

REDUCTION STUDY OF OXIDIZED TWO-DIMENSIONAL GRAPHENE-BASED
MATERIALS BY CHEMICAL AND THERMAL REDUCTION METHODS

by

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TABLE OF CONTENTS

	Page
ACKNOWLEDGEMENTS	iv
LIST OF TABLES	vii
LIST OF FIGURES	x
ABSTRACT	xx
 CHAPTER	
1. INTRODUCTION	1
1.1 Introduction	1
1.2 Oxidation methods for graphene/graphite oxide preparation	4
1.3 Graphene/graphite oxide reduction methods	4
1.3.1 Chemical reduction methods	5
1.3.1.1 Hydrazine reduction	6
1.3.1.2 Hydroxylamine reduction	9
1.3.1.3 Sodium borohydride reduction	10
1.3.1.4 Sodium bisulfite reduction	11
1.3.1.5 Benzyl alcohol reduction	12
1.3.2 Thermal reduction methods	13
1.4 Characterization methods	16
1.4.1 Energy dispersive X-ray spectroscopy (EDS)	16
1.4.2 Raman spectroscopy	17
1.5 Dissertation efforts	21
1.6 Technical relevance	21
2. EXPERIMENTAL METHODS	22
2.1 Material synthesis	22
2.1.1 Graphite oxide synthesis	22
2.1.2 Humic acid synthesis	23
2.2 Chemical reductions	23
2.2.1 Hydrazine reduction	23
2.2.2 Hydroxylamine reduction	24
2.2.3 Sodium borohydride reduction	25

2.2.4 Sodium bisulfite reduction.....	25
2.2.5 Benzyl alcohol reduction	26
2.3 Thermal reductions	26
2.4 Material characterization	28
2.4.1 Scanning electron microscopy/energy dispersive X-ray spectroscopy	28
2.4.2 Raman spectroscopy	28
3. GRAPHITE OXIDE REDUCTION: RESULTS AND DISCUSSION.....	30
4. HUMIC ACID REDUCTION: RESULTS AND DISCUSSION.....	37
5. CONCLUSIONS.....	47
5.1 Summary	47
5.2 Future Work	48
APPENDIX SECTION.....	49
LITERATURE CITED	126

LIST OF TABLES

Table	Page
1. Material abbreviations	2
2. Abbreviation list for graphite oxide materials.	31
3. Compilation of graphite oxide materials in order of descending % oxygen and correlated to G band position, $I_{(D)}/I_{(G)}$, and FWHM of G band.	35
4. Abbreviation list for humic acid materials.....	38
5. Compilation of humic acid materials in order of descending % oxygen and correlated to G band position, $I_{(D)}/I_{(G)}$, and FWHM of G band	46
A1-1. Graphite oxide standard C/O ratios	49
A1-2. Hydrazine reduced graphite oxide C/O ratios	51
A1-3. Hydroxylamine reduced graphite oxide C/O ratios	53
A1-4. Sodium borohydride reduced graphite oxide C/O ratios	55
A1-5. Sodium bisulfite reduced graphite oxide C/O ratios.....	57
A1-6. Benzyl alcohol reduced graphite oxide C/O ratios	60
A1-7. Thermally reduced graphite oxide at 500 °C C/O ratios.....	61
A1-8. Thermally reduced graphite oxide at 700 °C C/O ratios.....	63
A1-9. Thermally reduced graphite oxide at 900 °C C/O ratios.....	65
A1-10. Raman spectral data for graphite oxide standard.....	67
A1-11. Raman spectral data for hydrazine reduced graphite oxide.....	70
A1-12. Raman spectral data for hydroxylamine reduced graphite oxide	72

A1-13. Raman spectral data for sodium borohydride reduced graphite oxide	75
A1-14. Raman spectral data for sodium bisulfite reduced graphite oxide.....	77
A1-15. Raman spectral data for benzyl alcohol reduced graphite oxide	80
A1-16. Raman spectral data for thermally reduced graphite oxide at 500 °C	82
A1-17. Raman spectral data for thermally reduced graphite oxide at 700 °C	85
A1-18. Raman spectral data for thermally reduced graphite oxide at 900 °C	88
A2-1. Humic acid standard C/O ratios.....	91
A2-2. Hydrazine reduced humic acid C/O ratios.....	93
A2-3. Hydroxylamine reduced humic acid C/O ratios	93
A2-4. Sodium borohydride reduced humic acid C/O ratios	94
A2-5. Sodium bisulfite reduced humic acid C/O ratios.....	95
A2-6. Benzyl alcohol reduced humic acid C/O ratios	97
A2-7. Thermally reduced humic acid at 500 °C C/O ratios.....	98
A2-8. Thermally reduced humic acid at 700 °C C/O ratios.....	100
A2-9. Thermally reduced humic acid at 900 °C C/O ratios.....	102
A2-10. Raman spectral data for humic acid standard	103
A2-11. Raman spectral data for hydroxylamine reduced humic acid.....	107
A2-12. Raman spectral data for sodium borohydride reduced humic acid.....	110
A2-13. Raman spectral data for sodium bisulfite reduced humic acid	113
A2-14. Raman spectral data for benzyl alcohol reduced humic acid	115
A2-15. Raman spectral data for thermally reduced humic acid at 500 °C.....	118

A2-16. Raman spectral data for thermally reduced humic acid at 700 °C.....	120
A2-17. Raman spectral data for thermally reduced humic acid at 900 °C.....	123

LIST OF FIGURES

Figure	Page
1. Structure of materials used, (a) pristine graphene, (b) graphene oxide, and (c) proposed structure of humic acid	2
2. Oxidation and reduction process.....	5
3. Effect of amorphization on G band position vs. $I_{(D)}/I_{(G)}$ ratios	18
4. Amorphization of graphitic carbon.....	18
5. Thermal reduction at 500 °C, (a) GTO, (b) HA	27
6. Thermal reduction at 700 °C, (a) GTO, (b) HA	27
7. Thermal reduction at 900 °C, (a) GTO, (b) HA	27
8. SEM images of GTO prior to reduction, (a) evidence of exfoliated particles, scale bar = 2 μm , (b) evidence of agglomerated particles, scale bar = 5 μm	30
9. SEM image of GTO indicating particle size distribution	31
10. C/O ratios for all graphite oxide materials.....	32
11. SEM images of GTO and reduced GTOs, (a) HGTO, scale bar = 5 μm , (b) HAGTO, scale bar = 10 μm , (c) NBGTO, scale bar = 10 μm , (d) NBSGTO, scale bar = 5 μm , (e) BAGTO, scale bar = 30 μm , (f) Concentrated GTO prior to thermal reduction, scale bar = 20 μm , (g) GTO500, scale bar = 5 μm , (h) GTO700, scale bar = 10 μm , (i) GTO900 = 40 μm	33
12. G band positions for all GTO materials.....	34
13. Raman spectra for all GTO materials with correlating $I_{(D)}/I_{(G)}$ ratios.....	35
14. SEM images of HA prior to reduction, (a) Evidence of exfoliated particles and plate-like morphology, scale bar = 1 μm , (b) evidence of agglomerated particles, scale bar = 2 μm	37
15. SEM image of HA indicating the particle size distribution, scale bar = 1 μm	38

16. C/O ratios for all humic acid materials	39
17. SEM images of HA and reduced HA's. (a) HHA, scale bar = 2 μm , (b) HAHA, scale bar = 3 μm , (c) NBHA, scale bar = 400 nm, (d) NBSHA, scale bar = 1 μm , (e) BAHA, scale bar = 6 μm , (f) Concentrated HA prior to thermal reduction, scale bar = 20 μm , (g) HA500, scale bar = 50 μm , (h) HA700, scale bar = 50 μm , (i) HA900 = 50 μm	41
18. Drying of a dispersed material on a solid substrate	42
19. G band positions for all HA materials	43
20. Raman spectra for all HA materials with correlating $I_{\text{(D)}}/I_{\text{(G)}}$ ratios	45
A1-1. Image of EDS areas 1-11 for graphite oxide standard.....	49
A1-2. EDS spectra of areas 1-11 for graphite oxide standard	50
A1-3. Image of EDS areas 1 and 2 – sample 2 for hydrazine reduced graphite oxide	51
A1-4. EDS spectra for areas 1 and 2 – sample 2 for hydrazine reduced graphite oxide ..	51
A1-5. Image of EDS areas 1 and 2, spots 1-3 – sample 3 for hydrazine reduced graphite oxide.....	52
A1-6. EDS spectra for areas 1 and 2, spots 1-3 – sample 3 for hydrazine reduced graphite oxide.....	52
A1-7. Image of EDS area 1 – sample 1 for hydroxylamine reduced graphite oxide	53
A1-8. EDS spectra for area 1 – sample 1 for hydroxylamine reduced graphite oxide	53
A1-9. Image of EDS areas 1-3 – sample 2 for hydroxylamine reduced graphite oxide ...	54
A1-10. EDS spectra for areas 1-3 – sample 2 for hydroxylamine reduced graphite oxide.....	54
A1-11. Image of EDS areas 1 and 2 – sample 3 for hydroxylamine reduced graphite oxide.....	55

A1-12. EDS spectra for areas 1 and 2 – sample 3 for hydroxylamine reduced graphite oxide.....	55
A1-13. Image of EDS areas 1-4 – sample 1 for sodium borohydride reduced graphite oxide.....	56
A1-14. EDS spectra for areas 1-4 – sample 1 for sodium borohydride reduced graphite oxide.....	56
A1-15. Image of EDS areas 1 and 2 – sample 2 for sodium borohydride reduced graphite oxide.....	57
A1-16. EDS spectra for areas 1 and 2 – sample 2 for sodium borohydride reduced graphite oxide.....	57
A1-17. Image of EDS area 1 – sample 1 for sodium bisulfite reduced graphite oxide	58
A1-18. EDS spectrum for area 1 – sample 1 for sodium bisulfite reduced graphite oxide.....	58
A1-19. Image of EDS areas 1 and 2 – sample 2 for sodium bisulfite reduced graphite oxide.....	58
A1-20. EDS spectra for areas 1 and 2 – sample 2 for sodium bisulfite reduced graphite oxide.....	59
A1-21. Image of EDS areas 1 and 2 – sample 3 for sodium bisulfite reduced graphite oxide.....	59
A1-22. EDS spectra for areas 1 and 2 – sample 3 for sodium bisulfite reduced graphite oxide.....	59
A1-23. Image of EDS areas 1-3 – sample 1 for benzyl alcohol reduced graphite oxide..	60
A1-24. EDS spectra for areas 1-3 – sample 1 for benzyl alcohol reduced graphite oxide.....	60
A1-25. Image of EDS areas 1-3 – sample 2 for benzyl alcohol reduced graphite oxide..	61
A1-26. EDS spectra for areas 1-3 – sample 2 for benzyl alcohol reduced graphite oxide.....	61

A1-27. Image of EDS spots 1-6 for thermally reduced graphite oxide at 500 °C	62
A1-28. EDS spectra for spots 1-6 for thermally reduced graphite oxide at 500 °C.....	62
A1-29. Image of EDS spots 1-10 for thermally reduced graphite oxide at 700 °C	63
A1-30. EDS spectra for spots 1-10 for thermally reduced graphite oxide at 700 °C.....	64
A1-31. Image of EDS spots 1-8 for thermally reduced graphite oxide at 900 °C	65
A1-32. EDS spectra for spots 1-8 for thermally reduced graphite oxide at 900 °C.....	66
A1-33. Raman spectrum of pristine graphite.....	67
A1-34. Graphite oxide standard – spot 1	68
A1-35. Graphite oxide standard – spot 2	68
A1-36. Graphite oxide standard – spot 3	68
A1-37. Graphite oxide standard – spot 4	69
A1-38. Graphite oxide standard – spot 5	69
A1-39. Graphite oxide standard – spot 6	69
A1-40. Hydrazine reduced graphite oxide – spot 1a.....	70
A1-41. Hydrazine reduced graphite oxide – spot 1b	70
A1-42. Hydrazine reduced graphite oxide – spot 2	71
A1-43. Hydrazine reduced graphite oxide – spot 3	71
A1-44. Hydrazine reduced graphite oxide – spot 4	71
A1-45. Hydrazine reduced graphite oxide – spot 5	72
A1-46. Hydrazine reduced graphite oxide – spot 6	72
A1-47. Hydroxylamine reduced graphite oxide – spot 1	73

A1-48. Hydroxylamine reduced graphite oxide – spot 2	73
A1-49. Hydroxylamine reduced graphite oxide – spot 3	73
A1-50. Hydroxylamine reduced graphite oxide – spot 4	74
A1-51. Hydroxylamine reduced graphite oxide – spot 5	74
A1-52. Hydroxylamine reduced graphite oxide – spot 6	74
A1-53. Sodium borohydride reduced graphite oxide – spot 1	75
A1-54. Sodium borohydride reduced graphite oxide – spot 2	75
A1-55. Sodium borohydride reduced graphite oxide – spot 3	76
A1-56. Sodium borohydride reduced graphite oxide – spot 4	76
A1-57. Sodium borohydride reduced graphite oxide – spot 5	76
A1-58. Sodium borohydride reduced graphite oxide – spot 6	77
A1-59. Sodium borohydride reduced graphite oxide – spot 7	77
A1-60. Sodium bisulfite reduced graphite oxide – spot 1	78
A1-61. Sodium bisulfite reduced graphite oxide – spot 2	78
A1-62. Sodium bisulfite reduced graphite oxide – spot 3	78
A1-63. Sodium bisulfite reduced graphite oxide – spot 4	79
A1-64. Sodium bisulfite reduced graphite oxide – spot 5	79
A1-65. Sodium bisulfite reduced graphite oxide – spot 6	79
A1-66. Benzyl alcohol reduced graphite oxide – spot 1	80
A1-67. Benzyl alcohol reduced graphite oxide – spot 2	80
A1-68. Benzyl alcohol reduced graphite oxide – spot 3	81

A1-69. Benzyl alcohol reduced graphite oxide – spot 4.....	81
A1-70. Benzyl alcohol reduced graphite oxide – spot 5.....	81
A1-71. Benzyl alcohol reduced graphite oxide – spot 6.....	82
A1-72. Thermally reduced graphite oxide at 500 °C – spot 1.....	82
A1-73. Thermally reduced graphite oxide at 500 °C – spot 2.....	83
A1-74. Thermally reduced graphite oxide at 500 °C – spot 3.....	83
A1-75. Thermally reduced graphite oxide at 500 °C – spot 4.....	83
A1-76. Thermally reduced graphite oxide at 500 °C – spot 5.....	84
A1-77. Thermally reduced graphite oxide at 500 °C – spot 6.....	84
A1-78. Thermally reduced graphite oxide at 700 °C – spot 1.....	85
A1-79. Thermally reduced graphite oxide at 700 °C – spot 2.....	85
A1-80. Thermally reduced graphite oxide at 700 °C – spot 3.....	86
A1-81. Thermally reduced graphite oxide at 700 °C – spot 4.....	86
A1-82. Thermally reduced graphite oxide at 700 °C – spot 5.....	86
A1-83. Thermally reduced graphite oxide at 700 °C – spot 6.....	87
A1-84. Thermally reduced graphite oxide at 700 °C – spot 7.....	87
A1-85. Thermally reduced graphite oxide at 700 °C – spot 8.....	87
A1-86. Thermally reduced graphite oxide at 900 °C – spot 1.....	88
A1-87. Thermally reduced graphite oxide at 900 °C – spot 2.....	88
A1-88. Thermally reduced graphite oxide at 900 °C – spot 3.....	89
A1-89. Thermally reduced graphite oxide at 900 °C – spot 4.....	89

A1-90. Thermally reduced graphite oxide at 900 °C – spot 5.....	89
A1-91. Thermally reduced graphite oxide at 900 °C – spot 6.....	90
A2-1. Image of EDS areas 1-6 humic acid standard.....	91
A2-2. EDS spectra for areas 1-6 humic acid standard.....	92
A2-3. Image of EDS spots 1-6 for hydroxylamine reduced humic acid.....	93
A2-4. EDS spectra for spots 1-6 for hydroxylamine reduced humic acid.....	94
A2-5. Image of EDS spots 1-6 for sodium borohydride reduced humic acid.....	94
A2-6. EDS spectra for spots 1-6 for sodium borohydride reduced humic acid.....	95
A2-7. Image of EDS spots 1-6 for sodium bisulfite reduced humic acid.....	96
A2-8. EDS spectra for spots 1-6 for sodium bisulfite reduced humic acid.....	96
A2-9. Image of EDS spots 1-6 for benzyl alcohol reduced humic acid.....	97
A2-10. EDS spectra for spots 1-6 for benzyl alcohol reduced humic acid.....	97
A2-11. Image of EDS spots 1-6 for thermally reduced humic acid at 500 °C.....	98
A2-12. EDS spectra for spots 1-6 for thermally reduced humic acid at 500 °C.....	99
A2-13. Image of EDS for areas 1-10 for thermally reduced humic acid at 700 °C.....	100
A2-14. EDS spectra for areas 1-10 for thermally reduced humic acid at 700 °C.....	101
A2-15. Image of EDS for areas 1-8 for thermally reduced humic acid at 900 °C.....	102
A2-16. EDS spectra for areas 1-8 for thermally reduced humic acid at 900 °C.....	102
A2-17. Humic acid standard – spot 1.....	103
A2-18. Humic acid standard – spot 2.....	103
A2-19. Humic acid standard – spot 3.....	104

A2-20. Humic acid standard – spot 4.....	104
A2-21. Humic acid standard – spot 5.....	104
A2-22. Humic acid standard – spot 6.....	105
A2-23. Hydrazine reduced humic acid – spot 1.....	105
A2-24. Hydrazine reduced humic acid – spot 2.....	105
A2-25. Hydrazine reduced humic acid – spot 3.....	106
A2-26. Hydrazine reduced humic acid – spot 4.....	106
A2-27. Hydrazine reduced humic acid – spot 5.....	106
A2-28. Hydrazine reduced humic acid – spot 6.....	107
A2-29. Hydroxylamine reduced humic acid – spot 1	107
A2-30. Hydroxylamine reduced humic acid – spot 2	108
A2-31. Hydroxylamine reduced humic acid – spot 3	108
A2-32. Hydroxylamine reduced humic acid – spot 4	108
A2-33. Hydroxylamine reduced humic acid – spot 5	109
A2-34. Hydroxylamine reduced humic acid – spot 6	109
A2-35. Sodium borohydride reduced humic acid – spot 1	110
A2-36. Sodium borohydride reduced humic acid – spot 2	110
A2-37. Sodium borohydride reduced humic acid – spot 3	111
A2-38. Sodium borohydride reduced humic acid – spot 4	111
A2-39. Sodium borohydride reduced humic acid – spot 5	111
A2-40. Sodium borohydride reduced humic acid – spot 6	112

A2-41. Sodium borohydride reduced humic acid – spot 7	112
A2-42. Sodium bisulfite reduced humic acid – spot 1	113
A2-43. Sodium bisulfite reduced humic acid – spot 2	113
A2-44. Sodium bisulfite reduced humic acid – spot 3	114
A2-45. Sodium bisulfite reduced humic acid – spot 4	114
A2-46. Sodium bisulfite reduced humic acid – spot 5	114
A2-47. Sodium bisulfite reduced humic acid – spot 6	115
A2-48. Benzyl alcohol reduced humic acid – spot 1	116
A2-49. Benzyl alcohol reduced humic acid – spot 2	116
A2-50. Benzyl alcohol reduced humic acid – spot 3	116
A2-51. Benzyl alcohol reduced humic acid – spot 4	117
A2-52. Benzyl alcohol reduced humic acid – spot 5	117
A2-53. Benzyl alcohol reduced humic acid – spot 6	117
A2-54. Benzyl alcohol reduced humic acid – spot 7	118
A2-55. Thermally reduced humic acid at 500 °C – spot 1	118
A2-56. Thermally reduced humic acid at 500 °C – spot 2	119
A2-57. Thermally reduced humic acid at 500 °C – spot 3	119
A2-58. Thermally reduced humic acid at 500 °C – spot 4	119
A2-59. Thermally reduced humic acid at 500 °C – spot 5	120
A2-60. Thermally reduced humic acid at 500 °C – spot 6	120
A2-61. Thermally reduced humic acid at 700 °C – spot 1	121

A2-62. Thermally reduced humic acid at 700 °C – spot 2	121
A2-63. Thermally reduced humic acid at 700 °C – spot 3	121
A2-64. Thermally reduced humic acid at 700 °C – spot 4	122
A2-65. Thermally reduced humic acid at 700 °C – spot 5	122
A2-66. Thermally reduced humic acid at 700 °C – spot 6	122
A2-67. Thermally reduced humic acid at 700 °C – spot 7	123
A2-68. Thermally reduced humic acid at 900 °C – spot 1	123
A2-69. Thermally reduced humic acid at 900 °C – spot 2	124
A2-70. Thermally reduced humic acid at 900 °C – spot 3	124
A2-71. Thermally reduced humic acid at 900 °C – spot 4	124
A2-72. Thermally reduced humic acid at 900 °C – spot 5	125
A2-73. Thermally reduced humic acid at 900 °C – spot 6	125

ABSTRACT

Graphene is a two-dimensional (2D) sp^2 -hybridized carbon-based material possessing properties which include high electrical conductivity, ballistic thermal conductivity, tensile strength exceeding that of steel, high flexural strength, optical transparency, and the ability to adsorb and desorb atoms and molecules. Due to the characteristics of said material, graphene is a candidate for applications in integrated circuits, electrochromic devices, transparent conducting electrodes, desalination, solar cells, thermal management materials, polymer nanocomposites, and biosensors. Despite the above mentioned properties and possible applications, very few technologies have been commercialized utilizing graphene due to the high cost associated with the production of graphene. Therefore, a great deal of effort and research has been performed to produce a material that provides similar properties, reduced graphene oxide (RGO) to the ease of commercial scaling of the production processes. This material is typically prepared through the oxidation of graphite in an aqueous media to graphene oxide (GO) followed by reduction to yield RGO. Although this material has been extensively studied, there is a lack of consistency in the scientific community regarding the analysis of the resulting RGO material. In this dissertation, a study of the reduction methods for GO and an alternate 2D carbon-based material, humic acid (HA), followed by analysis of the materials using Raman spectroscopy and Energy Dispersive X-ray Spectroscopy (EDS). Means of reduction will include chemical and thermal methods. Characterization of the material has been carried out on both before and after reduction.

CHAPTER 1

INTRODUCTION

1.1 Introduction

Reduction of GO has been demonstrated by a variety of reduction methods including chemical and thermal treatment^{1,2}. Although the production of reduced graphene oxide (RGO) is not an expensive process, a recent report indicates that HA, a highly oxidized 2D carbonaceous material found in the mines of North Dakota as Leonardite coal, has the potential to produce graphene via thermal annealing on a copper substrate³. The use of HA as a starting material for graphene allows the researcher to bypass the oxidation process, as it is naturally oxidized and can be beneficial to the future of graphene and graphene-based materials. GO differs from graphene in that it possesses functional groups, including epoxide, carboxyl, and hydroxyl bonded to the basal plane and the edges⁴. The structure of HA is not fully understood due to the complex nature of the material, however, the proposed structure is a macromolecular material with high carbon content and includes both regions of sp^2 and sp^3 hybridized carbons. The functional groups are approximately the same as found in GO with the exception of nitrogen and sulfur moieties, however, complexity is introduced as the number and types of functional groups is dependent on where the material is found due to the manner in which the material is formed over time⁵. HA is produced via degradation of organic matter, therefore the structure is highly dependent upon location and age of the soil or coal⁵. Despite the material's complex nature, a structure was proposed in 1982 by Stevenson et al. and is widely cited in works containing HA⁶. The structure of graphene, GO and HA can be found in Figure 1 below. For purposes of clarity, graphite and

graphite oxide are terms used when the material is stacked. Therefore, the figure provided is demonstrative of graphene and graphene oxide. Although many authors in literature use the terms graphene oxide and graphite oxide interchangeably. Abbreviations utilized throughout the document are provided in Table 1 below.

Table 1. Material abbreviations

Abbreviation	Material
Graphene oxide	GO
Graphite oxide	GTO
Reduced graphene oxide	RGO
Reduced graphite oxide	RGTO

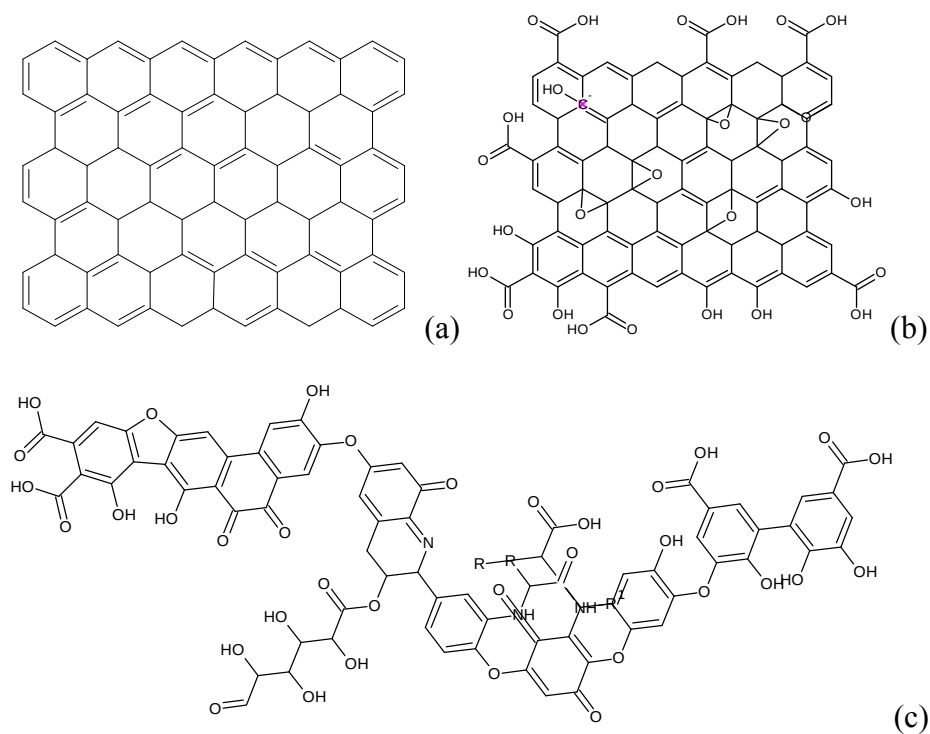


Figure 1. Structure of materials used, (a) pristine graphene, (b) graphene oxide, and (c) proposed structure of humic acid⁶

Although there are many sources of HA, the HA utilized within these studies comes from Leonardite coal, the lowest grade of Lignite coal, making the material inexpensive. Leonardite coal is often treated as a waste stream for coal mining as the power rating is too low for commercial use. Because the material is inexpensive and readily available in nature, the material is conducive to the commercialization of graphene-based materials. Several review articles and studies are available which provide extensive insight into the reduction of GO/GTO via chemical^{1,4,7} and thermal treatment^{2,8}. Despite the availability a wide array of data reported in the field of GO/GTO reduction, there is a lack of consistency in the collection and analysis thereof of the data collected during the characterization of the material, particularly in regards to Raman spectroscopy. In order to effectively understand the nature of the material, an understanding of the Raman spectrum both before and after reduction is necessary. All materials consisting of symmetrical bonding configurations are considered Raman active⁹. For example, diamond has a spectrum which is considerably different from graphene due to the bonding differences between the two materials⁹. Furthermore, GO falls into three regimes throughout the reduction process and knowledge of which regime the material falls into is fundamental to the characterization of the resulting reduced material⁹. Therefore, the work conducted within this study is an evaluation of the reducing efficacy of a variety of well-known chemical reductants and thermal reduction at various temperatures. Following the above described reductions, the materials are characterized to evaluate the extent of reduction and sp^2 restoration via Raman spectroscopy and Energy Dispersive X-ray Spectroscopy (EDS).

1.2 Oxidation methods for graphene/graphite oxide preparation

The first reported preparation of GO/GTO was in 1859 when a Professor at the University of Oxford inadvertently synthesized graphite oxide while attempting to determine the molecular weight of graphite¹⁰. Graphite was mixed with fuming nitric acid and combined with potassium chlorate and heated at 60 °C for several days¹⁰. The oxidation process was repeated four times resulting in a yellow solid after drying at 100 °C¹⁰. The material was determined to have a C:H:O ratio of 61.04:1.85:37.11 and was readily dispersed in aqueous or alkaline solvents and hence called the material “graphic acid”¹⁰. The next report of oxidation of graphite was in 1898 when potassium chlorate and concentrated sulfuric acid were used as oxidants¹¹. The report indicated that the oxidation yielded similar results in terms of C/O ratios but the process did not necessitate repetitive oxidation steps¹¹. In 1939, Hoffman successfully oxidized graphite without using fuming nitric acid¹². A safer alternative was developed by Hummer and Offeman where the oxidant was replaced by potassium permanganate mixed with sulfuric acid and sodium nitrate¹³. The “Hummers” method has since become widely utilized in the preparation of graphite/graphene oxide. However, all methods described above are dangerous as they involve the evolution of toxic gases, including NO₂, N₂O₄, and ClO₂¹. Finally in 2010, Tour et al. reported the oxidation of graphite with nitric and phosphoric acid and stated that the oxidized material was more thoroughly oxidized while the basal plane remained intact¹⁴.

1.3 Graphene/graphite oxide reduction methods

The following sections provide the background necessary for the reduction work performed in this study. To assist in the understanding of the oxidation and reduction steps which yield GO, a schematic of the process is provided in Figure 2. Graphite sheets first undergo an oxidation process to form GTO. The oxidation process introduces polar functional groups allowing dispersion of the material in aqueous media. Upon sonication, the oxidized sheets are separated and the material is then termed GO. Once the material is exfoliated, a reduction process is performed to remove the oxygen functionality from the material to restore the sp^2 domains. If the material is then deposited on a substrate and annealed, the material will be termed RGO, however, the material often ranges from single- to multi-layer RGO due to agglomeration. The material is not termed graphene because the oxidation produces defects which cannot be never fully repaired, however, graphene-like properties can be regained.

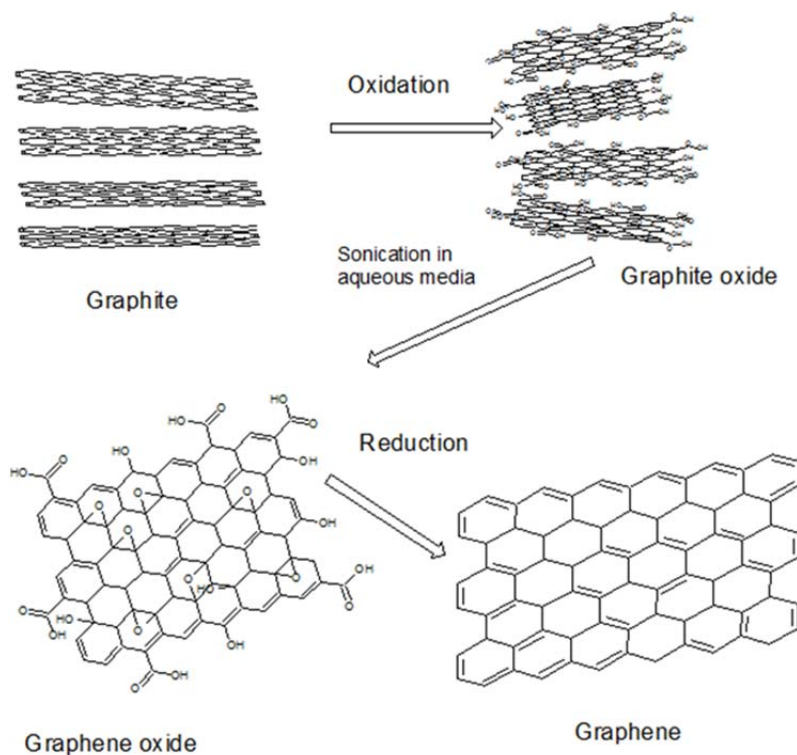


Figure 2. Oxidation and reduction process

1.3.1 Chemical reduction methods

The chemical reduction of GO/GTO has been widely studied. The first report of a chemical reduction of graphite oxide occurred in 1963, where Braur, et al. studied the effect of a variety of chemicals on graphite oxide including hydrazine, hydroxylamine, hydroiodic acid, Fe(II), and Sn(II) as reductants for the removal of oxygen¹. Because GO can be exfoliated and isolated upon oxidation, the focus of reduction methods for GO has increased. Because the material is chemically identical to GO, the information gained from the RGO can be correlated to RGTO. A qualitative method for indication of reduction of GO is a color change of the dispersion from a brownish color to black. Also, the material becomes more hydrophobic and aggregation of the platelets occur¹. Furthermore, an increase in the C/O ratio is noted¹. Some mechanism of reduction has been reported for a variety of reductants studied and are discussed in the literature as “well-supported”¹ and have been used in synthetic organic chemistry with supported modes of reaction. However, some reductants are less understood and are referred to as “proposed”¹, as they have not been utilized in synthetic organic chemistry and lack formal mechanisms for their reaction. Furthermore, they are not commonly used for the reduction of oxygen functional groups¹. Throughout the course of the study, reductants of both classes have been used and within the discussion to follow, their classification will be designated. For more information regarding chemical reductions, it is suggested that the reader refer to articles by Chua and Pumera¹. Below is a review of the reductants utilized within the current study and their efficacy in the reduction of GO/GTO. There is a lack of reduction studies with humic acid to achieve graphene-like structure and

properties with the exception of a study performed by Beall et al., therefore, the discussion will be limited to that study³.

1.3.1.1 Hydrazine reduction

Hydrazine has the chemical formula N_2H_4 and is a well-established reductant used in reduction reactions to remove carbonyl functionalities¹. It is often used in the Wolff-Kishner reduction and for in the synthesis of heterocyclic materials and is known for its antioxidant properties as the compound readily scavenges oxygen. This compound is highly toxic and can be dangerous if not properly handled. The first report of GO/GTO reduction by hydrazine was performed by Boehm et al. and is discussed in two separate studies in 1962 wherein the authors report the preparation and characterization of very thin carbon films^{15,16}. More recently, the reduction of GO/GTO was reported by Ruoff, et al. where C/O values of 10.3 were measured in comparison to 2.7 for GO/GTO. Furthermore, the conductivity was found to be 2420 Sm^{-1} , as compared to graphite which has a conductivity of 2500 Sm^{-1} ¹⁷. Raman spectroscopy was also used to evaluate the material and with an observed increase in the intensity of the D band attributed to a reduction in the size of in-plane sp^2 domains¹⁷. They further discuss that the observation is due to formation of new graphitic regions that are smaller than the regions in the GO/GTO prior to reduction with the number of regions being greater than that of GO/GTO¹⁷. When the reduction reaction of GO/GTO is complete, the material begins to aggregate and becomes less susceptible to dispersion in aqueous media due to a reduction in polar functional groups¹. In an attempt to determine the mechanism for reduction the group assumes that the Lerf-Klinowski model of GO/GTO functionalization is correct and that the primary source of oxygen functionality in GO/GTO can be assigned to

hydroxyl and epoxide groups^{18–20}. Furthermore, the model indicates that there exists carbonyl functionalities in the form of lactones, anhydrides, and quinones which are the functional groups which react with hydrazine and form hydrazides and hydrazones and are responsible for trace amounts nitrogen found in the material from elemental analysis^{17–20}. As the primary functional groups on GO/GTO include epoxides and hydroxyls, this mechanism is centered upon the hydrazine compound's reaction with epoxides via a nucleophilic attack on the epoxide producing an alcohol and hydrazine formation¹⁷. They propose that this reaction is followed by formation of an aminoaziridine, releases the alcohol in the form of water and is subsequently thermally eliminated, restoring the double bond¹⁷. The detailed mechanism can be found in references 17, 21, and 22^{17,21,22}. Despite the development of a mechanism for epoxide reduction, the group raises the question of hydroxyl reduction and suggest an area for future research¹⁷. In order to verify their own reports previously made, the group studied NMR and XPS of ¹³C- and ¹⁵N- labelled graphene prepared by reduction with hydrazine monohydrate²³.

Reports of GO/GTO reduction by hydrazine include preparation of a colloidal sample of GO/GTO without the use of stabilizers or surfactants. GO/GTO was suspended in a dimethylformamide (DMF) and water mixture and subsequently reduced with hydrazine²². The same group studied a variety of solvent mixtures including acetone, THF, ethanol, toluene, dichlorobenzene, dimethylsulfoxide, N-methylpyrrolidone, and acetonitrile which did not produce as good of results²². The material produced in the dimethylformamide and water had a measured conductivity as high as 1700 Sm⁻¹, which was increased to 16,000 Sm⁻¹ upon drying at 150 °C²². Another group attempted a similar

study with the addition of phenylhydrazine to assist in dispersion of the material in the solvent and reported that RGO/RGTO was dispersed in DMAc, DMF, NMP, and propylene carbonate and remained dispersed for a minimum of one year²⁴. The group discussed the possibility of a steric contribution of the phenylhydrazine upon reaction preventing aggregation of the platelets²⁴. Furthermore, they have reported a conductivity of $21,000 \text{ Sm}^{-1}$ measured after the material was dried at 150°C ²⁴.

Kaner et al. attempted reacting pure hydrazine with GO/GTO to mitigate the effects of agglomeration observed by the particles in aqueous media²⁵. The group prepared films of GO/GTO and then subsequently exposed them to hydrazine and reported that the resulting material was easily dispersed in organic solvents. The authors attributed this to the presence of N_2H_4^+ counter-ions on the reduced suspension in solvents such as DMSO or DMF which remained dispersed for months at a time²⁵. They reported an isolation of a single layer of RGO as large as $20 \times 40 \mu\text{m}$ ²⁵.

1.3.1.2 Hydroxylamine reduction

Hydroxylamine, with the formula name NH_2OH , is often used as a precursor in the synthesis of oxime and hydroxamic acid functionalities¹ and is also used in the synthesis of Nylon 6. Hydroxylamine is also known to reduce a variety of metal ions including Cu^{2+} , Pd^{2+} , Ag^+ , and Au^{3+} ¹. The use of hydroxylamine to reduce GO/GTO results from its antioxidant properties and is favored due to its non-reactive nature in water. The first group to report the reduction of GO/GTO with hydroxylamine was Guo et al. where they synthesized hydroxylamine *in situ* by mixing hydroxylamine hydrochloride and ammonia and subsequent introduction of GO/GTO²⁶. The reaction yielded a C/O of 9.7 and a conductivity of 1122 Sm^{-1} ²⁶. The resulting RGO/RGTO

remained in suspension upon completion of the reaction attributed to basicity of the media creating repulsive forces due to the negatively charged functional groups²⁶. They proposed a mechanism for reduction which can be found in reference 26. It was proposed that the epoxides are reduced by a ring-opening mechanism and a subsequent proton transfer causing an elimination of a water molecule producing a *N*-hydroxylaziridine intermediate²⁶. It was suggested that similar intermediates were formed during the reduction of the other functional groups. The *N*-hydroxylaziridine intermediate restores the double bond after nitrogen oxide and water was released²⁶. Furthermore, it was suggested that the hydroxylamine was not capable of carbonyl reduction²⁶.

The Chen group also reported the reduction of GO/GTO with hydroxylamine hydrochloride and found the C/O to be 1.5 which increased to 2.5 upon thermal annealing at 200 °C²⁷. XPS measurements indicated that nitrogen was doped in the reduced material²⁷. The sheet resistance measurements show a decrease in resistance from GO/GTO ($\sim 10^{10} \Omega$) by 5 orders of magnitude and after annealing resulted in a sheet resistance of $\sim 10^2 \Omega$ ²⁷. The proposed mechanism of reduction involved electron transfer from the negatively charged nitrogen species in hydroxylamine to the oxygen functionalities of the graphene oxide with a proton present during the reaction²⁷. It was described as possessing p-type semiconductor characteristics at ambient temperatures and pressure and a Dirac point greater than +40V upon FET analysis²⁷. Furthermore, the group tested the RGO/RGTO as a gas sensor sensitive to NO₂ down to 100 ppm and NH₃ diluted to 1% in dry air²⁷.

1.3.1.3 Sodium borohydride reduction

Sodium borohydride, NaBH_4 , is a commonly used reducing agent in synthesis reactions. It is a salt containing a tetrahedral BH_4^- anion readily dissolved in aqueous and polar solvents¹. When reacted with compounds containing carbonyl functional groups, the anion undergoes a hydride transfer forming an oxyanion and an electron-deficient BH_3 ¹. The BH_3 is stabilized forms favorable interaction with the resulting oxyanion. This allows for subsequent hydride transfers. Theoretically, this would continue until all B-H bonds have been cleaved, however, the reaction efficiency is limited by the nature of the carbonyl functional group. It is most efficient in the reduction of aldehydes and ketones to alcohols, however, esters and amides are not reducible¹.

Kamat et al. were the first to report the reduction of GO/GTO during a process of physisorption of gold nanoparticles to the surface of functionalized graphene²⁸. Meanwhile, another group reduced GO/GTO during the first step of a three part synthesis while attempting to reduce GO/GTO and functionalize with sulfonate moieties²⁹. The material was reported to be readily disperse in both aqueous and organic solvents²⁹. Prior to reduction, the material exhibited a conductivity value of 17 Sm^{-1} ²⁹. However, upon reduction, the conductivity increased to 1250 Sm^{-1} ²⁹. Ajayan et al. used NaBH_4 in a total reduction of graphene oxide study³⁰. Another group studied the concentration of NaBH_4 on the conductivity of the resulting RGO/RGTO³¹. A reported C/O of 8.6 and a conductivity measurement of up to 45 Sm^{-1} was measured when the material was reduced by dipping GO/GTO into 150 mM of NaBH_4 ³¹. Sheet resistance was less than that of RGO/RGTO produced by hydrazine reduction and attributed to the lack of functionalization of the material by the reductant³¹.

1.3.1.4 Sodium bisulfite reduction

There is a large variety of sulfur-containing compounds which behave as reductants and the efficacy said compounds in the reduction of GO/GTO was reported³². Sulfur-containing compounds including NaHSO₃, Na₂SO₃, Na₂S₂O₃, Na₂S·9H₂O, SOCl₂, and SO₂, were studied³². The reactions were performed in DMAc/H₂O due to previous reports of enhanced reduction of GO/GTO in DMAc³². SOCl₂ was reported to have the greatest reduction of GO/GTO. Unfortunately, the reaction with SOCl₂ was reported to undergo a highly exothermic reaction with GO/GTO³². The second highest reduction of GO was achieved with sodium bisulfite, NaHSO₃, with a C/O ratio of 7.89 in comparison to hydrazine-reduced GO/GTO with a C/O ratio of 11.4³². It was reported that although the difference in C/O ratios were large, only slight variations of the material's conductivity was observed³². Elemental analysis of the reduced material exhibited trace amounts of sulfur allowing for the formation of a proposed detailed mechanism of reduction that can be located in reference 38³². The mechanism is a two-step S_N2 nucleophilic reaction with a subsequent thermal elimination, where HSO³⁻ is oxidized to SO₄²⁻. This mechanism was confirmed by qualitative examination of the material where Ba²⁺ formed a precipitate of BaSO₄ when dispersed in aqueous media³². When in an aqueous solvent, SOCl₂ forms the HSO³⁻ anion readily, which is proposed to be directly responsible for the reduction of GO/GTO³². It was suggested that all other sulfur-containing species tested followed similar mechanisms upon formation of HSO³⁻³².

1.3.1.5 Benzyl alcohol reduction

In a study by Bielawski et al., alcohols including methanol, ethanol, isopropanol, and benzyl alcohol, were studied for their efficacy in the reduction of GO/GTO³³. Benzyl alcohol was found to have the greatest capacity to reduce the material with a C/O ratio of

30 and conductivity of 4600 Sm^{-1} measured³³. It was proposed that atmospheric oxygen behaving as the terminal reductant due to a previous report indicating that GO/GTO was capable of catalyzing benzylic and aliphatic alcohols³³. Furthermore, it was noted that the resulting RGO/RGTO possessed benzaldehyde and benzoic acid in the final solution suggesting that benzyl alcohol was directly involved in the reduction of GO/GTO³³.

1.3.2 Thermal reduction methods

Thermal annealing of GO/GTO often the most effective means of oxygen removal and restoration of the sp^2 domains⁸. Due to the input of energy into the material, oxygen is evolved from GO/GTO in the form of water, carbon dioxide, and carbon monoxide⁸. Typical treatment involves placing the sample into a pre-heated furnace at a temperature between 1000 and 1100 °C for 30-45 seconds under an inert atmosphere³⁴. As the oxygenated gases are evolved, the layer which comprise GO/GTO separate and the material is reduced to graphene⁸. One group reported the reduction of GO/GTO by placing the material in an alumina boat and inserting into a quartz tube which was sealed at one end³⁴. The tube had an argon inlet and a thermocouple that was put through a rubber stopper³⁴. The sample was purged with argon for 10 minutes and the tube was rapidly heated to 1050 °C³⁴. It was reported that the C/O ratio increased with increasing temperatures³⁴.

Another group reported the successful exfoliation and reduction of GO/GTO by thermal means and used TGA-FT-IR to monitor the reduction reaction³⁵. They discuss the decomposition of GO/GTO as having second order rate kinetics³⁵. Furthermore, it is

noted that the loss of mass with increasing temperature can be attributed to the removal of oxygen species³⁵. It is reported that the reaction is auto-catalyzed by local heat formation during the decomposition, increasing the reaction rate and causing an increase in internal temperatures³⁵. Due to a rapid increase in pressure, the resulting RGO/RGTO was extremely uniform with 80% of the final product comprised of single-layer RGO³⁵.

