship, and unwavering support. Without his direction, guidance and encouragement over the past 8 years, this work would not have been possible. I also acknowledge and thank Dr. Dean Edwards for his ongoing collaborative effort in GUITAR applications over the years, as well as his participation on the committee for this work. Dr. Peter Allen has also been an invaluable resource for figuring out clever solutions to the myriad of challenges encountered in the research lab, as well as a valued member of this committee. I wish to recognize the contributions of Dr. J. Franklin Bailey and Dr. Tom Williams, for their hours of assistance with electron microscopy as well as X-Ray diffraction. I also recognize Dr. David McIlroy, who has been an ongoing colleague in the venture who provided early X-Ray photoelectron spectroscopy support and assistance in early identification efforts. I extend special thanks to Dr. Paul Davis, Katie Yocham, Kari Livingston, Twinkle Pandhi, and Dr. David Estrada from Boise State University for their invaluable contributions to the Raman Spectroscopy as well as AFM studies performed on GUITAR. Additional thanks are extended to Dr. Alex Blumenfeld and Dr. Cecil Deybowski for their contributions to the NMR work performed. I also recognize Dr. Peter Griffiths, who first suggested that GUITAR may be a new allotrope and to his graduate student Dr. Ayuba Fasasi for his early work in obtaining Raman spectra. I express thanks to Haouyu Zhu for her many hours of assistance with electron microscopy, and to my other fellow graduate students in the Cheng laboratory as well as student collaborators in the University of Idaho Department of Chemical Engineering. I thank Arnold Schaid, whose friendship and many conversations urged me to make my decision to return to graduate school and finish what I started. Also, to Michael Pearson, uncle, friend and early collaborator in the discovery of GUITAR; although he has since passed away, I believe he would have been pleased with the conclusion which we present in this work. Furthermore, I wish to express special thanks to Cheri Cole, and Deb Cissel for their constant and often unrecognized administrative support and assistance in navigating the path to graduation. And to any left unmentioned, for there is too little space to include all of the contributions to this work, I simply say thank you.

## DEDICATION

To my Lord and my God,  
through Whom I can do all things,  
and without Whom I can do nothing.

I dedicate this work to my parents,  
Who believed in me and supported me  
no matter what;

And to my beautiful children,  
Stephanie, Gracie, Gabriel, Ashley, Levi and David,  
For the reason they give me for doing the impossible anyway,  
And to the love of my life, my best friend, my wife Michelle,  
For her unwavering love, endless patience, unfailing encouragement  
and constant support,  
Given each and every day,  
One day at a time,  
As we trudged the road to the finish line.

## TABLE OF CONTENTS

Authorization to Submit .....	ii
Abstract .....	iii
Acknowledgements .....	iv
Dedication.....	v
Table of Contents .....	vi
List of Figures .....	viii
List of Tables.....	ix
Chapter I: Discovery and Initial Characterization Efforts of GUITAR.....	1
Discovery .....	1
From Oil Shale to Roofing Tar .....	3
Optical Microscopy .....	3
Electron Microscopy.....	4
532 nm Raman Spectroscopy.....	8
X-Ray Photoelectron Spectroscopy.....	11
Chapter II: Gold Nanoparticle Deposition on GUITAR .....	13
Overview .....	13
Gold Nanoparticle Deposition on GUITAR vs. HOPG .....	13
Chapter III: A New Synthesis Method for GUITAR.....	16
Problems with the “Crucible Method” .....	16
Pure Starting Materials and the “Tube Furnace Method”.....	17
The IPA Method for Making Large Quantities of GUITAR.....	19
Chapter IV: Recent Characterization Efforts on GUITAR.....	21
GUITAR: Is it $sp^2$ , $sp^3$ , or something in between?.....	21
Elemental Analysis.....	22

X-Ray Diffraction .....	24
Density.....	26
Solid State NMR .....	28
Atomic Force Microscopy on Different Substrates .....	29
Multi-Wavelength Raman Studies .....	31
Chapter V: Summary, Conclusions and Future Work .....	35
Summary .....	35
Future Work .....	36
Conclusion .....	37
References .....	38

## LIST OF FIGURES

1. Piceance basin oil shale sample and GUITAR first observed .....	1
2. Map of the Piceance Basin in Colorado.....	2
3. Comparison of GUITAR's appearance with other graphitic materials .....	4
4. Morphology of graphitic materials.....	5
5. Comparison of GUITAR's basal plane with the basal plane of pyrolytic graphite .....	6
6. Comparison of GUITAR's edge plane with the edge plane of pyrolytic graphite.....	7
7. Transmission electron microscope images of GUITAR.....	7
8. Raman vibrational modes for graphitic carbon materials.....	8
9. The Tuinstra-Koenig equation.....	9
10. GUITAR's placement on Ferrari's amorphization trajectory .....	9
11. 532 nm Raman spectra of GUITAR .....	10
12. Raman spectra of graphite, graphitic oxide, and reduced graphitic oxide .....	11
13. Optical micrographs of AuNP's on BP-GUITAR and BP-HOPG.....	14
14. SEM images of AuNP's on BP-GUITAR and BP-HOPG .....	15
15. Schematic of the "Tube Furnace Method" .....	18
16. Ternary phase diagram of various forms of carbon.....	22
17. XRD diffractogram of GUITAR.....	25
18. Bragg's law .....	26
19. Scherrer's equation .....	26
20. Solid state NMR spectra of GUITAR.....	28
21. Atomic force microscopy of GUITAR.....	29
22. Plotting of D-band position versus Raman excitation energy .....	32
23. Plotting of G-band position versus Raman laser wavelength.....	33
24. Plotting of grain size ( $L_n$ ) value of GUITAR versus excitation energy .....	34
25. Proposed placement of GUITAR on the Ternary Phase Diagram for carbon materials.....	36



## LIST OF TABLES

1. Peak assignments for the deconvolved C 1s narrow scan XPS of GUITAR.....	12
2. Elemental analysis of GUITAR.....	23
3. Comparison of physical properties of various carbon materials .....	27
4. Kelvin Probe Force Microscopy Results of GUITAR vs. HOPG.....	31
5. Raman analysis of GUITAR deposited on a quartz substrate.....	32

## CHAPTER I: DISCOVERY AND EARLY CHARACTERIZATION

**Discovery**

In 2008, a metals analysis was performed on an oil shale sample (Fig 1a) taken from near Rifle, Colorado. The first step of the analysis was to combust the sample to remove any organics, after which the ashes would be dissolved in acid in preparation for mass spectroscopy.

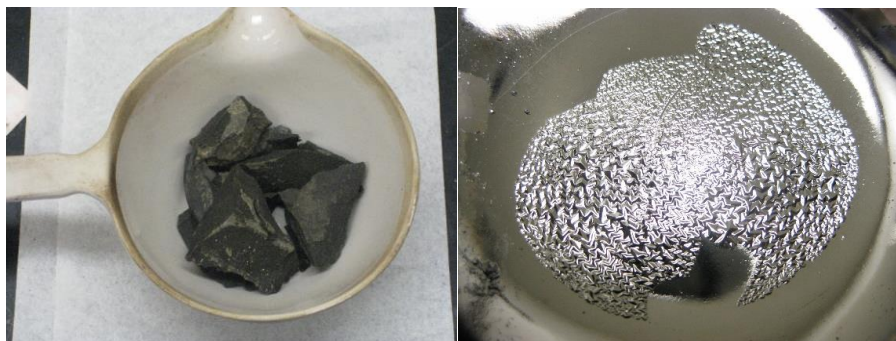


Figure 1. (a) Oil Shale sample from the Piceance Basin near Rifle, Colorado (Left). (b) Metallic Film observed on the interior of a porcelain crucible after the pyrolysis of oil shale (Right).

The pyrolysis of the oil shale was performed in a glazed porcelain crucible, a silvery coating with a metallic appearance was observed on the interior walls of the crucible (Fig 1b). The material was found to burn under a flame, and to be conductive with a voltmeter. These qualitative tests, taken along with the significant hydrocarbon content of oil shale, seemed to indicate that this material was likely a graphitic carbon deposit of some kind.

Oil shale from the Piceance Basin is part of the Green River Formation near Rifle, Colorado (Fig 2). The shale consists of between 9%-13% total organic carbon, and from  $\sim 0.74\%$ - $1.13\%$  sulfur<sup>1,2</sup>. The carbon present in Piceance basin oil shale comes from about 50%-70% resins and asphaltenes, 10%-30% aromatics, and from between 10% to up to 35% saturated hydrocarbons, and the sulfur present exists mostly in the form of thiophenes<sup>1</sup>.

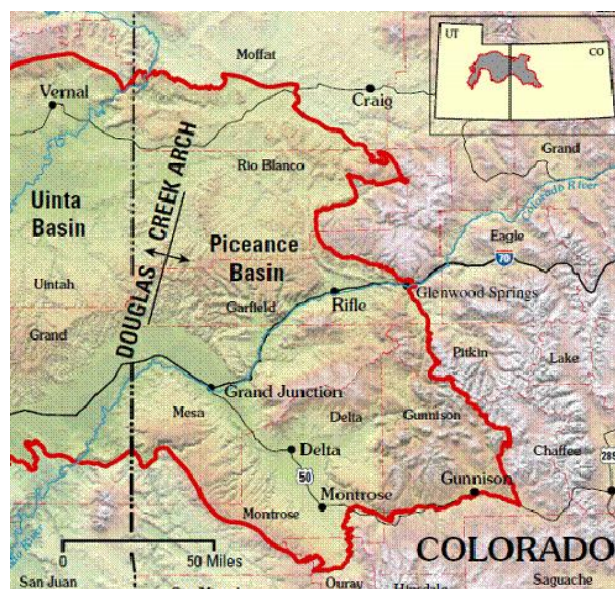


Figure 2. Map showing the Piceance Basin in Colorado, where the oil shale that produced GUITAR was taken from.

It was hypothesized that the formation of GUITAR was perhaps occurring due to the evolution of crude-oil hydrocarbon vapors coming into contact with a porcelain crucible surface heated to at least  $650^{\circ}\text{C}$ , a reaction was occurring to affect the formation of the GUITAR film. However, when the reaction was attempted with a number of pure hydrocarbon starting materials, no GUITAR was produced. It was then that the importance of the sulfur began to be questioned. The same reaction was attempted with the use of a number of hydrocarbon starting materials, both with and without the addition of elemental sulfur. In the absence of sulfur, the reaction did not occur. This indicated that sulfur was indeed a required co-factor for the formation of GUITAR<sup>3</sup>. Furthermore, it was determined that the ideal hydrocarbon starting material should be a liquid between  $80^{\circ}\text{C}$  –  $200^{\circ}\text{C}$ . Hydrocarbon starting materials that possessed a low boiling point vaporized too quickly to allow for the reaction to occur. Thermogravimetric analysis (TGA) was performed for the reaction between cyclohexanol and sulfur. From this it was apparent that a reaction between the two was occurring at around  $140^{\circ}\text{C}$ . Cyclohexanol was chosen for this analysis because it seemed to form GUITAR most successfully of the different hydrocarbons tested.

A mechanism was proposed for sulfur's important role in the formation of GUITAR. As sulfur is a well-known dehydrating agent, it is likely converting the cyclohexanol to cyclohexene (Step I), and then further reacts to form bridging polysulfide linkages. It was thought to then proceed through thermal degradation to a monosulfide. Subsequent dehydration results in the loss of H<sub>2</sub>S, and the formation of the predominantly sp<sup>2</sup> carbon material named GUITAR.

### **From Oil Shale to Roofing Tar**

Knowing that GUITAR is formed due to the reaction of hydrocarbon vapors in the presence of sulfur on a heated glassy substrate, a less expensive and more available substitute for oil shale was sought out. Many different materials were tested including candy bars, beans, and corn chips as a hydrocarbon source. All of these and many others were successful in the formation of GUITAR, as long as sulfur was present in the reaction chamber. In the absence of sulfur, the reaction was not observed to happen. The best alternative to oil shale was found to be roofing tar, which has between 1%-3% sulfur already present in the mixture.