Mattevi et al. demonstrated that thermal annealing at 450 °C or greater was equivalent to the reduction of GO/GTO with hydrazine monohydrate at 80 °C with subsequent thermal annealing at 200 °C³⁴. Another group used XPS to determine the C/O ratio and reported that thermally reduced GO/GTO at temperatures exceeding 450 °C contained only 8% oxygen post-reduction³⁶. A study of the thermal reduction of GO paper at 700 °C, under either argon or hydrogen atmosphere, demonstrated that the material was effectively reduced and the sp^2 character was restored with measured conductivities up to 8100 Sm^{-1} reported³⁷. The pre-reduced GO/GTO had measured conductivity values five orders of magnitude lower³⁷. The group also demonstrated the ability of the RGO/RGTO to be utilized as material for active electrodes in the positive half-cell of a vanadium redox flow battery and reported that the electrical behavior exceeded expectations in regards to current density and reversibility³⁷. The performance of the material was assigned to an increase in the sp^2 character of the material allowing the material to display an increase in conductivity³⁷. The authors postulate that the remaining oxygen serves active sites for the redox reaction with vanadium³⁷.

Acik et al. developed a mechanism to describe the thermal reduction process by measuring the material *in situ* with transmission infrared absorption spectroscopy while annealing GO/GTO from 60 to 850 °C under vacuum from 10^{-3} to 10^{-4} Torr³⁸. Reference

44 provides the mechanism by which the free radical reaction occur³⁸. The author proposes that the reaction goes through the typical processes of a free radical polymerization: initiation, propagation, and termination³⁸. The degradation of GO/GTO produces hydroxyl, hydronium, and hydroperoxyl free radicals at the edges of the material³⁸. The formation of said radicals are described as being the rate determining step of the reaction³⁸. The hydroxyl radicals react first with hydroxyl groups undergoing propagation reactions and the eventual formation of carbonyl free radicals³⁸. Also, carboxylate groups decompose upon heating through a process called decarboxylation and produces carbon dioxide free radicals³⁸. These free radicals on the carbon dioxide diffuse through GO/GTO until they reach another set of unpaired electrons re-establishing the covalent bond on the basal plane³⁸. They speculate that the hydroxyl free radicals are transformed into 1,2-diols at the defective sites on the carbonyl moiety and are further propagated by reacting with oxygen functional groups on GO/GTO or terminate by the formation of covalent bonds at sites where dangling bonds are present³⁸.

In 2012, Zhang et al. reports a method to produce graphene from GO/GTO by low temperature thermal exfoliation³⁹. The group builds upon the work of McAllister et al. discussed above and designs a system where enough pressure can be produced to efficiently reduce and exfoliate the material at lowered temperatures³⁹. Thermal analysis indicated the bulk of the functional groups decompose between 150 and 250 °C, a temperature well below the temperature at which the GO/GTO flakes begin to exfoliate, ~550 °C³⁹. Whereas the work that was reported by McAllister relied upon the generation of gas to increase the system pressure³⁵, the work by this group applied high vacuum to the thermogravimetric instrument, thereby assisting in the separation of sheets at 200

°C³⁹. They report that more than 60% of the annealed material was single-layer RGO³⁹. Furthermore, the group describes hydrogen promotes low temperature reduction and exfoliation as well as hydrochloric acid reduction and exfoliation³⁹. Confirmation of the reduction was achieved via XPS measurements where the carbon-to-oxygen ratios were calculated³⁹.

Finally, Huh at the Korea Institute of Ceramic Engineering and Technology depicts the Raman spectra of GO/GTO at various temperatures². This study invaluablely provides a story of GO/GTO and allows for future researchers to more accurately utilize Raman spectroscopy to characterize their graphene-based materials. As discussed previously, there remains a good deal inconsistency regarding these measurements and their interpretation. The samples are measured via Raman upon thermal annealing at temperatures ranging from 60 – 2000 °C². With lowered annealing temperatures, the sample is fairly representative of GO where the D band and G band are nearly equivalent in intensity². As the temperature is increased, the intensity of the D band continues to increase until approximately 1200 °C, at which point the intensity of the D band begins to decrease and finally becomes a small hump at 2000 °C². Furthermore, it can be noted that as reduction progresses, the full width half maximum of both peaks becomes smaller as thermal annealing allows for the relaxation of the atoms and rearrangements to occur, creating a higher degree of order in the material² Further discussion can be found in the following section provided on characterization of GO/GTO and RGO/RGTO.

1.4 Characterization methods

There exists a wide array of characterization techniques for GO/GTO and for evaluation of reduction. However for the purposes of this study, EDS and Raman spectroscopy will be the sole characterization techniques discussed.

1.4.1 Energy dispersive X-ray spectroscopy (EDS)

EDS is a material characterization technique by which a sample is bombarded by a highly focused beam of electrons followed by the measurement of X-rays ejected from the sample from the electron collisions⁴⁰. Theoretically, EDS can measure elements from beryllium to uranium, however, most detectors are not capable of analysis of elements smaller than carbon⁴⁰. Quantitative elemental analysis is performed by the measuring of elemental X-ray line intensities. Regarding accuracy and precision, elemental analysis of major elements can often have a precision of $> 2\sigma$ with a $\pm 1\%$ accuracy⁴⁰. However, the method is often considered semi-quantitative due to the spatial resolution of the electron beam. Penetration depth of the electron beam is determined by the density of the atom. Therefore information gained from the EDS is not necessarily spatially resolved⁴⁰.

1.4.2 Raman spectroscopy

Raman spectroscopy is a tool utilized in the characterization of any carbon-based material including graphite, carbon nanotubes, fullerenes, diamond, and aromatic molecules and has the potential to provide structural information of such materials. Carbon materials are often classified in terms of their bonding arrangements, either graphite-like with a high degree of sp^2 character or diamond-like for materials with primarily sp^3 hybridized carbons⁴¹. Diamond-like materials are characterized by possessing sp^3 hybridized carbons as their primary carbon source and by having mechanical hardness, being chemically inert, transparent, and electronically behaving as

a wide-band-gap semiconductor. For the purposes of this study, it can be clarified that GO/GTO and RGO/RGTO are graphitic carbon materials whereas HA falls somewhere between the two extremes and is more accurately described as a polyaromatic hydrocarbon. HA is known to possess both sp^2 and sp^3 C-C bonds, however the sp^3 regions are likely amorphous and vary in orientation and bonding from one particle to the next. Figure 3 is demonstrative of the effect that amorphization has on the Raman spectra of carbon materials.

In the context of this discussion, as carbon materials undergo amorphization, they transition from sp^2 (graphitic) to sp^3 (diamond-like) the Raman spectra will be effected throughout the entire process. Figure 4 is representative of the atomic transition from graphitic carbon to diamond-like carbon. Nano-crystalline graphite is chemically identical to graphite, however, the size of the sp^2 domains will decrease leading to a visual transition in the Raman spectra. As the material becomes amorphous, there are regions of sp^2 and sp^3 domains with little structural order. Furthermore, much of the rings remain intact in amorphous carbon. The transition from to tetrahedral amorphous carbon is characterized by the majority of the atoms being sp^2 (80-90%) and a disruption of the

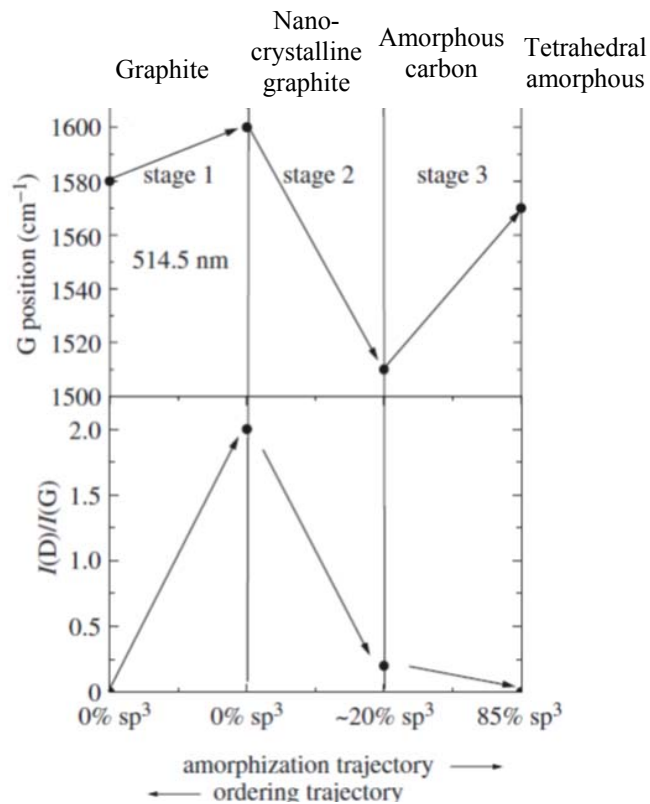


Figure 3. Effect of amorphization on G band position vs. $I_{(D)}/I_{(G)}$ ratio⁹

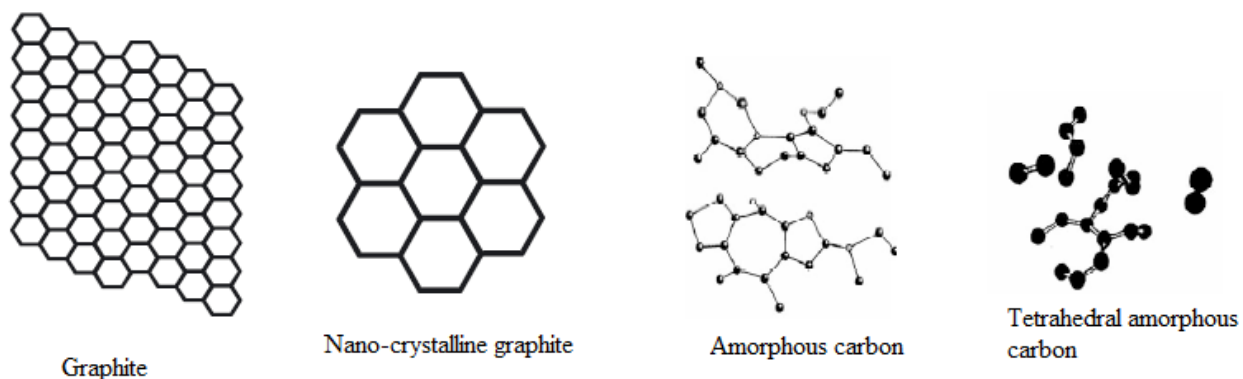


Figure 4. Amorphization of graphitic carbon

ring system (increase in aliphatic chains)^{9,42}. For analysis of these materials with Raman spectroscopy is important to understand the origin of the observed peaks. In graphitic carbons the primary peaks of interest are the D and G bands. For in depth theoretical reports on phonon symmetries, the Brillouin zone, and the band structure of graphite refer to references 49 and 50^{43,44}. Although both bands are attributed to sp^2 carbons, the G

band associated with the in-plane vibration of the graphite lattice measured at approximately 1575 cm^{-1} (sp^2 hybridized rings or chains) and a weak D band assigned to the breathing modes of the sp^2 rings at approximately 1355 cm^{-1} ⁴⁵. Therefore, the D band will not be present without the ring system and is not found in 100% sp^3 carbons. Note, the D band location is dependent upon source wavelength and can vary several wavenumbers⁴⁵. The D band is also found in pristine graphene, however, it is inactive until vibrations associated with the edges activate the frequency⁴⁵.

The primary factors which impact Raman spectra of carbon materials, include:

- The size of the sp^2 domain – small size leads to increase in G band frequency⁹
- Presence of defects/disorder – increase in FWHM of G band due to softening of the vibrational mode due to possession of weaker bonding⁹
- Presence of sp^2 rings or chains – increase in chains leads to a decrease in G band frequency⁹
- sp^2/sp^3 ratio – decrease in G band frequency until $\sim 20\%$ sp^3 , then increases with the continual decrease in $I_{(D)}/I_{(G)}$ ratio as the D band disappears⁹

Along with the position of the D and G band, the full width half maximum (FWHM) will increase as the number of sp^3 carbons increase⁴⁵. Reduction of GO/GTO creates regions of disorder associated with defects often associated with atomic rearrangements into 5-8-5 defect, one octagonal ring and two pentagonal rings, and the Stone-Wales defect (5-7-7-5) defect⁴⁵. It is reported that a transition from graphite to amorphous carbon is associated with an increase in observed G band frequency and broadness, however, the reduction by thermal means often displays similar characteristics, adding to the complexity⁴⁵.

The shift to higher frequencies in the G band is attributed to the presence of isolated double bonds, which resonate at higher frequencies than graphite⁴⁵. It is not until the defected areas restore sp^2 character that the G band is shifted down to frequencies measured in graphite. The source of G band broadening upon oxidation is attributed to other high-intensity bands which convolute with the G band of graphitic regions, such as the addition of the 1,4-hydroxyl pairs⁴⁵. Furthermore, the D band broadening is associated with the hydroxyl group which can produce a number of bands in the 1300 cm^{-1} region⁴⁵. Also, the sp^3 D band and the sp^2 D band will converge leading to increased broadness in the D band⁴⁵. Platelet size can have an effect on the location of the G band where frequencies as high as 1690 cm^{-1} have been measured in nano-ribbon graphitic materials⁴⁵. The narrow nature of nano-ribbon graphitic materials create a system where the sp^2 regions are highly isolated causing an increase in frequencies⁴⁵.

As the amount of hydrogenated carbons increase there is a photoluminescence effect where the background will become significantly noisier and data collection can become challenging. This is due to hydrogen saturation on non-radiative recombinant centers. As the amount of hydrogen increases (>40-50%), the Raman signal is drowned.

1.5 Dissertation efforts

The work performed within this dissertation is a comprehensive study of GO and HA prior to reduction including assessment of the materials via Raman spectroscopy, SEM, and EDS measurements. Both materials will undergo a series of reductions by chemical and thermal means. Chemical reductions will include hydrazine,

hydroxylamine, sodium borohydride, sodium bisulfite, and benzyl alcohol. Thermal reductions are to be performed at 500, 700, and 900 °C in a 10% hydrogen/argon atmosphere for a one hour period. Following reduction, the materials are studied using the above mentioned characterization techniques.

1.6 Technical relevance

The aim of this study is demonstrate the effectiveness of the reduction of both materials and demonstrate the production of a graphene-like material prepared from Leonardite coal. It is valuable to the technical community to have an alternative to GO/GTO for the preparation of graphene. Furthermore, the study seeks to clarify and study the use of Raman spectroscopy in the analysis of graphene-based materials.

CHAPTER 2

EXPERIMENTAL METHODS

2.1 Material synthesis

Different techniques were used in the synthesis of the starting materials. GTO was prepared by the Modified Hummers' method. HA was prepared by base extraction of Leonardite coal purchased from Amcol followed by filtration.

2.1.1 Graphite oxide synthesis

Graphite flakes were purchased from Sigma Aldrich and subsequently used for oxidation. A mixture of 9:1 sulfuric and phosphoric acid with volumes totaling 400 mL was added to 3.0 g of graphite. Then 18.0 g of potassium permanganate was added and allowed to mix. During this time, the mixture became warm due to an exothermic reaction following the addition of the potassium permanganate. The mixture was stirred and heated to 50 °C for 12 hours. Upon completion of the reaction, the mixture was allowed to cool to room temperature and then poured onto approximately 400 mL of ice, followed by the addition of 3 mL of 30% hydrogen peroxide. The material was filtered through a 0.2 µm cellulose nitrate filter, followed by washes of 200 mL of DI water, 200 mL of 30% HCl, and 200 mL of ethanol. The wash process was repeated a total of three times. The same batch of GTO was utilized throughout the study to allow for comparison.

The following is a list of the reagents and the vendors from which they were purchased. ACS grade sulfuric acid was obtained from BDH, 37% ACS grade hydrochloric acid was obtained from Sigma-Aldrich, 29-32% ACS grade hydrogen peroxide was purchased from Alfa Aesar, potassium permanganate, and ethanol.

2.1.2 Humic acid synthesis

Humic acid is prepared from pulverized Leonardite coal acquired from a mine in North Dakota. Approximately 100 grams of the coal is placed into 500 mL of DI water and then basified with ammonium hydroxide while stirring. Ammonium hydroxide was added drop wise until a pH of approximately 10 was achieved. The mixture was then filtered through VWR 415 filter paper to allow for separation of the large particle fraction of the coal from the humic and fulvic fractions. The filtrate is then acidified with concentrated HCl until a pH of approximately 4. HA is then collected by filtration with a 0.2 μm cellulose nitrate filter and dried under vacuum. All reactions discussed in this work used the same batch of HA for comparison.

The following is a list of the reagents and the vendors from which they were purchased. ACS grade ammonium hydroxide was obtained from Fisher Scientific, 37% ACS grade hydrochloric acid was obtained from Sigma-Aldrich, and Leonardite coal was obtained from Amcol International Corporation.

2.2 Chemical reductions

The following section is a description of the chemical reductions performed on GTO and HA. The reductions were performed with hydrazine, hydroxylamine, sodium borohydride, sodium bisulfite, and benzyl alcohol.

2.2.1 Hydrazine reduction

The reduction of GTO and HA was performed using hydrazine monohydrate purchased from Alfa Aesar. Prior to reduction, the 3 mg/mL suspensions of GTO and HA were sonicated via ultrasonication at 40% power for a 30 minute time period to facilitate exfoliation of the material. To 40 mL of deionized water, 4 mL of the appropriate

suspension and 1 mL of hydrazine monohydrate were added. For the HA reduction, the water was made basic by adding ammonia hydroxide until a pH of 9 was reached to ensure that HA would remain suspended. The reactions were stirred and heated to reflux in a fume hood for 24 hours. Upon completion of the reaction, the material was recovered by filtration with a 0.2 μm cellulose nitrate filter which was washed three times by methanol and deionized water. To facilitate recovery of HA, the reaction was made acidic by the addition of HCl until a pH of 4 was reached. After the recovered material was washed, it was placed in a vacuum oven at 60 °C and allowed to dry overnight. The material was then analyzed via Raman spectroscopy and SEM/EDS.

2.2.2 Hydroxylamine reduction

The reduction of GTO and HA was performed with hydroxylamine hydrochloride 100g/L and was purchased from Hach. Suspensions of 25 mL at 0.5 mg/mL of GTO and HA were prepared in deionized water and thoroughly mixed by ultrasonication for 30 minutes at 40% power. To prepare the hydroxylamine the suspensions were made basic by the addition of ammonia hydroxide was added until the pH exceeded 10²⁶. The reaction was heated to reflux for 2 hours and allowed to cool to room temperature. The material was recovered by filtration with a 0.2 μm cellulose nitrate filter which was washed three times by methanol and deionized water. To facilitate recovery of HA, the reaction was made acidic by the addition of HCl until a pH of 4 was reached. After the recovered material was washed, it was placed in a vacuum oven at 60 °C and allowed to dry overnight. The material was then analyzed via Raman spectroscopy and SEM/EDS.

2.2.3 Sodium borohydride reduction

Sodium borohydride was purchased as a 12% solution in 40% aqueous sodium hydroxide solution from Acros Organics and used as a reductant for GTO and HA. Suspensions of 15 mL of a 1 mg/mL solution of GTO and HA in deionized water were prepared and thoroughly mixed by ultrasonication for 30 minutes at 40% power. To the suspensions 1.24 mL (6.57 mmol) of sodium borohydride was added, followed by stirring and heating to reflux for 2 hours. Upon completion of the reaction, the mixture was allowed to cool to room temperature. The material was recovered by filtration with a 0.2 μ m cellulose nitrate filter which was washed three times by methanol and deionized water. To facilitate recovery of HA, the reaction was made acidic by the addition of HCl until a pH of 4 was reached. After the recovered material was washed, it was placed in a vacuum oven at 60 °C and allowed to dry overnight. The material was then analyzed via Raman spectroscopy and SEM/EDS.

2.2.4 Sodium bisulfite reduction

A reduction of GTO and HA was performed with sodium bisulfite purchased from Alfa Aesar. To 12 mL of deionized water, 3 mL of a 5 mg/mL suspension of the either GO or HA was added. However, the mixture of HA was made basic with ammonia hydroxide to ensure that material remained in suspension. Upon addition, the mixture was thoroughly mixed via ultrasonication for 30 minutes at 40% power. After mixing, 0.1509 g of sodium bisulfite was added followed by stirring and heating to reflux. The reaction was allowed to proceed for a total of three hours. Upon completion of the reaction, the mixture was allowed to cool to room temperature. The material was recovered by filtration with a 0.2 μ m cellulose nitrate filter which was washed three times by methanol

and deionized water. To facilitate recovery of HA, the reaction was made acidic by the addition of HCl until a pH of 4 was reached. After the recovered material was washed, it was placed in a vacuum oven at 60 °C and allowed to dry overnight. The material was then analyzed via Raman spectroscopy and SEM/EDS.

2.2.5 Benzyl alcohol reduction

Benzyl alcohol purchased from Fisher Scientific was used as a reductant for GTO and HA. To 25 mL of benzyl alcohol, 100 mg of the appropriate dried material. The reaction was stirred and heated to 120 °C for five days. Upon completion of the reaction, the mixture was allowed to reach room temperature. The GTO was recovered via filtration through a 0.2 µm cellulose nitrate filter and subsequent washing with methanol and deionized water for a total of 3 times. However, HA was not readily recovered by the same means described in the above methods. Even upon addition of HCl until acidic, the majority of the material passed directly through the filter paper. Because benzyl alcohol is only slightly soluble in water, a liquid-liquid extraction was performed with benzyl alcohol and basic water. The majority of the material was found to stay in the basic water and was subsequently dried via evaporation using a gentle stream of air to pass over the solution for 2 days. The material was then analyzed via Raman spectroscopy and SEM/EDS.

2.3 Thermal reductions

Thermal reductions of GTO and HA were performed in a tube furnace located in RFM 2210, Dr. Yu's laboratory. The tube furnace is equipped with digital gas flow and temperature controls. This allowed for precise dilution of hydrogen gas in argon. The gas mixture was maintained at 10% for each thermal reduction. Concentrated suspensions of

GTO and HA were placed on clean silicon wafer for the purpose of reduction. The reductions were performed at 500, 700, and 900 °C for a one hour period. After cooling to room temperature, the reduced materials were analyzed by Raman spectroscopy and SEM/EDS. The reduced material is depicted in Figures 5 – 7 below.

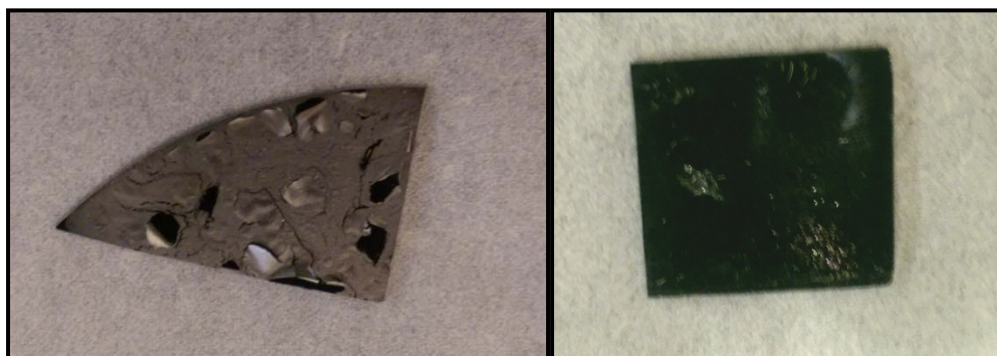


Figure 5. Thermal reduction at 500 °C, (a) GTO, (b) HA

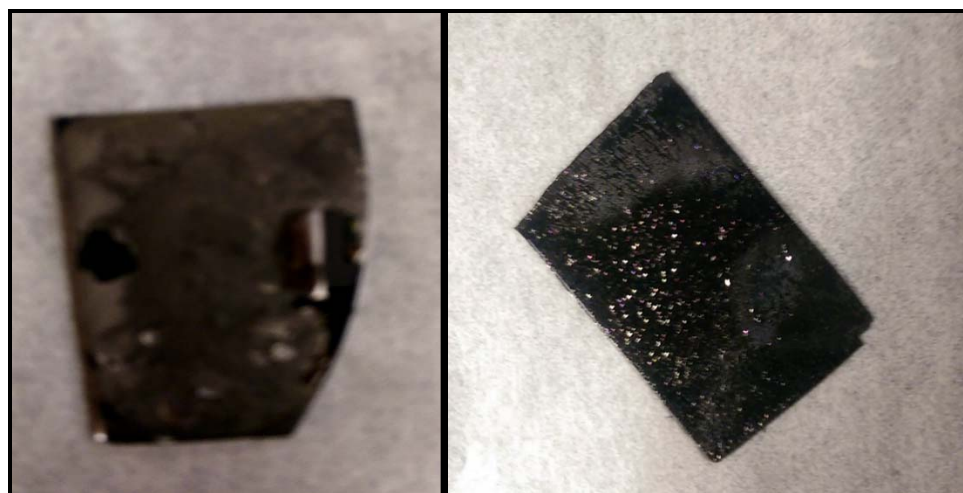


Figure 6. Thermal reduction at 700 °C, (a) GTO, (b) HA

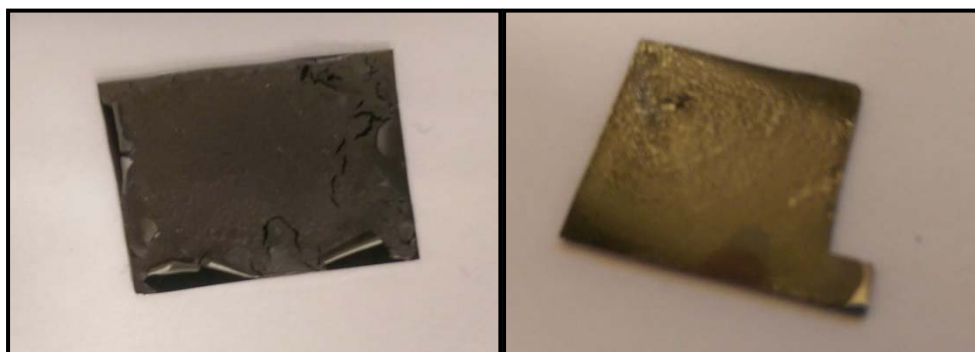


Figure 7. Thermal reduction at 900 °C, (a) GTO, (b) HA

2.4 Material characterization

All material was characterized by Raman spectroscopy and SEM/EDS both before and after reduction reactions. The following sections describe the analysis of the material

2.4.1 Scanning electron microscopy/energy dispersive X-ray spectroscopy

As previously discussed, the Helios NanoLab 400 was the SEM used throughout the study. Other than particle size determination, the SEM is used in the determination of relative percent carbon and oxygen in efforts to determine the C/O ratio. The Helios is equipped with an EDS detector to allow for the collection of characteristic X-rays which are ejected from the sample when bombarded with electrons. The EDS spectra was collected and analyzed with EDAX software. It should be noted that the penetration depth of the electron beam can extend microns into the surface and substrate peaks can mask the signal of the carbon and oxygen of the deposited sample film, therefore the reduction samples that were not abundant and low in concentration were analyzed at a 52° angle to allow for more of a surface measurement. Only the starting material was analyzed at a 0° angle. All samples were analyzed at 5kV and 86pA to prevent charging and decrease substrate signal. Furthermore, the chemically reduced samples were coated with Iridium with a Quorum EMS 150T ES sputter coating instrument to decrease the effects of charging facilitating higher quality imaging.

2.4.2 Raman spectroscopy

As discussed in the previous chapter, Raman spectroscopy is used in the study of order and disorder in graphene and graphene oxide. It is a helpful tool for studying carbonaceous materials, due to the symmetry in conjugated carbon-based materials. A

Thermo Scientific DXR Raman Microscope with excitation wavelength of 532 nm was used throughout the study. All samples were collected with a 10 collections per sample with a two second sampling time. The collection range was dependent upon the sample itself and is discussed in the results section.

CHAPTER 3

GRAPHITE OXIDE REDUCTION: RESULTS AND DISCUSSION

The following is a summation of the observed reduction in oxygen content for all chemical and thermal treatments and an analysis of the material prior to reduction. Figure 8 depicts GTO before reduction. It is apparent that complete exfoliation of the material was not achieved due to observed stacking for some of the material as can be seen in Figure 8b. However, several images appear to demonstrate that the majority of the material was present as single-layer GO as observed in Figure 8a and 9. As the material approaches single-layer the contrast with the substrate (silicon wafer) diminishes and is often difficult to image. As the appearance of the particles becomes darker and contrast increases suggests that the material is becoming more stacked. An attempt to determine the particle size using dynamic light scattering (DLS) was made, however, the data proved to be unreliable. The measured value from DLS was around 1 μm , however, the peak was extremely broad and the calculated error was high. Analysis of the particles in the SEM indicates that the particle size varied widely from several hundred nanometers to nearly ten microns in size.

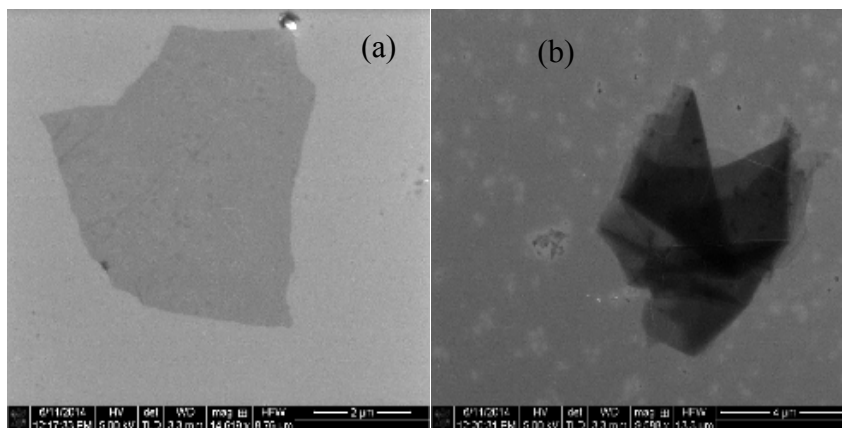


Figure 8. SEM images of GTO prior to reduction, (a) evidence of exfoliated particles, scale bar = 2 μm , (b) evidence of agglomerated particles, scale bar = 5 μm

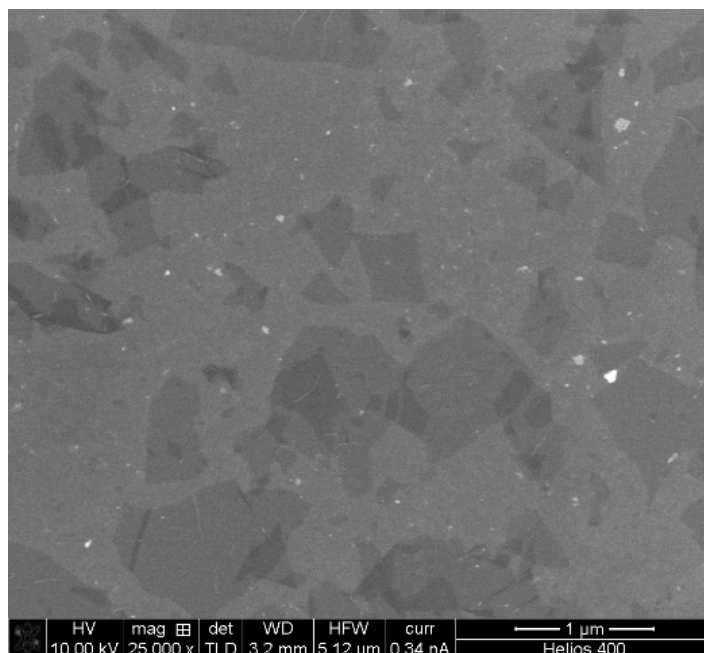


Figure 9. SEM image of GTO indicating the particle size distribution

To effectively discuss the reduced GO materials, all materials have been abbreviated and listed in Table 2 below.

Table 2. Abbreviation list for graphite oxide materials

Material	Abbreviation
GTO	Graphite Oxide
HGTO	Hydrazine reduced graphite oxide
HAGTO	Hydroxylamine reduced graphite oxide
NBGTO	Sodium borohydride reduced graphite oxide
NBSGTO	Sodium bisulfite reduced graphite oxide
BAGTO	Benzyl alcohol reduced graphite oxide
GTO500	Thermally reduced graphite oxide at 500 °C
GTO700	Thermally reduced graphite oxide at 700 °C
GTO900	Thermally reduced graphite oxide at 900 °C

A common measurement of reduction efficiency for graphene/graphite oxide is the determination of the C/O ratios. Figure 10 is a compilation of the C/O ratios for GTO and all reduced materials, both chemically and thermally, including error bars to indicate the standard deviation of the measurements. It is clear that the material reduced at 900 °C resulted in removing the most oxygen with an average oxygen value of 2.7%. The most

effective chemical reductant for removal of oxygen appeared to be benzyl alcohol with BAGTO having an average oxygen value of 12.3%.

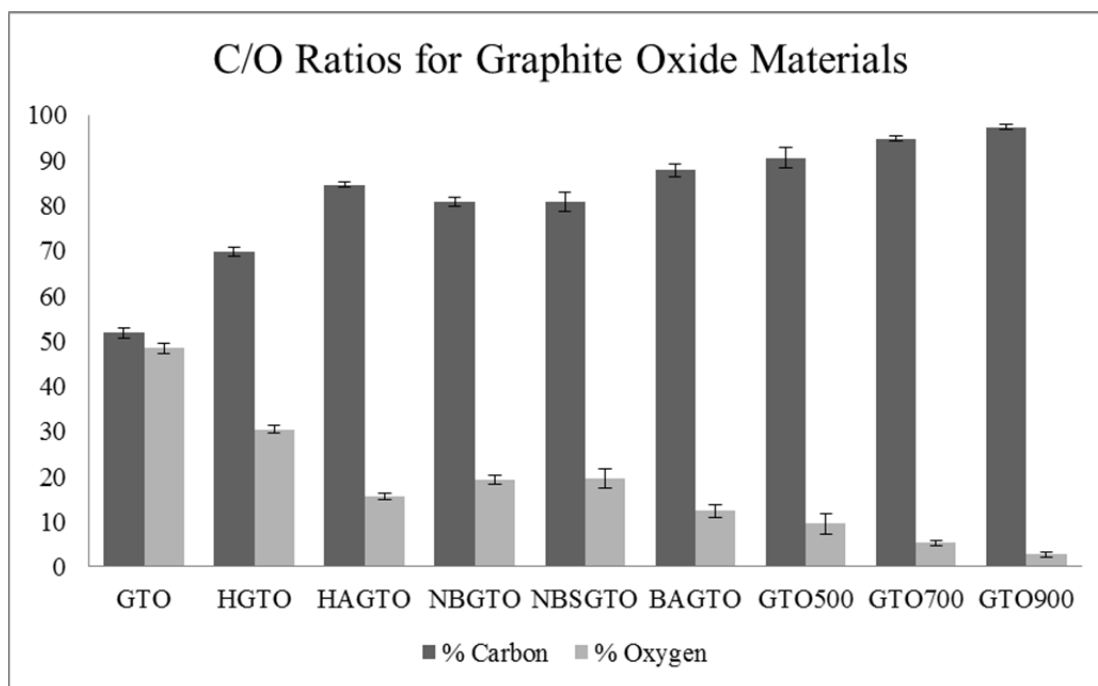


Figure 10. C/O ratios for all graphite oxide materials

Images of the all materials are provided below. When GO/GTO is chemically reduced, the removal of oxygen adds to the hydrophobicity of the material and effective exfoliation post-reduction is not maintained as seen in the images in Figure 11. HAGTO appeared to be the only material that when sonicated and solvent cast on a clean silicon wafer, provided a uniform film. The morphology of the reduced material remained consistent with GO/GTO and reduced GO/GTO seen in literature¹ where the lamellar morphology is maintained. As seen in Figure 10i, the material reduced at 900 °C appeared to have white particulates or nodules protruding from the surface. Upon examination by EDS, the source of the particulates remains unclear and did not appear to affect the C/O measurements. The EDS can measure areas or spots, so area

measurements were selected to include the particulates to verify the chemical nature of the particulates.

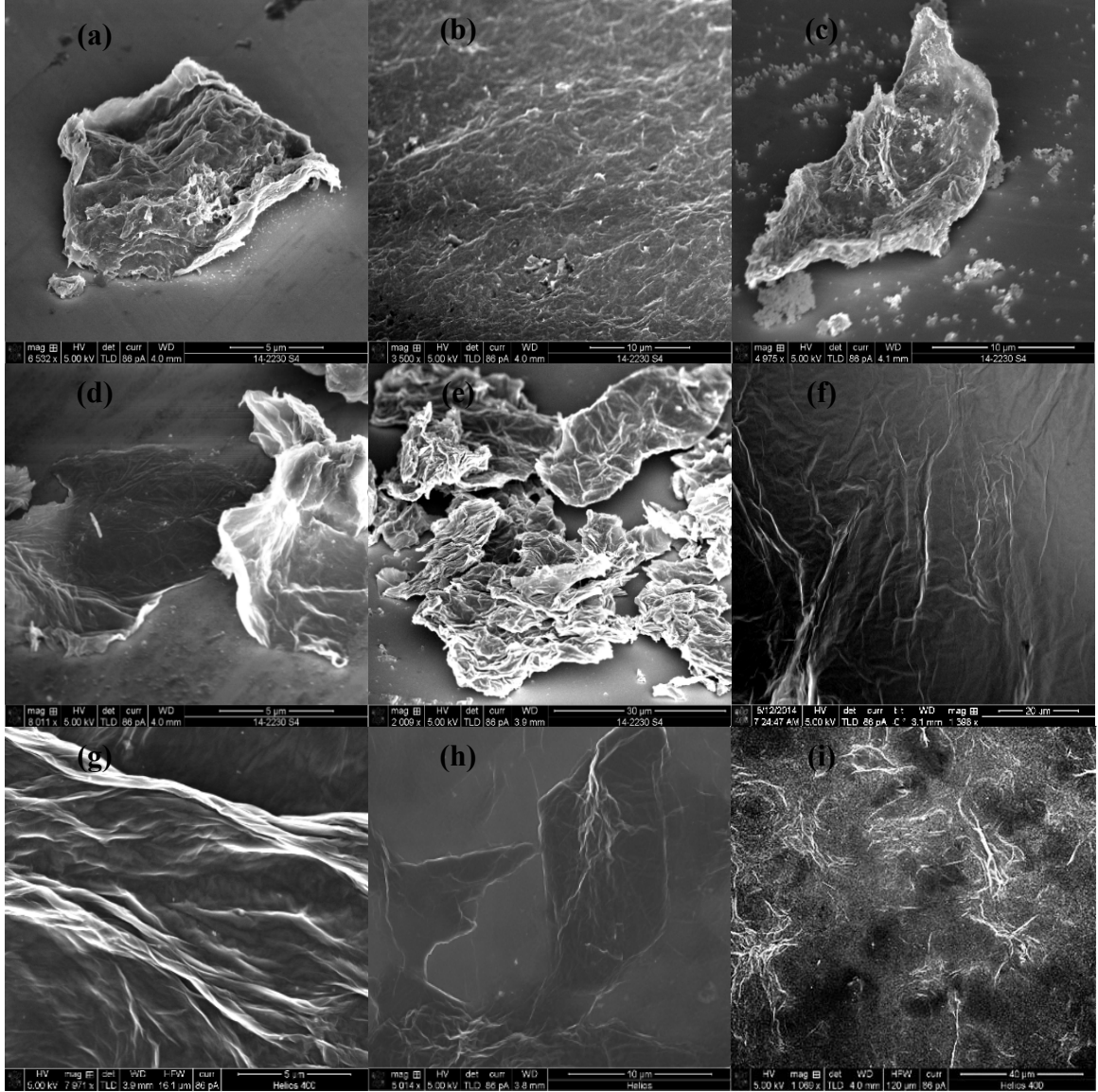


Figure 11. SEM images of GTO and reduced GTOs, (a) HGTO, scale bar = 5 μm , (b) HAGTO, scale bar = 10 μm , (c) NBGTO, scale bar = 10 μm , (d) NBSGTO, scale bar = 5 μm , (e) BAGTO, scale bar = 30 μm , (f) Concentrated GTO prior to thermal reduction, scale bar = 20 μm , (g) GTO500, scale bar = 5 μm , (h) GTO700, scale bar = 10 μm , (i) GTO900 = 40 μm

To correlate the EDS data with Raman spectral analysis of all materials, an analysis of the Raman data is given below. Traditionally, the $I_{\text{D}}/I_{\text{G}}$ ratio is utilized to

assess order and disorder in graphitic systems. As discussed in the background sections, the ratio is highly dependent upon which regime the material resides as well as stacking effects. As all materials prepared were agglomerated, comparisons between samples will be made. Figure 11 is a compilation of all materials demonstrating a trend in the position of the G band. As discussed in the background section of the paper the position of the G band can be attributed to several factors. In comparison to graphite, GTO has an observed increase in the frequency of the G band to approximately 1590.1 cm^{-1} . BAGTO had the lowest observed G band frequency. This is attributed to an increase in the size of sp^2 domains due to the decrease in oxygen species throughout the material as shown in Figure 12. To fully assess this material, the $I_{\text{(D)}}/I_{\text{(G)}}$ ratio and full width half maximum (FWHM) of the G band must also be taken into account. FWHM calculations were made using PeakFit 4.0 software fitted with mixed Voigt-Gaussian fitting to allow for the deconvolution of the D and G bands. Standard error and 95% confidence values can be obtained within the appendix.

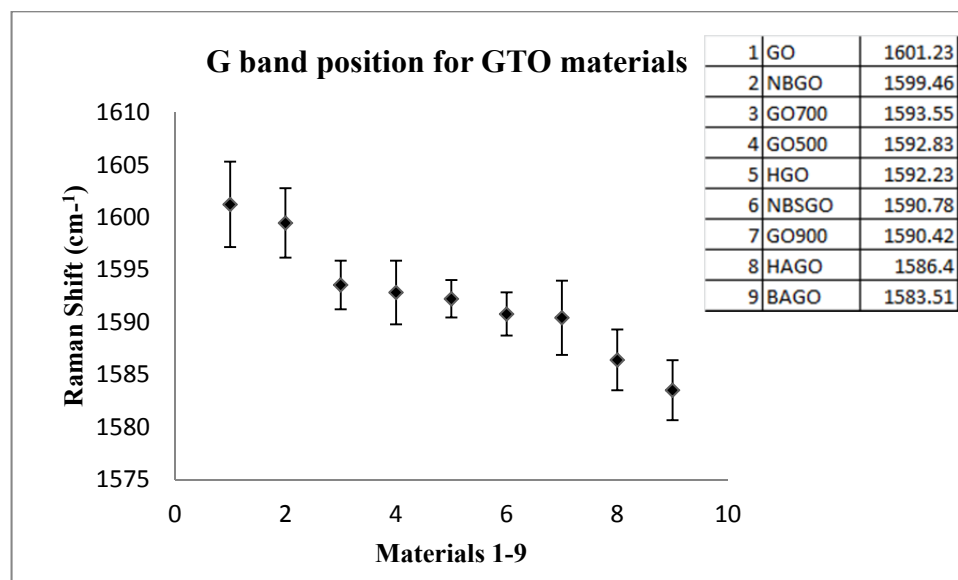


Figure 12. G band positions for GTO materials

As shown in Figure 13, the $I_{(D)}/I_{(G)}$ ratio for BAGTO is the lowest for all chemically reduced GTO's, however, the FWHM provided in Table 3 falls in the middle. This is due to regions of disorder/defects. It is likely that the removal of oxygen resulted in rearrangements of some of the carbon atoms creating defects such as the 5-7-5 or Stone-Wales defects.

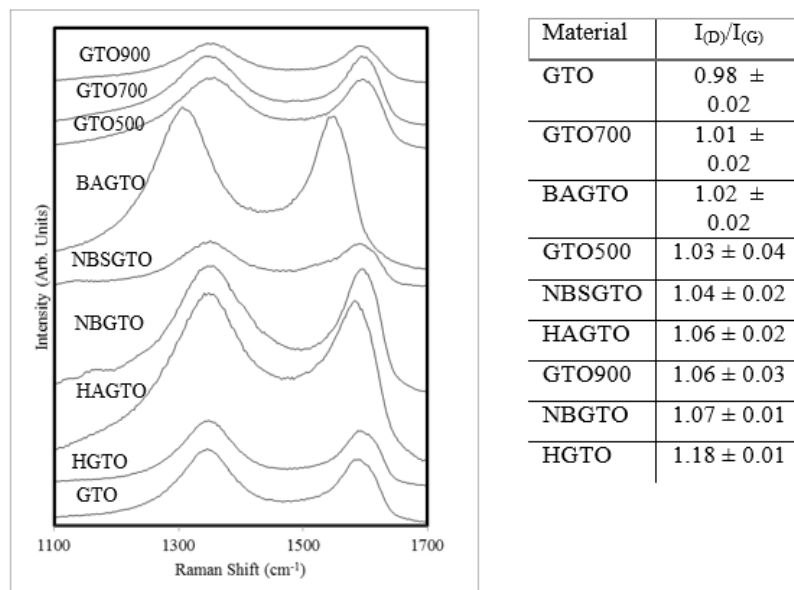


Figure 13. Raman spectra for all materials with corresponding $I_{(D)}/I_{(G)}$ ratios

Table 3. Compilation of graphite oxide materials in order of descending % oxygen and correlated to G band position, $I_{(D)}/I_{(G)}$, and FWHM of G band

Material	% Oxygen	G band position (cm ⁻¹)	$I_{(D)}/I_{(G)}$	FWHM
GTO	48.3	1590.5	0.98	92.4
HGTO	30.4	1599.1	1.18	72.2
NBSGTO	19.4	1588.5	1.04	79
NBGTO	19.2	1591.4	1.07	71.4
HAGTO	15.5	1586.4	1.06	89.2
BAGTO	12.3	1585.6	1.02	81.6
GTO500	9.6	1591.4	1.03	74.3
GTO700	5.3	1592.4	1.01	62.4
GTO900	2.7	1587.5	1.06	61.5

The location of the G band in the thermally reduced GTO's is higher than the most of the chemically reduced GTO's. This can be attributed to smaller sp^2 domains as the atoms attempt to rearrange and restore the sp^2 character. It is evident that this is occurring due to a decrease in G band frequency from GTO500 to GTO700. Furthermore, the FWHM follows the same trend. A decrease in oxygen content, i.e. reduction, does not necessarily increase the order of the material. Some of the chemical reductants are less effective in the removal of oxygen, but are more effective in restoration of the vinyl nature of the C-C bonds. And as previously discussed, thermal energy is effective in oxygen removal, but further treatment is necessary to restore all conjugation and repair defected regions.

CHAPTER 4

HUMIC ACID REDUCTION: RESULTS AND DISCUSSION

The following is a summation of the observed reduction in oxygen content for all chemical and thermal treatments and an analysis of the material prior to reduction. Figure 14a and 15 illustrates the plate-like morphology and exfoliation of the material prior to reduction. It is apparent that complete exfoliation of the material was not achieved due to observed stacking for some of the material as can be seen in Figure 14b. As the material approaches single-layer the contrast with the substrate (silicon wafer) diminishes and is often difficult to image. As the appearance of the particles becomes darker and contrast increases suggests that the material is becoming more stacked. Analysis of the particles in the SEM indicates that the particle size varied widely from several hundred nanometers to nearly ten microns in size.

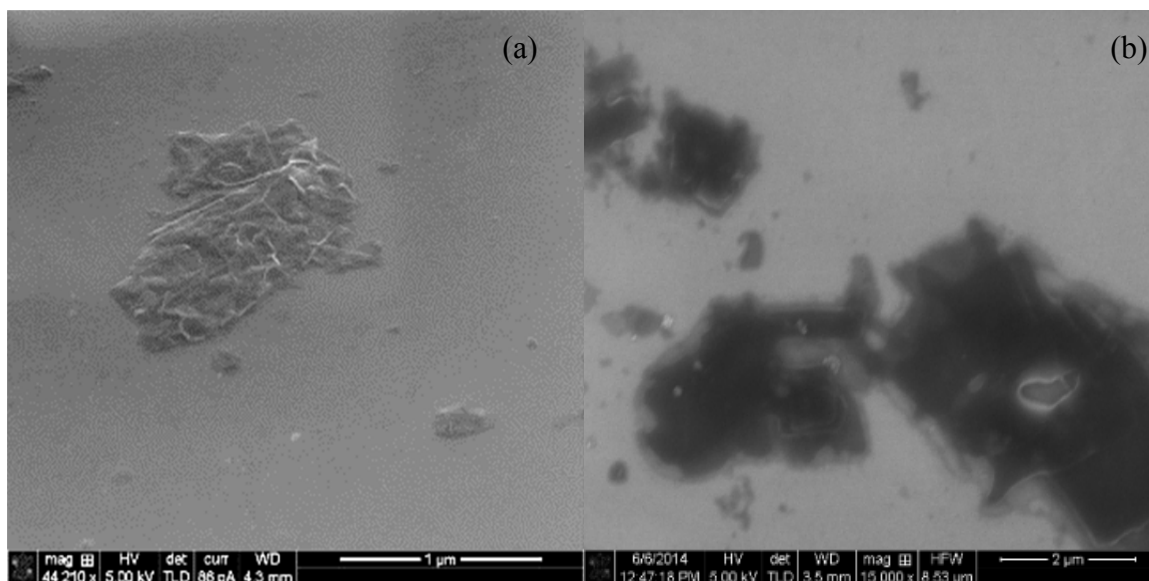


Figure 14. SEM images of HA prior to reduction, (a) Evidence of exfoliated particles and plate-like morphology, scale bar = 1 μ m, (b) evidence of agglomerated particles, scale bar = 2 μ m

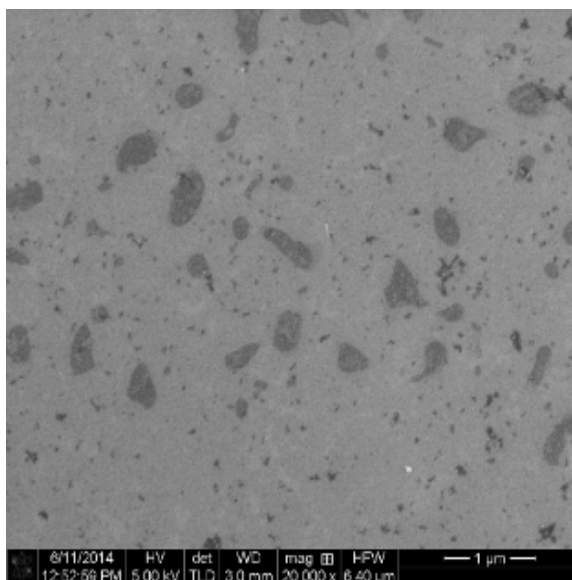


Figure 15. SEM image of HA indicating the particle size distribution, scale bar = 1 μ m

To effectively discuss the reduced HA materials, all materials have been abbreviated and are provided in Table 4.

Table 4. Abbreviation list for humic acid materials

Material	Abbreviation
HA	Humic acid
HHA	Hydrazine reduced humic acid
HAHA	Hydroxylamine reduced humic acid
NBHA	Sodium borohydride reduced humic acid
NBSHA	Sodium bisulfite reduced humic acid
BAHA	Benzyl alcohol reduced humic acid
HA500	Thermally reduced humic acid at 500 °C
HA700	Thermally reduced humic acid at 700 °C
HA900	Thermally reduced humic acid at 900 °C

The reduction of oxygen species was determined by obtaining C/O ratios for all reduced HA's by EDS. Figure 16 is a compilation of the C/O ratios for HA and all reduced materials, both chemically and thermally, including error bars to indicate the standard deviation of the measurements. The removal of oxygen was most effective by thermal treatment, however, the C/O ratios were not significantly different for the various temperatures. All were between 6 and 8 oxygen. The most effective chemical reductant

for removal of oxygen appeared to be HAHA having an average oxygen value of 9.1%. Unlike thermally reduced GTO, increase in the temperature of thermally reduced HA had little effect on oxygen removal. Oxygen content decreases from 40.1% in HA to an average of $\sim 7\%$ for all thermally reduced HA's. This finding can be attributed to the quinone functionalities due to the high thermal stability of quinone functional groups. It has been reported that temperatures exceeding 900 °C are required for the decomposition of benzoquinone due to resonance stabilization and the formation of hydroquinones during the thermal degradation process. The remaining oxygen require more thermal energy to effectively decompose the C-O bonds.

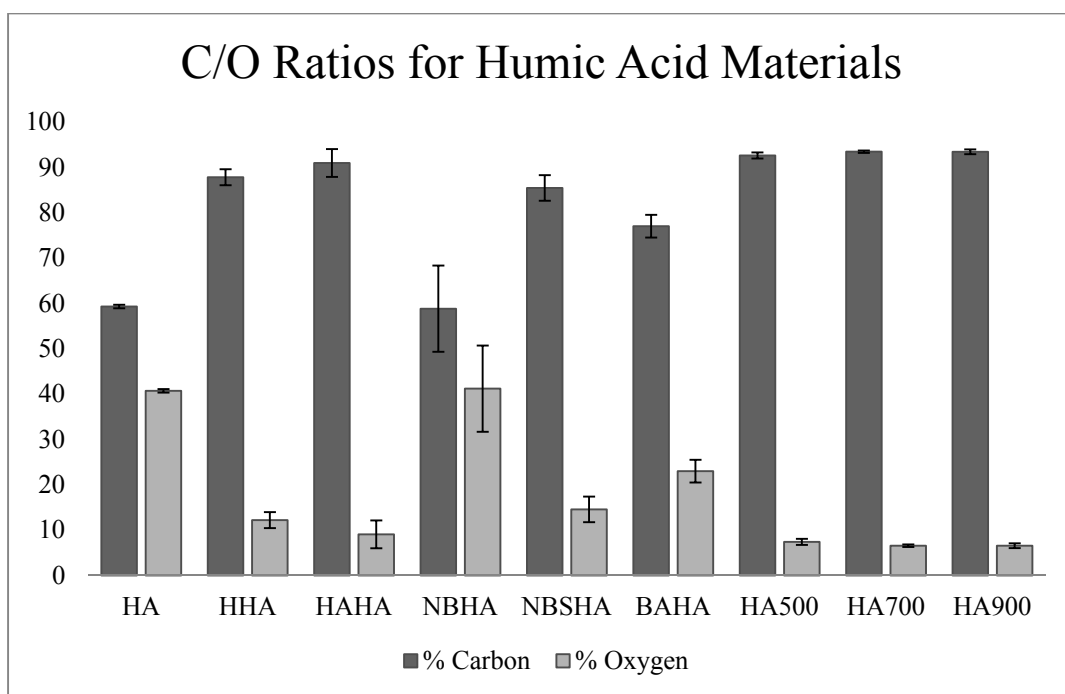


Figure 16. C/O ratios for all humic acid materials

Images for all materials are provided Figure 16. When HA is chemically reduced, the removal of oxygen adds to the hydrophobicity of the material and effective exfoliation post-reduction is not maintained. Depending on the reduction method, the morphology of the resulting material was altered. Some of the chemically reduced HA's,

such as HHA, HAHA, NBSHA, and NBSHA, possessed a coral-like appearance. This is much different than the plate-like appearance of the starting material. Because HA is an aromatic hydrocarbon, it is possible that the reductants were effective at polymerizing the platelets during the oxygen removal process forming a nano-ribbon morphology. Also, the quantity oxygen remaining for the above mentioned morphologically transformed materials were quite similar, ranging from ~ 9 to 15% oxygen (HAHA<HHA<NBSHA). It is likely that similar functional groups and oxygenated moieties are removed by the treatments. Both NBHA and BAHA appeared to retain their morphology, however, NBHA had measured oxygen values slightly above that of untreated HA and was ineffective in overall reduction. BAHA was reduced the oxygen content by a factor of two, but the appeared “fuzzy”, likely due to a lack of effective purification. As discussed in Chapter 2, the recovery of BAHA was difficult as the material remained well-suspended. An attempt at filtration was made with a 0.2 μm cellulose nitrate filter paper (hydrophilic) and the material readily passed through the filter paper. Because benzyl alcohol is slightly soluble in water, a liquid-liquid extraction was performed with alkaline DI water and phase-separation occurred with the treated material residing in the basic media.

Furthermore, the appearance of the material upon thermal reduction varied significantly from the image of non-reduced concentrated HA. Through the drying process of concentrated HA, the material will possess a cracked appearance, commonly described as “mud cracking”. Although all thermally reduced materials appeared cracked, it is evident that the cracking became more ordered⁴⁶. The cause for “mud cracking” can be quite complex, however, hydrophobicity and particle size often plays a significant role

in the geometry of the cracks⁴⁶. As depicted in Figure 17, as the solvent evaporates (in this case water), particles which have a high affinity for each other will exhibit an attractive force in the region of low pressure which exists between the two particles⁴⁶. There is a region of high pressure on the outer edges of the particles due to the forces exerted by the solvent evaporation⁴⁶.

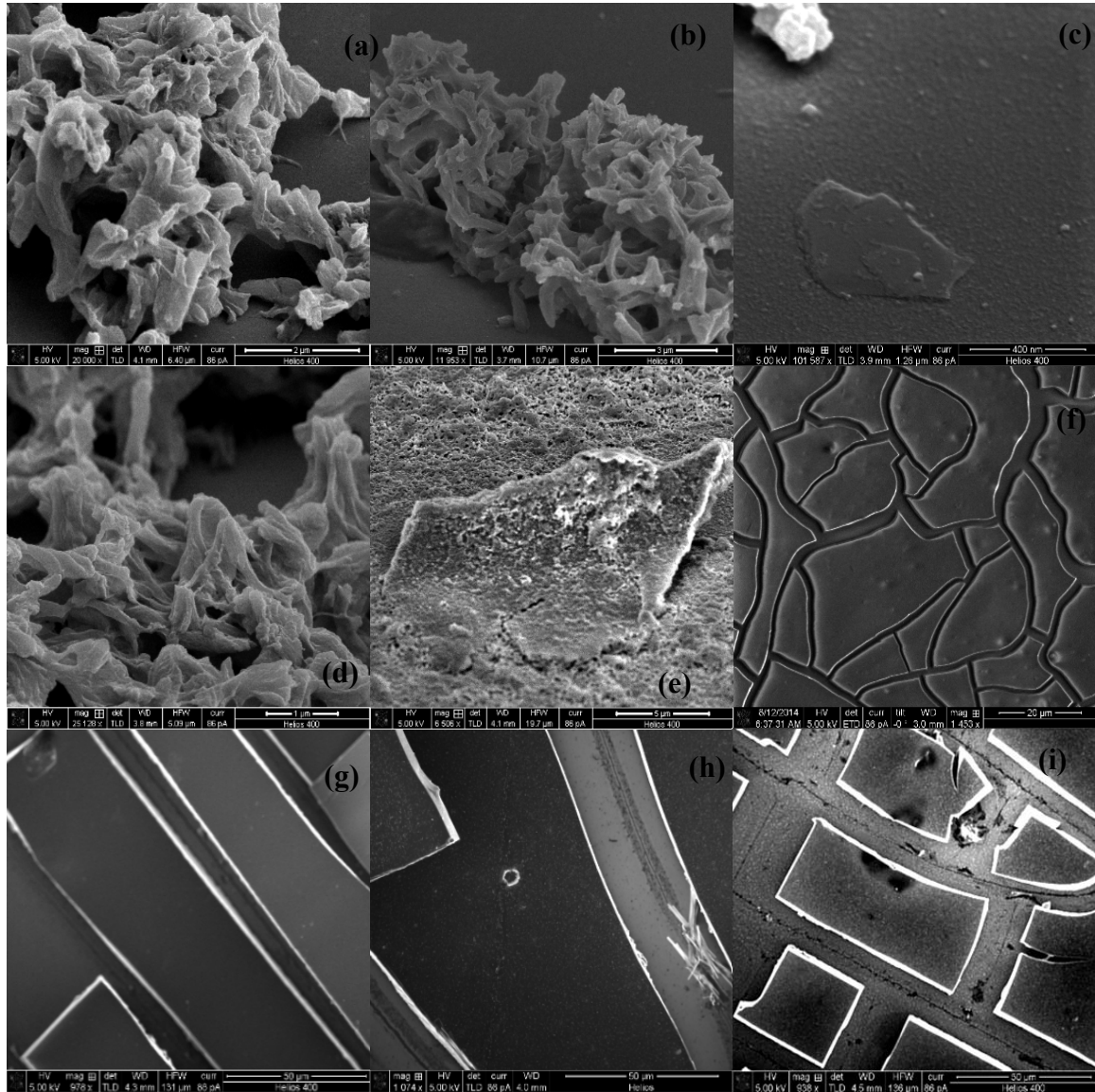


Figure 17. SEM images of HA and reduced HA's. (a) HHA, scale bar = 2 μ m, (b) HAHA, scale bar = 3 μ m, (c) NBHA, scale bar = 400 nm, (d) NBSHA, scale bar = 1 μ m, (e) BAHA, scale bar = 6 μ m, (f) Concentrated HA prior to thermal reduction, scale bar = 20 μ m, (g) HA500, scale bar = 50 μ m, (h) HA700, scale bar = 50 μ m, (i) HA900 = 50 μ m

Normal crack formation will nucleate at a particle defect sight and extend until a boundary is reached, often being another crack. Therefore, the appearance of the crack is curved and irregular, which is what was observed in the drying pattern of concentrated HA. The formation of regular arrays upon thermal reduction can be attributed to a decrease in defect sights, however, crack formation indicates that the material a high affinity from particle to particle, as the attractive force between the two forces is greater the forces exerted from solvent evaporation⁴⁶. This finding is consistent with the C/O ratios measured. It is apparent that the material still contained a minimum of 6% oxygenated species, therefore, the attractive forces are likely due to dipole-dipole interactions or hydrogen bonding between particles. Furthermore, the grain size produced by the cracking yield longer dimensions in the one dimension creating a more parallel morphology. Similar to “mud cracking”, is the formation of “coffee rings” upon solvent evaporation. “Coffee ring” formation is a phenomena whereby force exerted by solvent at the liquid/air interface is so great that the particles are forced to the edge of the evaporating droplet⁴⁶. When imaged, the particles at the outer rim of the evaporated droplet will have a cracks similar to those observed in the case of concentrated HA. However, because the chemically reduced HA’s were more dilute, the distribution of the particle on the substrate was confined to the region along the edge of the drying droplet.

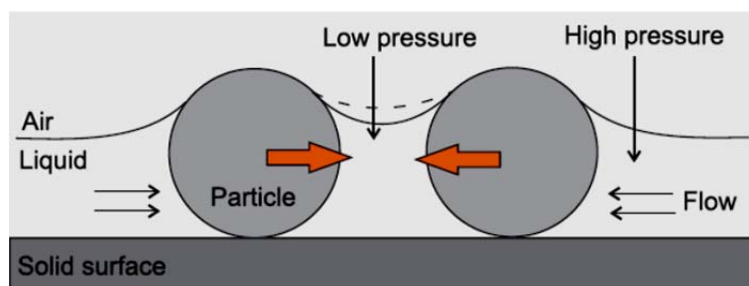


Figure 18. Drying of a dispersed material on a solid substrate⁴⁶

Similar to the observation in GTO900, the material reduced at 900 °C appeared to have white particulates or nodules protruding from the surface as shown in Figure 17i. Upon examination by EDS, the source of the particulates remains unclear and did not appear to affect the C/O measurements. The EDS can measure areas or spots, so area measurements were selected to include the particulates to verify the chemical nature of the particulates.

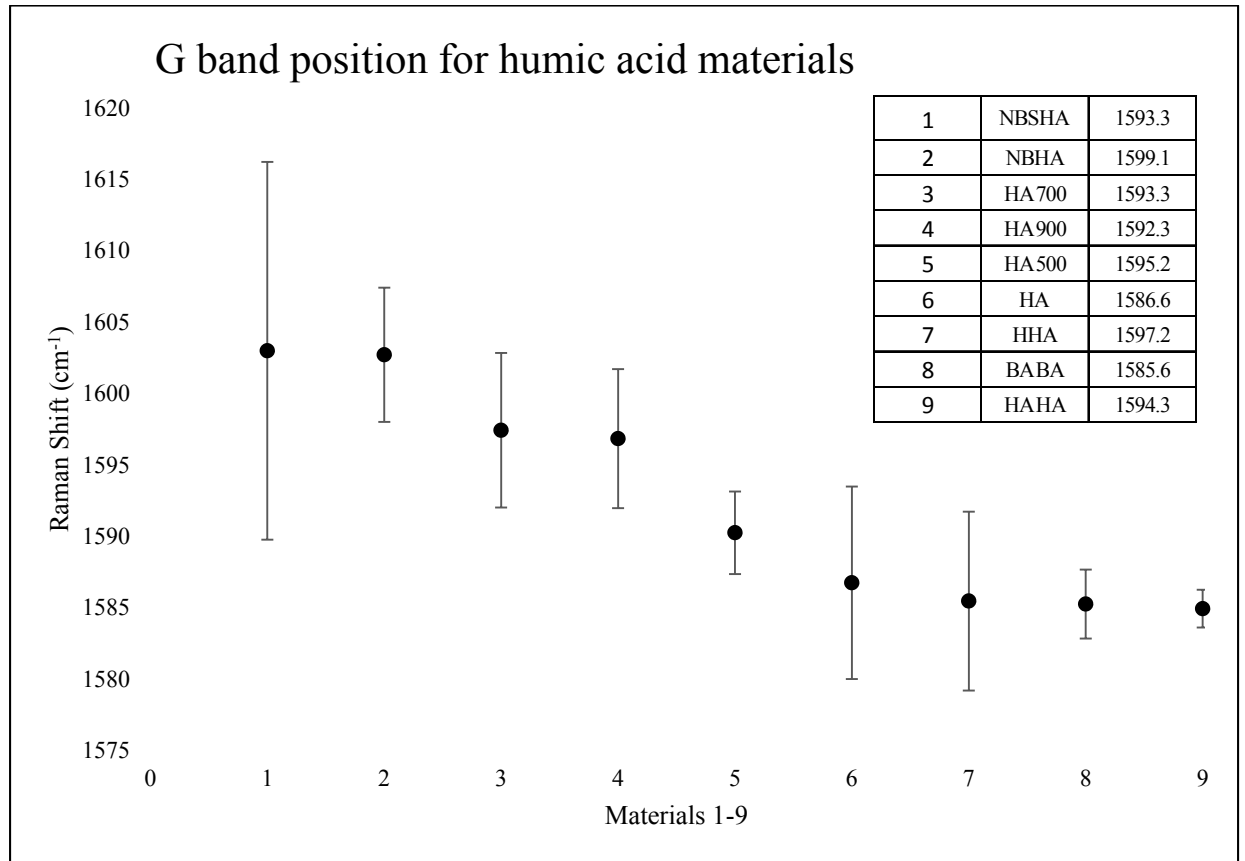


Figure 19. G band positions for all HA materials

To correlate the EDS data with Raman spectral analysis of all materials, an analysis of the Raman data is provided. Traditionally, the position of the G band and the $I_{(D)}/I_{(G)}$ ratio is utilized to assess order and disorder in graphitic systems. As discussed in the background sections, the band position and the ratio is highly dependent upon which

regime the material resides as well as stacking effects. As all materials prepared were agglomerated, comparisons between samples can confidently be made. Figure 20 compiles all materials, demonstrating a trend in the position of the G band versus oxygen content, $I_{(D)}/I_{(G)}$ ratio, and FWHM. HA falls in the regime more accurately described as an amorphous aromatic hydrocarbon. This can be observed in the Raman spectrum of HA as the $I_{(D)}/I_{(G)}$ ratio is low, ~ 0.66 , due to a large degree of disorder in the material. Furthermore, the aromatic hydrocarbons often have a competing fluorescent effect observed in the Raman as evidenced by the high background of the spectrums. The experimental setup was adjusted to minimize fluorescence effects and the range of analysis was decreased. As discussed in the background section of the paper the position of the G band can be attributed to several factors. The G band of HA is found in the same region as that of graphite due to a large number of sp^2 domains in HA, however, the size of the domains are small. The fluorescence background suggests that the material is slightly hydrogenated.

The position of the G band decreases in frequency from 1603 NBSHA to ~ 1585 cm^{-1} for HAHA. The shift alone cannot explain the changes observed in the Raman spectra. Therefore, comparison with a change in frequency with $I_{(D)}/I_{(G)}$ ratio is necessary. Table 5 is a direct comparison of the band position, the $I_{(D)}/I_{(G)}$ ratio, and % oxygen values by decreasing G band position. NBSHA has a ratio of 0.8 and HAHA had a ratio of 0.86. This indicates that although the amount of oxygen present and morphology are similar, HAHA is actually increasing in order as the oxygen is removed and increasing sp^2 domain size. The position of the G band also supports this argument. The remaining chemically treated HA's tend to follow a trend, increasing $I_{(D)}/I_{(G)}$ ratio as the % oxygen

is decreased, however, the intensity of the D band never surpasses that of the G band suggesting that there remains a significant amount of disorder.

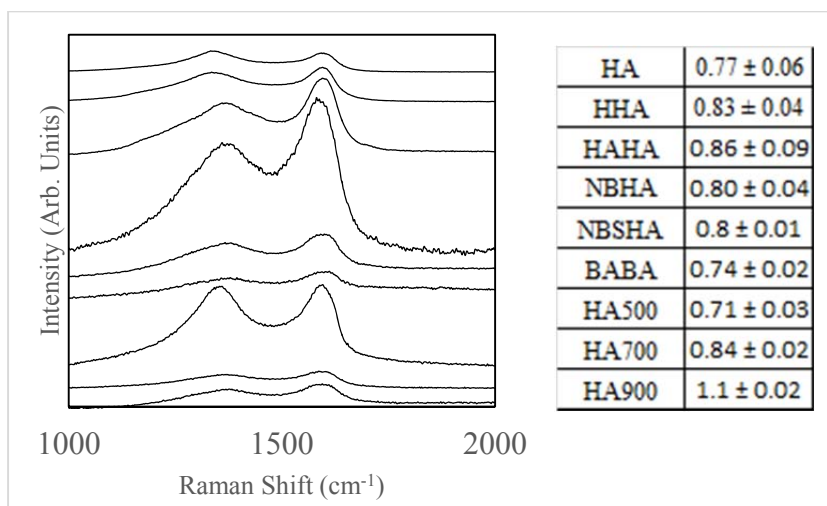


Figure 20. Raman spectra of HA materials and corresponding $I_{(D)}/I_{(G)}$ ratios

As previously discussed, thermal reduction of HA provided an immediate removal of ~33% of the oxygenated species, however, a limit of ~6.5% oxygen remained due to functional groups such as quinone structures which require additional thermal energy to cleave. Despite the lack in change in % oxygen, there is a clear trend in the Raman spectra. The $I_{(D)}/I_{(G)}$ ratio increases to the point where the D band intensity is greater than that of the G band. Thermal treatment appears to most effective in order restoration for HA materials. Thermal reduction provides energy to the system, allowing for atom rearrangement. The ratio changed by a total of 33% which is the greatest amount of change identified within this study. Future studies can attempt longer reduction times or higher temperatures to enhance reduction of the material.

To fully assess this material, the $I_{(D)}/I_{(G)}$ ratio and FWHM of the G band must also be taken into account. FWHM calculations were made using PeakFit 4.0 software fitted with Voigt Amp fitting to allow for the deconvolution of the D and G bands. All fits had an r^2 value > 0.94 . Error

Table 5. Compilation of humic acid material with decreasing % oxygen and correlated to G band position, $I_{(D)}/I_{(G)}$ values, and FWHM of G band

Material	% Oxygen	G band position (cm^{-1})	$I_{(D)}/I_{(G)}$	FWHM
NBHA	41.2	1599.1	0.80	107.4
HA	40.7	1586.6	0.77	112.3
BAHA	23.0	1585.6	0.74	107.0
NBSHA	14.6	1593.3	0.80	102.4
HHHA	12.2	1597.2	0.83	91.1
HAHA	9.1	1594.3	0.86	75.2
HA500	7.4	1595.2	0.71	82.1
HA700	6.6	1593.3	0.84	76.8
HA900	6.6	1592.3	1.10	68.2

and 95% confidence values can be found in the appendix. In the case of HA materials, the % oxygen values clearly follow a trend in regards to the FWHM, as the % oxygen decreased the FWHM decreased indicating a decrease in overall disorder of the material.

CHAPTER 5

CONCLUSIONS

5.1 Summary

In summary, both GTO and HA were characterized by a variety of methods including chemical and thermal methods. The reduction of oxygen in all GTO materials by all reduction methods all showed an increase in the $I_{(D)}/I_{(G)}$ ratio observed in the Raman measurements. Furthermore, the peak associated with the G band became more sharp and closer in wavenumber to the G band of graphite. This indicates that none of the reduction methods applied were successful in getting the material into the first regime in which the sp^2 domains are completely restored, the amorphous carbon to nano-graphite transformation. Within the first regime the material is decreasing the disorder on the basal plane by the removal of functional groups on the surface, but the removal of said groups does not translate to an increase in overall order. Dangling bonds, caused by the removed the functional groups produce a variety of rearrangements and the only means of defect repair occurs by thermal annealing at temperatures > 900 °C. These rearrangements to not necessarily correlate to restoration of graphene-like conjugation and rearrangement.

Unlike GTO, a decrease in oxygen content for HA by chemical necessitate a significant change in the Raman spectra. This is because, although the material begins with lowered amounts of oxygen, the data and extensive literature reports on the proposed structures of HA indicate, that the material is comprised of regions of both sp^2 and sp^3 character and the removal of oxygen species does not equate to the restoration of order in the material as a whole. Significant changes in the Raman spectra are not observed until the material undergoes thermal annealing, at which point the system has

been given an input of energy sufficient to allow for the evolution of oxygen and atom rearrangement to occur. During this process, the material displays a decrease in sp^3 carbon bonds and an increase in conjugation. The D peak increases in intensity, the G band sharpens, and the separation between the D and G band is observed.

Consistent with both materials is the fact that both reside within the first regime of regarding their Raman spectra. Both have some degree of sp^3 character and possess some degree of disorder. However, HA appears to have a much higher amount of both features and belongs to the very early stages of the first regime. GO begins in the latter stages of the first regime, but thermal treatment of either material results in the same level of order restoration per Raman analysis.

5.2 Future Work

Future work should include further evaluation of the materials via alternate means to included electrical characterizations and elemental analysis via X-ray photoelectron spectroscopy. Furthermore, as neither mode of reduction was successful in returning the graphitic nature of the material, it is proposed that the material could undergo further reduction or at elevated temperatures or pressure. It could be possible to calibrate the reduction of the material via Raman spectroscopy. Because HA is in the technical community as a graphene-like material, further analysis of the commercial relevance would be promising.

APPENDIX SECTION

Appendix I

Raw Data for Graphite Oxide Reductions

Section A. SEM/EDS raw data for graphite oxide materials

Table A1-1. Graphite oxide standard C/O ratios

Graphite Oxide Standard C/O Ratios		
Spot (S)/Area (A)	Atomic % Carbon	Atomic % Oxygen
A1	52.03	47.97
A2	51.21	48.79
A3	51.15	48.85
A4	54.18	45.82
A5	50.86	49.14
A6	50.81	49.19
A7	50.84	49.16
A8	52.62	47.38
A9	51.84	48.16
A10	51.21	48.79
A11	52.20	47.8
<i>Average</i>	<i>51.72</i>	<i>48.28</i>
<i>Standard Deviation</i>	<i>1.02</i>	

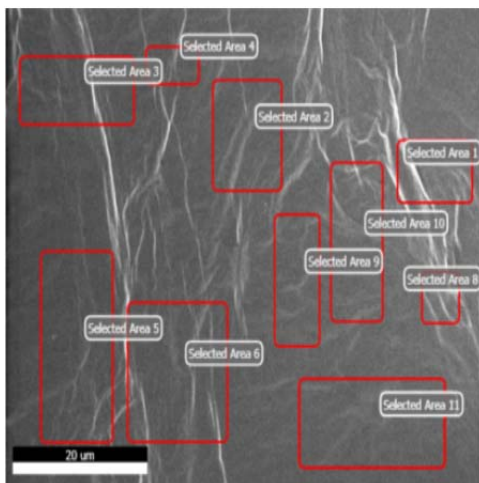


Figure A1-1. Image of EDS areas 1-11 of graphite oxide standard

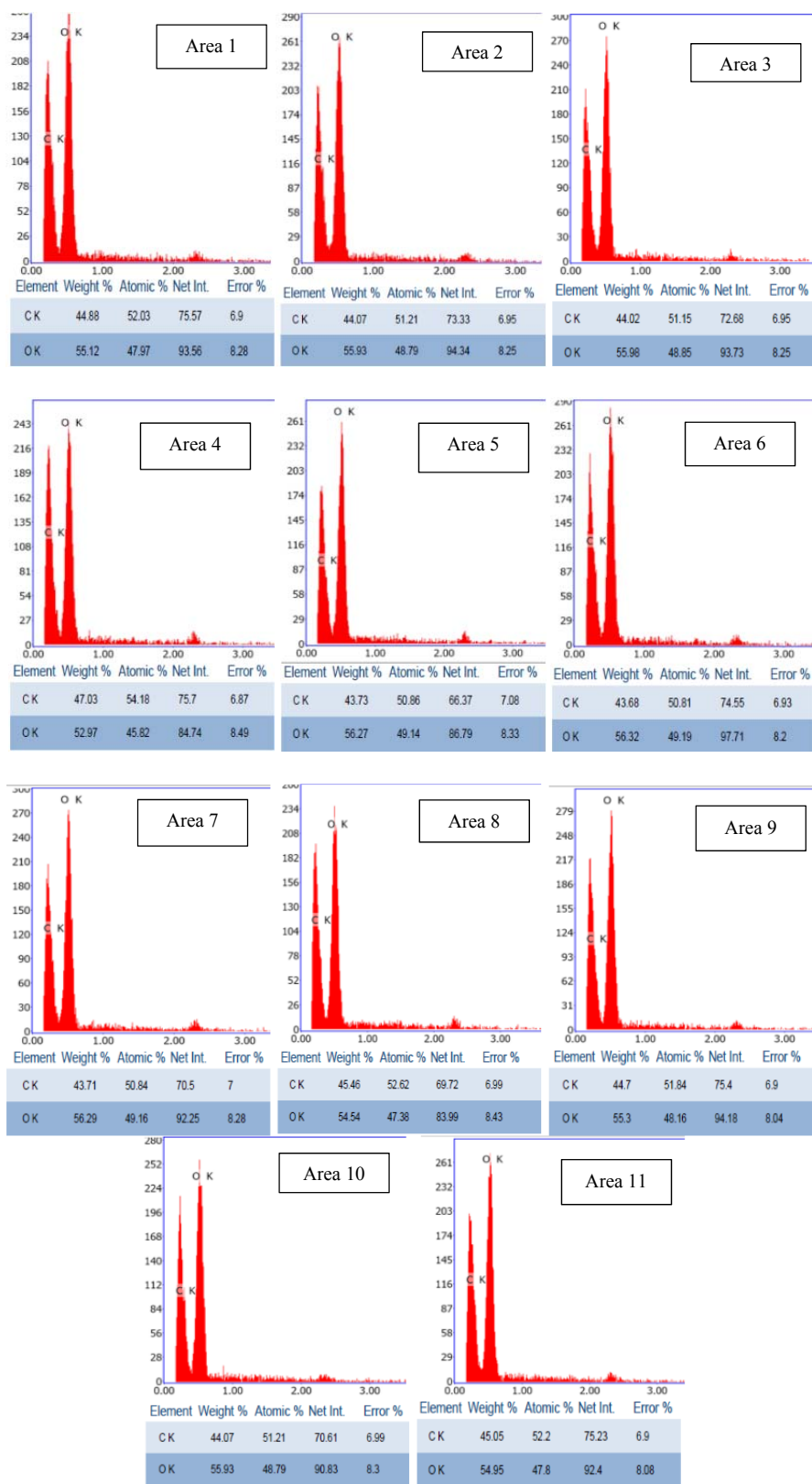


Figure A1-2. EDS spectra of areas 1-11 of graphite oxide standard

Table A1-2. Hydrazine reduced graphite oxide C/O ratios

Hydrazine Reduced Graphite Oxide C/O Ratios			
Sample #	Spot (S)/Area (A)	Atomic % Carbon	Atomic % Oxygen
2	A1	70.12	29.88
2	A2	70.09	29.91
3	A1	70.45	29.55
3	A2	70.78	29.22
3	S1	68.33	31.67
3	S2	68.61	31.39
3	S3	68.59	31.41
<i>Average</i>		69.57	30.43
<i>Standard Deviation</i>		0.95	

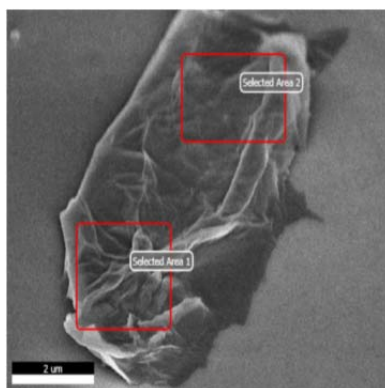


Figure A1-3. Image of EDS areas 1 and 2 – sample 2 for hydrazine reduced graphite oxide

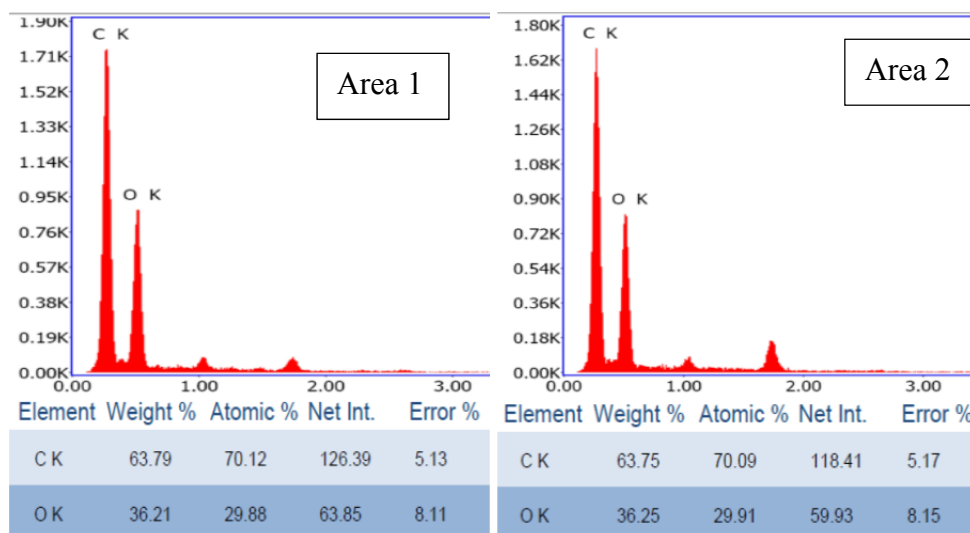


Figure A1-4. EDS spectra areas 1 and 2 – sample 2 for hydrazine reduced graphite oxide

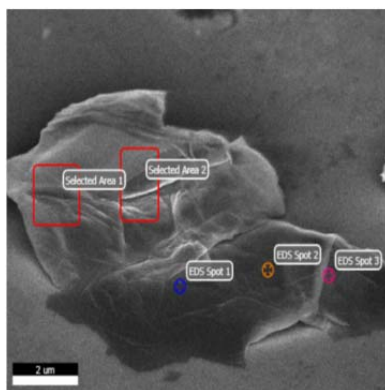


Figure A1-5. Image of EDS areas 1 and 2, spots 1-3 – sample 3 for hydrazine reduced graphite oxide

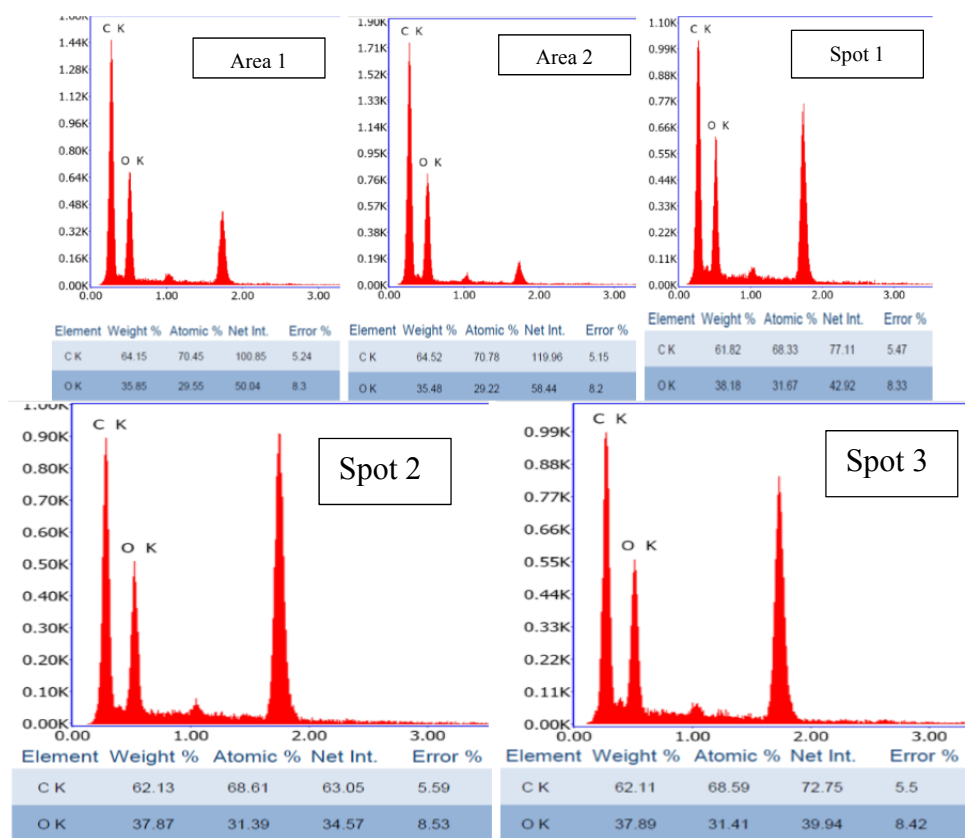


Figure A1-6. EDS spectra for areas 1 and 2, spots 1-3 – sample 3 for hydrazine reduced graphite oxide

Table A1-3. Hydroxylamine reduced graphite oxide C/O ratios

Hydroxylamine Reduced Graphite Oxide C/O Ratios			
Sample #	Spot (S)/Area (A)	Atomic % Carbon	Atomic % Oxygen
1	A1	85.50	14.50
2	A1	84.01	15.99
2	A2	84.49	15.51
2	A3	84.06	15.94
3	A1	84.96	15.04
3	A2	84.29	15.71
Average		84.55	15.45
Standard Deviation		0.63	

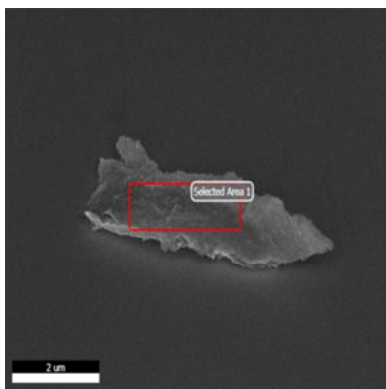


Figure A1-7. Image of EDS area 1 – sample 1 for hydroxylamine reduced graphite oxide

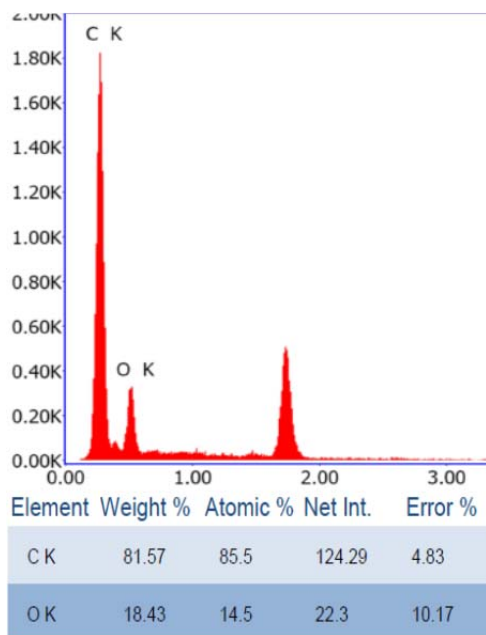


Figure A1-8. EDS spectrum area 1 – sample 1 for hydroxylamine reduced graphite oxide

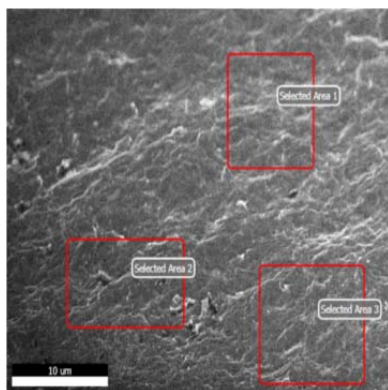


Figure A1-9. Image of EDS areas 1-3 – sample 2 for hydroxylamine reduced graphite oxide