A 25g-quantity of roofing tar was placed onto a square piece of glass matte and secured into a porcelain crucible. The glass matte was positioned so that it was slightly suspended above the deposition region where the silicon wafer was then placed as the target substrate. A Bunsen burner was then ignited and the tar was allowed to pyrolyze to completion, which took 25 minutes to occur. After cooling, the burned tar and glass matte were removed and GUITAR was seen to coat both the substrate as well as the porcelain surface of the crucible below the glass matte. GUITAR was synthesized and used for all studies using this method up until 2016, when pure starting materials were substituted for roofing tar. This is discussed in greater detail in Chapter III.

### **Optical Microscopy**

With the naked eye, GUITAR looks similar to highly oriented pyrolytic graphite (HOPG) or graphene paper, with its characteristic silvery grey metallic sheen. It can also be seen that the material is a thin film-like deposit, and relatively featureless on the surface. It appears grey/black unless light is directly incident on the surface (Fig 3), causing the light to reflect making it appear

silver. At 80x magnification via an optical microscope, there also appears to be extremely small reflective particles dispersed heterogeneously on the surface. We believe that they are likely small light- reflective divots on the mostly flat surface. It is not currently well understood what these divots are, however they may correlate with similar microscopic surface features seen in the AFM imaging that will be discussed in Chapter IV.

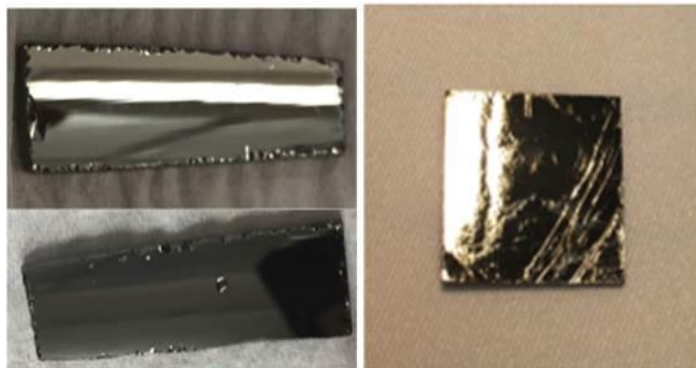


Figure 3. GUITAR coated onto a quartz glass wafer (Left top and bottom). Notice that under direct light, GUITAR has a reflective, mirror-like silver appearance (Left top). From a non-reflective angle, GUITAR is grey/black in color (Left –bottom). Highly oriented pyrolytic graphite (Right)

### Electron Microscopy

It is appropriate here to give a brief overview of the morphology of graphitic materials. Graphitic materials essentially consist of stacks of planar,  $sp^2$ -bonded carbon sheets held together by weak Van der Waals forces. The individual sheets are separated by a distance of 0.348 nm for a typical graphite. The stacked sheets of planar carbon have then a flat terminal plane on the top and bottom of the stack, referred to as the basal plane (BP), as well as a plane consisting of the exposed terminating edges of each planar sheet, called the edge plane (EP). “Steps” or “step edges” occur where a planar sheet or sheets of carbon terminate to an edge prior to reaching the edge of the bulk material (Fig 4). These step edges are also referred to as “step defects.” The BP and EP of a graphitic material exhibit significant differences in electrochemical behavior. These differences are discussed in greater detail in Chapter II.

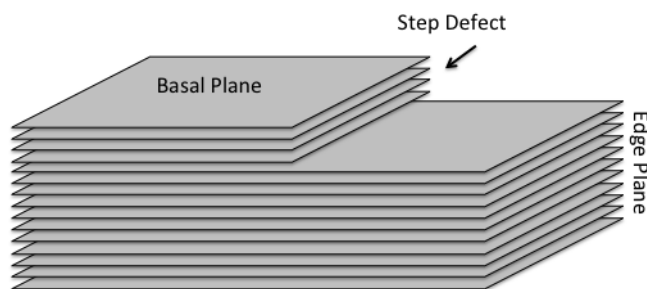


Figure 4. The morphology of a typical graphitic material consisting of the BP, EP, and a step defect.

Scanning electron microscopy (SEM) imaging clearly shows that GUITAR has a flat BP, which is relatively featureless when compared to other graphitic materials. Figure 5 contains images of GUITAR's BP compared to a typical pyrolytic graphite, graphene paper, as well as HOPG. From these comparisons, we see that GUITAR's BP is most similar in appearance to HOPG's BP. However, GUITAR's BP lacks the step defects that are readily visible as the diagonal white lines on HOPG's BP. This has especially important implications in the context of GUITAR's electrochemical behavior, as compared to other graphitic materials, and will be discussed in greater detail in Chapter 2. GUITAR also displays a layered morphology at the EP which is very similar in appearance to both graphene paper and pyrolytic graphite (Fig 6)<sup>4,5</sup>. Early GUITAR films were measured for thickness using imaging tools built in the SEM software and found to be around 3  $\mu\text{m}$  thick.

Transmission electron microscopy (TEM) was also used to acquire additional images of the EP of GUITAR (Fig 7). From the TEM images and SEM images combined, it was very clear that there are discrete layers making up the EP of GUITAR.

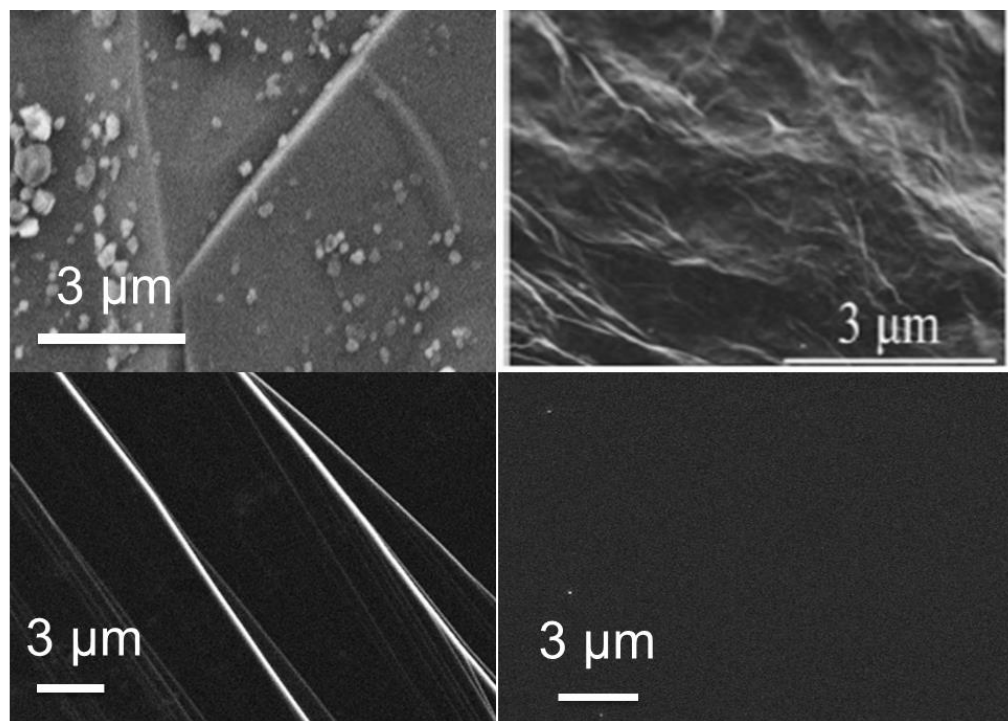


Figure 5. SEM images of the BP of (top left) Panasonic Pyrolytic graphite, (top right) graphene paper<sup>4</sup> (Copyright 2015 by The Minerals, Metals & Materials Society. Reprinted with permission.), (bottom left) HOPG, and (bottom right) GUITAR.

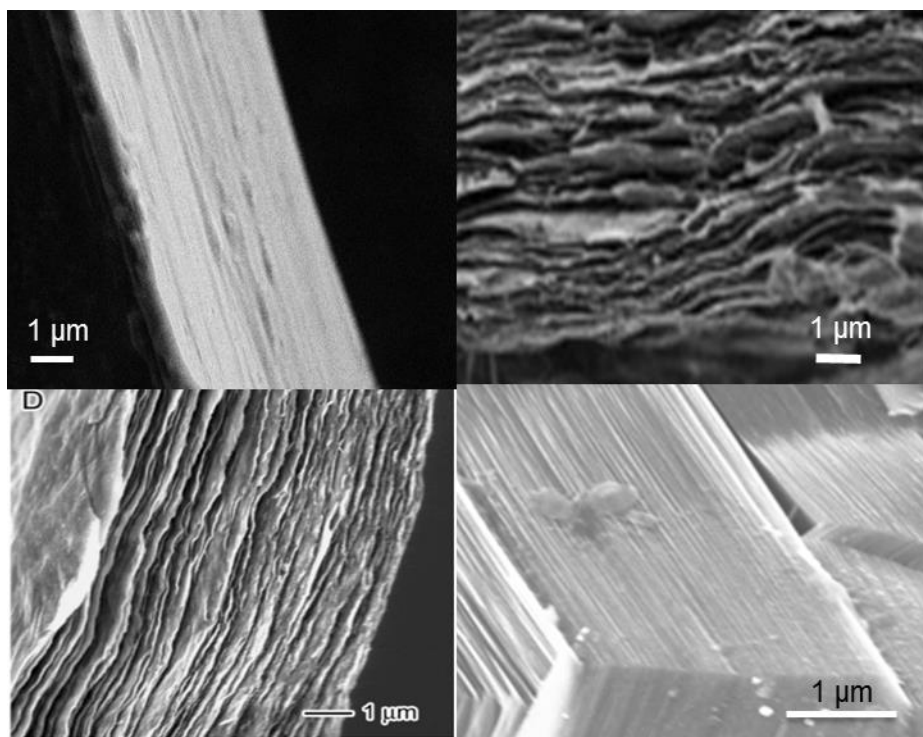


Figure 6. EP SEM images of GUITAR (top left), RGO or reduced graphene oxide paper<sup>4</sup> (top right) (Copyright 2015 by The Minerals, Metals & Materials Society. Reprinted with permission). Graphene oxide paper (used by permission Adv. Mat.) (bottom left), and Panasonic pyrolytic graphite (bottom right).

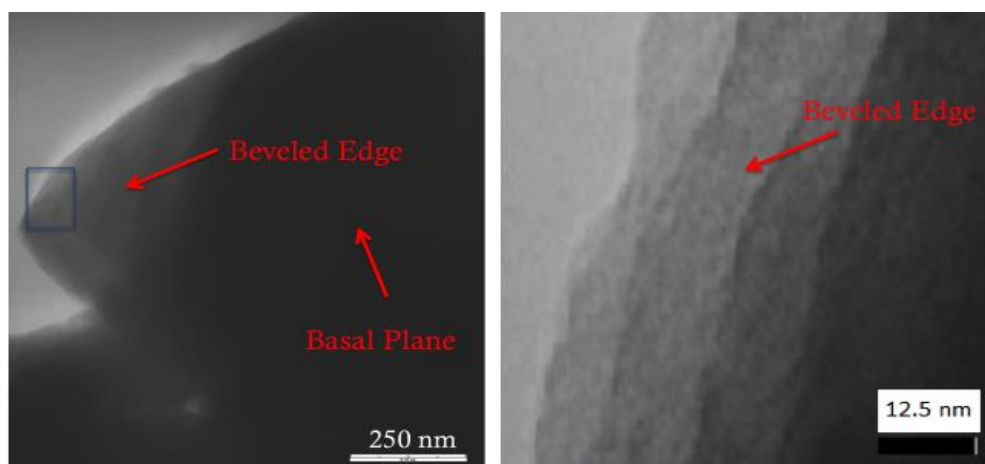


Figure 7. 2010 TEM images of the BP and edge plane of GUITAR made from roofing tar. The layers are more apparent in these images. The image on the right shows that, according to the scale bar of 12.5 nm, spacing between GUITAR is  $\sim 10$  nm (right).



## 532 nm Raman Spectroscopy

Raman spectroscopy is a widely established and extremely useful tool for the characterization of nano-crystalline, micro-crystalline, amorphous, as well as diamond-like carbon materials. This is due to the highly symmetric covalent bonds and the absence of a dipole moment found within both graphitic as well as diamond-like carbons. For disordered graphitic carbons two primary modes exist; the D band at around  $1350\text{ cm}^{-1}$ , and the G band which appears from  $1580 - 1600\text{ cm}^{-1}$ <sup>6</sup>. The G mode is due to an in-plane bond-stretching motion of paired  $\text{sp}^2$  carbon atoms displaying  $E_{2g}$  symmetry (Fig 8). It is important to note that this G mode occurs at all  $\text{sp}^2$  bonded carbon pair locations, and not only those that are part of a six-membered ring arrangement. The D mode arises from what is referred to as a “breathing mode” and only occurs in disordered graphite, as it is forbidden in perfect hexagonal carbon lattices. Because of this, the presence and intensity of the D peak gives a good qualitative indication of the presence of defects in a carbon material.