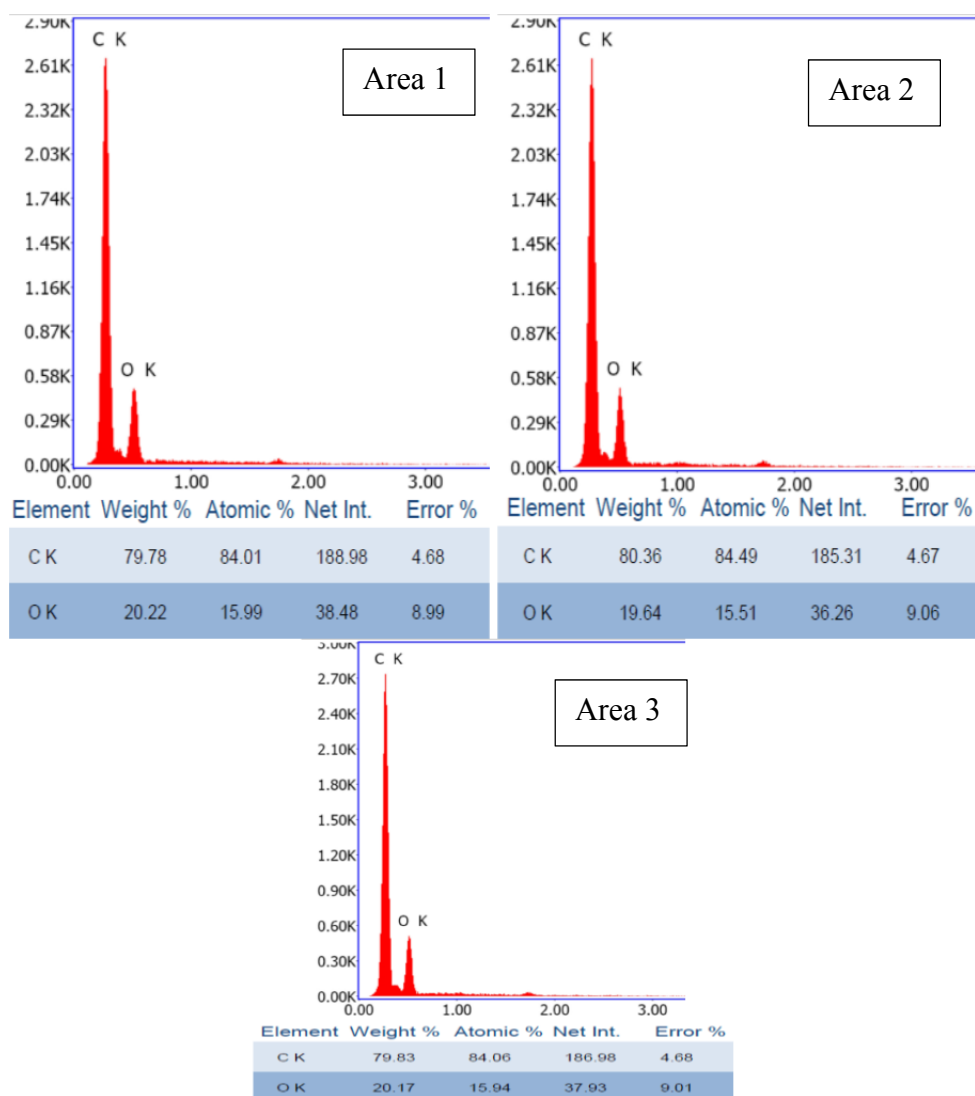


Figure A1-10. EDS spectra areas 1-3 – sample 2 for hydroxylamine reduced graphite oxide

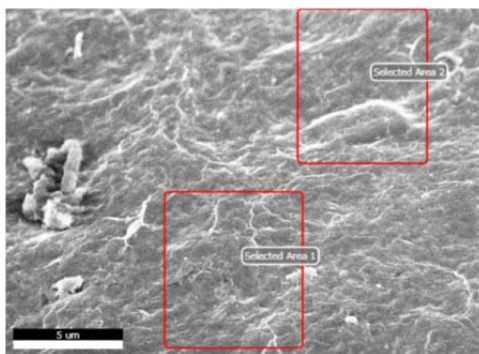


Figure A1-11. Image of EDS areas 1 and 2 – sample 3 for hydroxylamine reduced graphite oxide

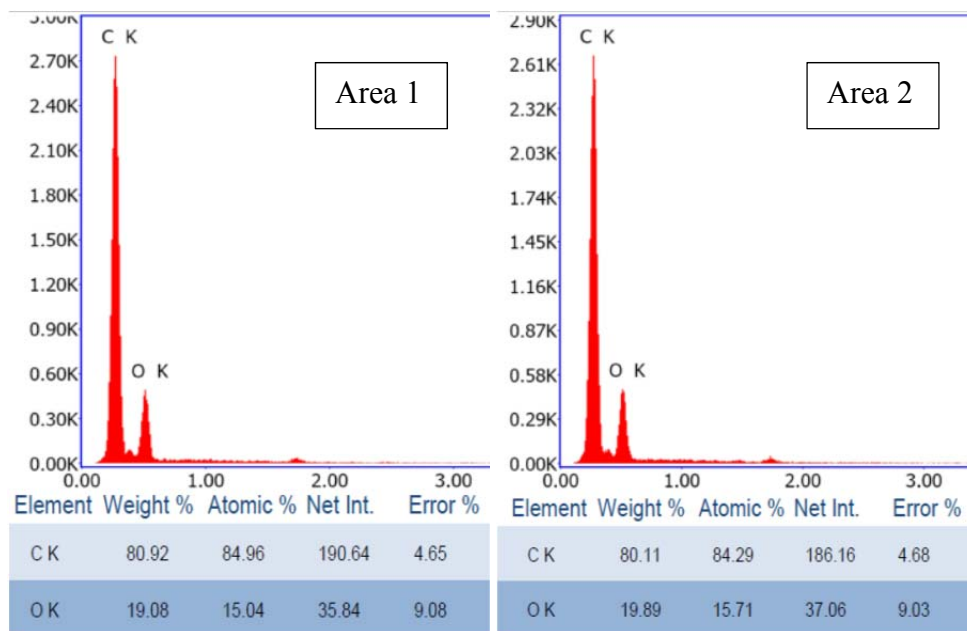


Figure A1-12. EDS spectra for areas 1 and 2 – sample 3 for hydroxylamine reduced graphite oxide

Table A1-4. Sodium borohydride reduced graphite oxide C/O ratios

Sodium Borohydride Reduced Graphite Oxide C/O Ratios			
Sample #	Spot (S)/Area (A)	Atomic % Carbon	Atomic % Oxygen
1	A1	79.47	20.53
1	A2	82.15	17.85
1	A3	80.78	19.22
1	A4	80.95	19.05
2	A1	81.07	18.93
2	A2	80.07	19.93
Average		80.75	19.25
Standard Deviation		0.96	

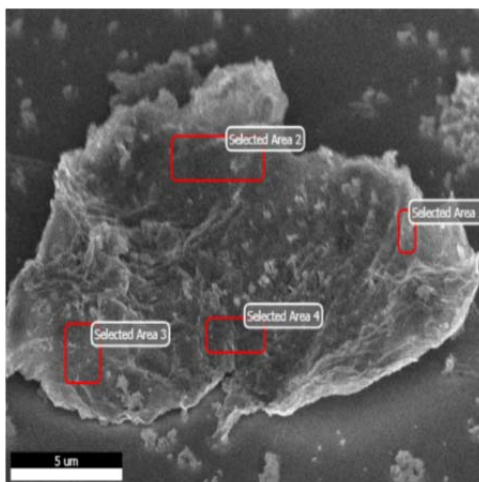


Figure A1-13. Image of EDS areas 1-4 – sample 1 for sodium borohydride reduced graphite oxide

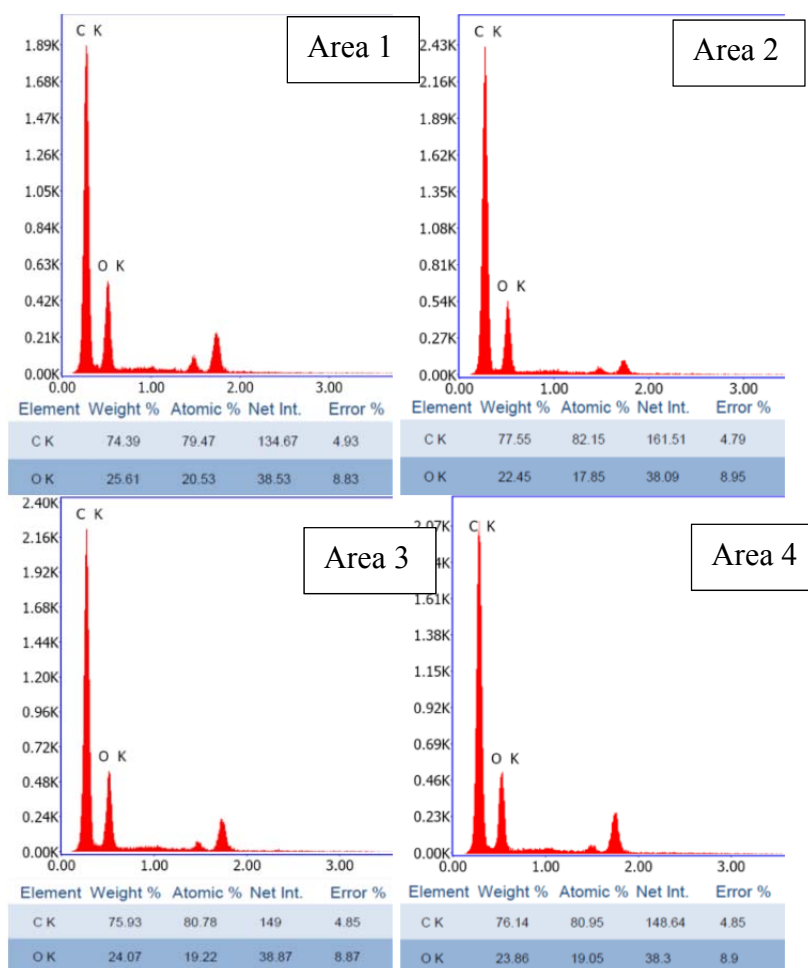


Figure A1-14. EDS spectra for areas 1-4 – sample 1 for sodium borohydride reduced graphite oxide

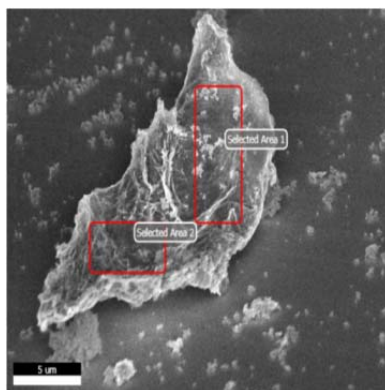


Figure A1-15. Image of EDS areas 1 and 2 – sample 2 for sodium borohydride reduced graphite oxide

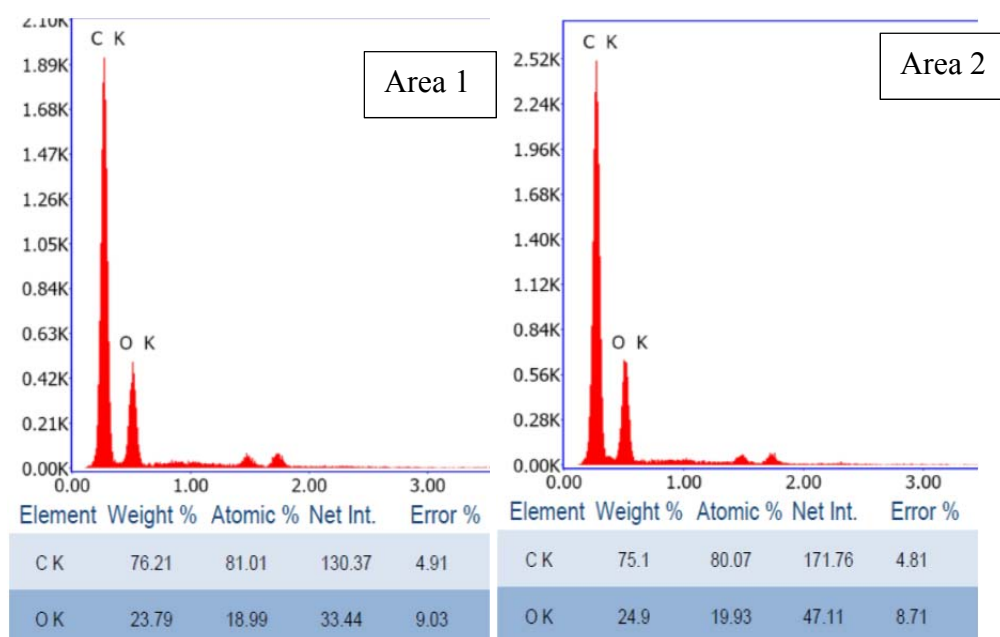


Figure A1-16. EDS spectra areas 1 and 2 – sample 2 for sodium borohydride reduced graphite oxide

Table A1-5. Sodium bisulfite reduced graphite oxide C/O ratios

Sodium Bisulfite Reduced Graphite Oxide C/O Ratios			
Sample #	Spot (S)/Area (A)	Atomic % Carbon	Atomic % Oxygen
1	A1	78.45	21.55
2	A1	80.51	19.49
2	A2	80.43	19.57
3	A1	83.59	16.41
3	A2	80.07	19.93
<i>Average</i>		80.61	19.39
<i>Standard Deviation</i>		2.12	

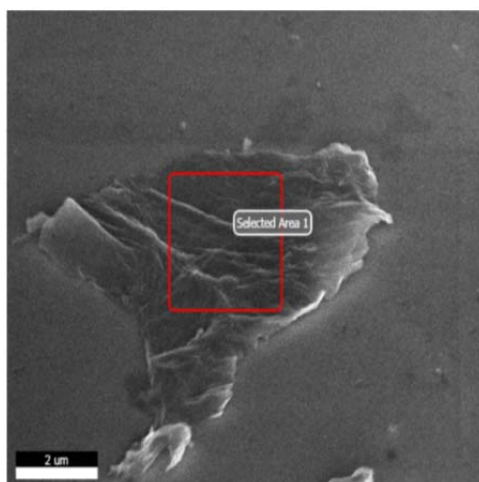


Figure A1-17. Image of EDS area 1 – sample 1 for sodium bisulfite reduced graphite oxide

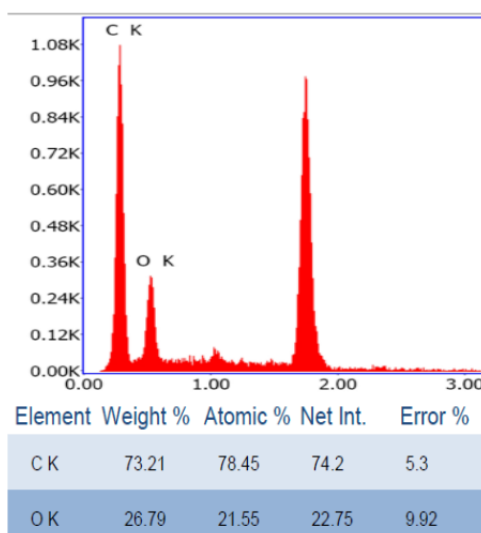


Figure A1-18. EDS spectrum for area 1 – sample 1 for sodium bisulfite reduced graphite oxide

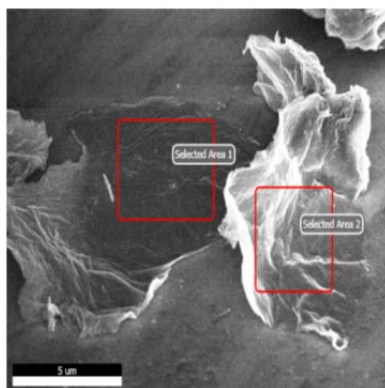


Figure A1-19. Image of EDS areas 1 and 2 – sample 2 for sodium bisulfite reduced graphite oxide

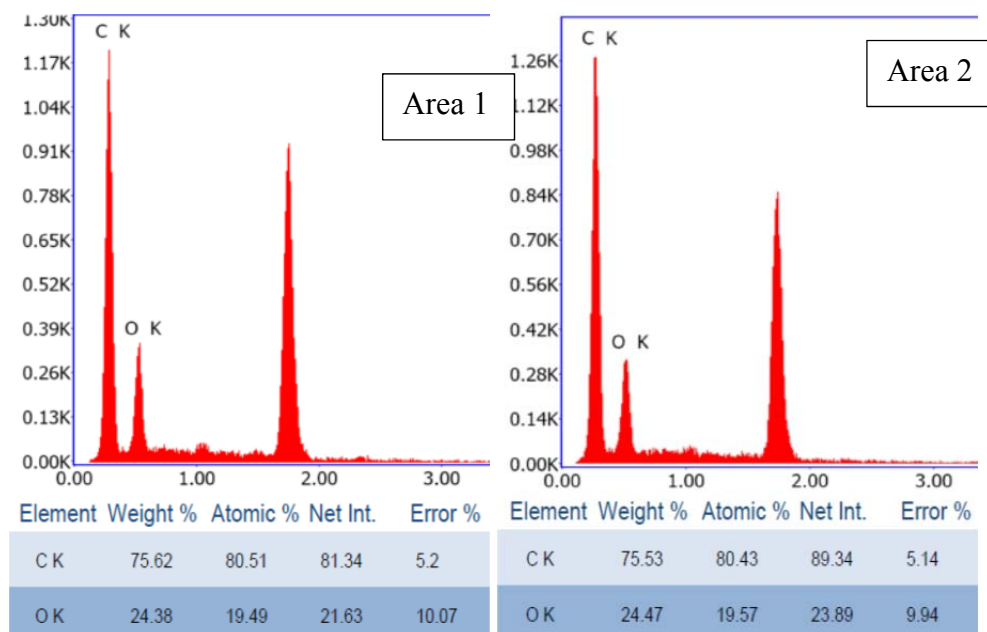


Figure A1-20. EDS spectra for areas 1 and 2 – sample 2 for sodium bisulfite reduced graphite oxide

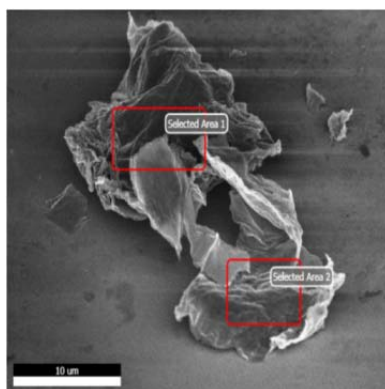


Figure A1-21. Image of EDS areas 1 and 2 – sample 3 for sodium bisulfite reduced graphite oxide

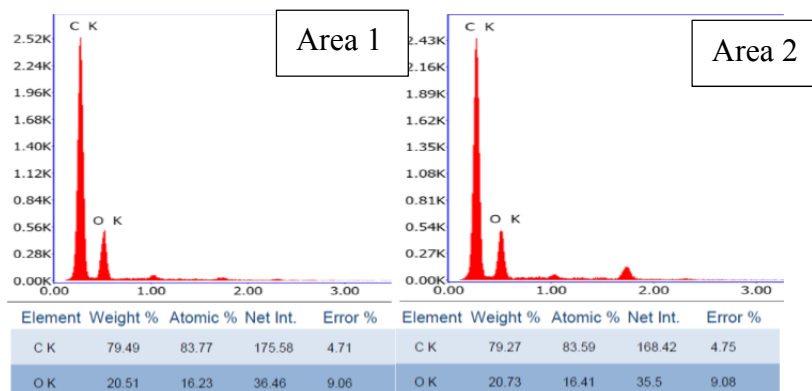


Figure A1-22. EDS spectra for areas 1 and 2 – sample 3 for sodium bisulfite reduced graphite oxide

Table A1-6. Benzyl alcohol reduced graphite oxide C/O ratios

Benzyl Alcohol Reduced Graphite Oxide C/O Ratios			
Sample #	Spot (S)/Area (A)	Atomic % Carbon	Atomic % Oxygen
1	A1	89.75	10.25
1	A2	87.24	12.76
1	A3	88.91	11.09
2	A1	87.02	12.98
2	A2	85.87	14.13
2	A3	87.23	12.77
Average		87.67	12.33
Standard Deviation		1.41	

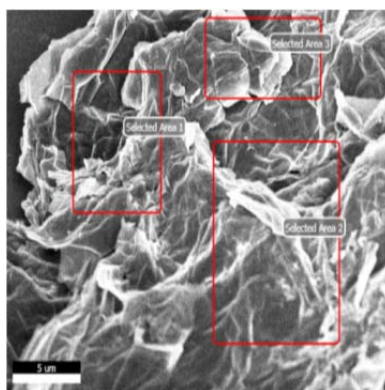


Figure A1-23. Image of EDS areas 1-3 – sample 1 for benzyl alcohol reduced graphite oxide

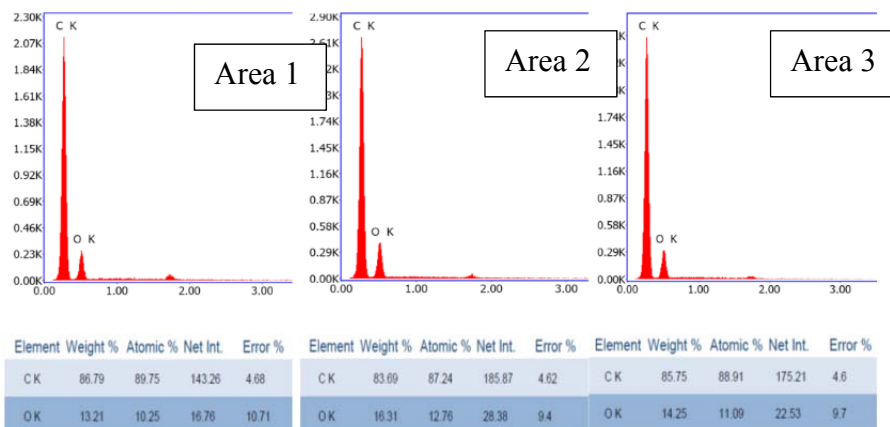


Figure A1-24. EDS spectra for areas 1-3 – sample 1 for benzyl alcohol reduced graphite oxide

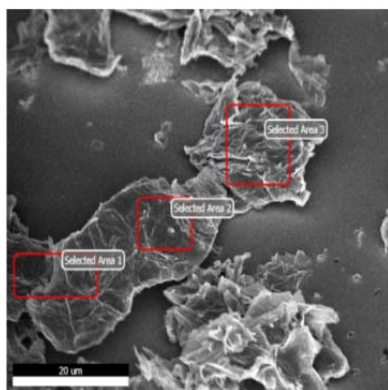


Figure A1-25. Image of EDS areas 1-3 – sample 2 for benzyl alcohol reduced graphite oxide

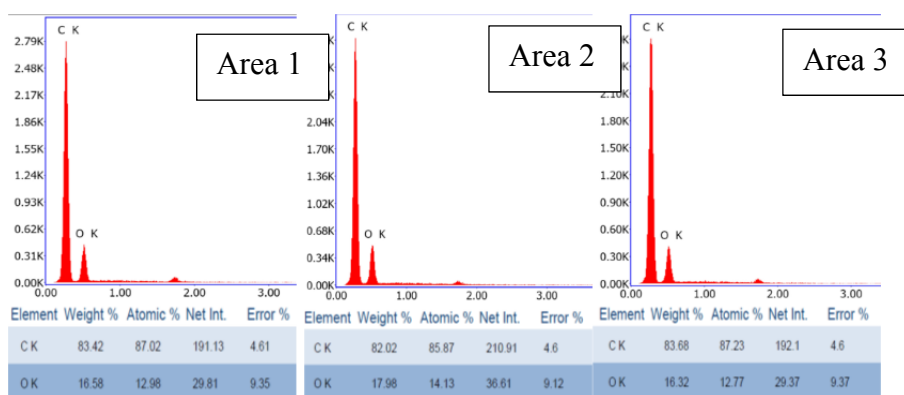


Figure A1-26. EDS spectra for areas 1-3 – sample 2 for benzyl alcohol reduced graphite oxide

Table A1-7. Thermally reduced graphite oxide at 500 °C C/O ratios

Graphite Oxide Thermally Reduced at 500 °C C/O ratios		
Spot (S)/Area (A)	Atomic % Carbon	Atomic % Oxygen
S1	91.64	8.36
S2	87.52	12.48
S3	92.40	7.60
S4	93.19	6.81
S5	88.88	11.12
S6	89.03	10.97
<i>Average</i>	<i>90.44</i>	<i>9.56</i>
<i>Standard Deviation</i>	<i>2.27</i>	

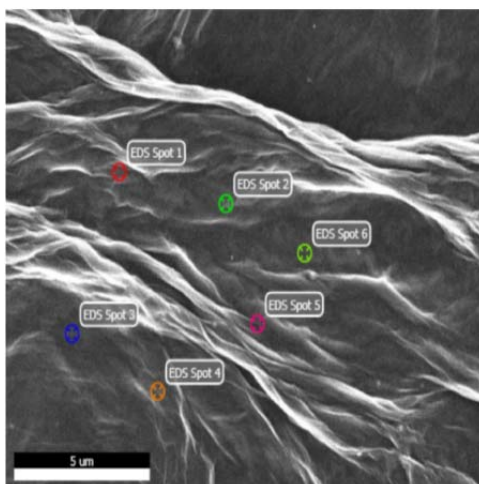


Figure A1-27. Image of EDS spots 1-6 for thermally reduced graphite oxide at 500 °C

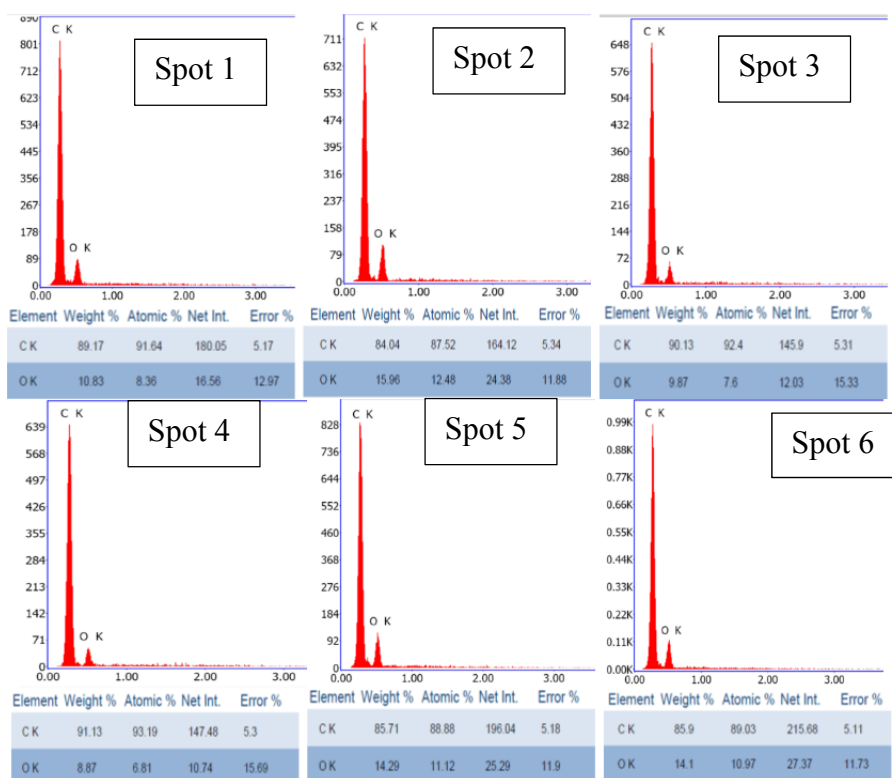


Figure A1-28. EDS spectra for spots 1-6 for thermally reduced graphite oxide at 500 °C

Table A1-8. Thermally reduced graphite oxide at 700 °C C/O ratios

Graphite Oxide Thermally Reduced at 700 °C		
Spot (S)/Area (A)	Atomic % Carbon	Atomic % Oxygen
A1	95.82	4.18
A2	95.42	4.58
A3	94.26	5.74
A4	94.69	5.31
A5	94.97	5.03
A6	94.75	5.25
A7	94.17	5.83
A8	94.39	5.61
A9	94.77	5.23
A10	93.99	6.01
<i>Average</i>	94.72	5.28
<i>Standard Deviation</i>	0.57	

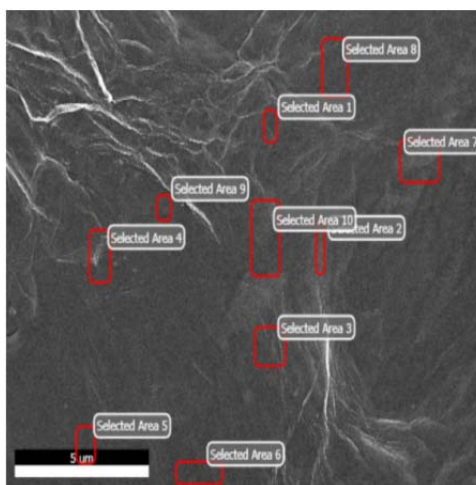


Figure A1-29. Image of EDS areas 1-10 for thermally reduced graphite oxide at 700 °C

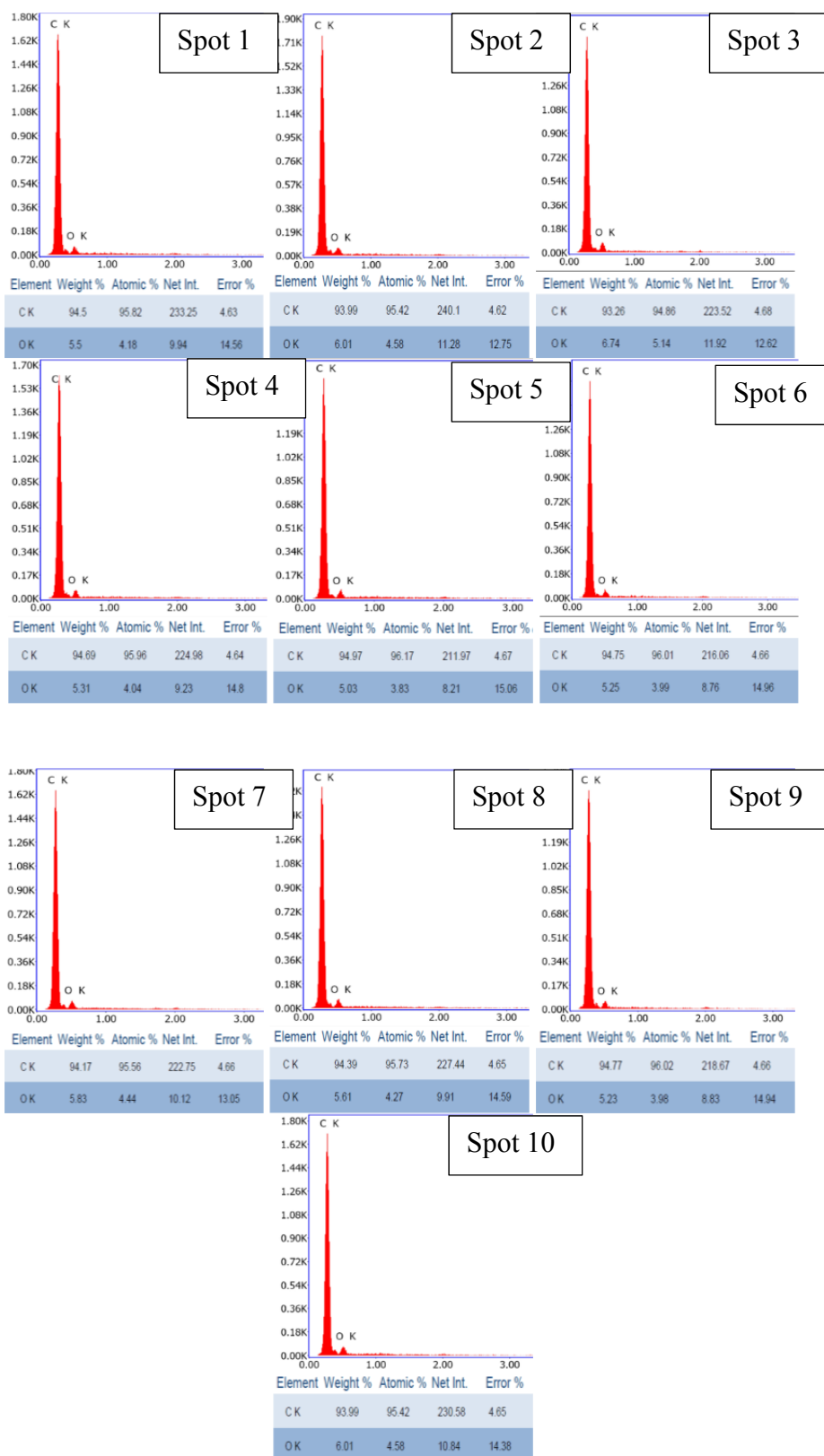


Figure A1-30. EDS spectra for areas 1-10 for thermally reduced graphite oxide at 700 °C

Table A1-9. Thermally reduced graphite oxide at 900 °C C/O ratios

Graphite Oxide Thermally Reduced at 900 °C		
Spot (S)/Area (A)	Atomic % Carbon	Atomic % Oxygen
A1	96.42	3.58
A2	97.32	2.68
A3	98.47	1.53
A4	97.34	2.66
A5	96.62	3.38
A6	97.51	2.49
A7	97.15	2.85
A8	97.59	2.41
<i>Average</i>	<i>97.30</i>	<i>2.70</i>
<i>Standard Deviation</i>	<i>0.63</i>	

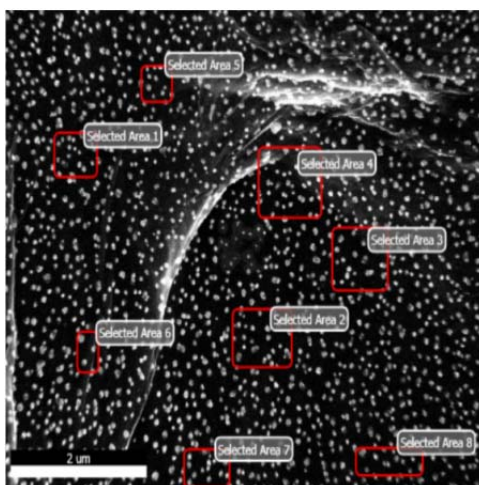


Figure A1-31. Image of EDS areas 1-8 for thermally reduced graphite oxide at 900 °C

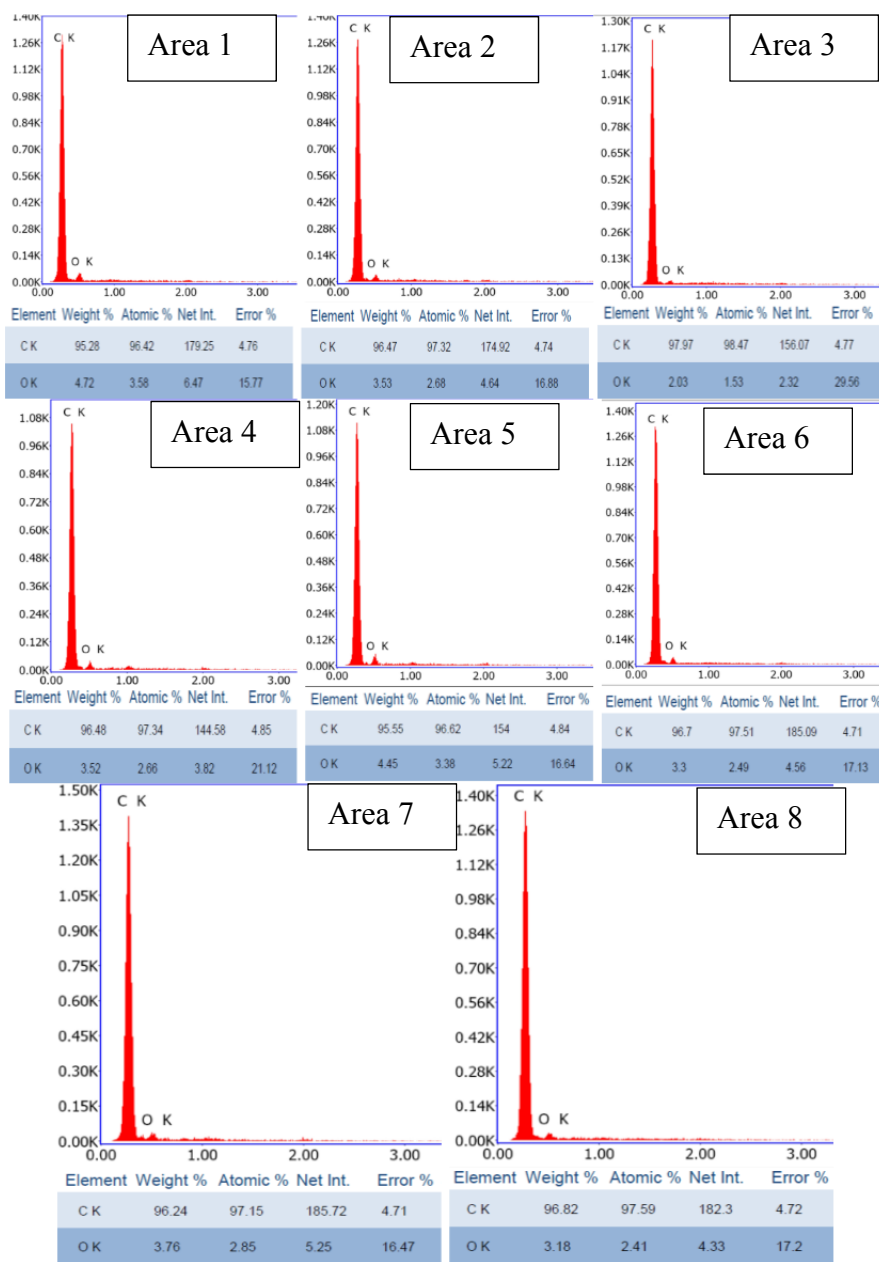


Figure A1-32. EDS spectra areas 1-8 for thermally reduced graphite oxide at 900 °C

Section B. Raman Spectroscopy Raw Data for Graphite Oxide and Reduced Graphite Oxide

Section B.1 Raman Spectral Data for Graphite

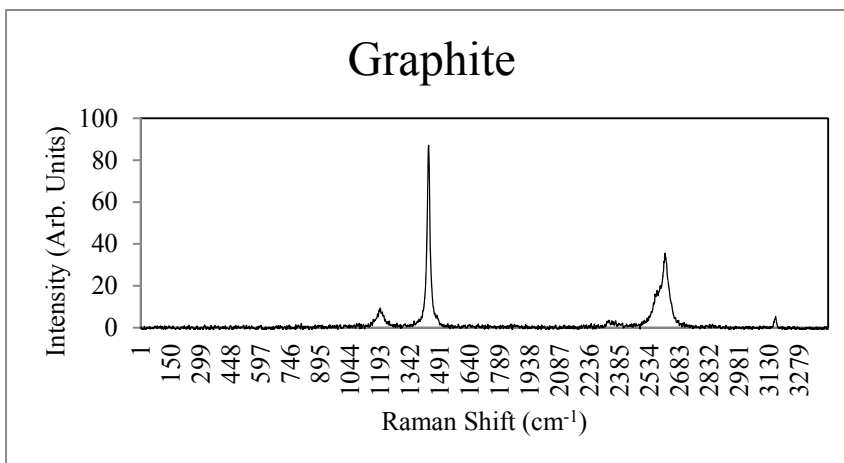


Figure A1-33 Raman spectrum of pristine graphite

Section B.2 Raman spectral data for graphite oxide standard

Table A1-10. Raman spectral data for graphite oxide standard

Raman Analysis for Graphite Oxide Standard					
Sample #	D Raman Shift (cm ⁻¹)	I _(D)	G Raman Shift (cm ⁻¹)	I _(G)	I _(D) /I _(G)
1	1358.08	1087.68	1603.96	1094.05	0.99
2	1354.22	1100.89	1592.39	1087.50	1.01
3	1353.26	1134.34	1601.07	1173.01	0.97
4	1353.26	973.47	1603.96	995.65	0.98
5	1350.36	1125.17	1602.99	1145.39	0.98
6	1360.01	1117.95	1602.99	1150.24	0.97
Average	1354.87		1601.23		0.98
Standard Deviations	3.23		4.07		0.02

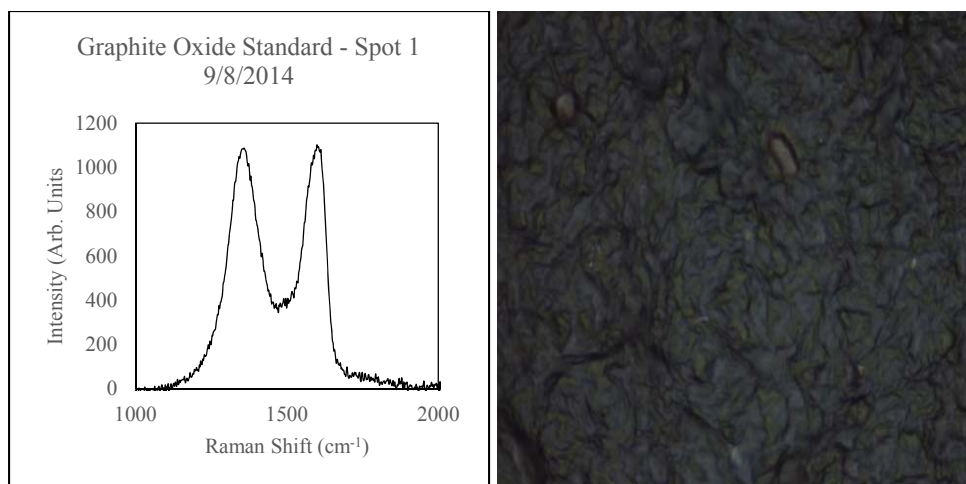


Figure A1-34. Graphite oxide standard – spot 1

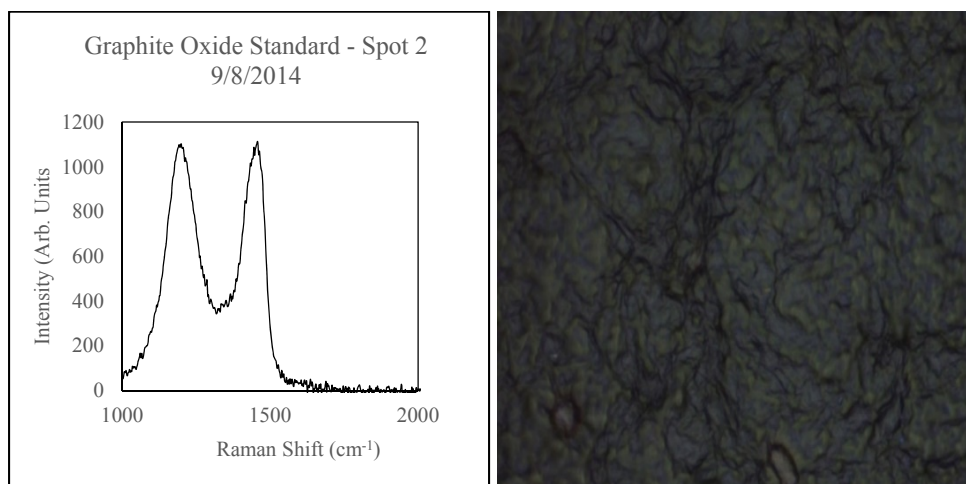


Figure A1-35. Graphite oxide standard – spot 2

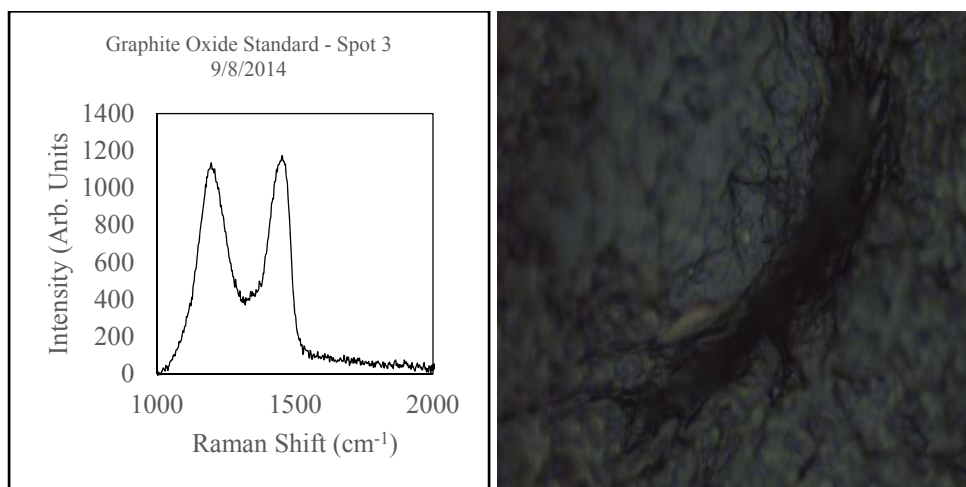


Figure A1-36. Graphite oxide standard – spot 3

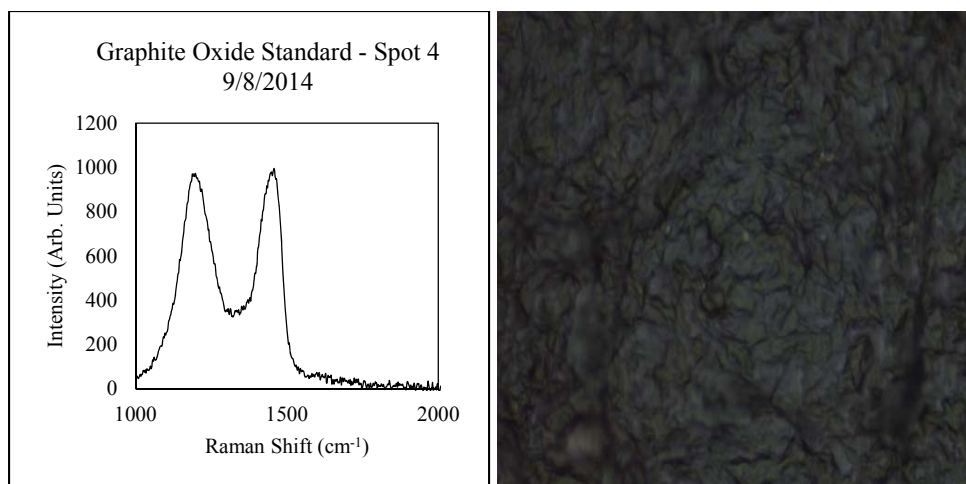


Figure A1-37. Graphite oxide standard – spot 4

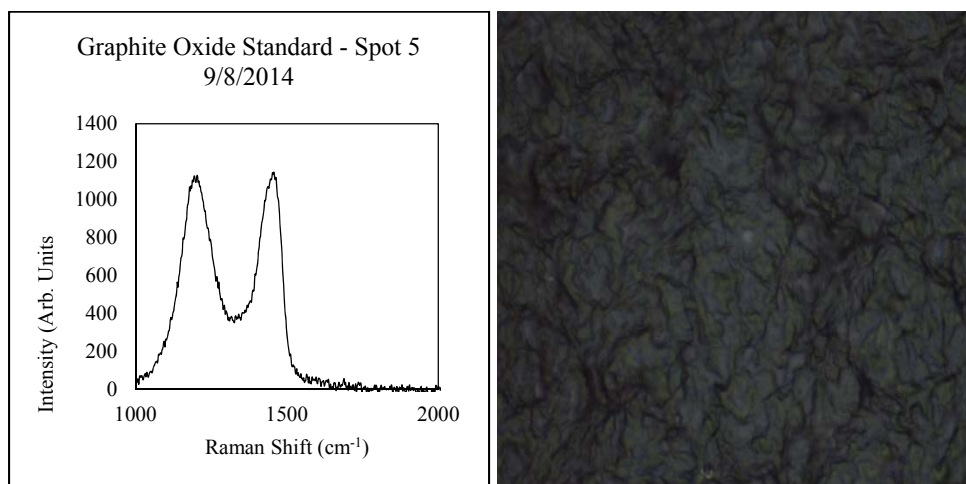


Figure A1-38. Graphite oxide standard – spot 5

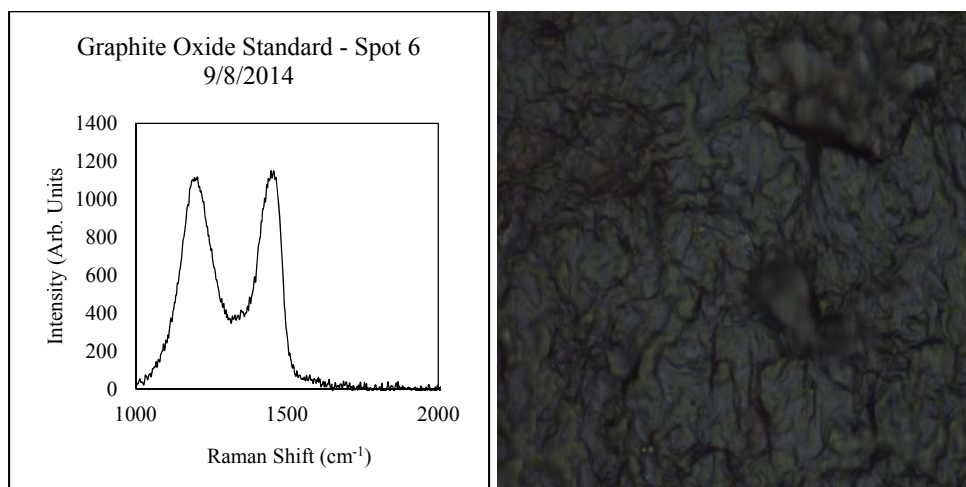


Figure A1-39. Graphite oxide standard – spot 6

Section B3. Raman spectral data for hydrazine reduced graphene oxide

Table A1-11. Raman spectral data for hydrazine reduced graphite oxide

Raman Analysis for Hydrazine Reduced Graphite Oxide					
Sample #	D Raman Shift (cm ⁻¹)	I _(D)	G Raman Shift (cm ⁻¹)	I _(G)	I _(D) /I _(G)
1	1348.44	545.71	1588.53	464.10	1.18
2	1350.36	225.67	1593.35	193.45	1.17
3	1351.33	169.99	1595.28	141.59	1.20
4	1349.40	328.10	1594.32	276.24	1.19
5	1346.51	619.83	1587.57	533.12	1.16
6	1345.54	610.01	1594.32	510.79	1.19
Average	1348.60		1592.23		1.18
Standard Deviation	2.23		3.31		0.02

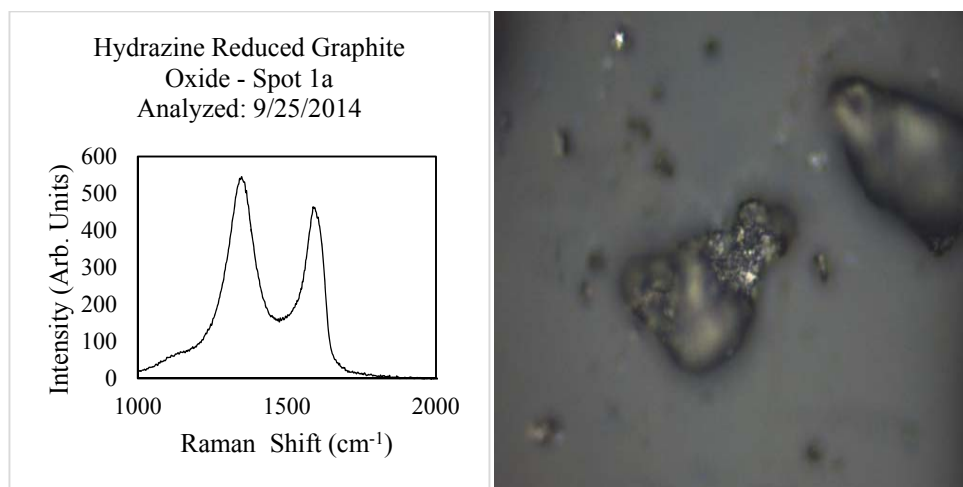


Figure A1-40. Hydrazine reduced graphite oxide standard – spot 1a

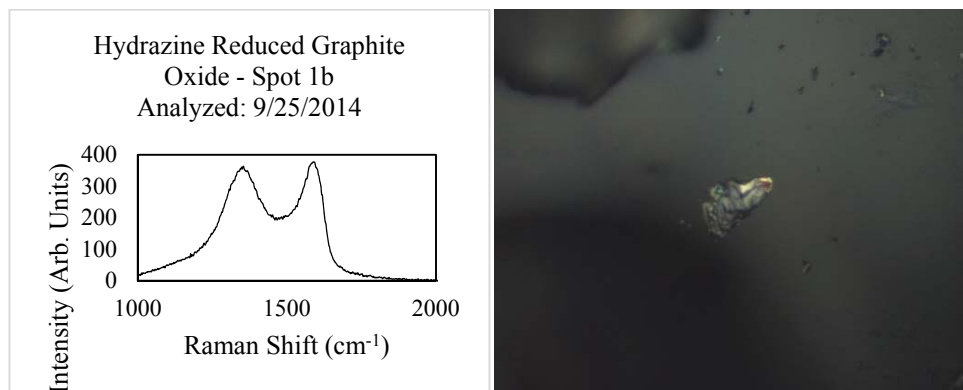


Figure A1-41. Hydrazine reduced graphite oxide standard – spot 1b

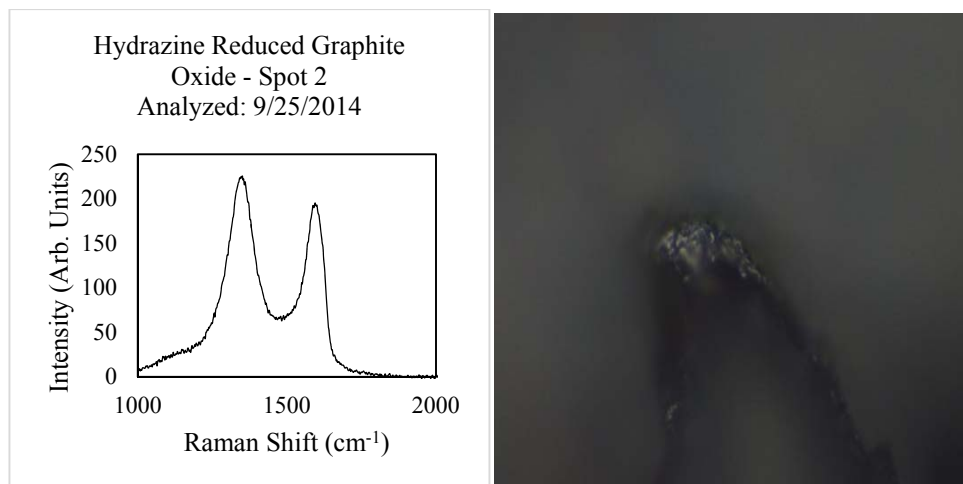


Figure A1-42. Hydrazine reduced graphite oxide standard – spot 2

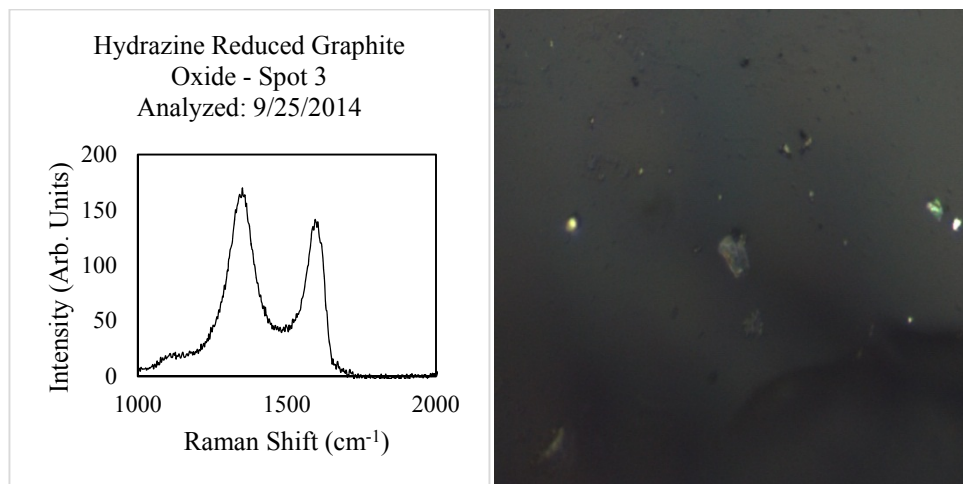


Figure A1-43. Hydrazine reduced graphite oxide standard – spot 3

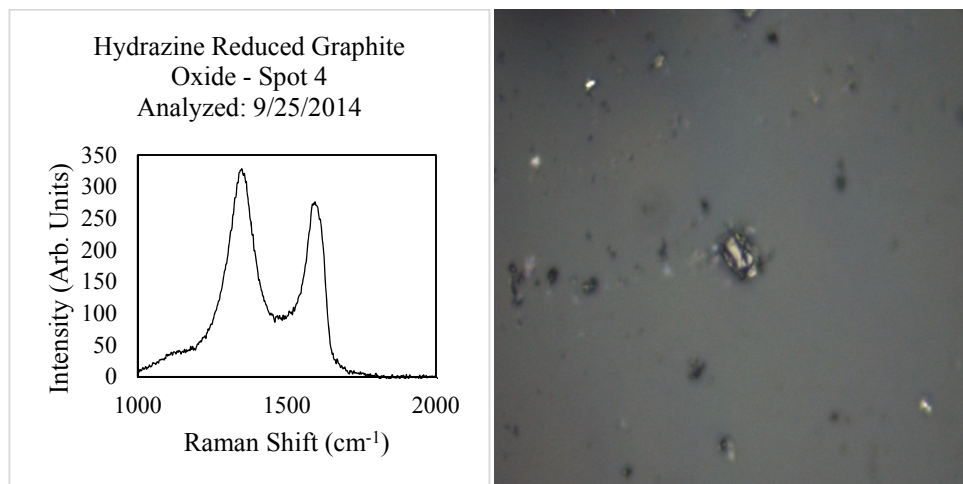


Figure A1-44. Hydrazine reduced graphite oxide standard – spot 4

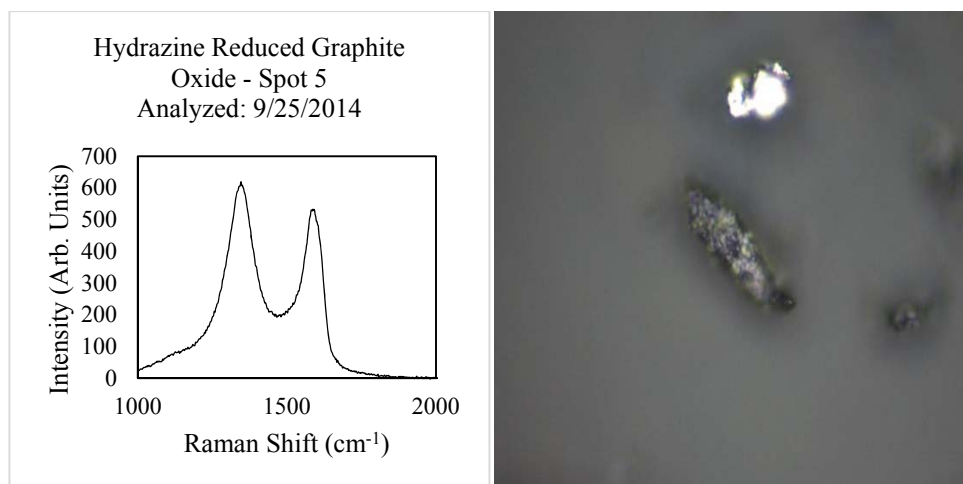


Figure A1-45. Hydrazine reduced graphite oxide standard – spot 5

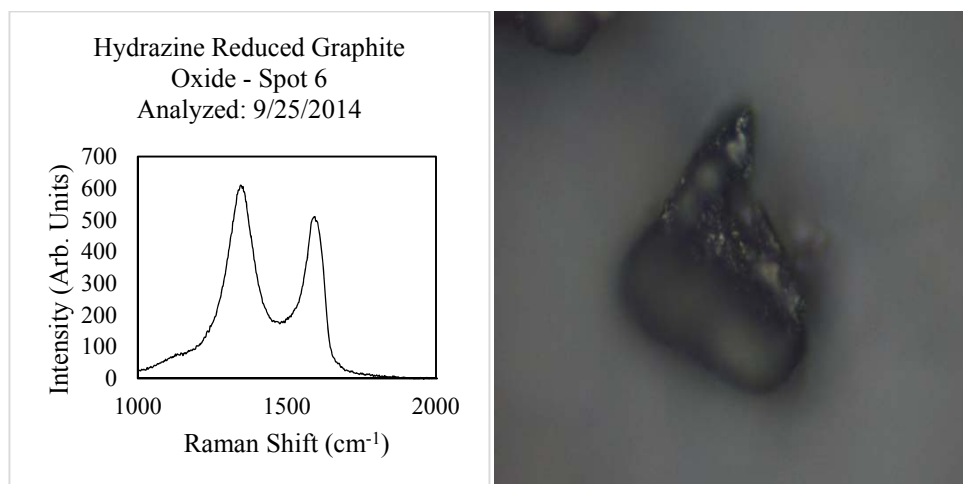


Figure A1-46. Hydrazine reduced graphite oxide standard – spot 6

Section B4. Raman spectral data for hydroxylamine reduced graphite oxide

Table A1-12. Raman spectral data for hydroxylamine reduced graphite oxide

Raman Analysis for Hydroxylamine Reduced Graphite Oxide					
Sample #	D Raman Shift (cm⁻¹)	I(D)	G Raman Shift (cm⁻¹)	I(G)	I(D)/I(G)
1	1348.39	1381.48	1584.63	1325.48	1.04
2	1357.07	714.12	1588.48	684.44	1.04
3	1351.29	1501.67	1587.52	1378.07	1.09
4	1348.39	534.85	1588.48	494.39	1.08
5	1348.39	1496.27	1582.70	1434.63	1.04
6	1346.47	1299.85	1586.56	1210.49	1.07
Average	1350.00		1586.40		1.06
Standard Deviation	3.79		2.32		0.02

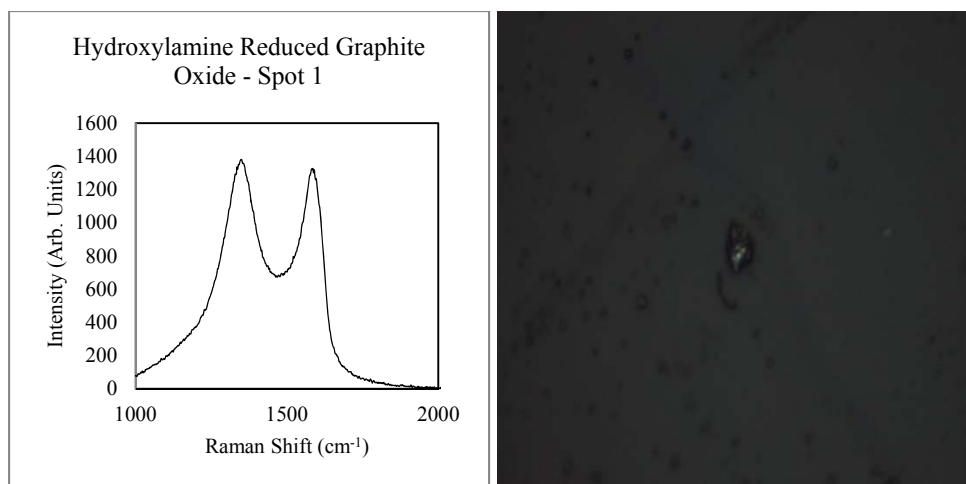


Figure A1-47. Hydroxylamine reduced graphite oxide standard – spot 1

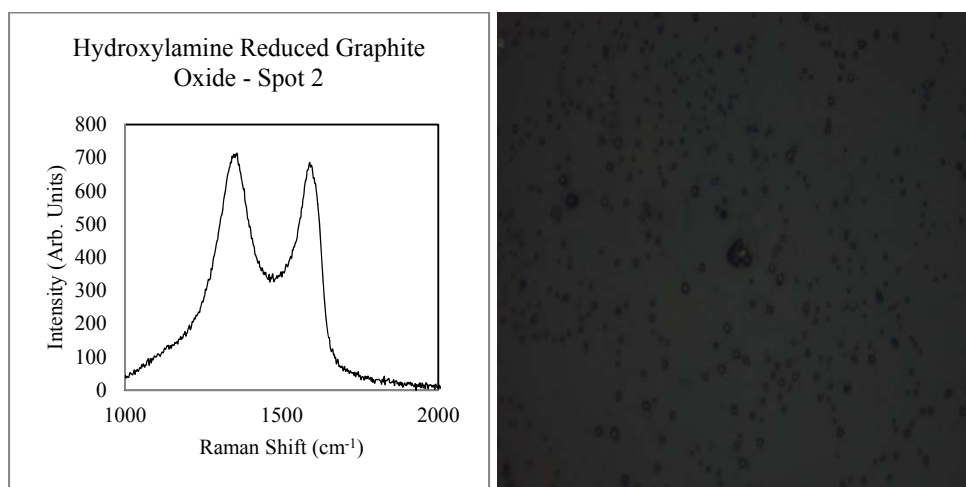


Figure A1-48. Hydroxylamine reduced graphite oxide standard – spot 2

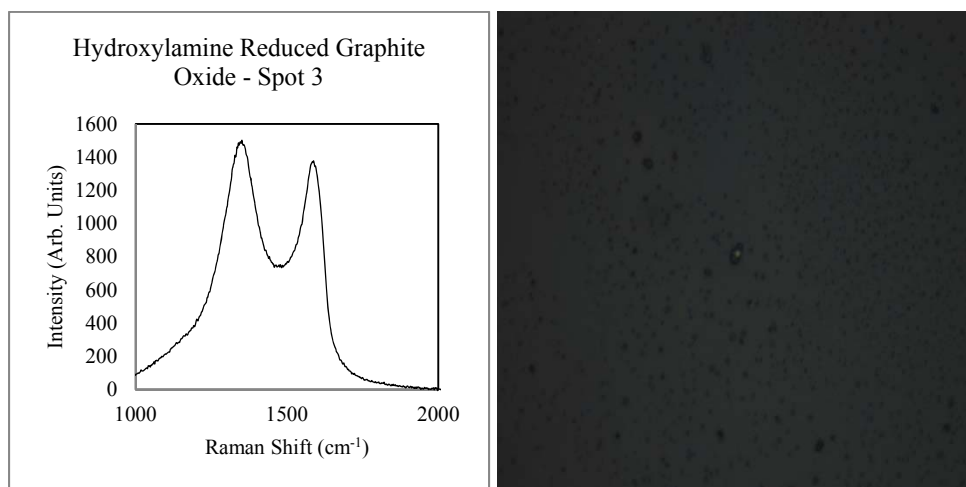


Figure A1-49. Hydroxylamine reduced graphite oxide standard – spot 3

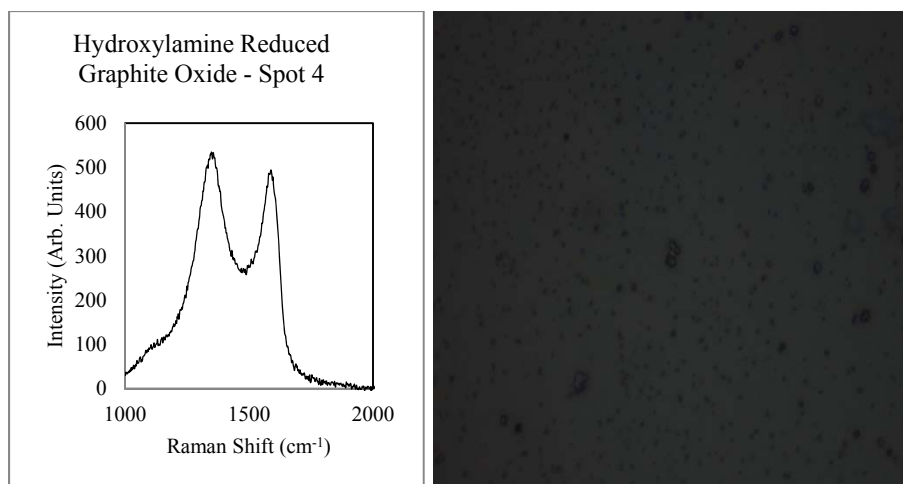


Figure A1-50. Hydroxylamine reduced graphite oxide standard – spot 4

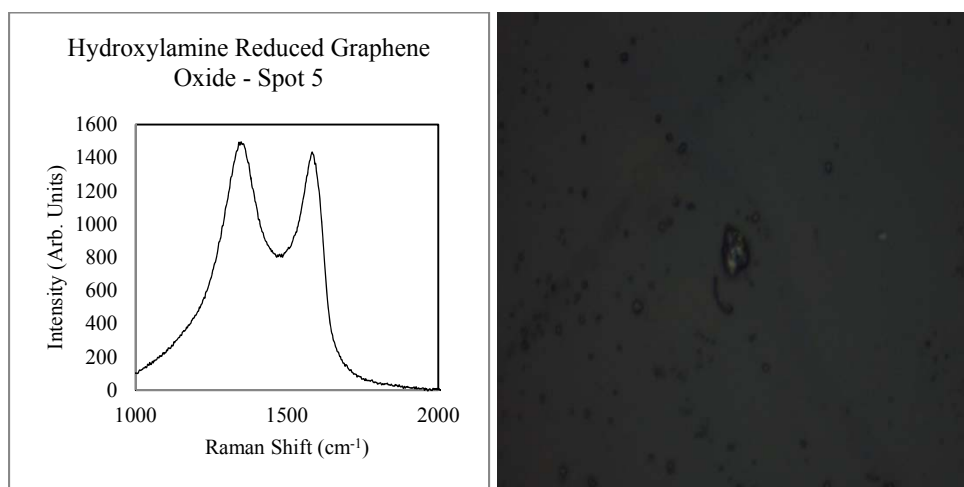


Figure A1-51. Hydroxylamine reduced graphite oxide standard – spot 5

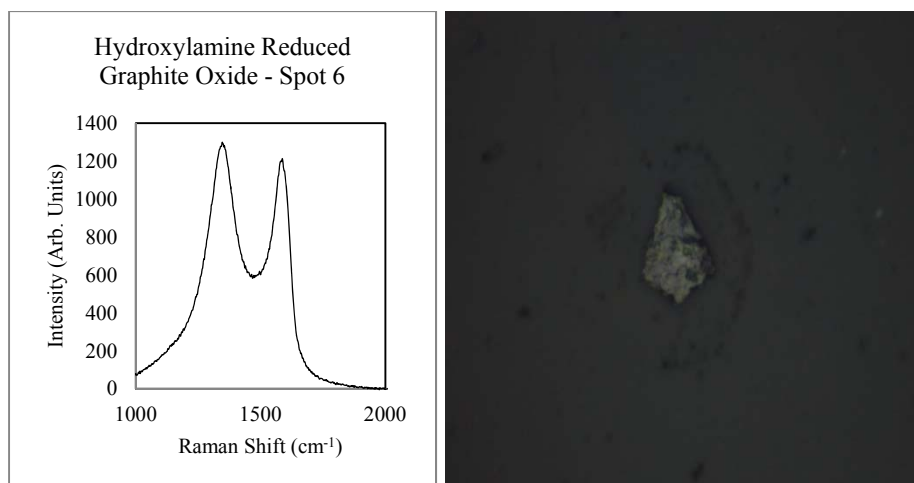


Figure A1-52. Hydroxylamine reduced graphite oxide standard – spot 6

Section B4. Raman spectral data for sodium borohydride reduced graphite oxide

Table A1-13. Raman spectral data for sodium borohydride reduced graphite oxide

Raman Analysis of Sodium Borohydride Reduced Graphite Oxide					
Sample #	D Raman Shift (cm ⁻¹)	I _(D)	G Raman Shift (cm ⁻¹)	I _(G)	I _(D) /I _(G)
1	1348.44	447.03	1602.99	425.66	1.05
2	1353.26	471.08	1599.14	456.76	1.03
3	1343.61	107.13	1603.96	95.07	1.13
4	1347.47	197.99	1594.32	180.88	1.09
5	1353.26	411.56	1597.21	385.42	1.07
6	1346.51	476.17	1599.14	442.43	1.08
7	1344.58	300.17	1599.14	293.26	1.02
Average	1348.76		1599.46		1.07
Standard Deviation	3.57		3.04		0.04

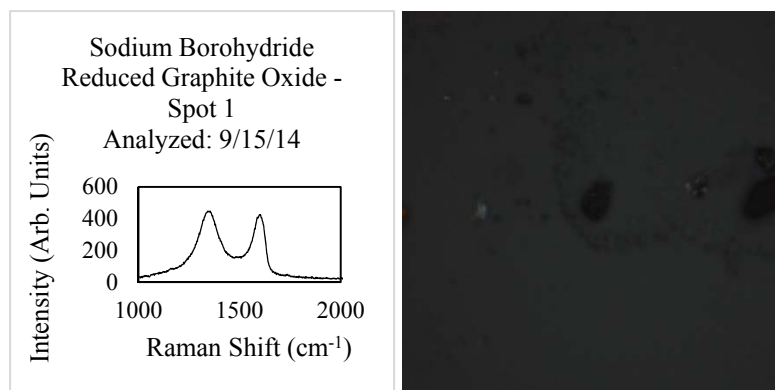


Figure A1-53. Sodium borohydride reduced graphite oxide – spot 1

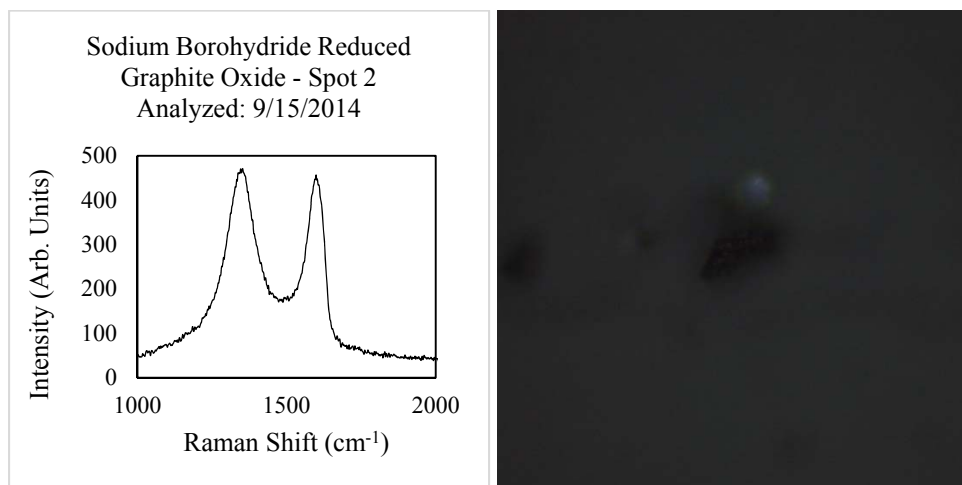


Figure A1-54. Sodium borohydride reduced graphite oxide – spot 2

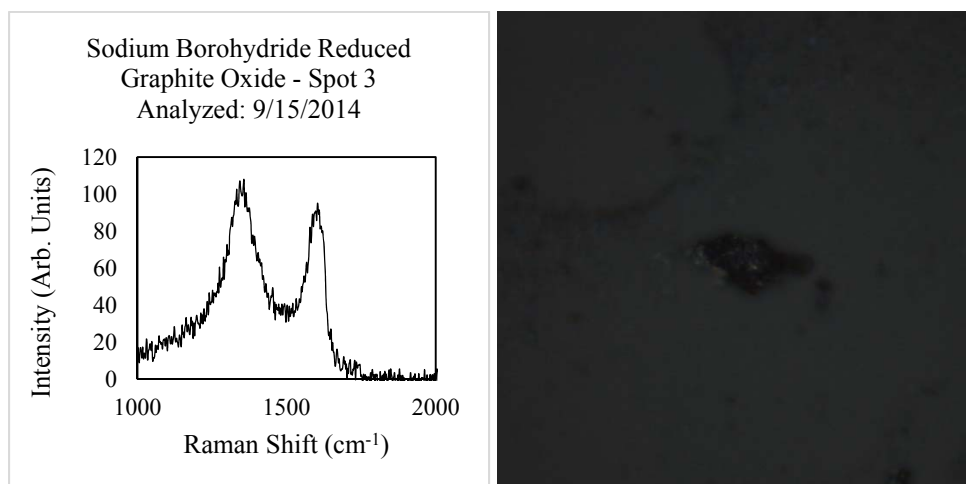


Figure A1-55. Sodium borohydride reduced graphite oxide – spot 3

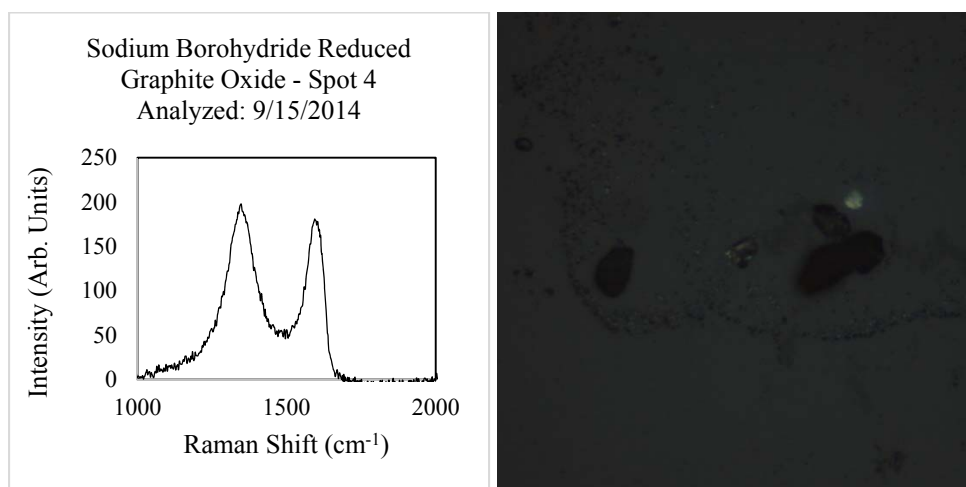


Figure A1-56. Sodium borohydride reduced graphite oxide – spot 4

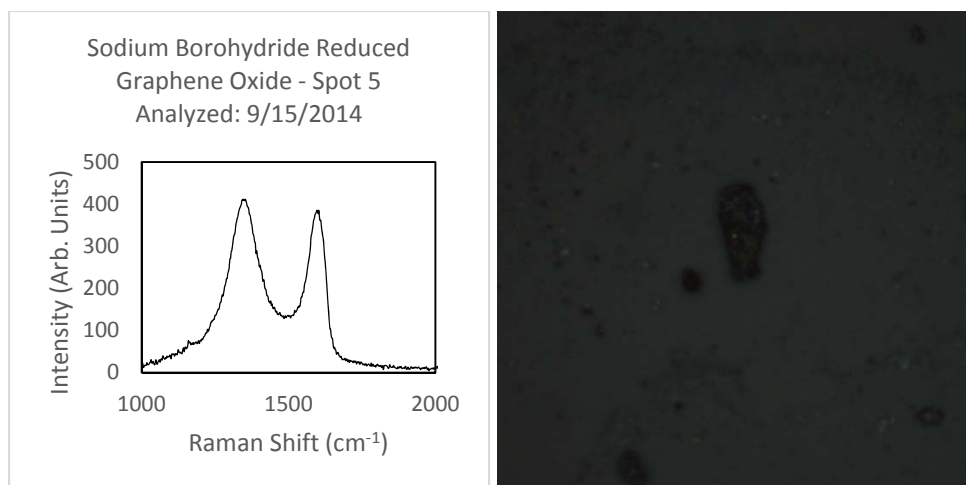


Figure A1-57. Sodium borohydride reduced graphite oxide – spot 5

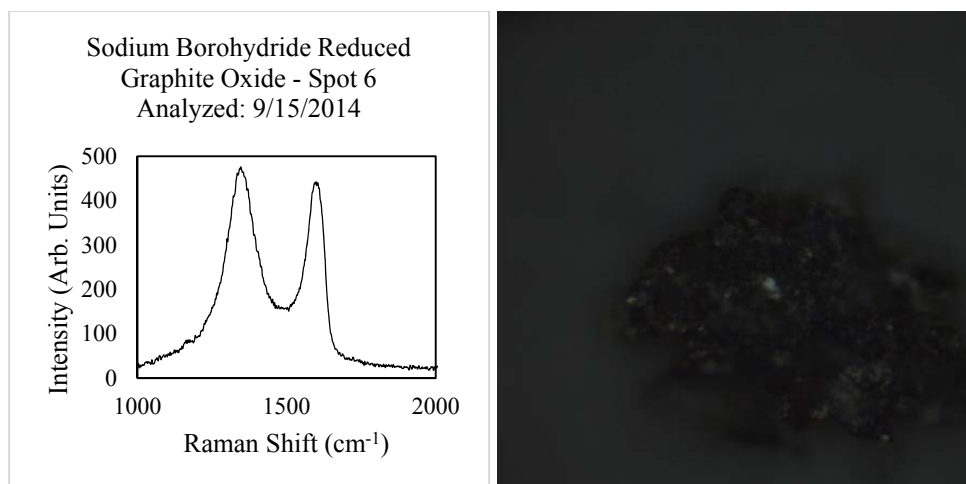


Figure A1-58. Sodium borohydride reduced graphite oxide – spot 6

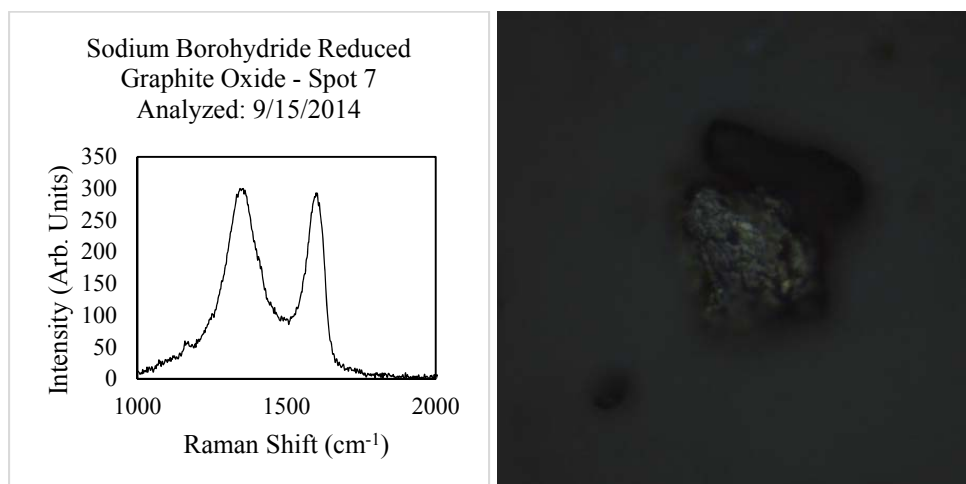


Figure A1-59. Sodium borohydride reduced graphite oxide – spot 7

Section B5. Raman spectral data for sodium bisulfite reduced graphite oxide

Table A1-14. Raman spectral data for sodium bisulfite reduced graphite oxide

Raman Analysis for Sodium Bisulfite Reduced Graphite Oxide					
Sample #	D Raman Shift (cm ⁻¹)	I _(D)	G Raman Shift (cm ⁻¹)	I _(G)	I _(D) /I _(G)
1	1351.33	365.95	1590.46	351.02	1.04
2	1355.19	399.97	1592.39	388.79	1.03
3	1347.47	408.18	1587.57	390.17	1.05
4	1351.33	390.76	1590.46	368.42	1.06
5	1350.36	328.37	1591.42	311.82	1.05
6	1352.29	370.64	1592.39	363.47	1.02
Average	1351.33		1590.78		1.04
Standard Deviation	2.52		1.79		0.02

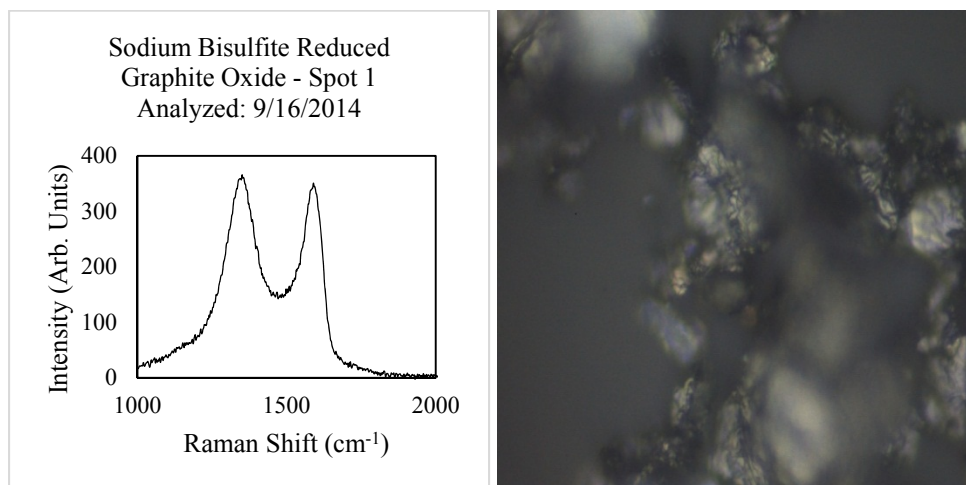


Figure A1-60. Sodium bisulfite reduced graphite oxide – spot 1

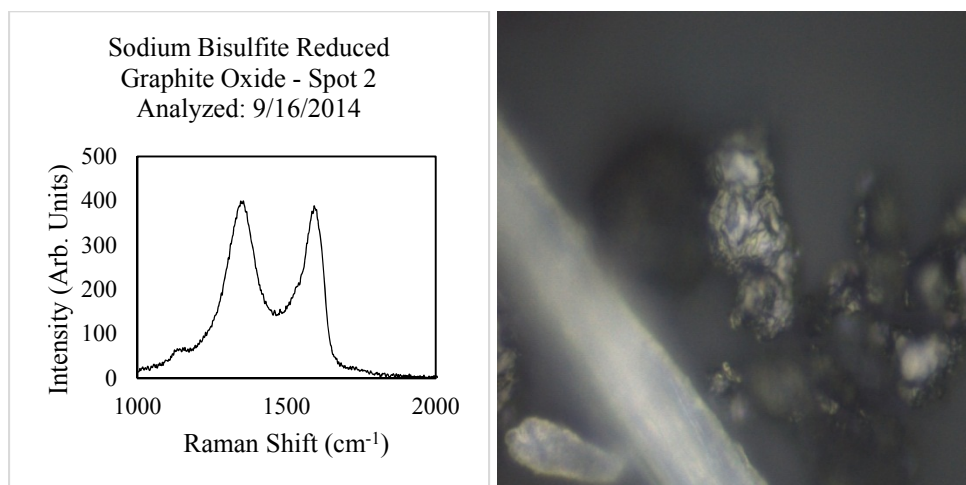


Figure A1-61. Sodium bisulfite reduced graphite oxide – spot 2

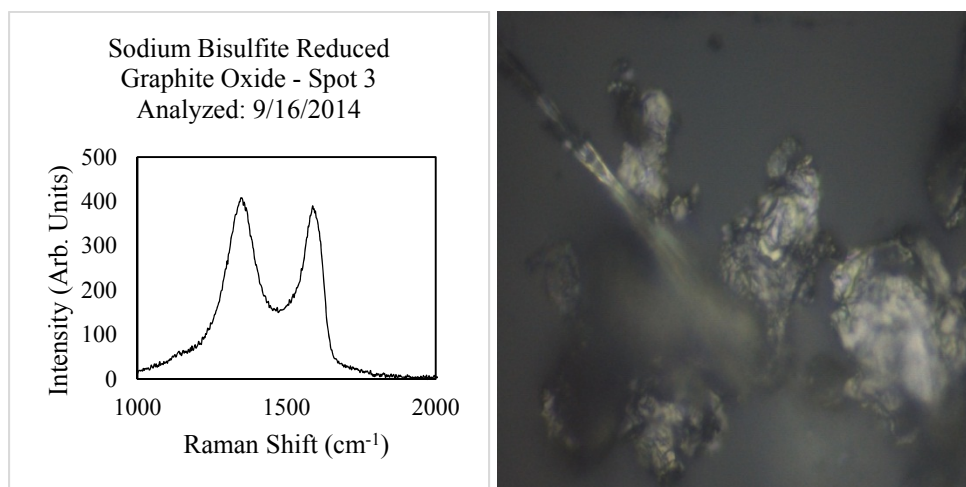


Figure A1-62. Sodium bisulfite reduced graphite oxide – spot 3

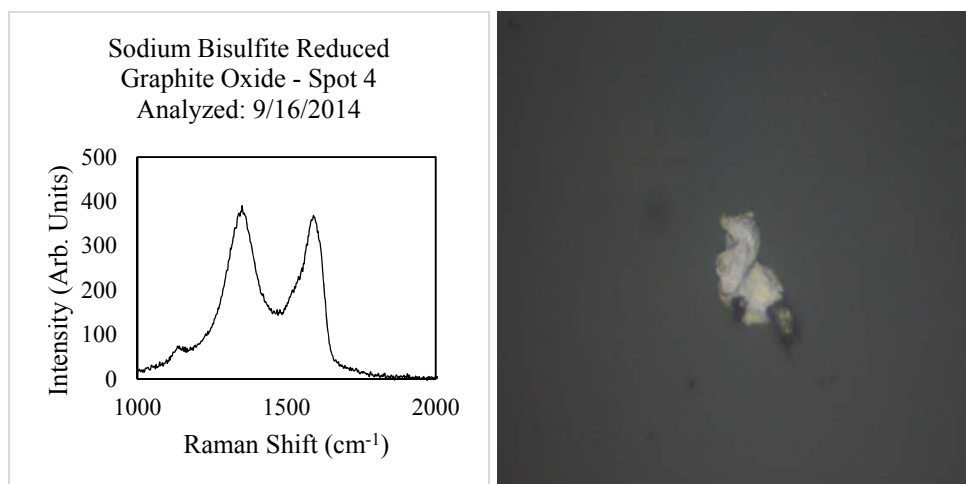


Figure A1-63. Sodium bisulfite reduced graphite oxide – spot 4

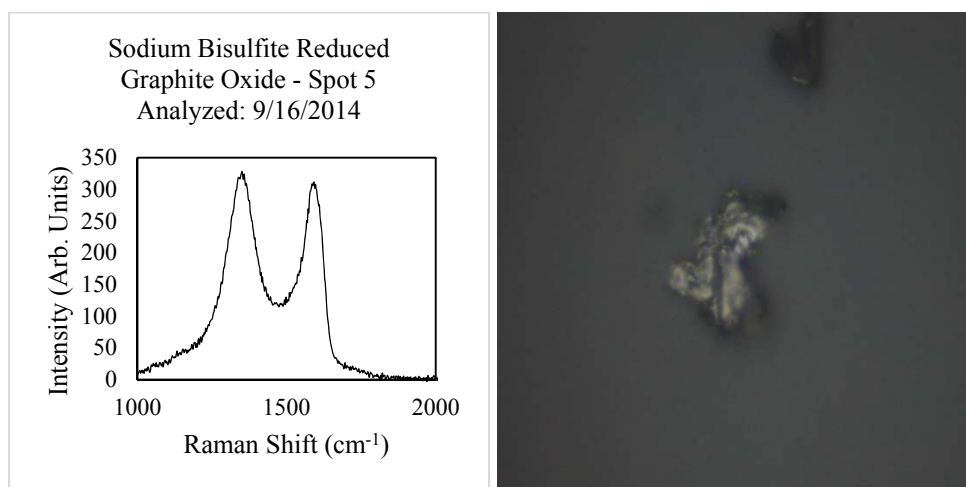


Figure A1-64. Sodium bisulfite reduced graphite oxide – spot 5

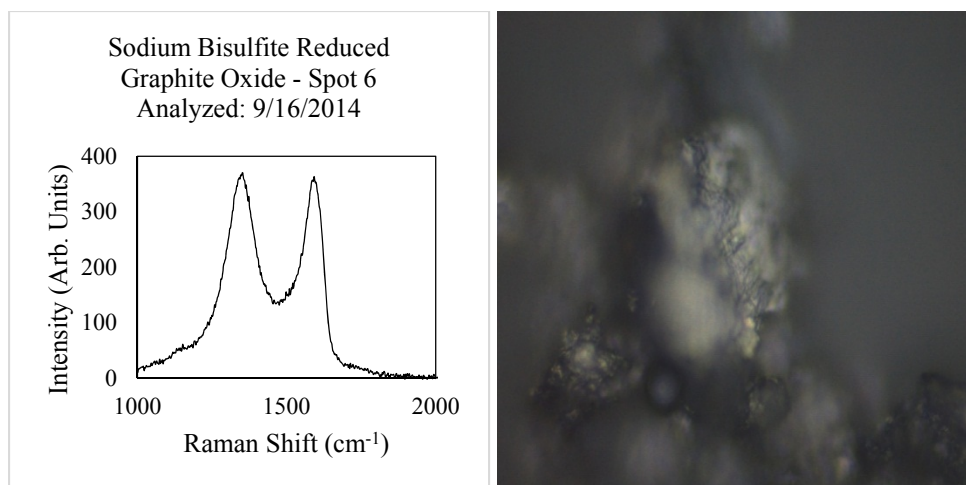


Figure A1-65. Sodium bisulfite reduced graphite oxide – spot 6

Section B6. Raman spectral data for benzyl alcohol reduced graphite oxide

Table A1-15. Raman spectral data for benzyl alcohol reduced graphite oxide

Raman Analysis for Benzyl Alcohol Reduced Graphite Oxide					
Sample #	D Raman Shift (cm ⁻¹)	I _(D)	G Raman Shift (cm ⁻¹)	I _(G)	I _(D) /I _(G)
1	1342.61	632.98	1585.60	621.98	1.02
2	1343.57	759.24	1585.60	762.10	1.00
3	1341.65	1362.25	1584.63	1290.05	1.06
4	1348.39	1666.92	1581.74	1654.26	1.01
5	1339.72	1615.54	1580.78	1578.99	1.02
6	1339.72	1682.75	1582.70	1604.84	1.05
Average	1342.61		1583.51		1.02
Standard Deviation	3.23		2.06		0.02