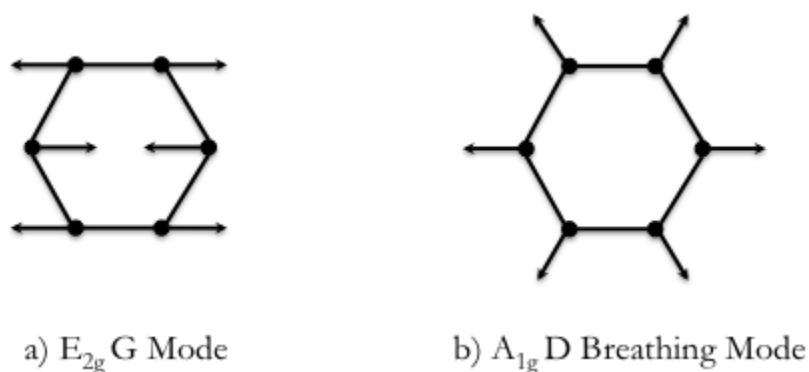


Figure 8. Raman-induced carbon motion in the a) G and b) D modes.

One useful piece of information that can be obtained for carbon via Raman spectroscopy is the size of the individual grains, or crystalline regions in a graphitic material. Tuinstra and Koenig reported that the ratio of the intensities of the D and G peaks, abbreviated as  $I(D)$  and  $I(G)$ , respectively, were inversely proportional to the grain size,  $L_a$ , where  $C(515.5\text{ nm})$  is approximately  $44\text{ \AA}$  (Fig 9)<sup>7</sup>. The  $C(\lambda)$  for a 532 nm laser is  $49.6\text{ \AA}$ , which is what was used for the Raman spectra of GUITAR in 2009.

$$\frac{I(D)}{I(G)} = \frac{C(\lambda^4)}{L_a}$$

Figure 9. The Tuinstra-Koenig Equation.

Additionally, Ferrari and Robertson developed an amorphization trajectory as a tool to assist in identification of various carbon materials analyzed via Raman spectroscopy (Fig 10)<sup>1</sup>. From the 532 nm Raman spectra of GUITAR (Fig 11), the intensities (I) of the D and G bands were used to determine the I(D)/I(G) ratio. Using this in conjunction with the position of the G peak allowed for a rough categorization of the nature of GUITAR, as well as an approximate idea of the sp<sup>2</sup>/sp<sup>3</sup> content.

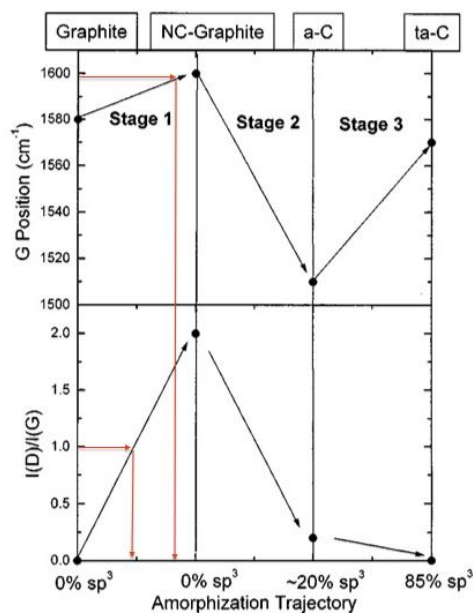


Figure 10. Ferrari's amorphization trajectory, showing the variation of the G position and the I(D)/I(G) ratio. GUITAR's placement on Ferrari's amorphization trajectory using the 532 nm raman spectra's I(D)/I(G) ratio of 0.97, and a G peak position of 1593 cm<sup>-1</sup> is shown in red.

GUITAR's Raman spectra taken at 532 nm revealed a broad D band peak at  $1354\text{ cm}^{-1}$ , as well as a narrower G band peak at  $1593\text{ cm}^{-1}$  (Fig 11). Reference spectrum for typical graphite and graphite oxide are included for comparison (Fig 12). It should be noted that the wavenumber on the x-axis is displayed decreasing from right to left, which is opposite of the reference spectra of graphite and graphite oxide. The large D peak in GUITAR's spectra indicated that GUITAR has significant grain defects present in its structure.

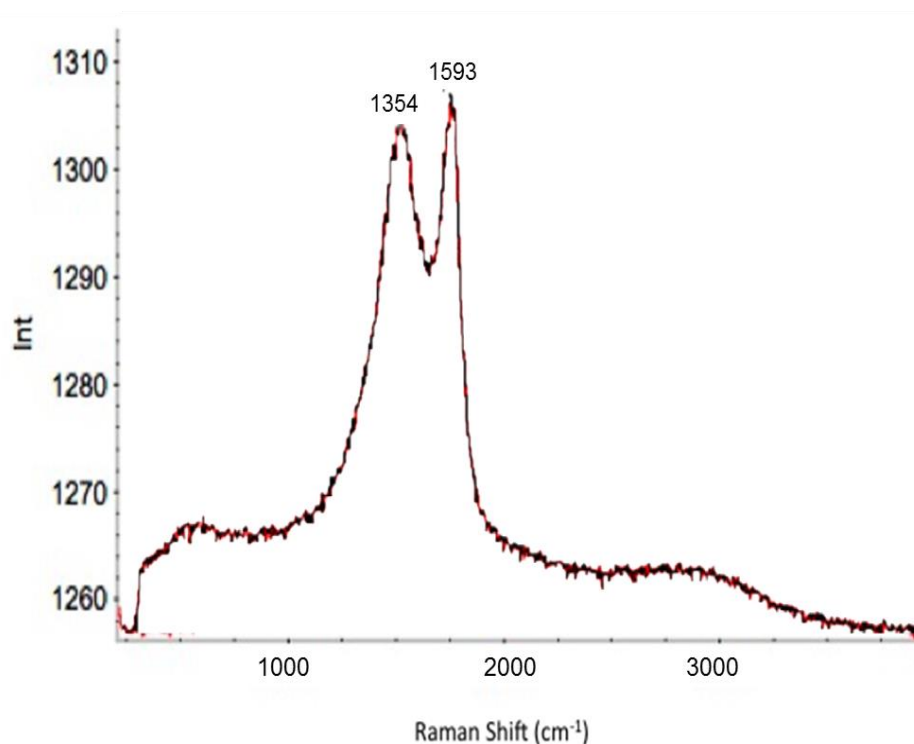


Figure 11. Raman spectra of GUITAR acquired in ambient air using 532 nm excitation; the G mode peak is at  $1593\text{ cm}^{-1}$  and D mode peak is at  $1354\text{ cm}^{-1}$ .

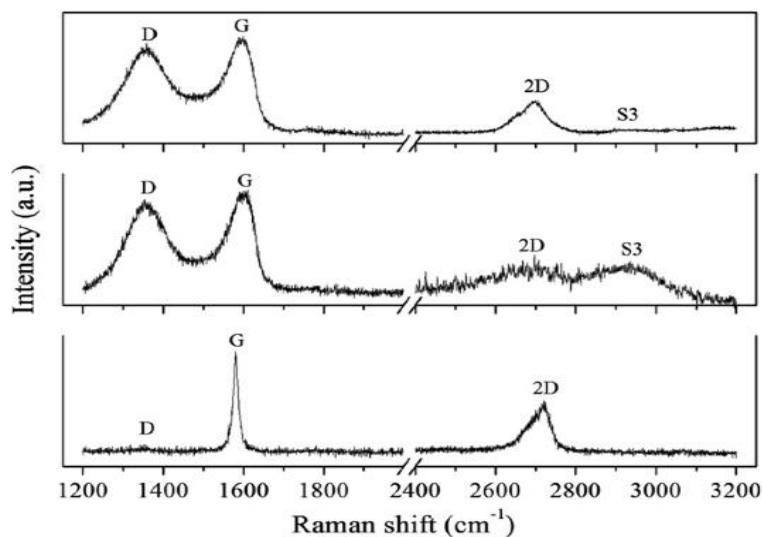


Figure 12. Raman spectra of (top) graphite, (middle) graphitic oxide – GOx, and (bottom) reduced GOx. (Reproduced with permission, Elsevier, CARBON).

From the intensity of both the D and G peaks the  $I(D)/I(G)$  ratio of GUITAR at 532 nm was determined to be 0.93. Using the Tuinstra-Koenig relationship, the grain size ( $L_a$ ) of GUITAR was found to be 5.3 nm. The  $I(D)/I(G)$  ratio of 0.93 and G peak position of  $1593\text{ cm}^{-1}$  from the Raman spectra, placed GUITAR in the  $\sim 100\%$   $sp^2$  region of Ferrari's amorphization trajectory (Fig 10). This data indicated that GUITAR was likely a nano-crystalline graphite.

### X-Ray Photoelectron Spectroscopy

A GUITAR sample was analyzed in 2009 via X-ray photoelectron spectroscopy. A wide XPS scan revealed a large C 1s peak, and smaller N 1s and O 1s peaks. Two silicon peaks also appeared due to a silicon wafer substrate on which the GUITAR was deposited. An additional annealing step at  $800^\circ\text{C}$  in vacuum was applied to drive off any adsorbed  $\text{N}_2$ ,  $\text{O}_2$ , CO or  $\text{CO}_2$ . Additional scanning after annealing showed no change in binding energy or intensity of the N 1s and O 1s peaks, confirming that the oxygen and nitrogen peaks were, in fact, due to a small amount of O and N incorporated into GUITAR's structure.

Curve fitting of the XPS demonstrated the presence of bands at 284.24, 285.15, and 286.15 eV. The 284.24 band corresponds well with literature values of  $sp^2$ -bonded carbon found in a variety of graphitic materials.

Table 1. XPS Peak Assignments for the deconvolved C 1s peak.

XPS Peak Assignments			
XPS Peak		Assignment	Reference
284.24 eV		C=C, $sp^2$	8,9,10,11,12
285.15 eV		C=N, $sp^2$	3,4,7
286.15 eV		C-OH, C-O-C, or C=N $sp^2$	3,4,5,6,7

The 285.15 eV peak could also be due to an  $sp^3$  hybridized carbon bond, but this received little attention back in 2009. This was in large part due to the presence of the N 1s peak at 401.2 eV in wide scan XPS spectrum and the absence of any C-H stretching peaks in the IR spectrum of GUITAR. XPS peak assignments are summarized in Table 1.

## CHAPTER II: GOLD NANOPARTICLE DEPOSITION ON GUITAR

### Overview

Electrochemical studies performed in 2015 established GUITAR as having distinct characteristics as an electrode material when compared to most other graphitic materials<sup>13</sup>. One of the defining differences between GUITAR and these other graphites is that GUITAR's BP allows for facile electron transfer as observed in cyclic voltammetric studies of the  $\Delta E_p$  for the  $\text{Fe}(\text{CN})_6^{3-/4-}$ , and  $\text{Ru}(\text{NH}_3)_6^{3+/2+}$  redox systems. This is unusual among graphites. For instance, both HOPG and graphene demonstrate an energetic barrier to heterogeneous electron transfer at the BP. This is likely due to a lower density of electronic states (DOS) possessed by the highly ordered hexagonal carbon networks present in both HOPG as well as graphene. Facile electron transfer is seen to occur, however, at step defects as well as the EP of graphitic materials, including HOPG. The other defining difference between GUITAR's electrochemistry when compared to other graphitic materials is its exceptionally high anodic limit of 2.7 V vs. SHE in 1 M  $\text{H}_2\text{SO}_4$ . Combined with GUITAR's excellent anodic stability in aqueous solutions, this makes it a potentially ideal electrode in a number of applications including dimensionally stable anodes, organic pollutant remediation, water purification, energy conversion and storage as well as an ultra capacitor material.

### Gold Nanoparticle Deposition on GUITAR vs. HOPG

As has already been stated, the BP of GUITAR exhibits facile HET kinetics, while the BP of HOPG exhibits slow kinetics due to an energetic barrier. While this has been observed via  $\Delta E_p$  measurements through the use of cyclic voltammetry, a more practical experiment was designed to demonstrate this behavior in a visual way. An electrochemical deposition of gold nanoparticles (AuNP's) was chosen to accomplish this.

A BP-GUITAR and BP-HOPG electrode was immersed in a 10 mM  $\text{AuCl}_4^-$  solution, with 100 mM KCl as a supporting electrolyte. A 200 mV pulse was applied for two seconds, and then both electrodes were immediately removed from the plating solution.

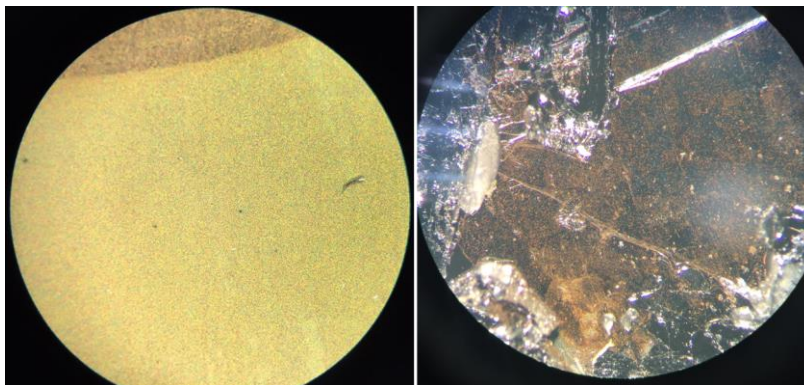


Figure 13. Optical microscope images (40x) of gold nanoparticles deposited on both GUITAR (left) and HOPG (right).

Optical micrographs of both the BP-GUITAR as well as the BP-HOPG electrodes were taken (Fig 13). A stark contrast can be seen in the comparison of the two AuNP-decorated electrodes. The BP-GUITAR electrode clearly shows a dense and mostly homogenous AuNP deposit, whereas the BP-HOPG electrode displays only sparse patches of gold discoloration, in addition to a gold-colored line traversing diagonally across a step defect on the BP of the HOPG. This makes good sense, as step defects are known to be more electrochemically active due to a higher DOS.

SEM images were also obtained for both AuNP-decorated electrodes (Fig 14). In addition, pristine BP-GUITAR and BP-HOPG electrodes were also taken as control images. The AuNP size as well as distribution is very uniform in the BP-GUITAR electrode. In comparison, the AuNP distribution clearly favors the sites of step defects, and the BP is only sparsely populated with AuNP's compared to the BP of GUITAR. This is consistent with the relatively small HET rate constant,  $k_0$ , of BP-HOPG ( $1 \times 10^{-9}$ - $1 \times 10^{-6} \text{ cm s}^{-1}$ ) as compared to BP-GUITAR's HET rate constant,  $k_0$ , of  $1.2 \times 10^{-2}$ . The SEM images clearly demonstrate in a visual way that BP-GUITAR's HET rate constant is 4-7 orders of magnitude higher than BP-HOPG. In addition to the visual confirmation of the facile HET observed in the cyclic voltammetry of BP-GUITAR, it can also be concluded that there exists a uniformity of DOS's across the BP of GUITAR.

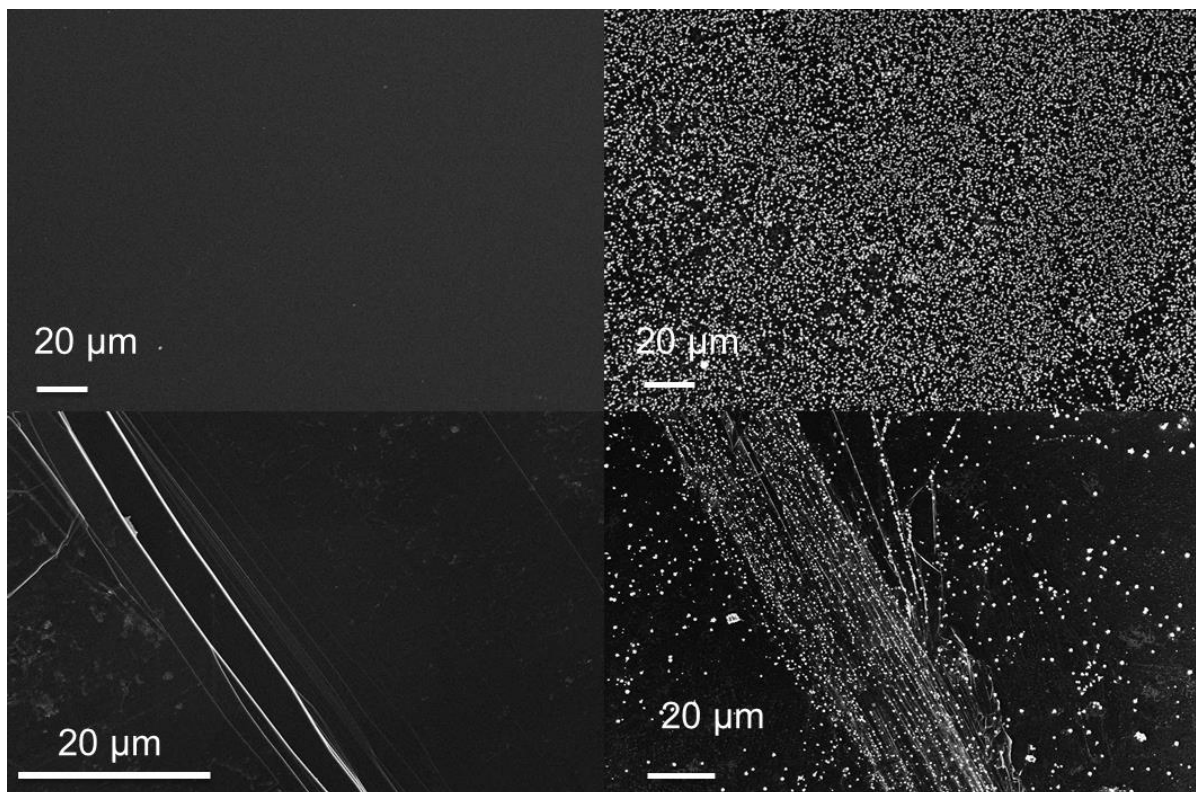


Figure 14. A pristine GUITAR (top left) and HOPG (bottom left) electrode was immersed in a 10 mM  $\text{AuCl}_4^-$  solution with 100 mM KCl as a supporting electrolyte. A voltage of 200 mV was applied for 2 seconds without stirring to achieve deposition. Gold nanoparticles deposited onto the surface of GUITAR (top right) and HOPG (bottom right). This is a clear visual demonstration of GUITAR's electrochemical behavior at the BP compared to HOPG's BP electrochemistry.



## CHAPTER III: A NEW SYNTHESIS METHOD FOR GUITAR

### Problems with the “Crucible Method”

Up until the Spring of 2016, GUITAR was synthesized using the “Crucible Method,” which consisted of placing 25 g of roofing tar on a glass mat, suspended above a target substrate which was placed in the bottom of a porcelain crucible. A second crucible was then placed on top to minimize the entry of air into the reaction chamber, and the vessel was heated over a Bunsen flame which caused the subsequent pyrolysis of the roofing tar. GUITAR synthesis occurred as the hydrocarbon vapors evolving from the roofing tar came in contact with the heated substrate at the bottom of the crucible. The Bunsen flame was turned off when the evolution of hydrocarbon vapor ceased, which occurred after 25 minutes for 25 grams of roofing tar.

There were several issues with the crucible method that led us to seek out an improved method for synthesis. One problem was variability from batch to batch in the quality of the GUITAR that was synthesized. The  $\Delta E_p$ , which is an electrochemical property of any electrode material, was used as a quantitative test to gauge consistency and quality from run to run. The  $\Delta E_p$  was seen to vary considerably at times depending on the person doing the synthesis, where the tar was taken from in the container, which can the tar came from and in many cases for no apparent reason at all. Some synthesis runs produced GUITAR that was clean and without soot, while other runs produced considerable soot on the target substrate which compromised the quality and electrochemical performance of the GUITAR electrode. Another issue was the lack of temperature control. A Bunsen burner can provide crude temperature control at best. However, measuring the temperature of the crucible with a standard high temperature thermocouple, as well as an infrared thermocouple proved to be problematic and unreliable. The high temperature thermocouple probe was used initially, but the extraneous heat from the Bunsen heat source rising around the edges of the crucible caused false high readings. There also appeared to be different temperature zones in the crucible during the heating, as evidenced by the bottom of the crucible reaching a refractory temperature which could be seen as a reddish-orange glow. This glow can be seen to fade away at about 3/8” up the crucible exterior, indicating both cooler temperatures as well as a rather sharp temperature gradient at increasing distances from the Bunsen flame. An

infrared beam temperature reading was attempted as well although it was doubtful if it would be effective, due to the requirement that surface temperatures measured via infrared thermocouple should typically be non-reflective for accurate results. The glazed porcelain crucible surface proved to be less than ideal, and the temperature readings obtained from this method were highly varied and unreliable.

Another growing concern was the inconsistency of the composition of the source starting material, roofing tar. Due to the nature of the material, as the by-product of the crude oil refining process, the chemical composition of roofing tar is not highly regulated. While there was never a great deal of time invested to understand the extent to which this variability source was affecting GUITAR synthesis, several cans of roofing tar simply had to be labeled as “bad” and were thrown out due to the consistently poor-quality GUITAR that was formed from a particular container. This led us to further believe that a pure reagent-grade starting material synthesis should be developed.

### **Pure Starting Materials and the “Tube Furnace Method”**

A new and improved apparatus and scheme for GUITAR synthesis has been developed, and is illustrated in Figure 15. From a previous study performed in 2011 a wide selection of pure hydrocarbon starting materials were tested in the presence of elemental sulfur to further understand the GUITAR synthesis reaction. In addition to showing that sulfur is a necessary cofactor in the GUITAR synthesis, there also appeared to be a correlation of successful GUITAR synthesis to the boiling point of the hydrocarbon starting material. The ideal range for the boiling point of hydrocarbon precursors to GUITAR formation was  $\sim 160^{\circ}\text{C}$  to  $300^{\circ}\text{C}$ . Of the solvents that were tested, cyclohexanol was the best pure reagent starting material for producing a GUITAR film (Table 3).

To address the issue of temperature control, a Lindberg quartz tube furnace which had a temperature controller accurate to  $\pm 2^{\circ}\text{C}$  was set at  $900^{\circ}\text{C}$  as a substitute for the Bunsen flame heat source. A 1.5” quartz tube was used in place of the porcelain crucible to provide a reaction environment where the target substrate could be placed, and the GUITAR synthesis could occur. Initially, testing was performed in an oxygen-starved environment by simply plugging both ends of

the quartz tube with glass matte plugs. However, nitrogen is currently being used as an inert gas to prevent unsafe combustion of the hydrocarbon/sulfur fumes within the high temperature quartz tube environment. For the starting material reaction mixture, 50 ml of cyclohexanol was mixed with ~2% (1.7 g) of powdered elemental sulfur. The sulfur amount of 2% was chosen as a median value between the sulfur percentage of the Piceance Basin oil shale (1.0 %) and Black Jack Roofing Tar (2.42 %).

A 500 ml round bottom flask containing the cyclohexanol and sulfur was placed in a heating mantle where the temperature was set to approximately 280°C. A glass connecting tube, with a gas inlet for nitrogen, joined the round bottom flask with the quartz tube via a ball and socket joint. Additionally, due to the high boiling point of cyclohexanol, heating tape was used to heat the glass tubing to approximately 180°C, to help prevent condensation of the vapors prior to reaching the reaction zone. A nitrogen flow of 5 standard cubic feet per minute (SCFM) was used as an inert carrier gas.