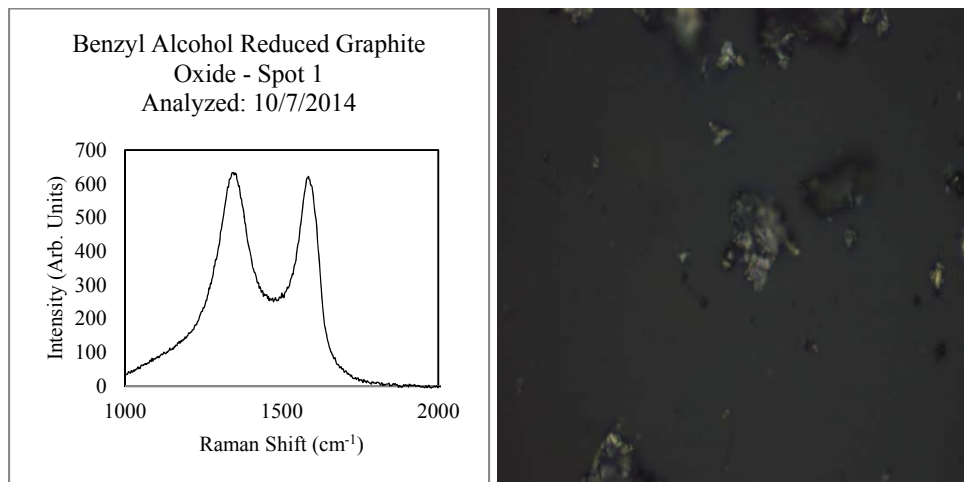


Figure A1-66. Benzyl alcohol reduced graphite oxide – spot 1

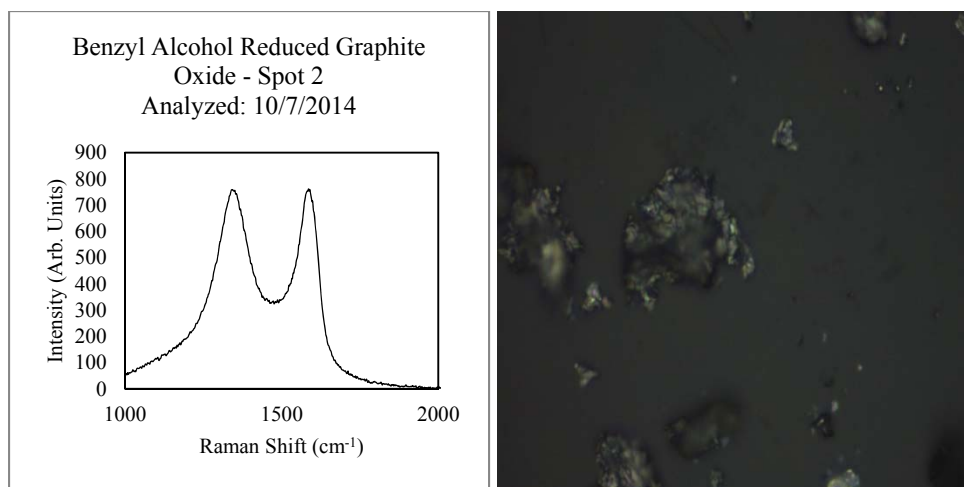


Figure A1-67. Benzyl alcohol reduced graphite oxide – spot 2

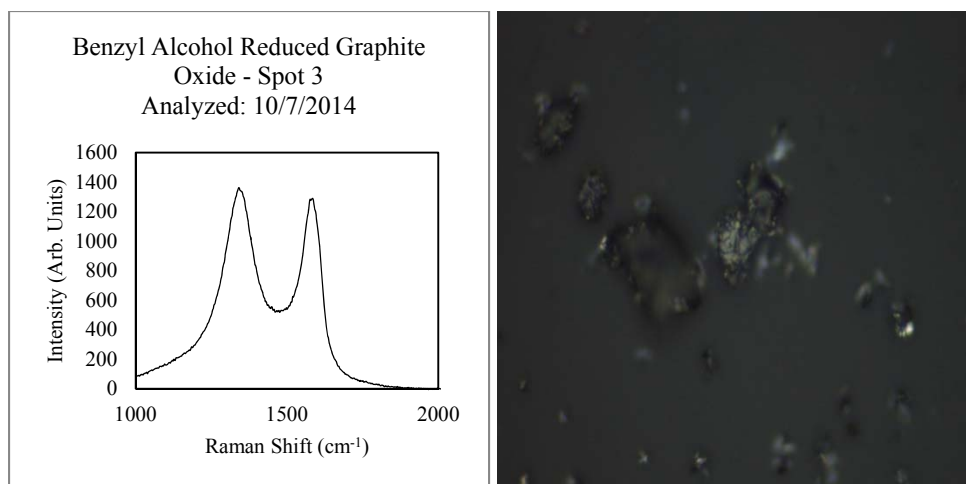


Figure A1-68. Benzyl alcohol reduced graphite oxide – spot 3

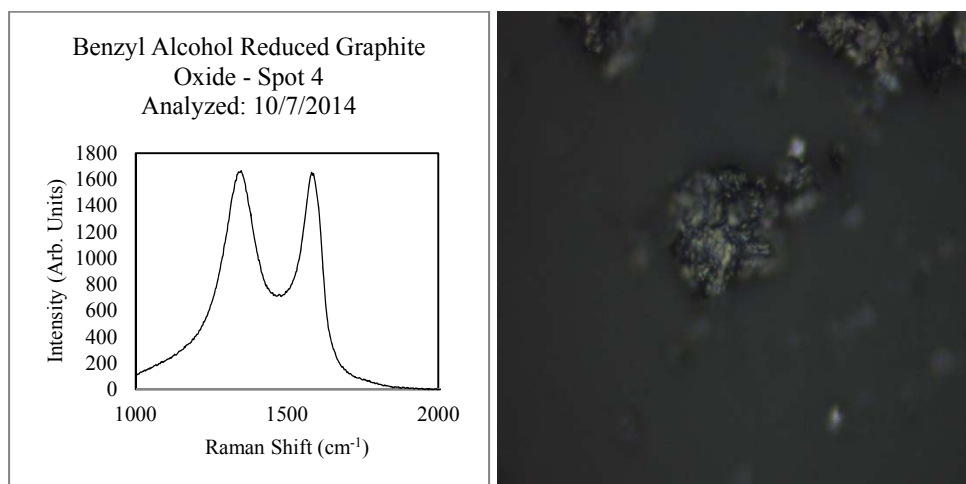


Figure A1-69. Benzyl alcohol reduced graphite oxide – spot 4

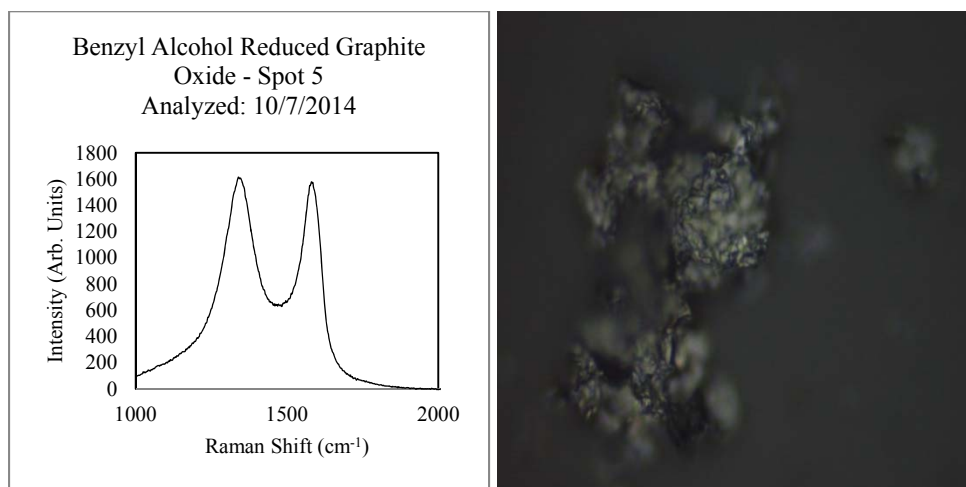


Figure A1-70. Benzyl alcohol reduced graphite oxide – spot 5

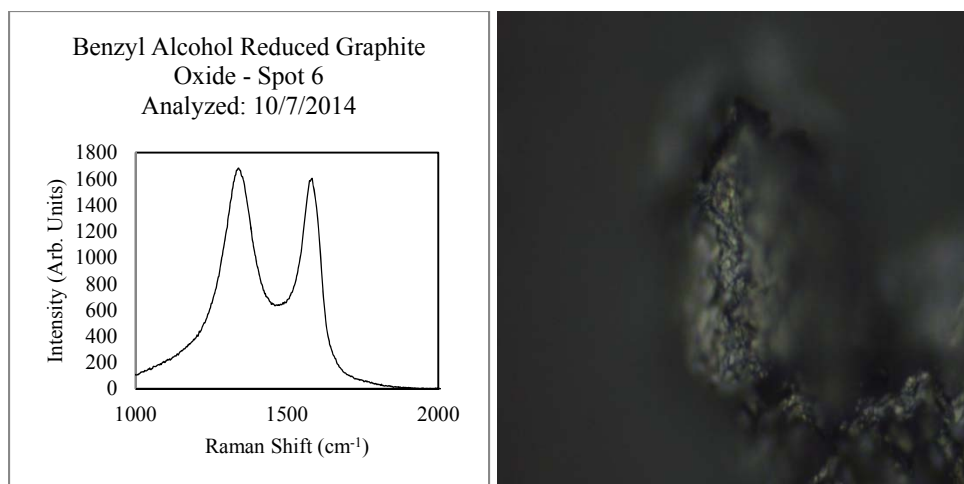


Figure A1-71. Benzyl alcohol reduced graphite oxide – spot 6

Section B7. Raman spectral data for graphite oxide thermally reduced at 500 °C

Table A1-16. Raman spectral data for thermally reduced graphite oxide at 500 °C

Raman Analysis for Thermally Reduced Graphite Oxide at 500 °C					
Sample #	D Raman Shift (cm⁻¹)	I_(D)	G Raman Shift (cm⁻¹)	I_(G)	I_(D)/I_(G)
1	1357.07	504.22	1595.24	516.24	0.98
2	1346.47	595.83	1596.20	593.86	1.00
3	1358.04	603.77	1595.24	588.40	1.03
4	1350.32	514.93	1593.31	495.49	1.04
5	1353.22	458.93	1589.45	431.32	1.06
6	1348.39	435.18	1587.52	415.10	1.05
Average	1352.25		1592.83		1.03
Standard Deviation	4.68		3.54		0.03

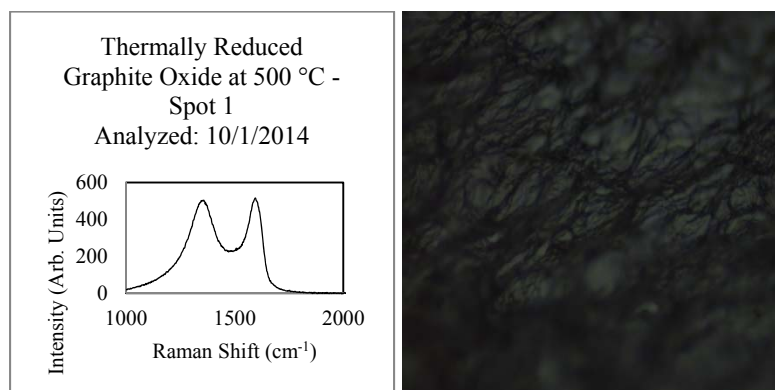


Figure A1-72. Thermally reduced graphite oxide at 500 °C - spot 1

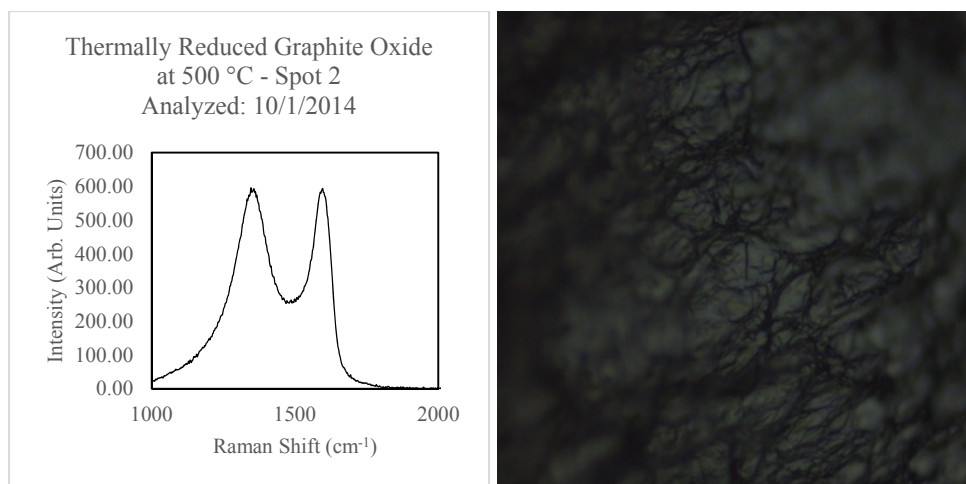


Figure A1-73. Thermally reduced graphite oxide at 500 °C - spot 2

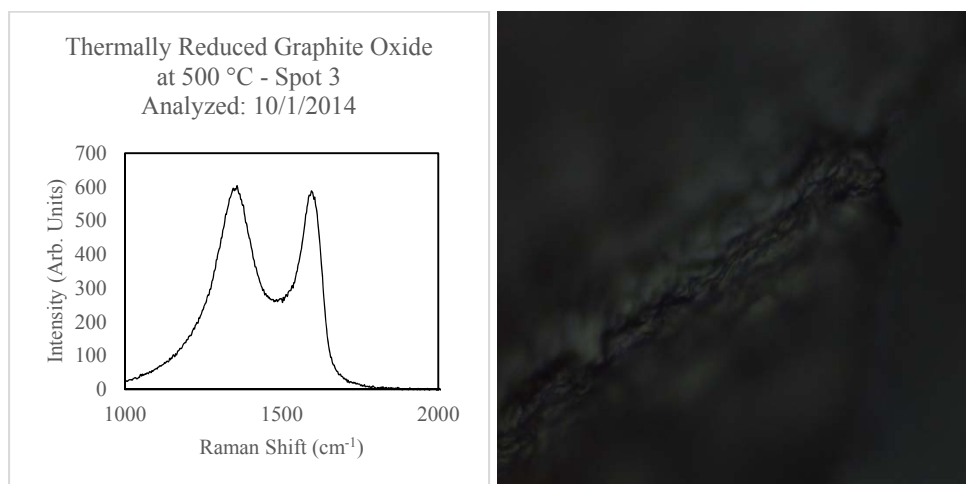


Figure A1-74. Thermally reduced graphite oxide at 500 °C - spot 3

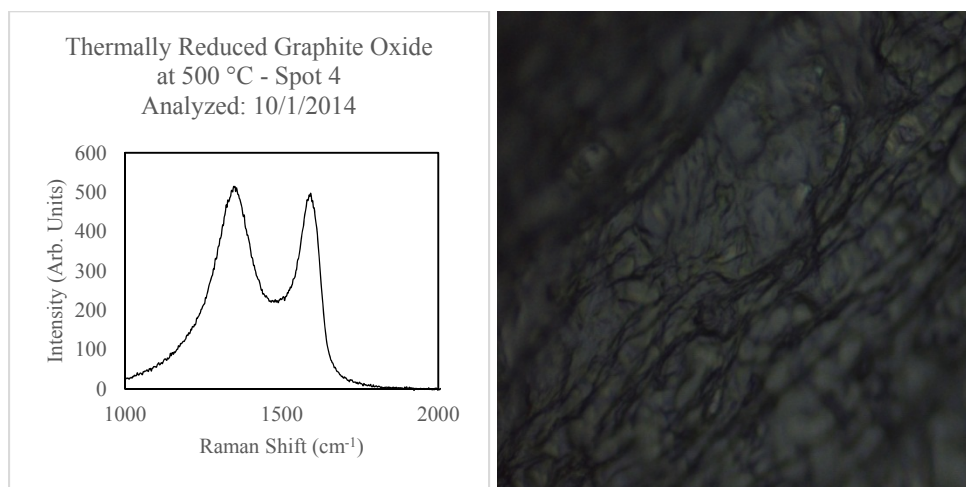


Figure A1-75. Thermally reduced graphite oxide at 500 °C - spot 4

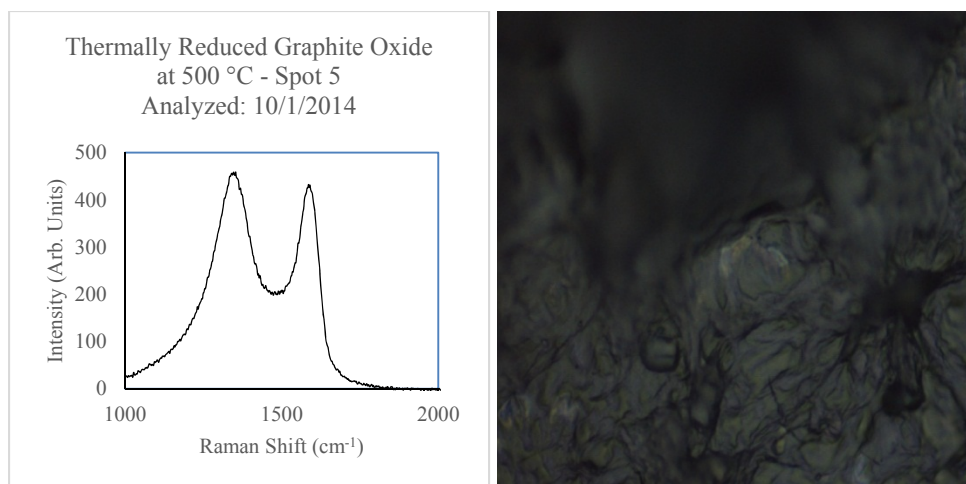


Figure A1-76. Thermally reduced graphite oxide at 500 °C - spot 5

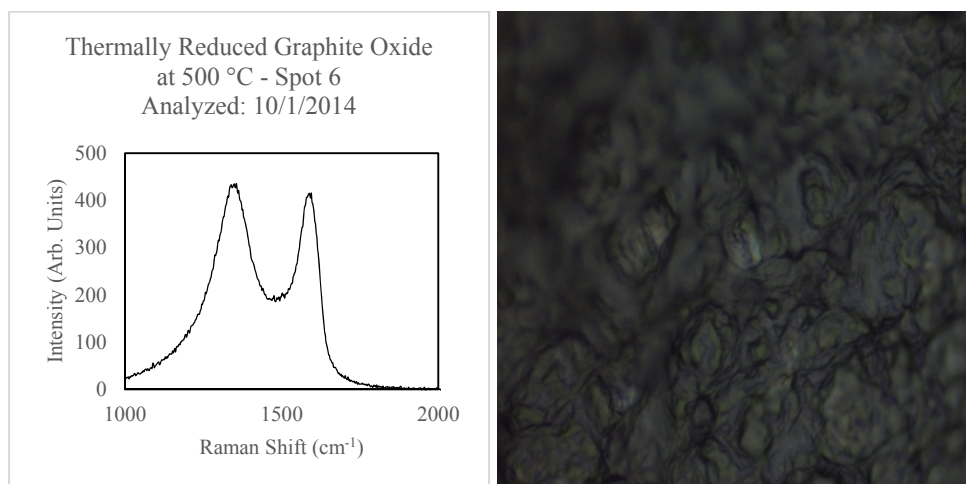


Figure A1-77. Thermally reduced graphite oxide at 500 °C - spot 6

Section B8. Raman spectral data for graphite oxide thermally reduced at 700 °C

Table A1-17. Raman spectral data for thermally reduced graphite oxide at 700 °C

Raman Analysis for Thermally Reduced Graphite Oxide at 700 °C					
Sample #	D Raman Shift (cm ⁻¹)	I _(D)	G Raman Shift (cm ⁻¹)	I _(G)	I _(D) /I _(G)
1	1348.39	545.22	1594.27	540.82	1.01
2	1345.5	538.67	1588.49	520.99	1.03
3	1341.65	406.43	1590.42	396.42	1.03
4	1348.39	494.15	1594.27	495.53	1.00
5	1341.65	479.94	1594.27	483.14	0.99
6	1343.57	573.06	1594.27	570.81	1.00
7	1353.22	579.26	1598.13	569.84	1.02
8	1344.54	559.41	1594.27	553.67	1.01
Average	1345.86		1593.55		1.01
Standard Deviation	3.96		2.90		0.01

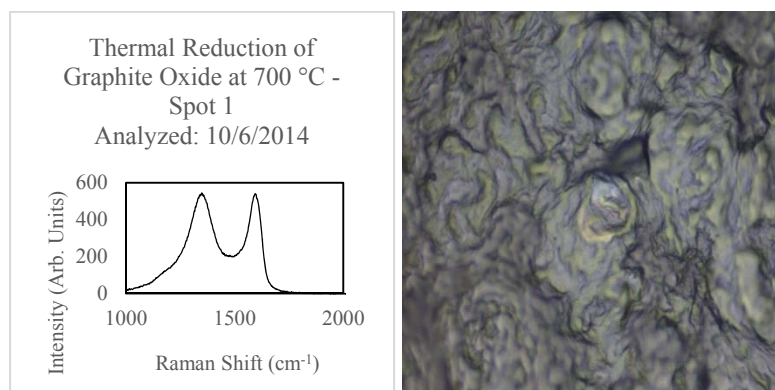


Figure A1-78. Thermally reduced graphite oxide at 700 °C - spot 1

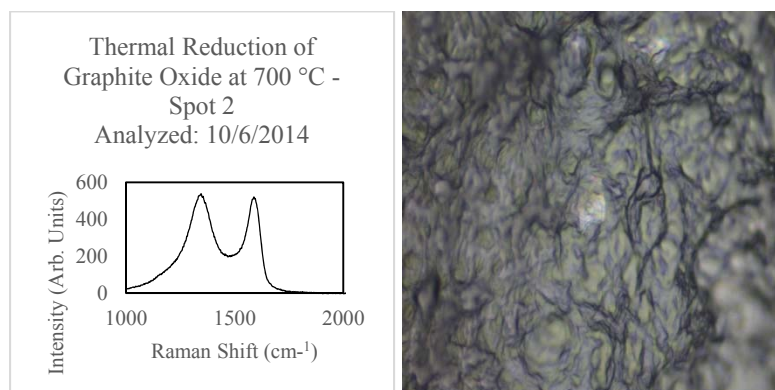


Figure A1-79. Thermally reduced graphite oxide at 700 °C - spot 2

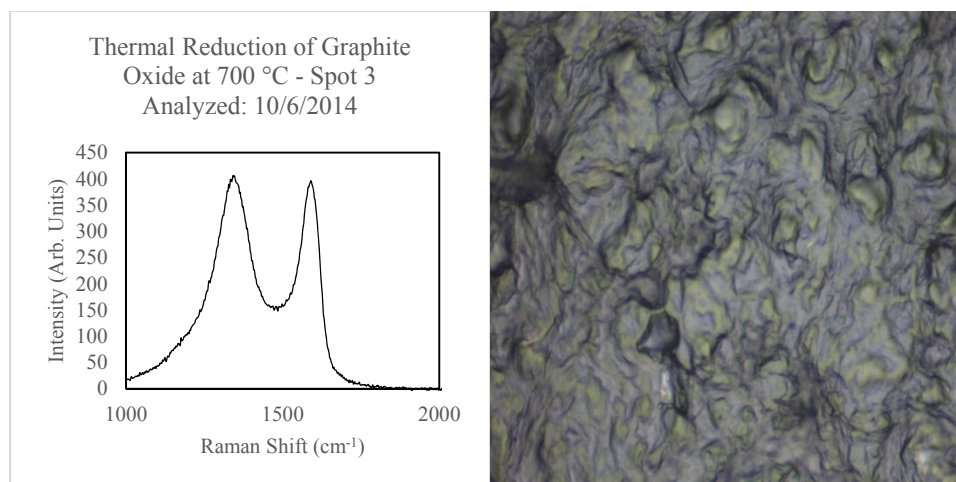


Figure A1-80. Thermally reduced graphite oxide at 700 °C - spot 3

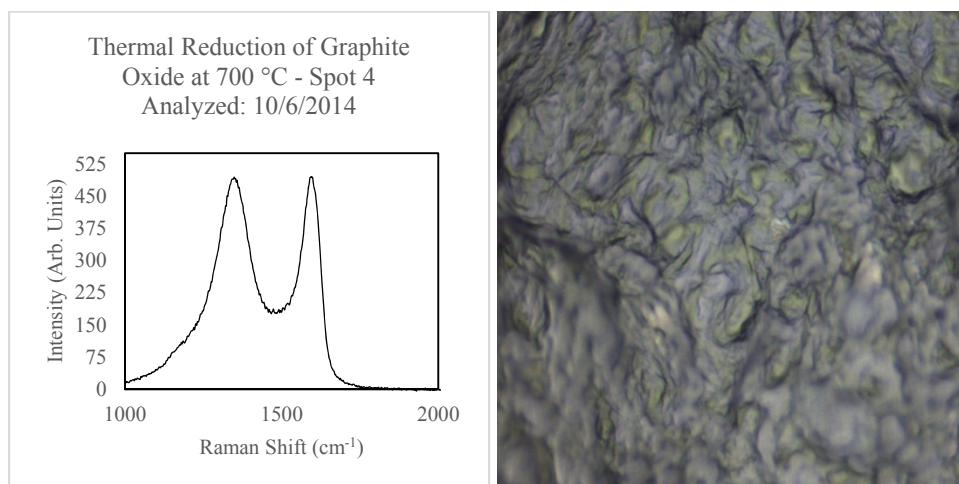


Figure A1-81. Thermally reduced graphite oxide at 700 °C - spot 4

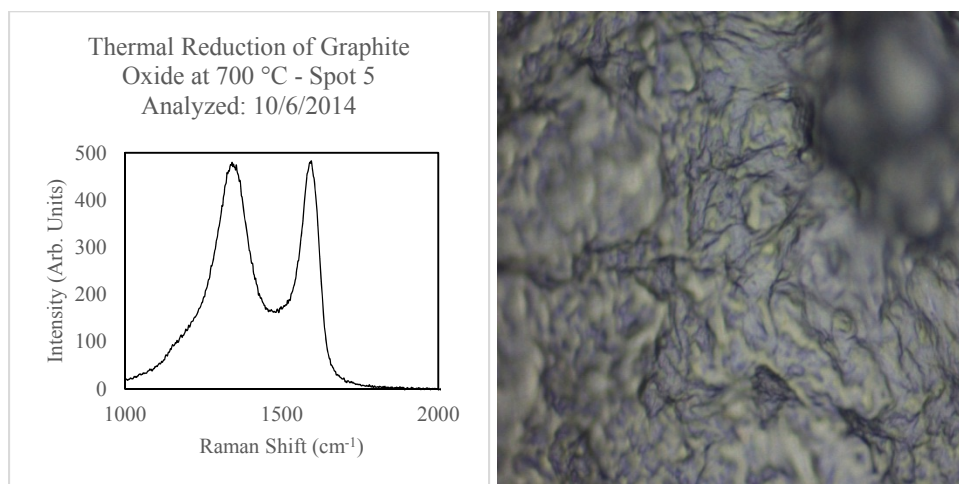


Figure A1-82. Thermally reduced graphite oxide at 700 °C - spot 5

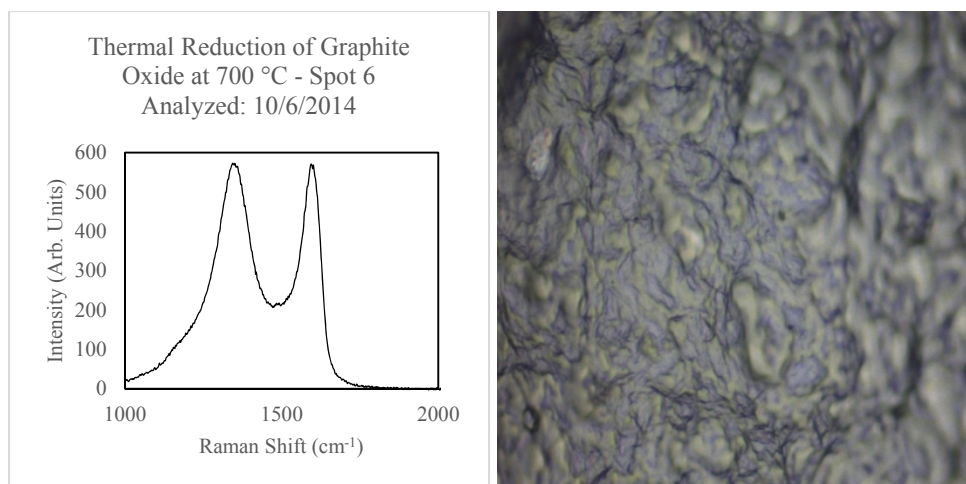


Figure A1-83. Thermally reduced graphite oxide at 700 °C - spot 6

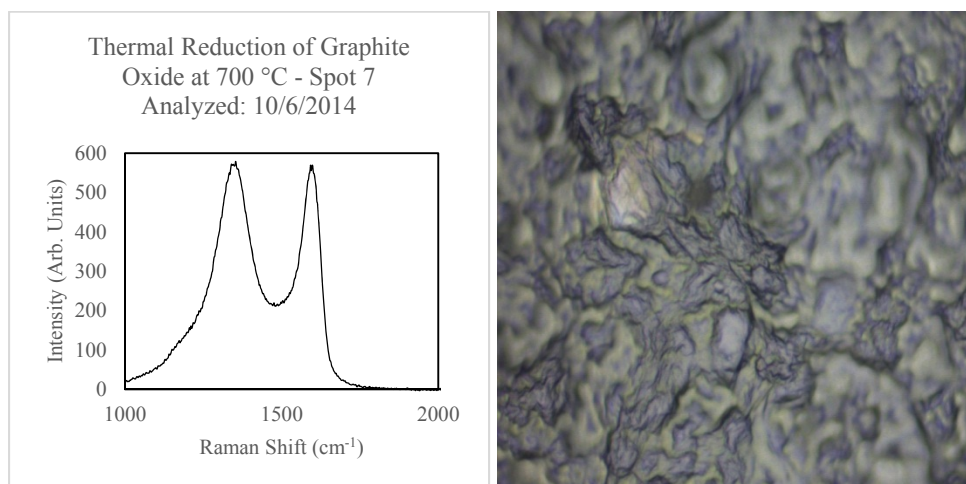


Figure A1-84. Thermally reduced graphite oxide at 700 °C - spot 7

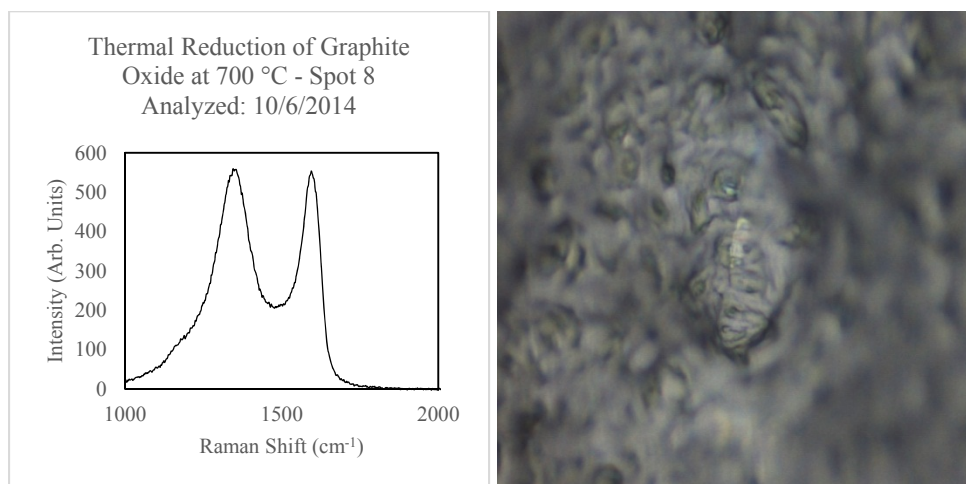


Figure A1-85. Thermally reduced graphite oxide at 700 °C - spot 8

Section B9. Raman spectral data for graphite oxide thermally reduced at 900 °C

Table A1-18. Raman spectral data for thermally reduced graphite oxide at 900 °C

Raman Analysis for Thermally Reduced Graphite Oxide at 900 °C					
Sample #	D Raman Shift (cm ⁻¹)	I _(D)	G Raman Shift (cm ⁻¹)	I _(G)	I _(D) /I _(G)
1	1353.22	381.57	1594.27	355.43	1.07
2	1353.22	334.64	1593.31	310.76	1.08
3	1348.39	325.52	1589.45	304.80	1.07
4	1345.50	268.67	1587.52	256.58	1.05
5	1347.43	322.60	1587.52	302.97	1.06
6	1354.18	329.69	1590.42	314.00	1.05
Average	1350.32		1590.42		1.06
Standard Deviation	3.66		2.86		0.01

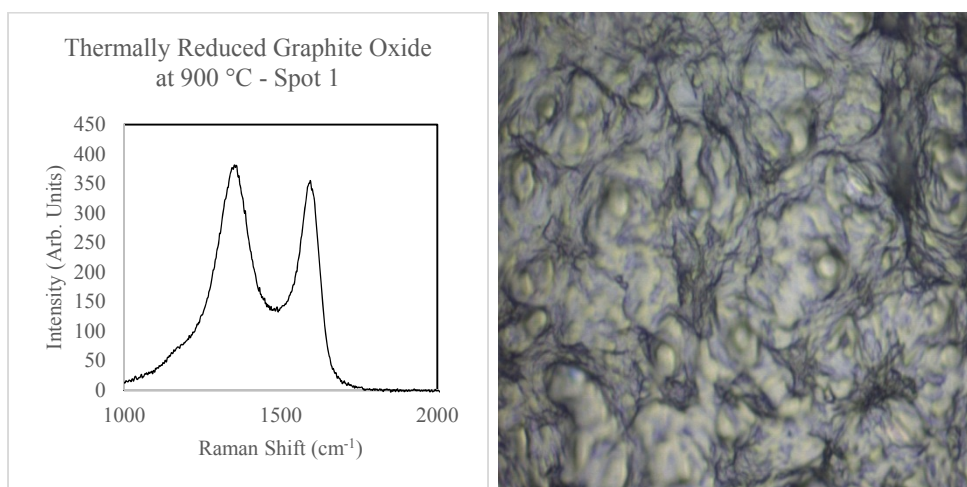


Figure A1-86. Thermally reduced graphite oxide at 900 °C - spot 1

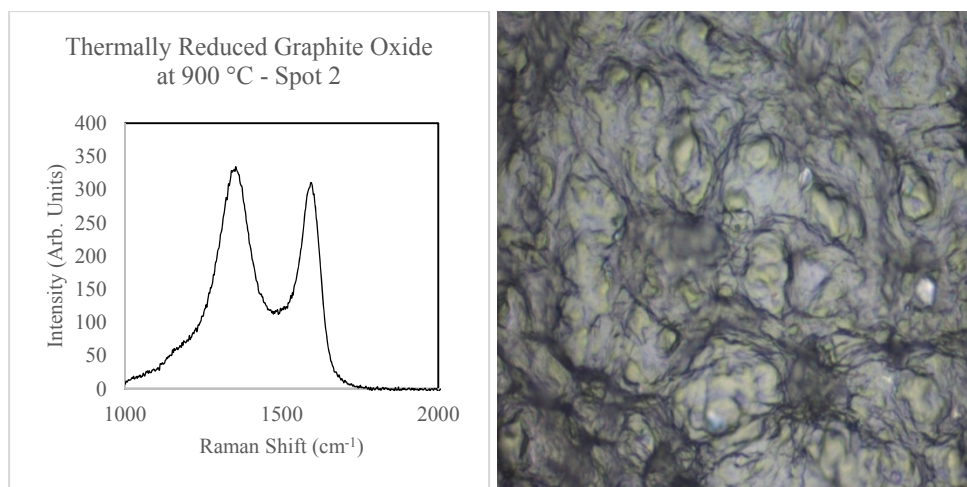


Figure A1-87. Thermally reduced graphite oxide at 900 °C - spot 2

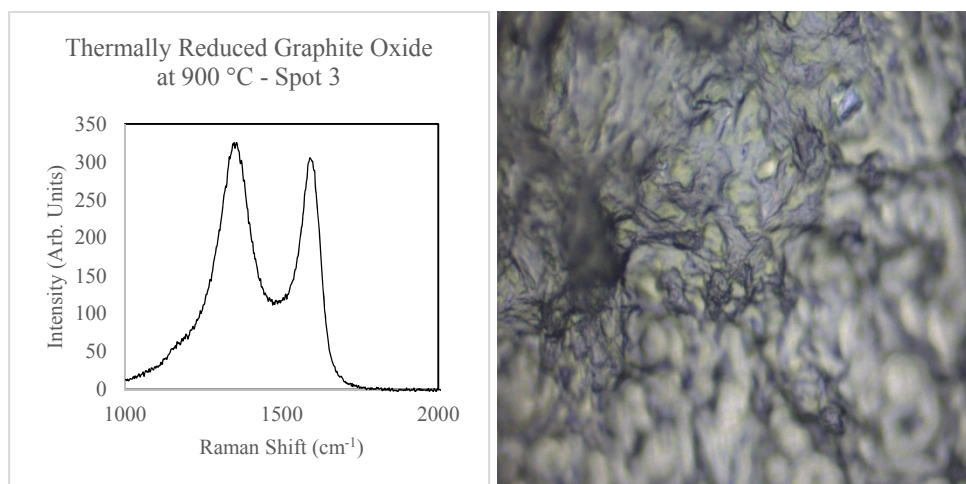


Figure A1-88. Thermally reduced graphite oxide at 900 °C - spot 3

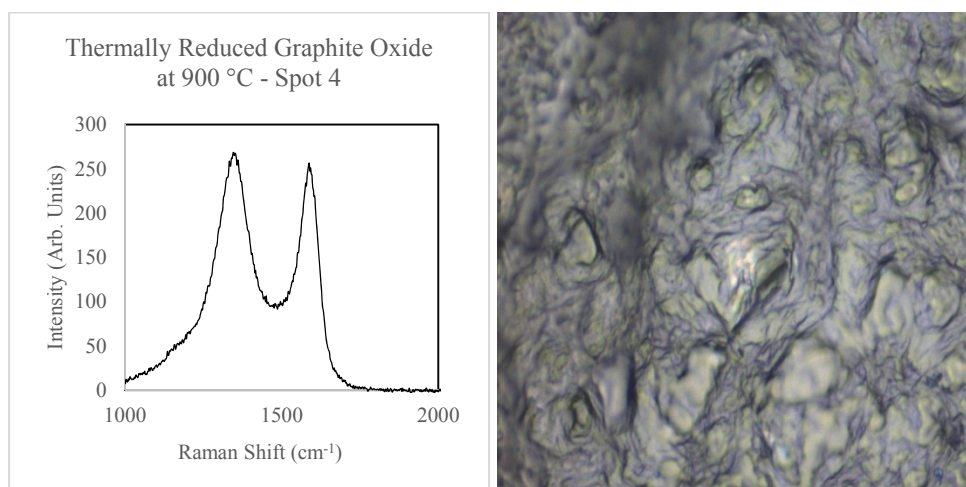


Figure A1-89. Thermally reduced graphite oxide at 900 °C - spot 4

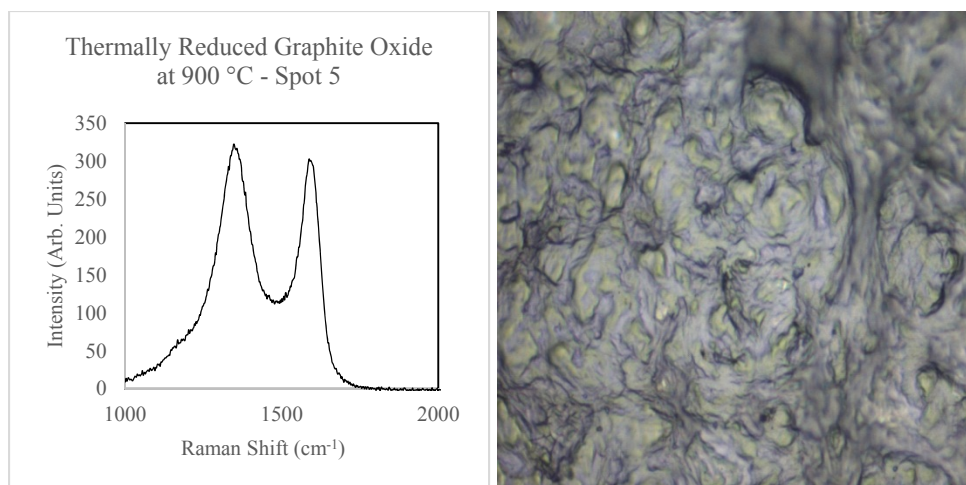


Figure A1-90. Thermally reduced graphite oxide at 900 °C - spot 5

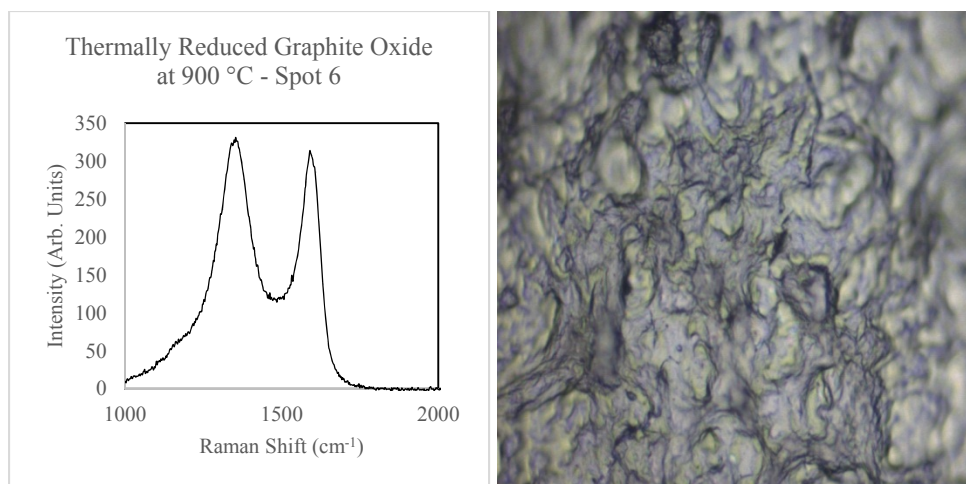


Figure A1-91. Thermally reduced graphite oxide at 900 °C - spot 6

Appendix II

Raw Data for Humic Acid Reductions

Section C.1 SEM/EDS for humic acid standard and reduced humic Acid

Table A2-1. Humic acid standard C/O ratios

Humic Acid Standard C/O Ratios		
Spot (S)/Area (A)	Atomic % Carbon	Atomic % Oxygen
A1	59.53	40.47
S1	59.85	40.15
S2	59.05	40.95
S3	59.32	40.68
S4	59.14	40.86
S5	59.74	40.26
S6	58.61	41.39
S7	59.25	40.75
S8	59.56	40.44
<i>Average</i>	<i>59.34</i>	<i>40.66</i>
<i>Standard Deviation</i>	<i>0.38</i>	