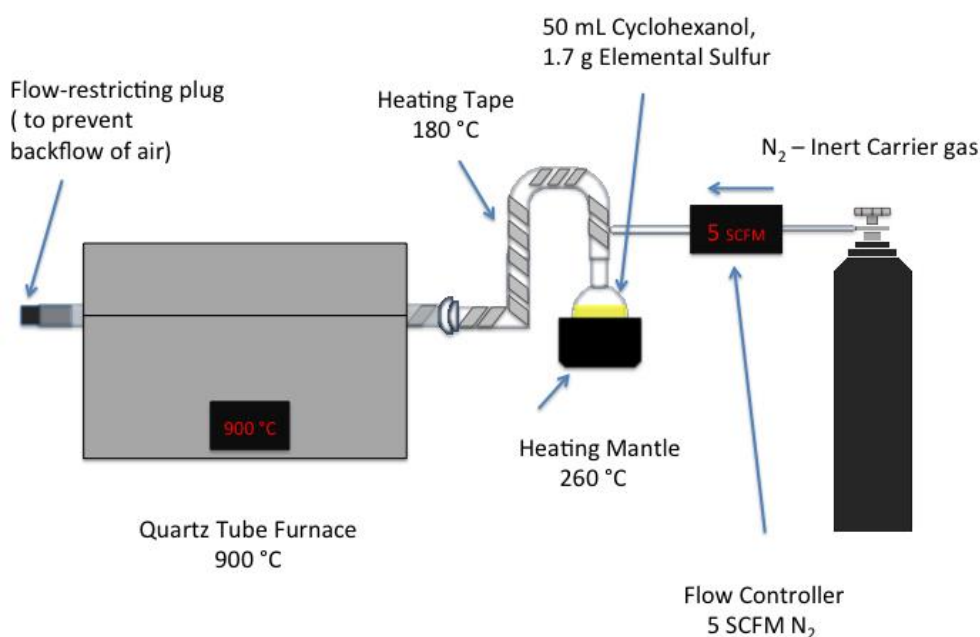


Figure 15. The “Tube Furnace Method” for GUITAR synthesis uses a quartz –tube furnace to synthesize GUITAR with cyclohexanol and sulfur as the starting materials.

The target substrate is then positioned within the center region of the quartz tube and preheated. Once the preheat process is completed, the sulfur/cyclohexanol mixture is heated to begin evolving the vapors which are responsible for the synthesis of GUITAR once they come in contact with the heated substrate surface.

Prior to the use of the Tube Furnace (TF) method, silicon wafer was the primary substrate for GUITAR synthesis. GUITAR films would delaminate, however, during the cooling phase of GUITAR synthesis. This required a transfer of the GUITAR film to a secondary substrate for electrode fabrication and testing. This transfer step was difficult to perform without the GUITAR film cracking, which greatly affects electrode performance. However, researchers in the University of Idaho Chemical Engineering department discovered that GUITAR films would remain adhered to a polished quartz surface, unlike the silicon wafer which GUITAR would delaminate from upon cooling. It is believed that this is likely due to the differences in the coefficient of thermal expansion of quartz and silicon. Silicon has a relatively large coefficient of thermal expansion ( $2.6 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ ) as compared to quartz ( $0.54 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ ). GUITAR will not delaminate from quartz even with rapid cooling. From this, it can be concluded that the thermal expansion coefficient of GUITAR is probably quite near the value of quartz.

### **The IPA Method for Making Large Quantities of GUITAR**

The reaction yield of the GUITAR synthesis is very low and therefore requires a relatively large quantity of starting material for the synthesis. Because of this limitation, several basic analyses that require relatively large amounts of sample, such as density, XRD and BET for surface area, could not be performed. Therefore, an improved method for harvesting large quantities of GUITAR was desired. The Tube Furnace Method process could be operated in a continuous mode utilizing a very large reservoir of starting material, whereas the Crucible Method (CM) was limited to single batches containing 25 g of starting material. The inherent increase in synthesis yield of the Tube Furnace method was further improved upon using multiple quartz tubes of decreasing size to be placed one-within-another, creating a high surface area deposition surface for harvesting GUITAR films. After the reaction was completed, the GUITAR-coated quartz tubes were placed in a large test tube filled with isopropyl alcohol (IPA) and sonicated for 4 hours. The GUITAR would

delaminate in the IPA as a finely-divided particulate with some larger flakes present as well. The particulate GUITAR remained well suspended in the IPA. The GUITAR/IPA suspension could then be filtered leaving a finely divided GUITAR powder which could then be dried and stored. This allowed for density measurements, BET analysis, as well as XRD to be performed.

## CHAPTER IV: RECENT CHARACTERIZATION EFFORTS ON GUITAR

**GUITAR: Is it  $sp^2$ ,  $sp^3$ , or something in between?**

The molecular structure of GUITAR has been difficult to ascertain. SEM and TEM images clearly show that it is a layered material, however the electrochemistry reveals that electrolyte intercalation does not occur, as in the case of a typical graphite. The lack of intercalation indicates that GUITAR's interplanar space is not accessible to electrolyte species. TEM images of GUITAR's EP obtained in 2015 indicated that the layers may be separated by more than typical graphite's well established inter-planar distance of 0.334 nm. It was also suggested by a colleague that this may be due to amorphous carbon regions occurring interstitially between planes.

A fundamental question then needs to be answered: Is GUITAR a pure  $sp^2$  carbon material, or is it located somewhere on the spectrum of  $sp^2/sp^3$  hybrid materials? Pure  $sp^2$  carbon materials are referred to as graphitic carbons, and then in order of increasing  $sp^3$  content are sputtered amorphous carbon (a-C), tetrahedral amorphous carbon (ta-C) and diamond-like carbon (DLC). Until recently, we believed that GUITAR was located on the far lower left of the ternary phase diagram (Fig 16). This was determined from the initial single-wavelength (532 nm) Raman analysis which was performed in 2009 and indicated that GUITAR is a nano-crystalline graphite (n-c G). However, from an electrochemical standpoint, GUITAR behaves more like a diamond-like carbon/amorphous carbon or boron-doped diamond (BDD) electrode.

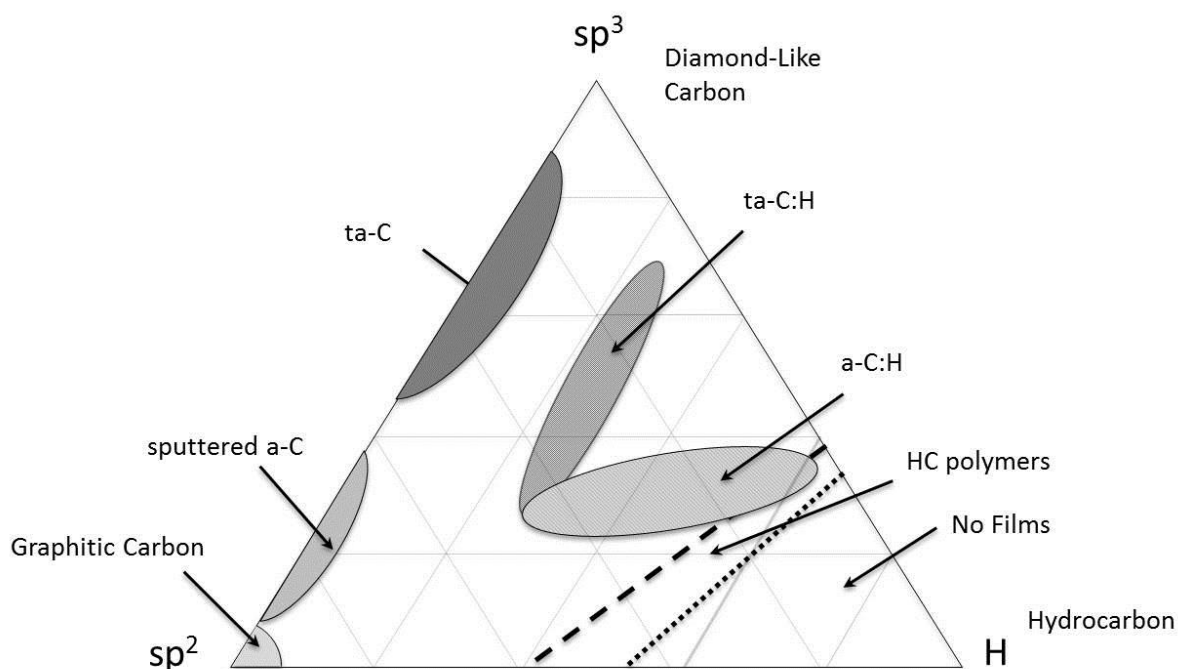


Figure 16. Ternary phase diagram showing the relative hybridization of various forms of carbon after Jacob and Moller<sup>19</sup>.

### Elemental Analysis

The results from a recent elemental analysis of GUITAR from the TF method are displayed in Table 3 in comparison to crucible method GUITAR data from 2014. A direct comparison can't be made as oxygen and sulfur analyses were not performed for the CM-GUITAR batch.

However, some general trends are useful to note.

The amount of nitrogen in GUITAR has decreased to a value below the limit of detection (LOD) for analysis. The 1.56% nitrogen present in CM-GUITAR agrees with the XPS information from 2009 that showed the presence of nitrogen in CM-GUITAR. It is probably that nitrogen-containing hydrocarbons in the roofing tar are acting as a nitrogen dopant in CM-GUITAR. The only source of nitrogen present in the TF method is from the N<sub>2</sub> carrier gas, which is inert to the

reaction. This gives a reasonable indication, as a side note, that GUITAR may be electrochemically modified via n-doping. Future studies may explore this possibility.

For GUITAR, the sulfur quantity is also below the LOD for sulfur analysis. This is consistent with the lack of a sulfur peak in the XPS of cleaved GUITAR. This indicates that while sulfur may catalyze GUITAR synthesis, it does not directly incorporate into the final structure.

Table 2. Elemental analysis of GUITAR made from roofing tar in the CM and the TF METHOD which used cyclohexanol and sulfur.

Elemental Analysis	% Carbon	% Hydrogen	% Nitrogen	% Oxygen	% Sulfur
GUITAR from roofing tar	92.35	1.16	1.56	--	--
GUITAR from cyclohexanol/sulfur (TF METHOD)	96.8	1.3	<0.05	3.08	<0.2

The amount of hydrogen reported from “Tube Furnace” GUITAR’s elemental analysis is 1.30% compared to 1.16% hydrogen present in “Crucible method” GUITAR. It should be mentioned however, that the commercial laboratory that performed this analysis for hydrogen reports a low threshold of 0.5% for hydrogen analysis. Due to being near the limit of detection of this method, as well as the potential for carryover from previous analysis in a commercial lab setting we cannot confidently report that GUITAR has any significant hydrogen content. If any at all is present in GUITAR, it could be attributed to the surface where dangling- $\pi$  bonds are terminated with hydrogen. There is currently no experimental data supporting the presence of hydrogen on the interior of GUITAR’s structure.

Oxygen wasn’t analyzed for GUITAR, so we have no data for comparison. However, GUITAR showed the presence of 3.08% oxygen, which is significant considering that GUITAR is synthesized in an inert atmosphere to prevent side reactions, as well as combustion of the hydrocarbon vapors produced during the synthesis. While it is possible that some air may have



adsorbed to the surface of the GUITAR prior to running the elemental analysis, it is also possible that some oxygen is incorporating into the GUITAR structure during synthesis from the hydroxyl group present in cyclohexanol. A significant oxygen peak is also clearly visible in the wide scan XPS that was obtained in 2009. Even with cleaving the GUITAR sample just right prior to initiating the test, the oxygen peak persisted. This indicates that either GUITAR has oxygen contained within its structure or that it has a strong affinity for oxygen adsorbed to the surface.

### **X-Ray Diffraction**

Early X-Ray diffraction (XRD) spectra of GUITAR were obtained in 2009. The amount of sample required for XRD, however, was difficult to achieve since the synthesis method being used at the time was only capable of producing very small amounts of GUITAR. From the diffractograms, it is apparent that the signal was quite weak compared to the background. GUITAR's XRD signal from the 2009 diffractogram should not be referred to as a "peak" but rather an "amorphous hump." GUITAR is rigid, flakes easily and is difficult to pulverize without losing significant quantities of sample. These factors in addition to extremely small sample quantities made XRD analysis difficult. The only conclusion that could be safely drawn from this study was that XRD should be repeated when a larger sample quantity became available.