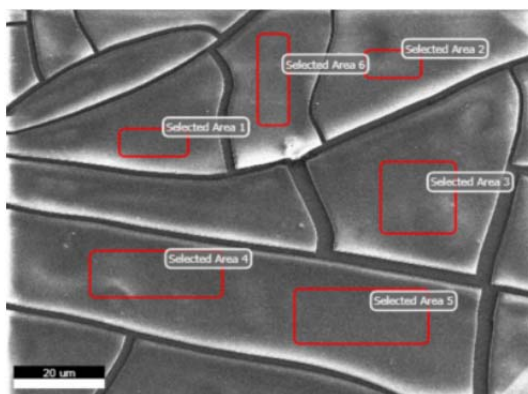


Figure A2-1. Image of EDS areas 1-6 of humic acid standard

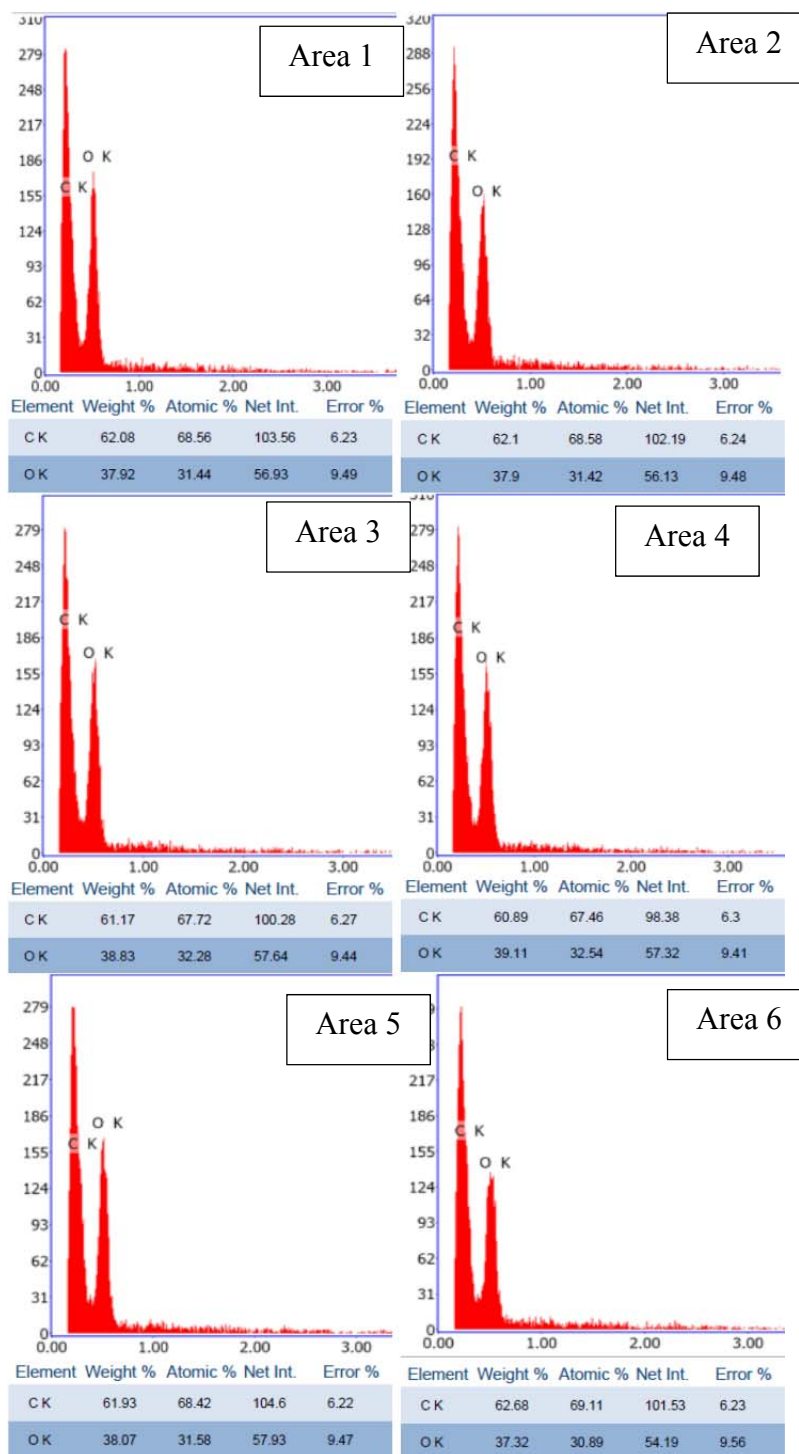


Figure A2-2. EDS spectra for areas 1-6 for humic acid standard

Table A2-2. Hydrazine reduced humic acid C/O ratios

Hydrazine Reduced Humic Acid C/O Ratios			
Sample #	Spot (S)/Area (A)	Atomic % Carbon	Atomic % Oxygen
1	S1	87.40	12.60
1	S2	86.41	13.59
1	S3	91.30	8.70
1	S4	88.60	11.40
2	S1	87.64	12.36
2	S2	87.39	12.61
2	S3	85.87	14.13
Average		87.80	12.20
Standard Deviation		1.77	

Table A2-3. Hydroxylamine reduced humic acid C/O ratios

Hydroxylamine Reduced Humic Acid C/O Ratios		
Spot (S)/Area (A)	Atomic % Carbon	Atomic % Oxygen
S1	89.16	10.84
S2	89.74	10.26
S3	91.03	8.97
S4	88.45	11.55
S5	90.34	9.66
S6	96.9	3.1
Average	90.94	9.06
Standard Deviation	3.06	

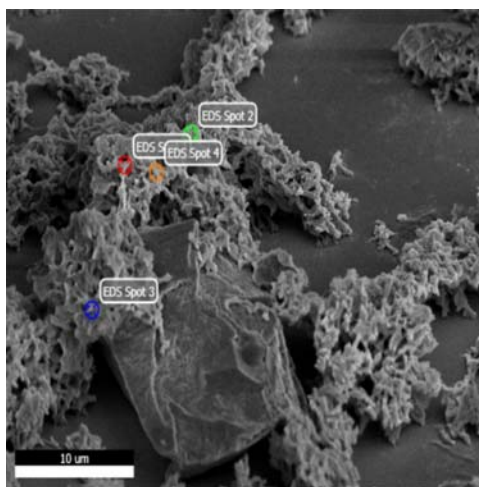


Figure A2-3. Image of EDS of areas 1-6 hydroxylamine reduced humic acid

Element	Weight %	Atomic %	Net Int.	Error %
C K	83.9	87.4	136.93	5.18
O K	16.1	12.6	20.57	11.33

C K	82.68	86.41	134.46	5.22
O K	17.32	13.59	22.22	11.16

C K	88.52	91.13	138.35	5.04
O K	11.48	8.87	13.65	12.18

C K	85.69	88.86	149.81	5.05
O K	14.31	11.14	19.37	11.43

Figure A2-4. EDS spectra of areas 1-6 for hydroxylamine reduced humic acid

Table A2-4. Sodium borohydride reduced humic acid C/O ratios

Sodium Borohydride Reduced Humic Acid C/O Ratios		
Spot (S)/Area (A)	Atomic % Carbon	Atomic % Oxygen
S1	67.54	32.46
S2	67.36	32.64
S3	62.34	37.66
S4	53.1	46.9
S5	42.8	57.2
S6	59.75	40.25
<i>Average</i>	<i>58.82</i>	<i>41.19</i>
<i>Standard Deviation</i>	<i>9.50</i>	

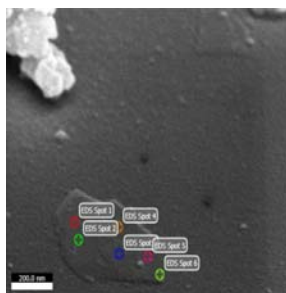


Figure A2-5. Image of EDS areas 1-6 sodium borohydride reduced humic acid

Element	Weight %	Atomic %	Net Int.	Error %
C K	60.87	67.45	15.3	8.95
O K	39.13	32.55	8.92	14.01
C K	60.87	67.45	15.3	8.95
O K	39.13	32.55	8.92	14.01
C K	60.77	67.36	13.89	9.6
O K	39.23	32.64	8.14	17.6
C K	55.41	62.34	10.88	10.39
O K	44.59	37.66	8.23	14.08
C K	45.94	53.1	10.74	10.53
O K	54.06	46.9	12.65	12.56
C K	35.97	42.8	13.29	10.11
O K	64.03	57.2	25.32	9.4
C K	52.7	59.75	9.67	10.78
O K	47.3	40.25	8.3	17.21

Figure A2-6. EDS spectra areas 1-6 for sodium borohydride reduced humic acid

Table A2-5. Sodium bisulfite reduced humic acid C/O ratios

Sodium Bisulfite Reduced Humic Acid C/O Ratios		
Spot (S)/Area (A)	Atomic % Carbon	Atomic % Oxygen
S1	88.88	11.12
S2	88.02	11.98
S3	83.71	16.29
S4	82.47	17.53
S5	84.19	15.81
<i>Average</i>	85.45	14.55
<i>Standard Deviation</i>	2.82	

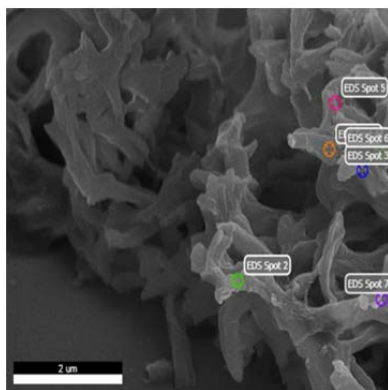


Figure A2-7. Image of EDS spots 1-6 for sodium bisulfite reduced humic acid

Element	Weight %	Atomic %	Net Int.	Error %
C K	86.06	89.16	111.77	5.3
O K	13.94	10.84	13.98	13.66
C K	86.78	89.74	134.65	5.1
O K	13.22	10.26	15.76	11.88
C K	88.4	91.03	121.42	5.18
O K	11.6	8.97	12.12	14.04
C K	85.18	88.45	108.96	5.34
O K	14.82	11.55	14.72	13.57
C K	87.53	90.34	125.63	5.18
O K	12.47	9.66	13.69	13.73
C K	95.91	96.9	108.01	5.1
O K	4.09	3.1	3.35	21.74

Figure A2-8. EDS spectra for spots 1-6 for sodium bisulfite reduced humic acid

Table A2-6. Benzyl alcohol reduced humic acid C/O ratios

Benzyl Alcohol Reduced Humic Acid C/O Ratios		
Spot (S)/Area (A)	Atomic % Carbon	Atomic % Oxygen
S1	80.55	19.45
S2	76.52	23.48
S3	73.13	26.87
S4	75.85	24.15
S5	77.45	22.55
S6	78.5	21.5
Average	77.00	23.00
Standard Deviation	2.51	

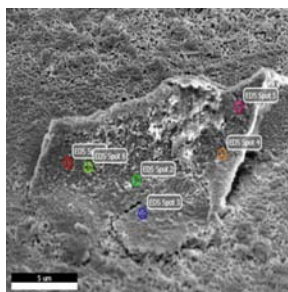


Figure A2-9. Image of EDS spots 1-6 for benzyl alcohol reduced humic acid

Element	Weight %	Atomic %	Net Int.	Error %
C K	75.67	80.55	103.23	5.51
O K	24.33	19.45	27.37	10.64
C K	70.98	76.52	97.59	5.71
O K	29.02	23.48	33.9	10.21
C K	67.14	73.13	78.46	6
O K	32.86	26.87	33.44	10.11
C K	70.23	75.85	98.73	5.66
O K	29.77	24.15	35.74	10.1
C K	72.06	77.45	86.12	5.73
O K	27.94	22.55	28.18	10.52
C K	73.27	78.5	96.88	5.69
O K	26.73	21.5	29.58	10.52

Figure A2-10. EDS spectra for spots 1-6 for benzyl alcohol reduced humic acid

Table A2-7. Thermally reduced humic acid at 500 °C

Thermally Reduced Humic Acid at 500 °C		
Spot (S)/Area (A)	Atomic % Carbon	Atomic % Oxygen
S1	91.85	8.15
S2	92.66	7.34
S3	93.83	6.17
S4	92.68	7.32
S5	92.45	7.55
S6	92.14	7.86
<i>Average</i>	<i>92.60</i>	<i>7.40</i>
<i>Standard Deviation</i>	<i>0.68</i>	

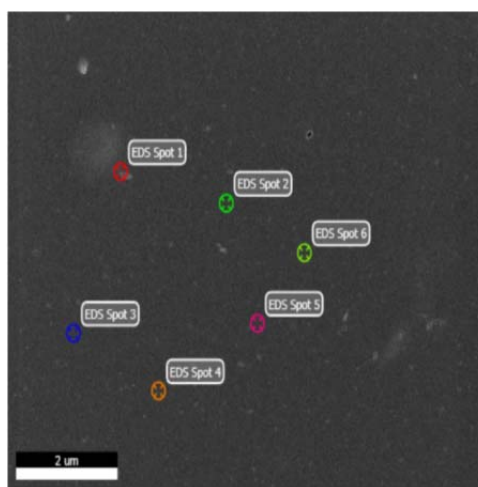


Figure A2-11. Image of EDS spots 1-6 of thermally reduced humic acid at 500 °C

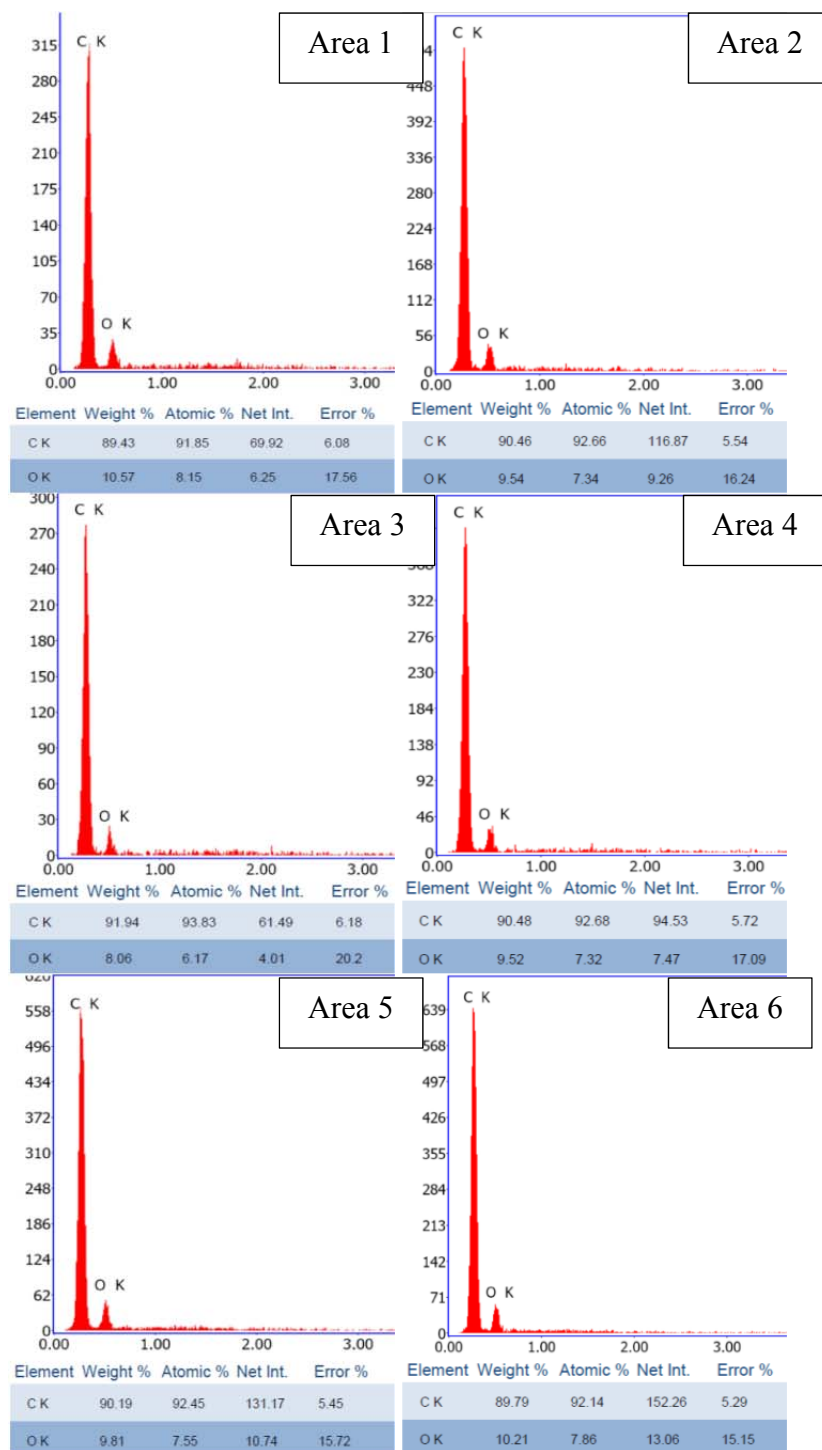


Figure A2-12. EDS spectra for spots 1-6 of thermally reduced humic acid at 500 °C

Table A2-12. Thermally reduced humic acid at 700 °C

Humic Acid Thermally Reduced at 700 °C		
Spot (S)/Area (A)	Atomic % Carbon	Atomic % Oxygen
A1	93.13	6.87
A2	93.37	6.63
A3	93.56	6.44
A4	93.73	6.27
A5	93.77	6.23
A6	93.80	6.20
A7	93.43	6.57
A8	93.39	6.61
A9	93.08	6.92
A10	93.15	6.85
<i>Average</i>	93.44	6.56
<i>Standard Deviation</i>	0.27	

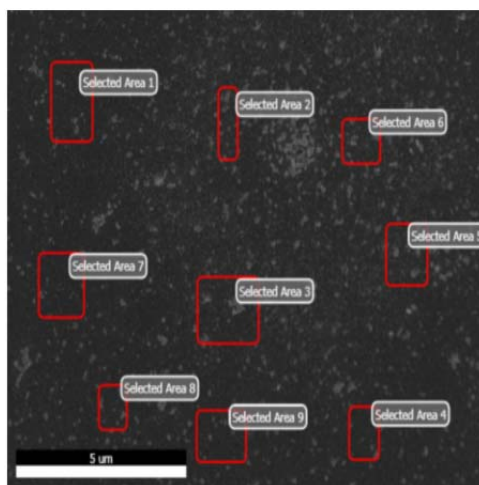


Figure A2-13. Image of EDS for areas 1-6 of thermally reduced humic acid at 700 °C

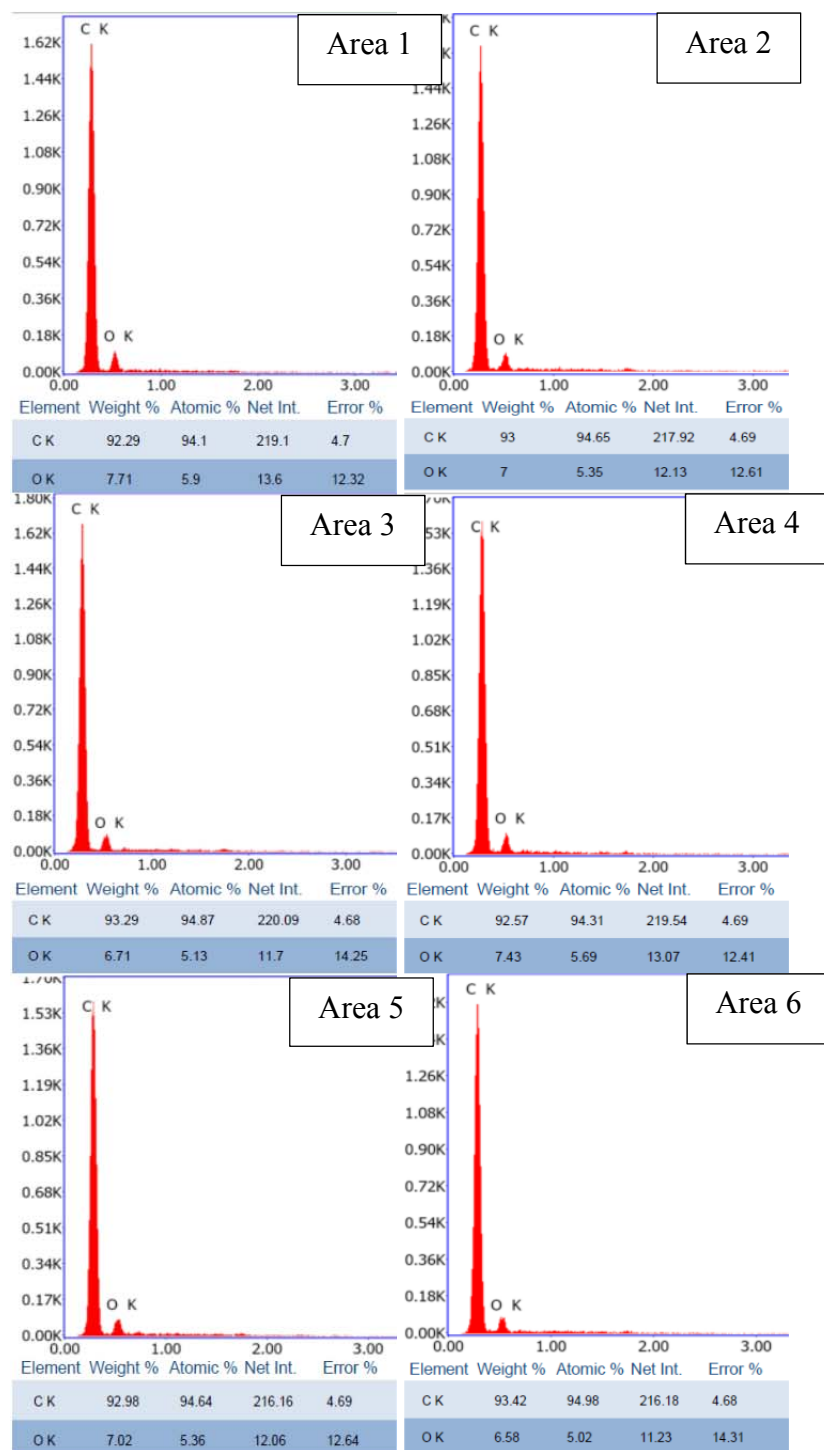


Figure A2-14. EDS spectra for areas 1-6 of thermally reduced humic acid at 700 °C

Table A2-13. C/O ratios for humic acid thermally reduced at 900 °C

Humic Acid Thermally Reduced at 900 °C		
Spot (S)/Area (A)	Atomic % Carbon	Atomic % Oxygen
A1	92.95	7.05
A2	93.05	6.95
A3	93.71	6.29
A4	93.78	6.22
A5	93.21	6.79
A6	94.34	5.66
A7	92.95	7.05
<i>Average</i>	<i>93.43</i>	<i>6.57</i>
<i>Standard Deviation</i>	<i>0.53</i>	

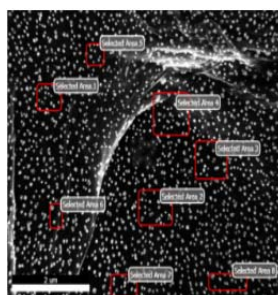


Figure A2-15. EDS for areas 1-7 of thermally reduced humic acid at 900 °C

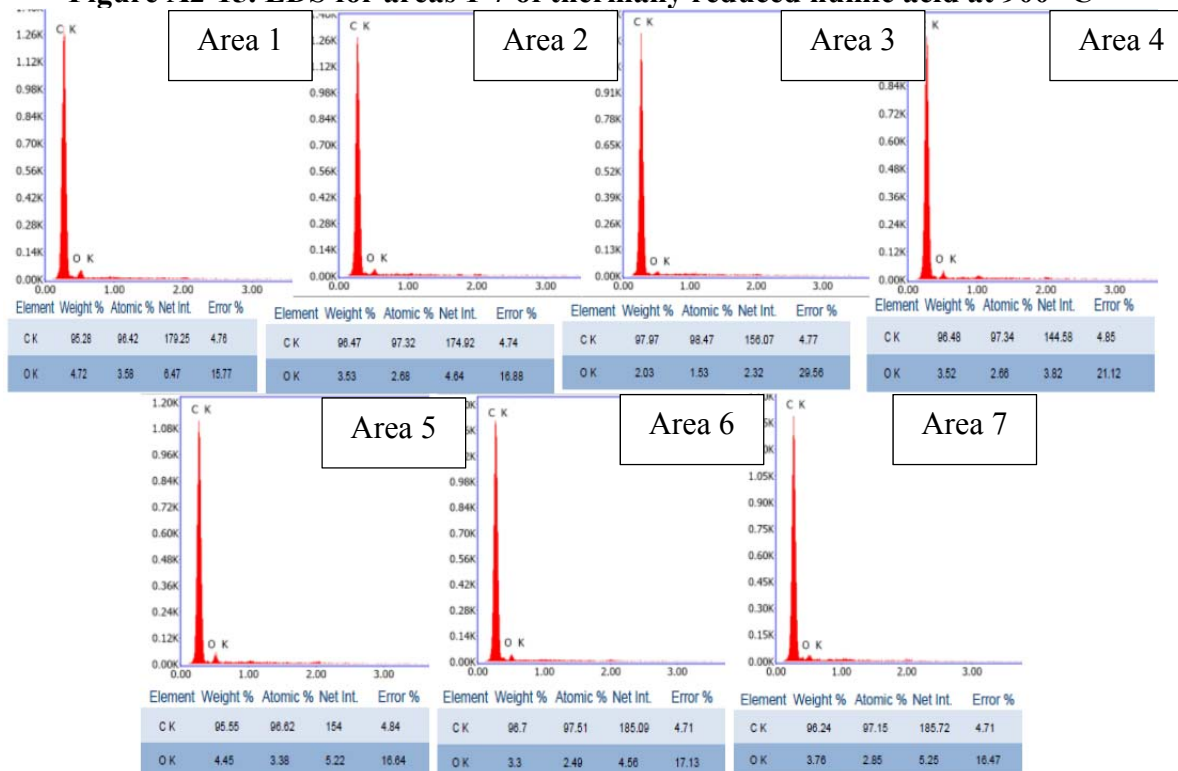


Figure A2-16. EDS spectra for areas 1-7 of thermally reduced humic acid at 900 °C

Section C.2 Raman spectral data for humic acid standard and reduced humic acid standard

Table A2-14. Raman spectral data for humic acid standard

Raman Analysis for Humic Acid Standard					
Sample #	D Raman Shift (cm⁻¹)	I_(D)	G Raman Shift (cm⁻¹)	I_(G)	I_(D)/I_(G)
1	1405.33	407.59	1581.78	582.07	0.70
2	1359.04	373.58	1592.39	510.31	0.73
3	1371.58	411.88	1559.6	462.12	0.89
4	1380.26	401.92	1599.14	517.65	0.78
5	1367.72	462.87	1594.32	610.81	0.76
6	1371.58	526.68	1593.35	675.74	0.78
Average	1375.92		1586.76		0.77
Standard Deviation	14.57		13.22		0.06

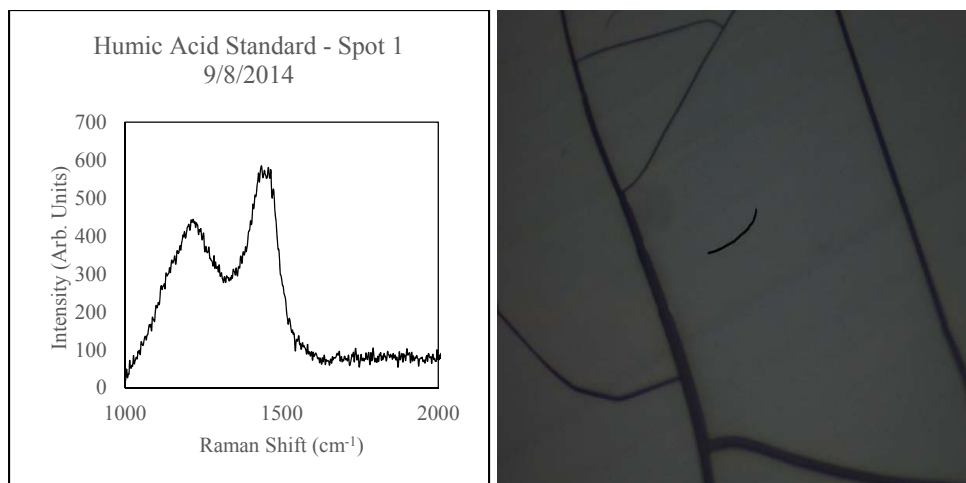


Figure A2-17. Humic acid standard - spot 1

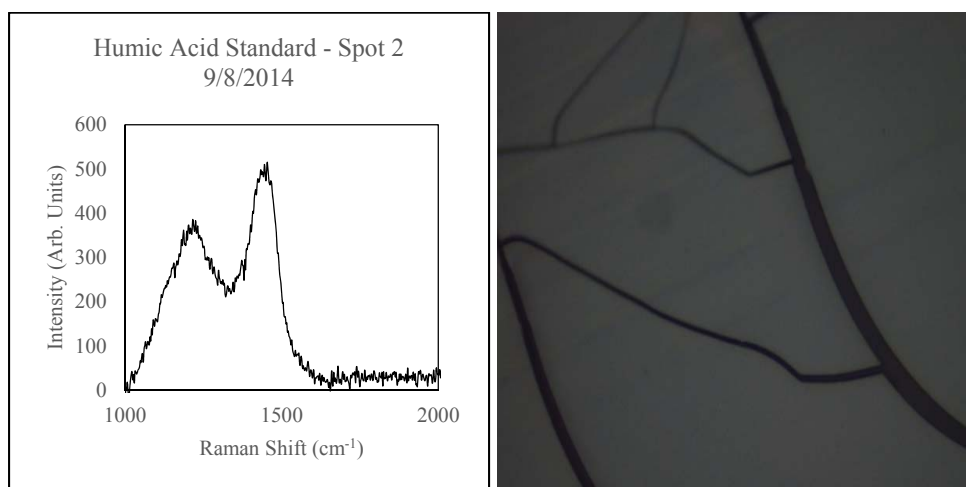


Figure A2-18. Humic acid standard - spot 2

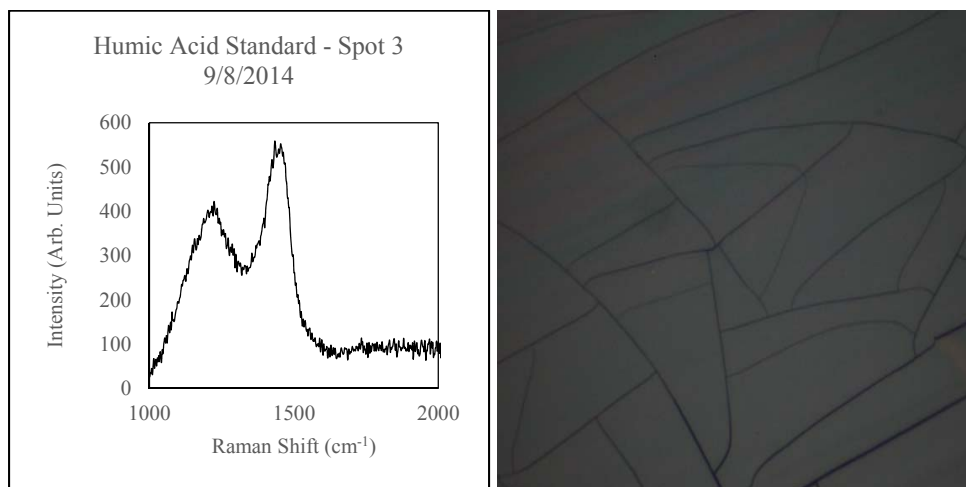


Figure A2-19. Humic acid standard - spot 3

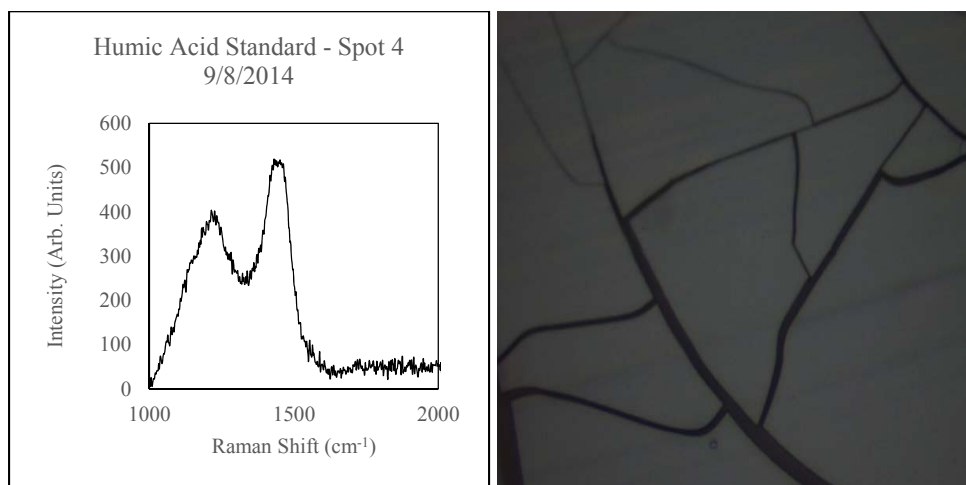


Figure A2-20. Humic acid standard - spot 4

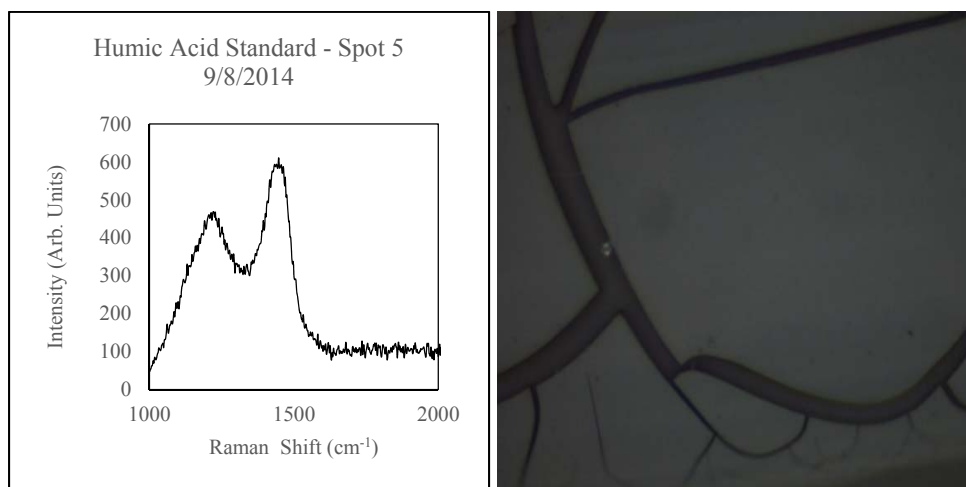


Figure A2-21. Humic acid standard - spot 5

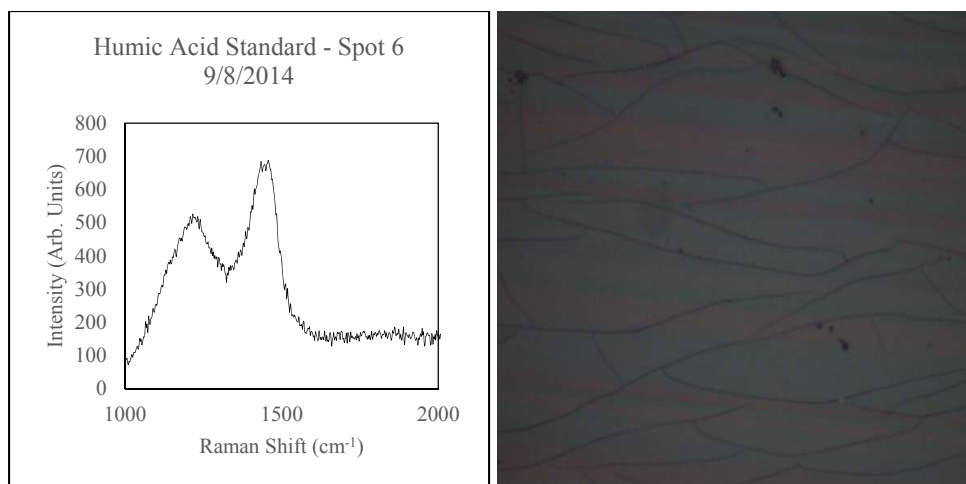


Figure A2-22. Humic Acid Standard - Spot 6

Section C3. Raman spectral data for hydrazine reduced humic acid

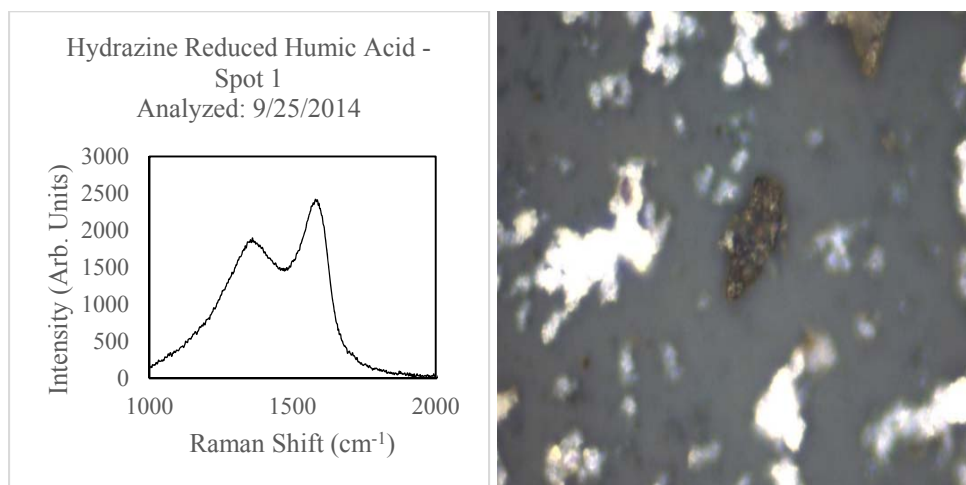


Figure A2-23. Hydrazine reduced humic acid - spot 1

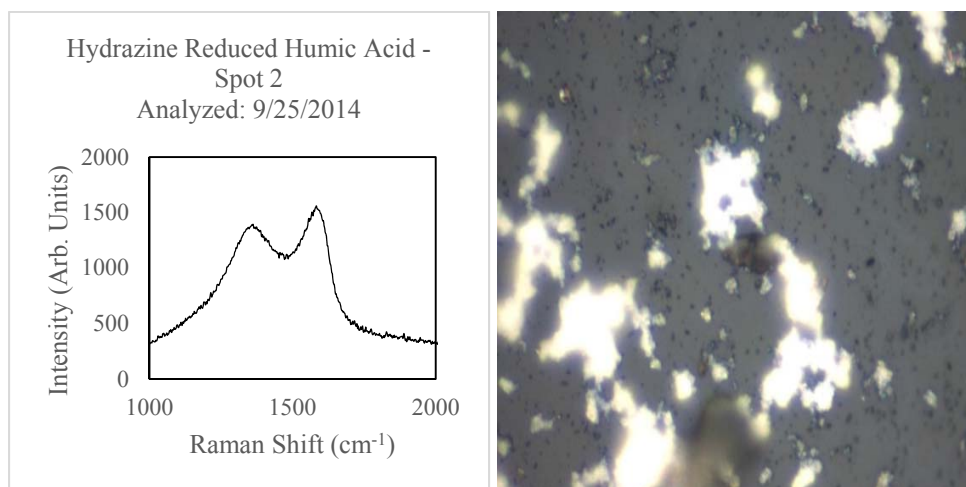


Figure A2-24. Hydrazine reduced humic acid - spot 2

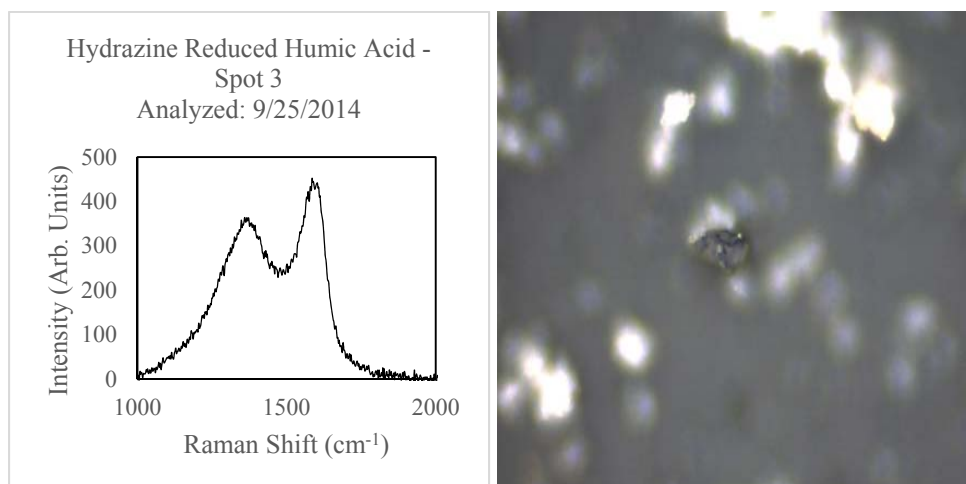


Figure A2-25. Hydrazine reduced humic acid - spot 3

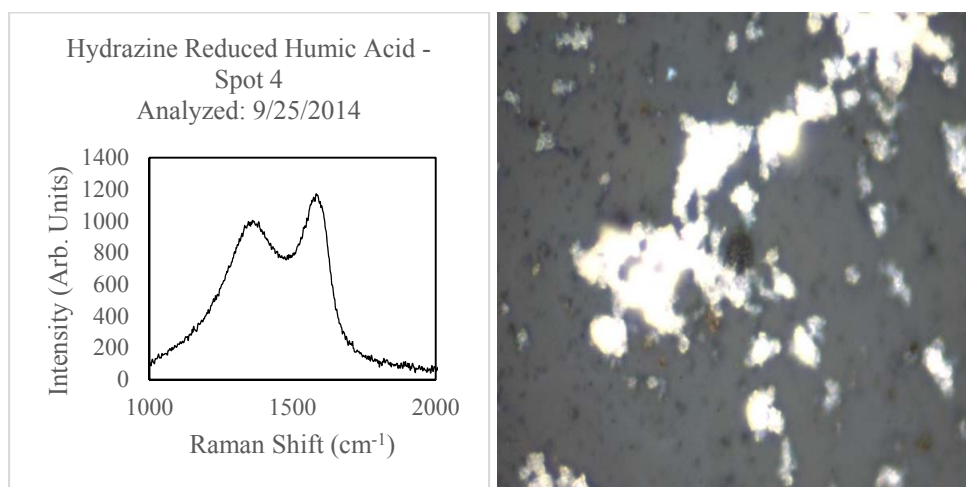


Figure A2-26. Hydrazine reduced humic acid - spot 4

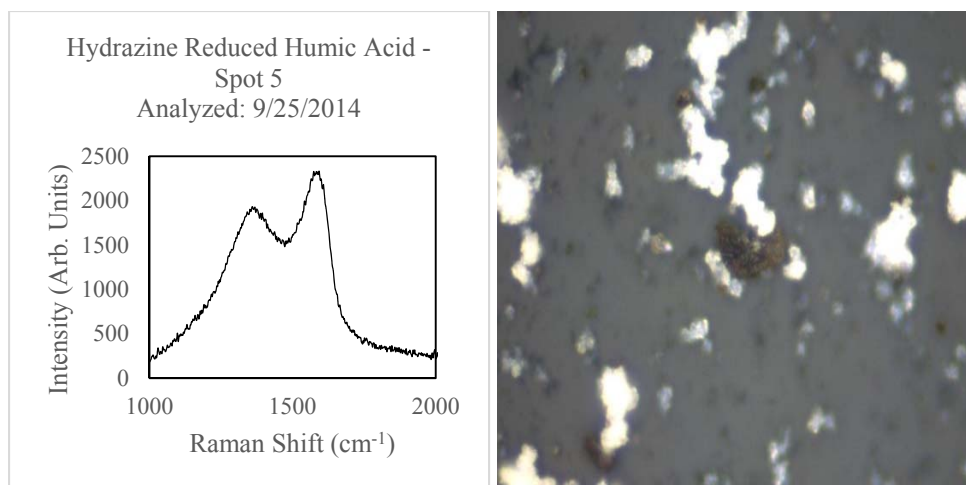


Figure A2-27. Hydrazine reduced humic acid - spot 5

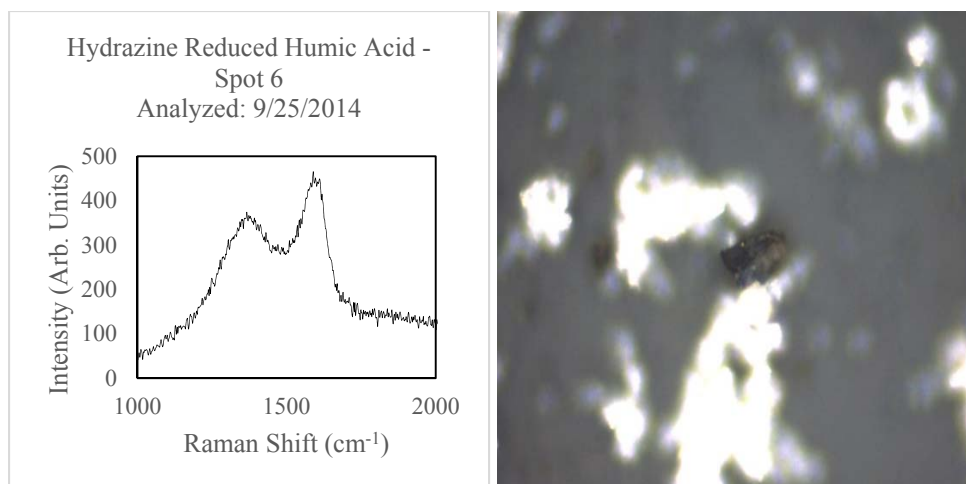


Figure A2-28. Hydrazine reduced humic acid - spot 6

Section C3. Raman spectral data for hydroxylamine reduced humic acid

Table A2-15. Raman spectral data for hydroxylamine reduced humic acid

Raman Analysis for Hydroxylamine Reduced Humic Acid					
Sample #	D Raman Shift (cm ⁻¹)	I _(D)	G Raman Shift (cm ⁻¹)	I _(G)	I _(D) /I _(G)
1	1374.43	2289.91	1579.81	3010.73	0.76
2	1373.46	1142.91	1580.78	1351.55	0.85
3	1381.18	1861.59	1580.78	2334.08	0.80
4	1359.00	2334.52	1593.31	2366.97	0.99
5	1358.04	2649.69	1588.49	2810.39	0.94
6	1378.29	2158.83	1586.56	2630.25	0.82
Average	1370.73		1584.95		0.86
Standard Deviations	9.86		5.41		0.09