Through the use of the IPA method in conjunction with Tube Furnace method GUITAR synthesis, a sufficiently large quantity of GUITAR was produced to initiate a new XRD study. The IPA method produces finely-divided GUITAR which greatly simplifies sample preparation for XRD. Sample handling and subsequent sample loss is minimized by eliminating the pulverization step, and allowing for immediate analysis via XRD.

The 2016 XRD diffractogram for GUITAR shows a broad, strong, crystalline peak at a  $2\theta$  value of  $25.44^\circ$  (Fig 17). Through the use of Bragg's Law (Fig 18), an interlayer spacing distance of 0.350 nm was determined for GUITAR, as compared to 0.338 nm for a typical graphite d-spacing.

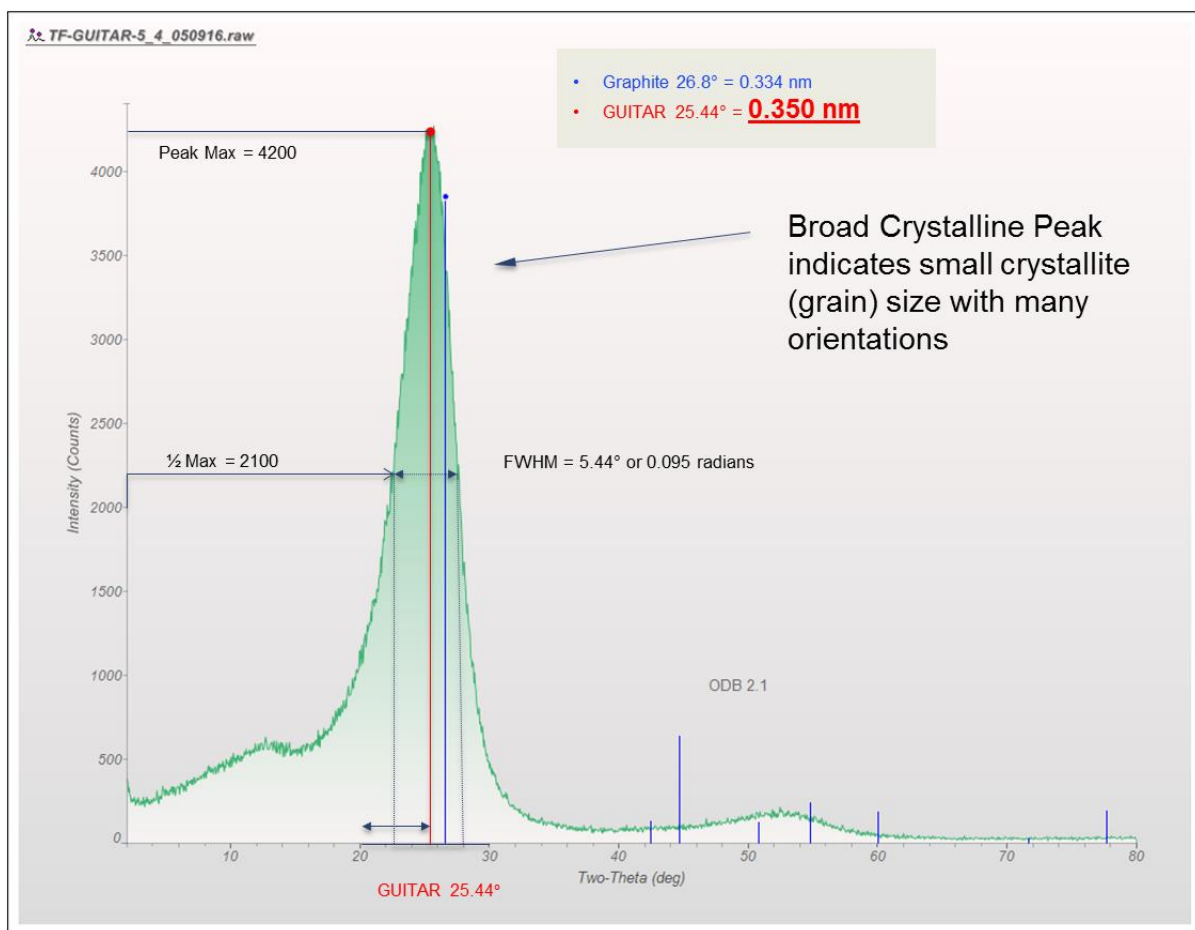


Figure 17. XRD diffractograms of GUITAR grown using the Tube Furnace method. Using Bragg's law, the interplanar distance of GUITAR was determined to be 0.350 nm, which is significantly higher than for a typical graphite (0.338 nm). The broad crystalline peak indicates nanometer scale grain size, as well as many planar orientations of the grains. Using the FWHM of the GUITAR peak, Scherrer's equation was used to determine a grain size ( $L_a$ ) of 1.66 nm for GUITAR.

The broadening of diffraction peaks is observed when the crystallite size is smaller than approximately 100 nm<sup>14</sup>. The crystallite size or grain size of a material can be determined by measuring the broadening given by the Scherrer equation (Fig 19). The Scherrer equation takes the full width at half maximum (FWHM) of the broadened diffraction peak, the Bragg angle  $\theta$ , and a crystallite shape factor  $C$  and allows for calculation of crystallite size,  $d$ . The FWHM of GUITAR's diffraction peak is 5.44° or 0.095 radians.

$$n \lambda = 2 d \sin \theta$$

Figure 18. Bragg's Law relates the Bragg's angle,  $\theta$ , of a diffraction peak to the distance between crystal planes. Also called "d-spacing, in graphitic materials this distance is known as the "interlayer spacing," or distance between individual graphene sheets.

According to the Scherrer equation and the current XRD diffractograms for GUITAR, the grain size  $L_a$  of GUITAR is calculated to be 1.66 nm. This is significantly lower than the previously calculated 5 nm grain size which was predicted in 2009 through the use of Ferrari's Amorphization Trajectory, and the 532 nm Raman spectral analysis of GUITAR.

$$d = \frac{C \lambda}{B \cos \theta}$$

Figure 19. The Scherrer equation allows for the determination of grain size by measuring the degree of broadening of a diffraction peak of a nanocrystalline material. As grain size ( $d$ ) increases, the FWHM or breadth ( $B$ ) of the peak decreases.

## Density

With the larger quantity of GUITAR available via the TF METHOD/IPA method, density analysis was able to be performed. GUITAR's density is 1.79 g cm<sup>-3</sup>(Table 3). This places GUITAR within the density range of a hard amorphous carbon (a-C:H hard).

Table 3. Comparison of physical properties of various amorphous carbons, graphite, diamond and GUITAR.

Material	sp <sup>3</sup> (%)	H (%)	Density (g cm <sup>-3</sup> )	Hardness (GPa)	Reference
Diamond	100	0	3.515	100	15
ta-C	80-88	0	3.1	80	16 17 18
ta-C:H	70	30	2.4	50	19
Graphite	0	0	2.267		20
Sputtered C	5	0	2.2		18
a-C:H hard	40	30-40	1.6-2.2	10-20	21
Evaporated C	0	0	1.9	3	22
GUITAR	-	1.3	1.79	2.85-8.21	23
a-C:H soft	60	40-50	1.2-1.6	<10	21
Glassy C	0	0	1.3-1.55	3	22
Polyethylene	100	67	0.92	0.01	24
C60	0	0			22

## Solid State NMR

The most direct measurement of the  $sp^3$  fraction of a carbon material is by  $C^{13}$  NMR. The Solid State NMR was performed on a 20 mg GUITAR sample, using Magic Angle Spinning (MAS) to decrease peak broadening. As you can see in Fig 20 (top), GUITAR shows a distribution of  $sp^2$  and  $sp^3$  carbon chemical shifts. This is evident in the spectra in the asymmetry of the peak shape. Specifically, the asymmetric region spanning from  $\sim 100 - 50$  ppm indicates a broad distribution or "mixing" of  $sp^2$  and  $sp^3$  carbon bonding throughout the bulk of the material, instead of isolated regions or "pockets" of  $sp^2$  and  $sp^3$  carbon. The pure  $sp^2$  control sample of crystalline graphite is shown in Fig 20 (bottom).

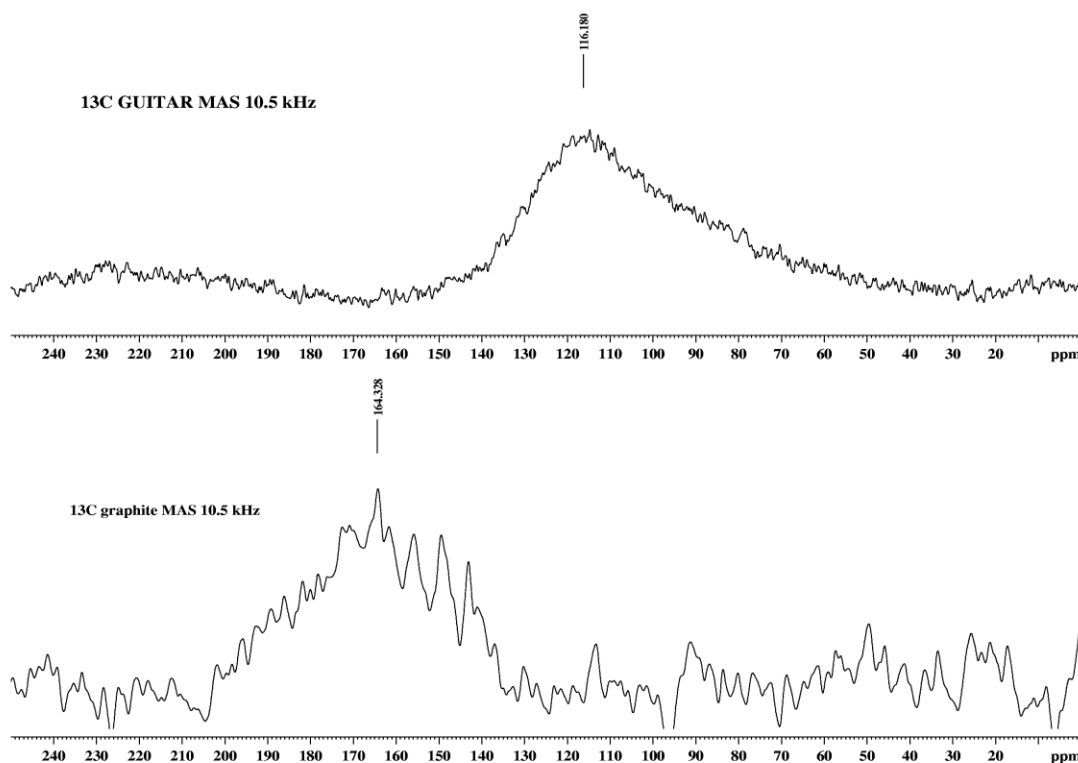


Figure 20. Solid state NMR spectra for GUITAR (top) and powdered graphite (bottom).

## Atomic Force Microscopy on Different Substrates

AFM studies on GUITAR were performed during 2016 with colleagues from Boise State. Samples of GUITAR were synthesized onto both silicon wafer and quartz. Free standing GUITAR flakes were obtained through exfoliation of GUITAR grown on silicon wafer. GUITAR deposited onto quartz, adheres very well, and was analyzed directly without attempting to remove the quartz substrate.

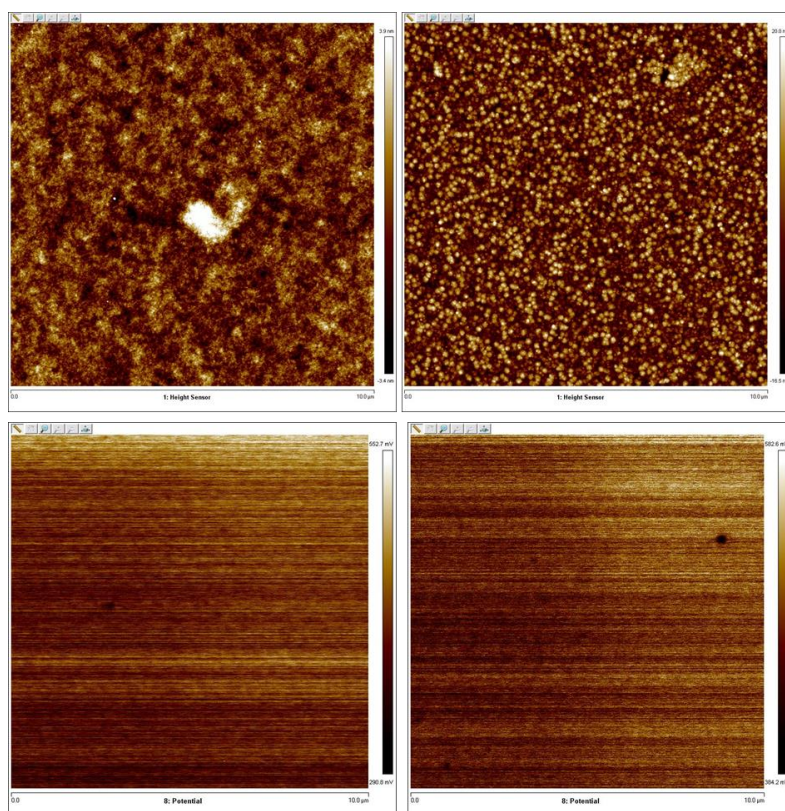


Figure 21. Atomic force microscopy images of GUITAR grown on Si wafer (top left) and GUITAR grown on polished quartz wafer (top right), showed the dependence of the morphology of the deposited GUITAR on deposition substrate used. The corresponding Kelvin Probe Force Microscopy images are also displayed for GUITAR grown on Si wafer (bottom left) and quartz (bottom right) (Courtesy Paul Davis, Boise State University).

The AFM images that were obtained for the GUITAR flake, which was grown on silicon wafer, looked similar to previous AFM images for GUITAR with the surface displaying a rough, cratered morphology (Fig 21). The surface roughness value for the GUITAR flake is 0.915 nm. However, the AFM's of GUITAR adhered onto quartz showed a completely different surface morphology. GUITAR on quartz forms an array of agglomerated nanospheres. The roughness values obtained via nanoindentation showed an average value for flake GUITAR of 0.915 nm while GUITAR on quartz roughness value of 6.6 nm. A similar nanosphere patterned deposition was observed via AFM when GUITAR was deposited on the surface of Panasonic pyrolytic graphite. Although further studies are necessary to fully understand the effect of deposition substrate, we have concluded nonetheless that GUITAR's synthesis is strongly influenced by the target substrate material.

In addition to surface roughness, nanoindentation was also used to attempt to acquire a hardness value for GUITAR. Due to GUITAR's very thin films, and the inherent limitations of the instrument, only a range of 2.85-8.21 GPa was able to be reported. This places GUITAR within the hardness range of soft amorphous carbon, evaporated carbon, and glassy carbon. GUITAR is too soft to be in the hard amorphous carbon category.

Kelvin Probe Force Microscopy (KPFM) was also performed on the surface of GUITAR films. This technique measures the work function of a material, as compared to a gold standard. GUITAR displays a significantly higher surface potential than HOPG; in fact GUITAR's surface potential is very similar to the surface potential of the gold standard, suggesting that GUITAR is highly noble, and likely to resist oxidation. This has been observed electrochemically.

Table 4. KPFM results showing the potential difference of the work was measured relative to gold. The GUITAR sample's potential difference from gold was an average of 35 mV while the potential difference between gold and HOPG is -426 mV. The potential difference between the sample and HOPG was 419 mV. The potential measurements for GUITAR are much closer to gold than to HOPG. (Courtesy Paul Davis, Boise State University)

Sample	Raw $\Delta$ Potential (mV)	$\sigma$	Sample - Au Stan.
GUITAR Flake A	449	27	36
GUITAR Flake B	416	29	3
GUITAR on quartz	481	24	68
HOPG	62	22	-351
Au Standard	413	28	0

### Multi-Wavelength Raman Studies

As mentioned earlier in Chapter I, it was from early Raman spectroscopic data that initial conclusions were drawn that GUITAR was likely a disordered nano-crystalline graphite. These conclusions were based on Raman analysis performed at a single wavelength of 532 nm. There are several additional benefits, however, to a Raman analysis performed at multiple wavelengths, such as the ability to verify the grain size,  $L_a$ , as well as the ability to measure the dispersion of the location of the G and D-bands which can be compared to other carbon materials.

In early 2016, a collaboration began with colleagues at Boise State University to perform a multi-wavelength Raman spectroscopy study of GUITAR deposited on quartz. The wavelengths chosen for the study were 442, 488, 515, 532, and 633 nm. Lorentzian fitting was used to obtain the G and D band locations, the peak intensities  $I(D)$ , and  $I(G)$ , as well as the grain size  $L_a$  from the Tuinstra-Koenig equation (Table 5).



Table 5. Results from the Raman analysis of GUITAR deposited on a quartz substrate.

Laser $\lambda$ (nm)	eV	D-Band (cm <sup>-1</sup> )	G-Band (cm <sup>-1</sup> )	I(D)	I(G)	I(D)/I(G)	La(nm)
442	2.81	1374	1581	3675	4384	0.838276	10.92732
488	2.54	1367	1589	0.12161	0.09611	1.265321	10.75697
514	2.41	1359	1591	0.27515	0.23614	1.165199	14.37685
532	2.33	1346	1575	6063	5496	1.103166	17.42677
633	1.96	1333	1580	336	251	1.338645	28.78462

The D-band peak values were seen to increase with higher laser energy, giving a linear plot of D-band position versus the laser energy (eV) with a slope of  $51.27 \text{ cm}^{-1} \text{ eV}^{-1}$ . Nanocrystalline graphites show this same trend, with a slope of  $50 \text{ cm}^{-1} \text{ eV}^{-1}$ .

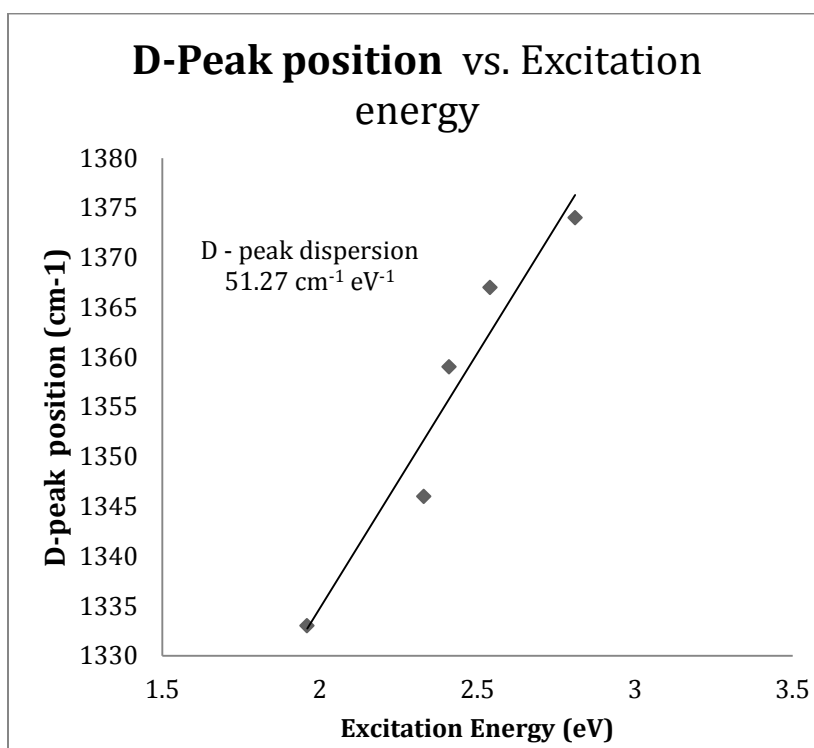


Figure 22. Plotting of the D-band position vs. Raman laser energy. The relationship is linear and the slope is  $51.27 \text{ cm}^{-1} \text{ eV}^{-1}$ . The same plot for nanocrystalline graphite gives a slope of  $50 \text{ cm}^{-1} \text{ eV}^{-1}$ .

The G-band positions for GUITAR did not show dispersion (shifting) with varying wavelength. This is also consistent with both nanocrystalline graphite as well as HOPG. Amorphous carbons, hydrogenated polymeric amorphous carbons, as well as tetrahedral amorphous carbons all show dispersion with varying excitation wavelength.

It is important to note that the Tuinstra-Koenig Equation is only valid for materials possessing grain sizes ( $L_a$ )  $>2$  nm. So as a confirmation to the 1.66 nm grain size value through the use of XRD and Scherrer's equation,  $L_a$  was calculated from the  $I(D)/(IG)$  ratio values for each of the Raman spectra.  $L_a$  values can then be plotted against Raman laser wavelength and, for materials with a grain size larger than 2 nm, will reveal a linear relationship with a slope of 0. In other words, the grain size should be the same regardless of excitation energy. This makes practical sense, as the grain size of a material is a physical property that does not change once the material has formed. In the case of GUITAR, however,  $L_a$  is seen to vary with wavelength as in Figure 24. This clearly indicates that GUITAR's grain size is  $<2$  nm according to the limitations of the Tuinstra-Koenig equation.

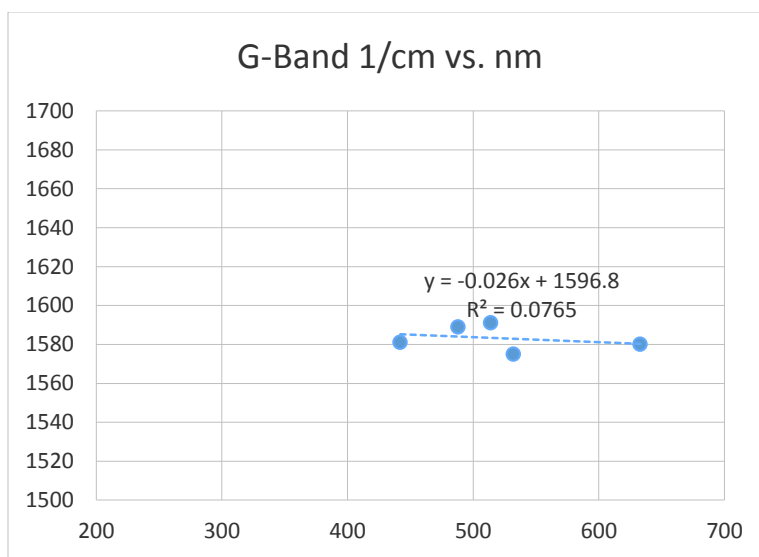


Figure 23. Plotting of the G-band position vs. Raman laser energy. The relationship is also seen to be linear, with a slope of near 0. This is typical of  $sp^2$  graphitic material.

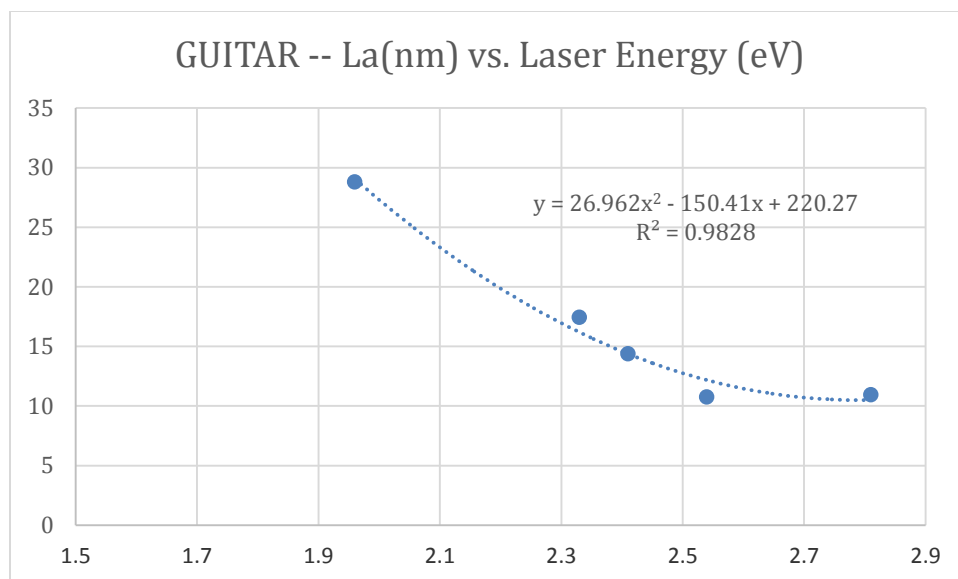


Figure 24.  $L_a$  values (nm) for GUITAR as calculated via the Tuinstra-Koenig equation versus laser excitation energy. The non-zero quadratic slope raised many questions initially, but was later explained by the  $<2$  nm grain size (1.66 nm) of GUITAR. The Tuinstra-Koenig equation is only accurate for  $L_q$  values  $>2$  nm.

## CHAPTER V: SUMMARY, FUTURE WORK, AND CONCLUSION

**Summary**

Much information has been presented on the characterization of the carbon allotrope GUITAR. The main conclusions that can be made from this work are as follows:

- I. XRD spectra of GUITAR indicates a poly-orientated, polycrystalline (not amorphous) structure, with a d-spacing of .350 nm, compared to 0.334 nm for typical graphite. This suggests the presence of interplanar bonding defects within the layers of GUITAR, which could be responsible for the inflated d-spacing value.
- II. GUITAR's absolute density of  $1.76 \text{ g/cm}^3$  places it within the range of hard amorphous carbon, but we know from (I) that GUITAR is polycrystalline, and not amorphous.
- III. GUITAR's low skeletal density,  $0.57 \text{ g/cm}^3$  indicates that it is a nano-porous material, but electrochemical data shows that intercalation of electrolyte does not occur.
- IV. G-Band position does not shift, which agrees with graphitic carbon such as HOPG.
- V. The grain size  $L_a$  as obtained from the I(D)/I(G) ratio via Multi-wavelength Raman analysis changes with laser wavelength, which isn't plausible since grain size is a physical property that is fixed. This indicates that the grain size must be less than 2 nm, which is the lower limit of the Tuinstra-Koenig relationship.
- VI. SSNMR shows that GUITAR has a distribution of chemical shifts. It is not a pure  $sp^2$  material as was previously thought. It may contain up to 50%  $sp^3$  hybridized bonding.
- VII. GUITAR contains very little, if any hydrogen.
- VIII. GUITAR displays a significantly higher surface potential than HOPG; in fact GUITAR's surface potential is very similar to the surface potential of the gold standard, suggesting that GUITAR is highly noble, and therefore resistant to oxidation. This has been observed electrochemically.

Electrochemical data presented in previous work had already established GUITAR as unique from other forms of carbon. As has been stated previously, electrochemically it behaves most closely to

that of a diamond-like amorphous carbon (DLC). However, its density is around 50% lower than DLC, likely due to its porosity.

Recent XPS work performed that is not included here, further supports that GUITAR is indeed a graphene-like material with a up to 50%  $sp^3$ -hybridized bonding. With all of these factors taken together, we propose a placement for GUITAR on the ternary phase diagram mentioned earlier (Figure 25).

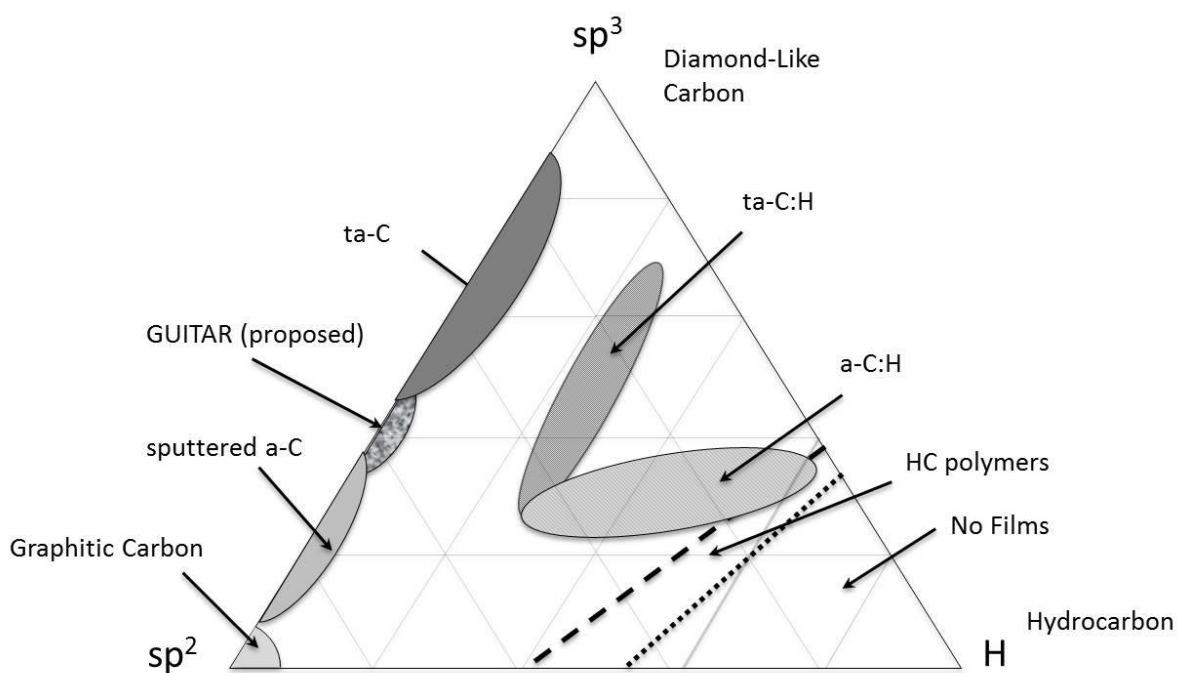


Figure 25. GUITAR's proposed placement on Jacob and Muller's Ternary Phase Diagram for various carbon materials.

### Future Work

Additional studies that will be useful to further understand GUITAR's fundamental properties and potential applications should include transport measurements and bandgap opening determination. Angular resolved photoemission spectroscopy (ARPES) may also reveal the orientation of the stacked graphene layers in GUITAR. UV-Raman analysis is also very useful in quantifying the  $sp^3$

content of a carbon material. Confocal UV-Raman spectroscopy could be employed to determine the  $sp^2$  and  $sp^3$  distribution on both the surface as well as into the bulk of the material, giving insight into the type of bonding and defects that exist internally as well as at the exterior. Coupling this data with atomic-level modeling could provide a starting point to elucidate a molecular structure of the strange material called GUITAR.

## **Conclusion**

GUITAR is a highly noble, porous material, consisting of nanometer-sized grains of two-dimensional graphene-like layers, which are interconnected by three-dimensional diamond-like “defects.” This unique structure begins to give some explanation as to why GUITAR displays many of the useful and superior qualities of both graphene and diamond.

The simple fact that has been constant throughout this work, is that GUITAR’s physical and chemical profile does not align neatly with any known form of carbon. This is in agreement with the electrochemical evidence previously presented by Gyan et al.<sup>13</sup> Therefore, we here confirm that GUITAR is indeed an altogether new, and truly unique allotrope of carbon. It is our hope to have presented information here that will be useful in the continuation of GUITAR research as well as the development of the many applications that are both currently being explored, and yet to be discovered.

## References:

- <sup>1</sup> T. V. Le Doan, N. W. Bostrom, A. K. Burnham, R. L. Kleinberg, A. E. Pomerantz, and P. Allix. 2013. "Green River Oil Shale Pyrolysis: Semi-Open Conditions." *Energy & Fuels* 6447-6459.
- <sup>2</sup> Alan K. Burnham, Robert W. Taylor. 1982. "Occurrence and Reactions of Oil Shale Sulfur." *Occurrence and Reactions of Oil Shale Sulfur*. Golden, Colorado: Lawrence Livermore Laboratory. 1-24.
- <sup>3</sup> Yuqun Xie, Simon D. McAllister, Seth A. Hyde, Jency Pricilla Sundararajan, B. A. Fouetio Kengne, David N. McLroy and I. Francis Cheng. 2012. "Sulfur as an important co-factor in the formation of multilayer graphene in the thermolyzed asphalt reaction." *Journal of Materials Chemistry* 5723-5729.
- <sup>4</sup> JIE GAO, CHENGYAN LIU, LEI MIAO, XIAOYANG WANG, and YU CHEN. 2015. "Free-Standing Reduced Graphene Oxide Paper with High Electrical Conductivity." *Journal of Electronic Materials* 1290-1295.
- <sup>5</sup> Haiqun Chen, Marc B. Muller, Kerry J. Gilmore, Gordon G. Wallace, and Dan Li. 2008. "Mechanically Strong, Electrically Conductive, and Biocompatible Graphene Paper." *Advanced Materials* 3557-3561.
- <sup>6</sup> A.C. Ferrari, J. Robertson. 2000. "Interpretation of Raman spectra of disordered and amorphous carbon." *Physical Review B* 14095 14107
- <sup>7</sup> Kabir, Humayun, Isaiah O. Gyan, Jeremy D. Foutch, Haoyu Zhu, and I. Francis Cheng. 2016. "Application of GUTTAR on the Negative Electrode of the Vanadium Redox Flow Battery: Improved V<sup>3+</sup>/V<sup>2+</sup> Heterogeneous Electron Transfer with Reduced Hydrogen Gassing." *Journal of Carbon Research* 13.
- <sup>8</sup> Wei D, Liu Y, Wang Y, Zhang H, Huang L, Yu G. 2009. "Synthesis of N- doped graphene by chemical vapor deposition and its electrical properties." *Nano Letters* 1752.
- <sup>9</sup> Blyth R, Buqa H, Netzer F, Ramsey M, Besenhard J, Golob P, et al. " XPS studies of graphite electrode materials for lithium ion batteries." *Applied Surface Sciences*, 2000: 99-106
- <sup>10</sup> Arsat R, Breedon M, Shafiei M, Kalantar-zadeh K, Wlodarski W, Gilje S, et al. 2008. "Graphene-like nano-Sheets/36 LiTaO<sub>3</sub> surface acoustic wave hydrogen gas sensor." *IEEE SENSORS Conference* 188-191.
- <sup>11</sup> Su C, Xu Y, Zhang W, Hao J, Tang X, Tsai C, et al. 2009. "Electrical and spectroscopic characterizations of ultra-large reduced graphene oxide monolayers." *Chemical Materials* 5674-80.
- <sup>12</sup> Jang J, Lee C, Lyu S, Lee T, Lee C. 2004. " Structural study of nitrogen- doping effects in bamboo-shaped multiwalled carbon nanotubes." *Applied Physics Letters* 2877-9.
- <sup>13</sup> Isaiah O. Gyan, Peter M. Wojcik, D. Eric Aston, David N. McLroy, I. Francis Cheng. "A Study of the Electrochemical Properties of New Graphitic Material: GUTTAR." *ChemElectroChem*, 2015: 700-706
- <sup>14</sup> He, Bob B. Two-Dimensional X-Ray Diffraction. New Jersey: Wiley, 2009.
- <sup>15</sup> Field, J.E. *Properties of Diamond*. London: Academic Press, 1993
- <sup>16</sup> McKenzie, D.R. *Rep. Prog. Phys.*, 1996: 1611
- <sup>17</sup> P.J. Fallon, V.S. Veerasamy, C.A. David, J. Robinsen, GAJ Amaratunga, W.I. Milne, J. Koskinen, *Physics Review B*, 1993: 4777.
- <sup>18</sup> G.M. Pharr, D.LCallahan, S.D. McAdams, T.Y. Tsui S. Anders, A Anders, J.W. Ager, I.G. Brown, C.S. Bhatia, S.R.P. Silva, J. Robinson." *Applied Physical Letters*, 1996: 779.
- <sup>19</sup> W. Jacob, W. Moller. *Applied Physics Letters*, 1993: 1771
- <sup>20</sup> Kelly, B.T. *Physics of Grpabite*. London: Applied Science Publishers, 1981
- <sup>21</sup> P. Koidl, C. Wagner, B. Dischler, J. Wagner, M. Ramsteiner, *Material Science Forum*, 1990
- <sup>22</sup> Robertson, J. *Advanced Physics*, 1986: 317
- <sup>23</sup> M.S. Dressshaus, G. Dresselhaus, P.C. Eklund, *Science of Fullerenes and Carbon Nanotubes*. London: Academic Press, 1996

---

<sup>24</sup> M.F. Ashby, D.R.H. Jones. *Engineering Materials*. Oxford: Pergamon Press, 1980.

<sup>25</sup> Andrea C. Ferrari, Denis M. Basko. "Raman spectroscopy as a versatile tool for studying the properties of graphene." *Nature Nanotechnology*, 2010: 235-246