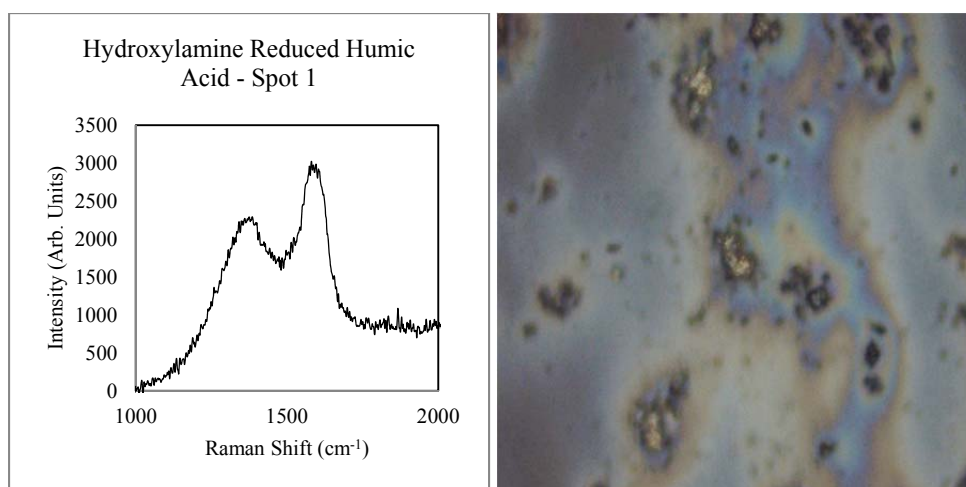


Figure A2-29. Hydroxylamine reduced humic acid - spot 1

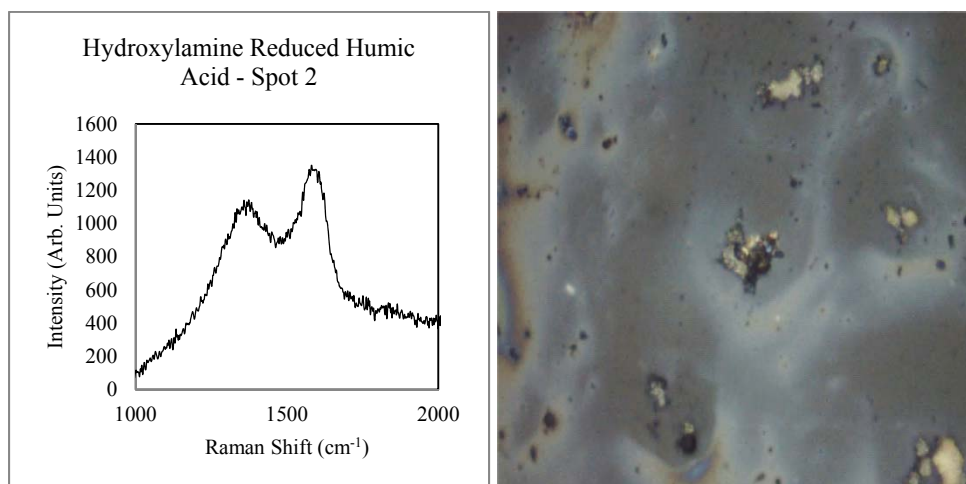


Figure A2-30. Hydroxylamine reduced humic acid - spot 2

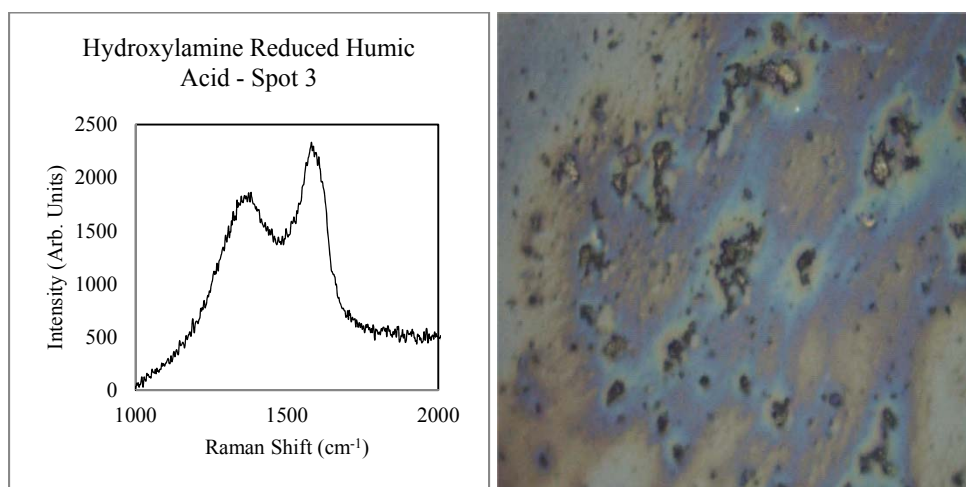


Figure A2-31. Hydroxylamine reduced humic acid - spot 3

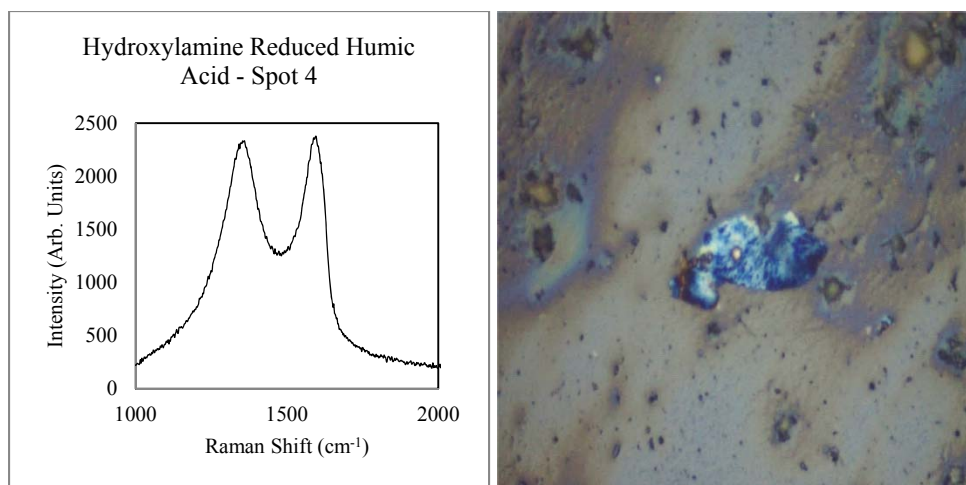


Figure A2-32. Hydroxylamine reduced humic acid - spot 4

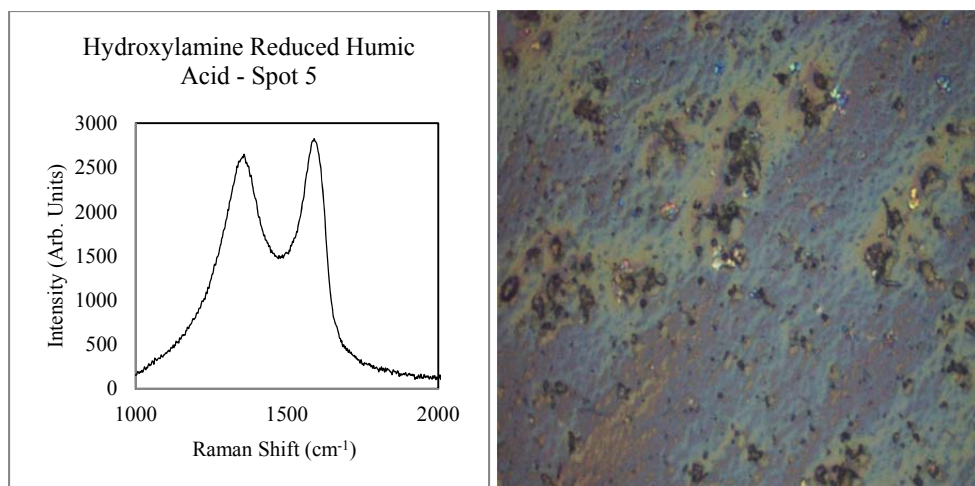


Figure A2-33. Hydroxylamine reduced humic acid - spot 5

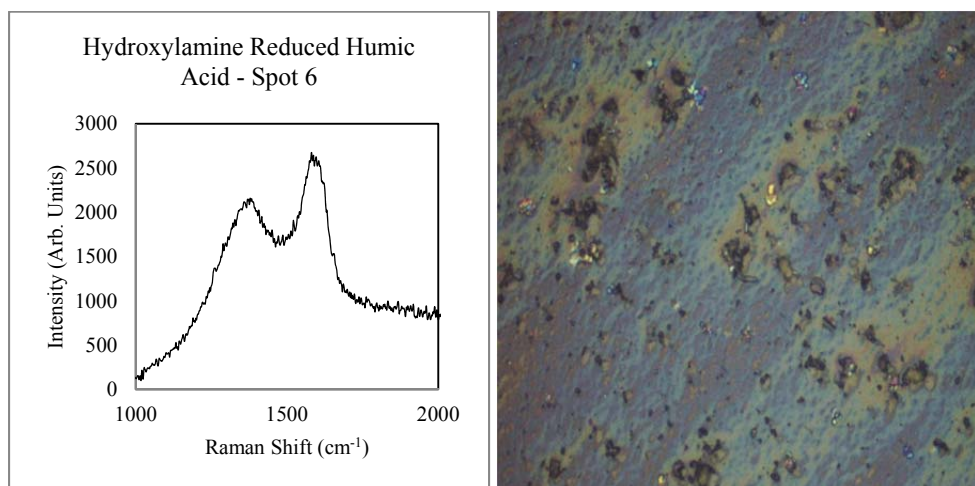


Figure A2-34. Hydroxylamine reduced humic acid - spot 6

Section C4. Raman spectral data for sodium borohydride reduced humic acid

Table A2-16. Raman spectral data for sodium borohydride reduced humic acid

Raman Analysis for Sodium Borohydride Reduced Humic Acid					
Sample #	D Raman Shift (cm ⁻¹)	I _(D)	G Raman Shift (cm ⁻¹)	I _(G)	I _(D) /I _(G)
1	1366.76	1312.15	1604.92	1822.44	0.72
2	1359.04	2796.82	1592.39	3519.56	0.79
3	1366.76	1520.30	1603.96	1838.38	0.83
4	1358.08	858.01	1602.03	1028.19	0.83
5	1385.08	692.54	1607.81	852.64	0.81
6	1373.51	1029.04	1603.96	1239.90	0.83
7	1380.26	431.96	1603.96	533.43	0.81
Average	1369.93		1602.72		0.80
Standard Deviation	10.23		4.87		0.04

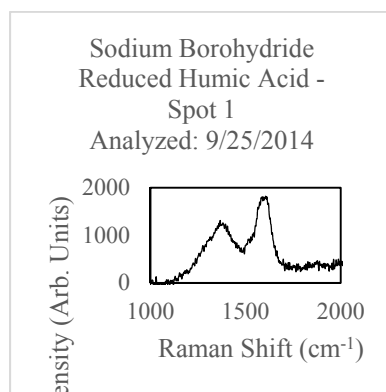


Figure A2-35. Sodium borohydride reduced humic acid - spot 1

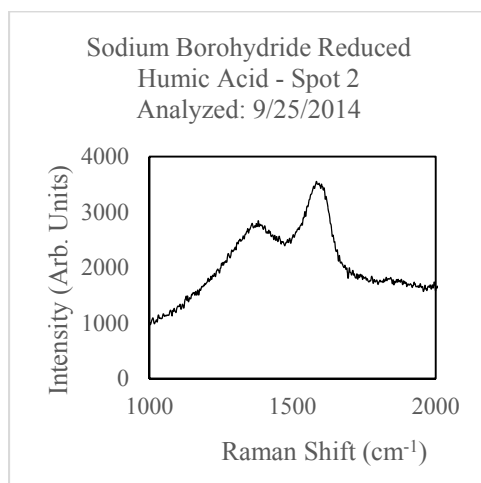


Figure A2-36. Sodium borohydride reduced humic acid - spot 2

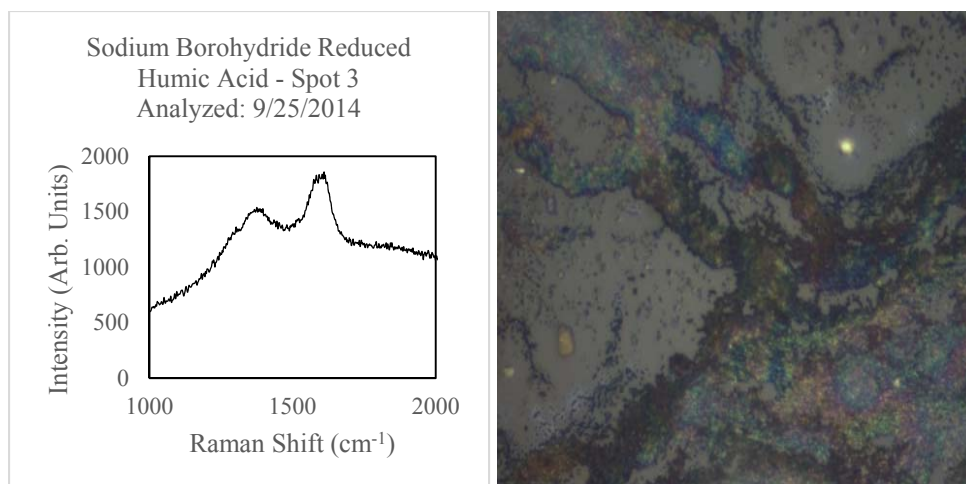


Figure A2-37. Sodium borohydride reduced humic acid - spot 3

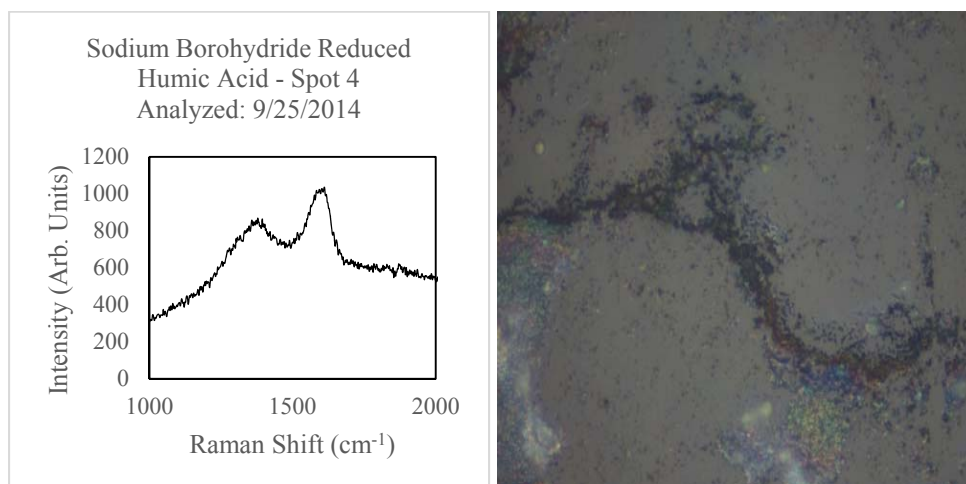


Figure A2-38. Sodium borohydride reduced humic acid - spot 4

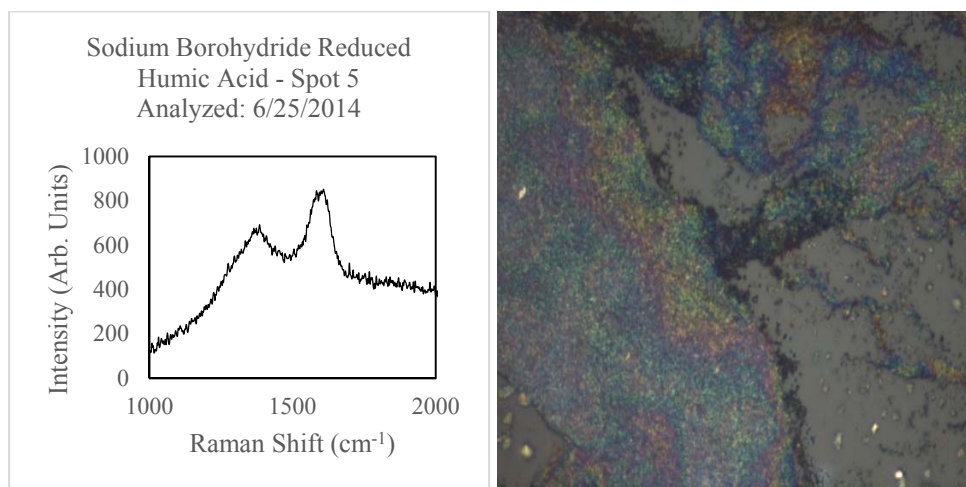


Figure A2-39. Sodium borohydride reduced humic acid - spot 5

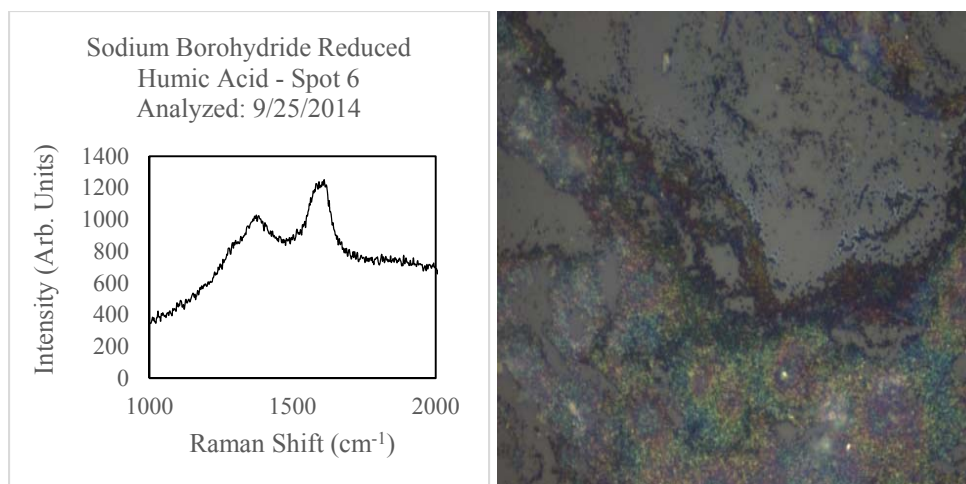


Figure A2-40. Sodium borohydride reduced humic acid - spot 6

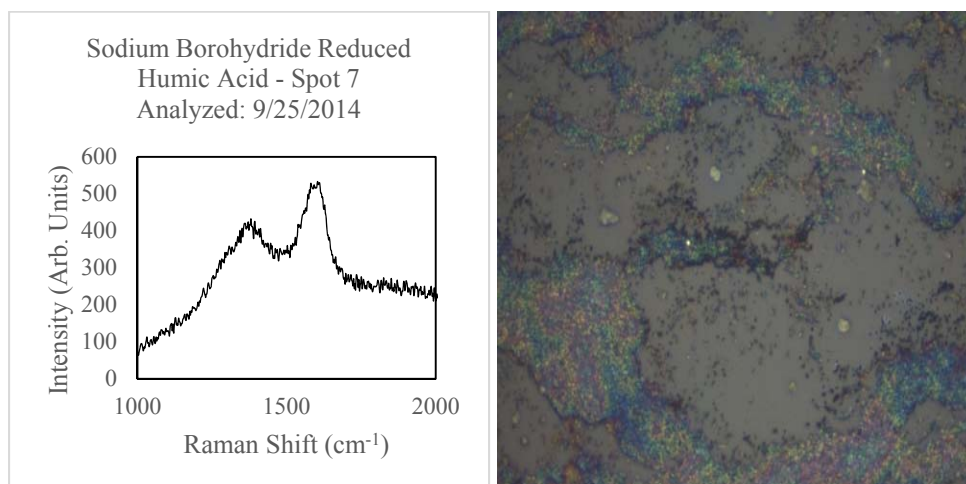


Figure A2-41. Sodium borohydride reduced humic acid - spot 7

Section C5. Raman spectral data for sodium bisulfite reduced humic acid

Table A2-17. Raman spectral data for sodium bisulfite reduced humic acid

Raman Analysis of Sodium Bisulfite Reduced Humic Acid					
Sample #	D Raman Shift (cm⁻¹)	I_(D)	G Raman Shift (cm⁻¹)	I_(G)	I_(D)/I_(G)
1	1371.58	562.54	1599.14	706.05	0.80
2	1362.90	282.04	1602.99	349.48	0.81
3	1366.76	910.74	1599.14	1138.15	0.80
4	1368.68	936.37	1605.89	1176.43	0.80
5	1374.47	847.54	1605.89	1055.35	0.80
6	1360.01	174.35	1604.92	226.70	0.77
Average	1367.40		1603.00		0.80
Standard Deviation	4.91		2.89		0.01

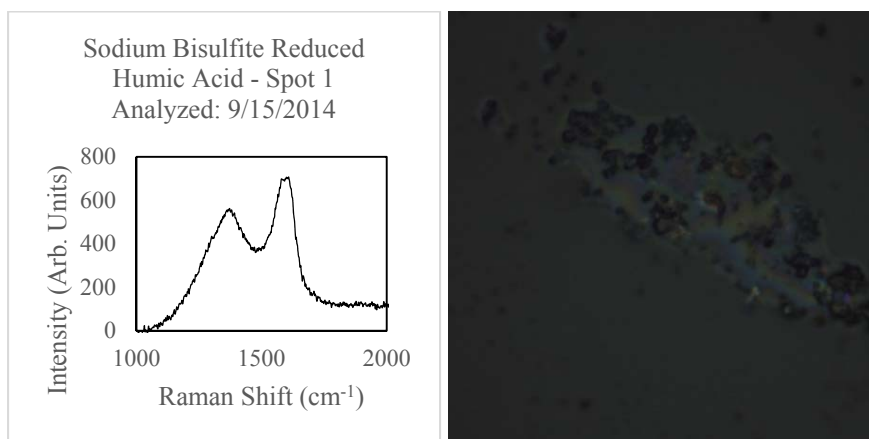


Figure A2-42. Sodium bisulfite reduced humic acid – spot 1

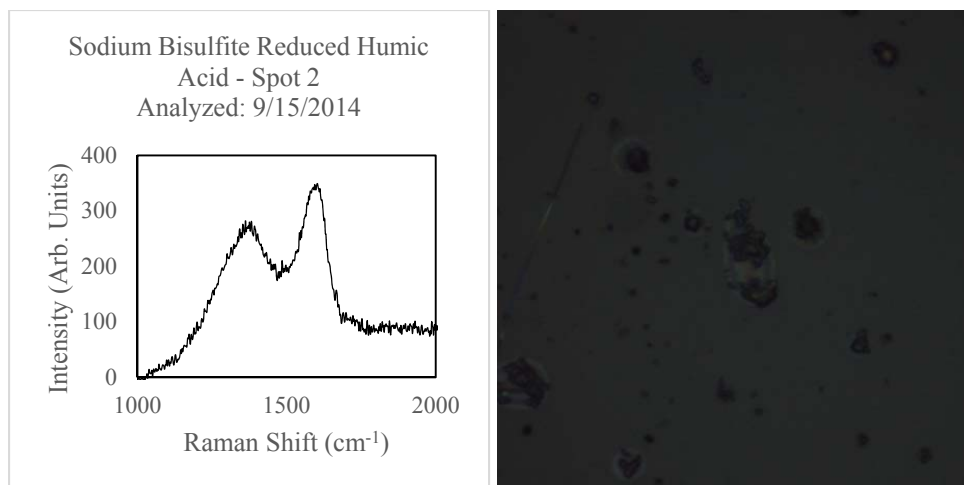


Figure A2-43. Sodium bisulfite reduced humic acid – spot 2

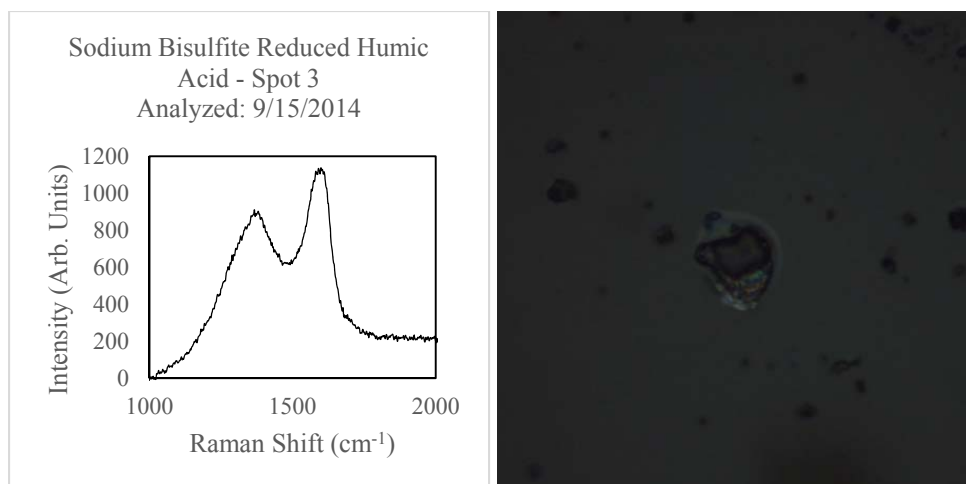


Figure A2-44. Sodium bisulfite reduced humic acid – spot 3

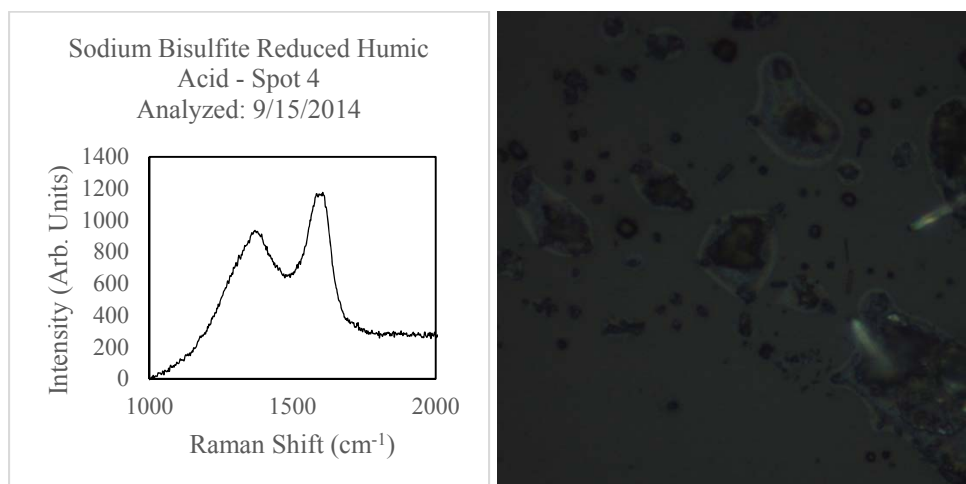


Figure A2-45. Sodium bisulfite reduced humic acid – spot 4

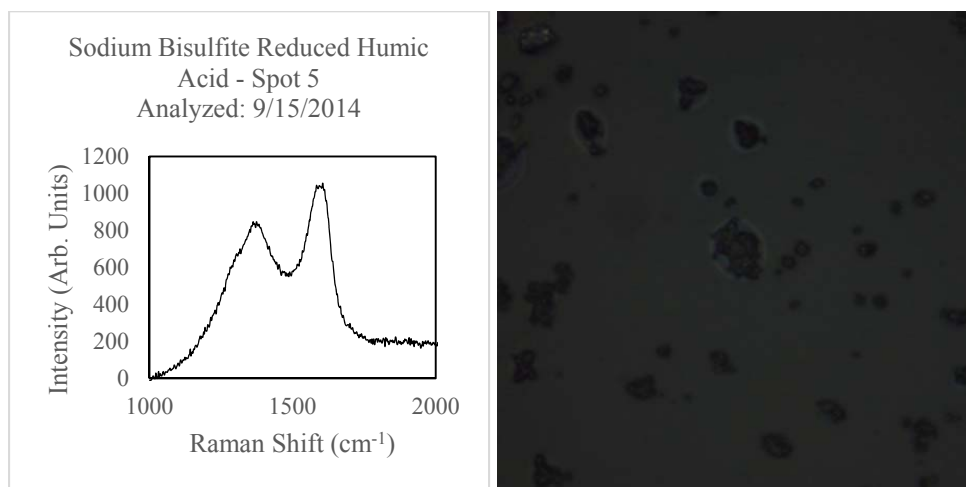


Figure A2-46. Sodium bisulfite reduced humic acid – spot 5

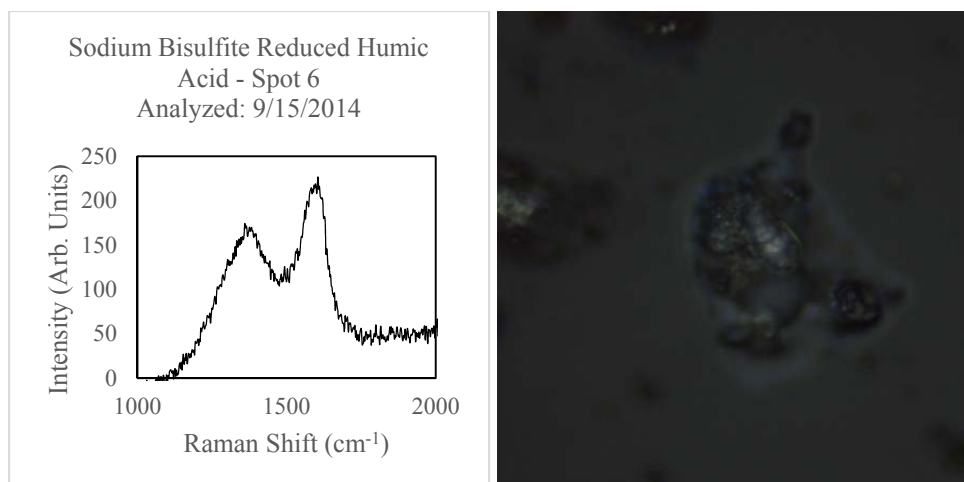


Figure A2-47. Sodium bisulfite reduced humic acid – spot 6

Section C6. Raman spectral data for benzyl alcohol reduced humic acid

Table A2-18. Raman spectral data for benzyl alcohol reduced humic acid

Raman Analysis for Benzyl Alcohol Reduced Humic Acid					
Sample #	D Raman Shift (cm ⁻¹)	I _(D)	G Raman Shift (cm ⁻¹)	I _(G)	I _(D) /I _(G)
1	1362.86	1021.46	1595.24	1371.96	0.74
2	1375.39	1990.24	1593.31	2576.45	0.77
3	1372.50	3317.59	1579.81	4488.16	0.74
4	1377.32	2511.46	1581.74	3434.87	0.73
5	1378.29	2864.82	1580.78	4105.38	0.70
6	1373.46	3876.82	1580.78	5323.72	0.73
7	1375.39	772.38	1579.81	1031.64	0.75
Average	1373.60		1585.27		0.74
Standard Deviations	5.15		6.74		0.02

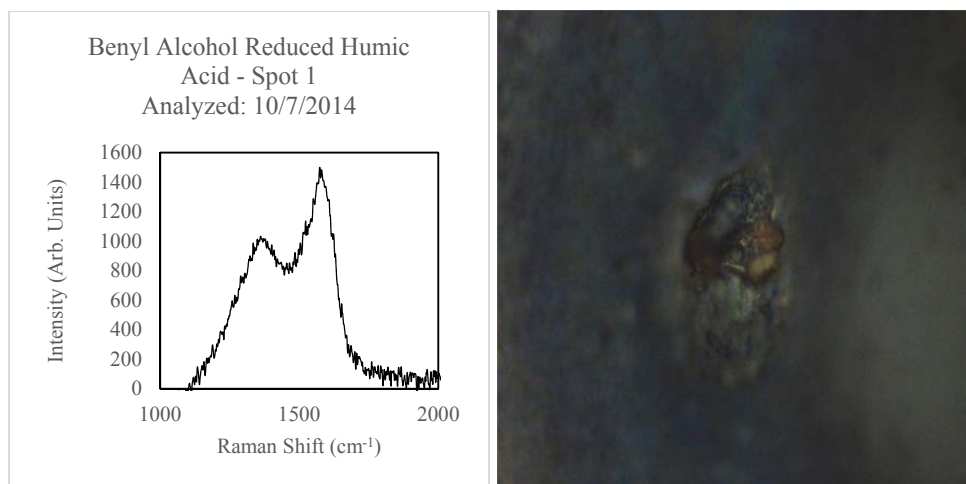


Figure A2-48. Benzyl alcohol reduced humic acid – spot 1

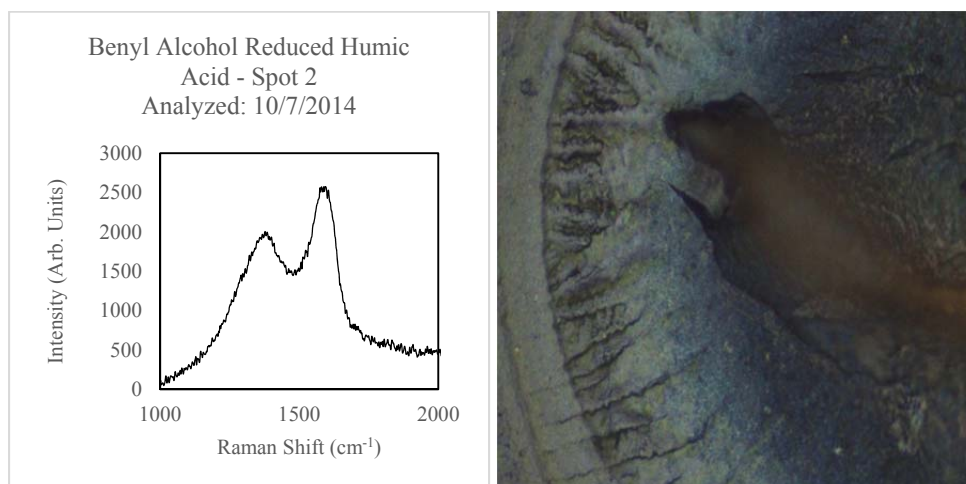


Figure A2-49. Benzyl alcohol reduced humic acid – spot 2

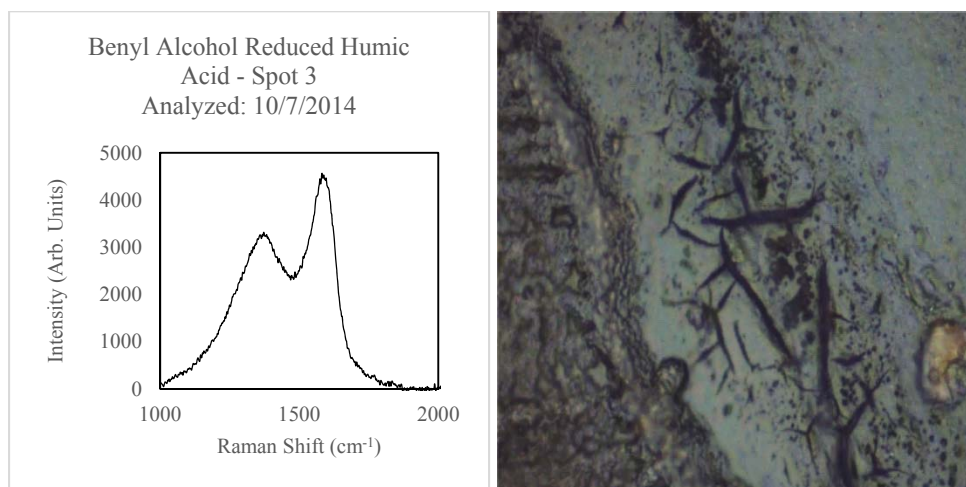


Figure A2-50. Benzyl alcohol reduced humic acid – spot 3

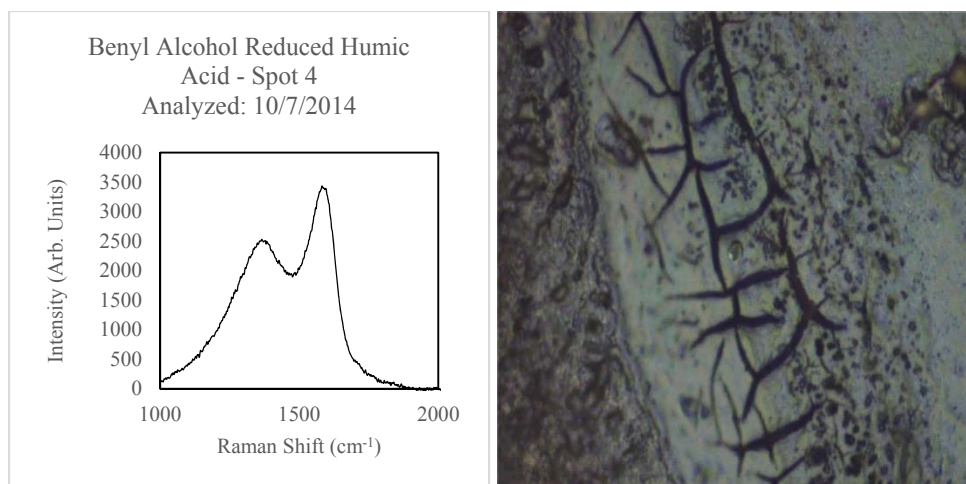


Figure A2-51. Benzyl alcohol reduced humic acid – spot 4

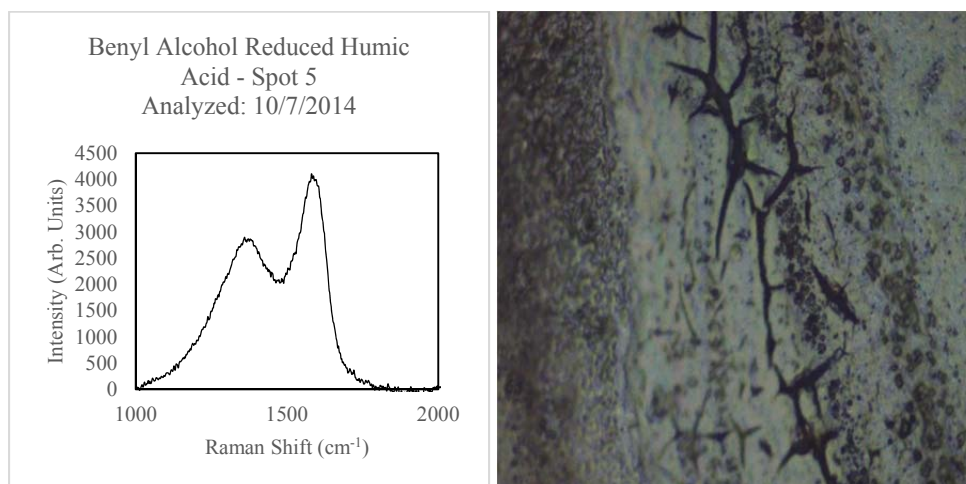


Figure A2-52. Benzyl alcohol reduced humic acid – spot 5

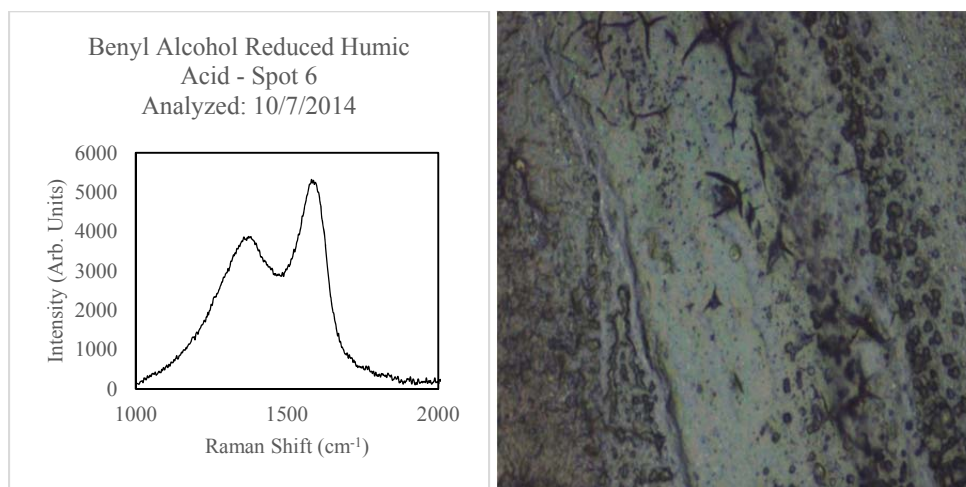


Figure A2-53. Benzyl alcohol reduced humic acid – spot 6

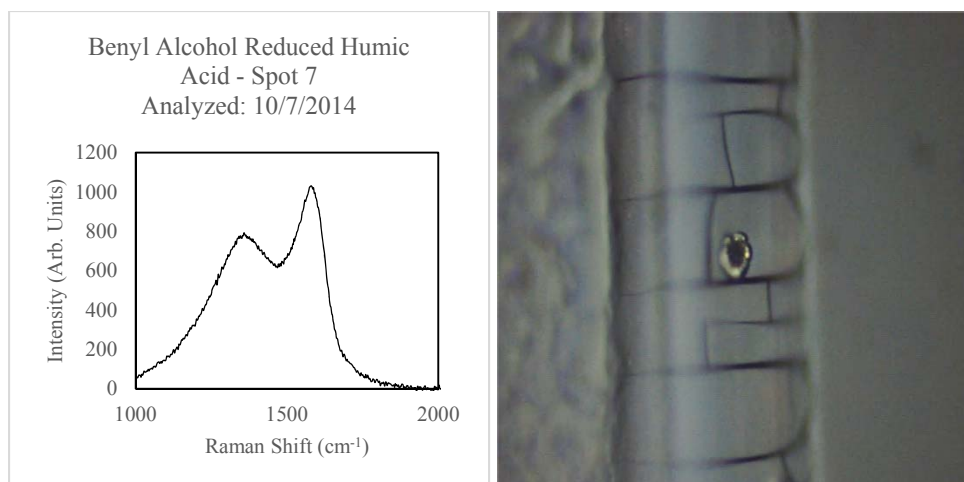


Figure A2-54. Benzyl alcohol reduced humic acid – spot 7

C7. Raman spectral data for thermally reduced humic acid at 500 °C

Section A2-19. Raman spectral data for thermally reduced humic acid at 500 °C

Raman Analysis for Thermally Reduced Humic Acid at 500 °C					
Sample #	D Raman Shift (cm ⁻¹)	I _(D)	G Raman Shift (cm ⁻¹)	I _(G)	I _(D) /I _(G)
1	1367.68	1403.12	1579.81	1841.50	0.76
2	1359.97	2043.90	1587.52	2813.93	0.73
3	1369.61	823.67	1588.49	1188.71	0.69
4	1369.61	1462.98	1595.24	2128.52	0.69
5	1368.64	2260.52	1596.20	3240.07	0.70
6	1368.64	2169.88	1594.27	3137.50	0.69
Average	1367.36		1590.26		0.71
Standard Deviations	3.69		6.26		0.03

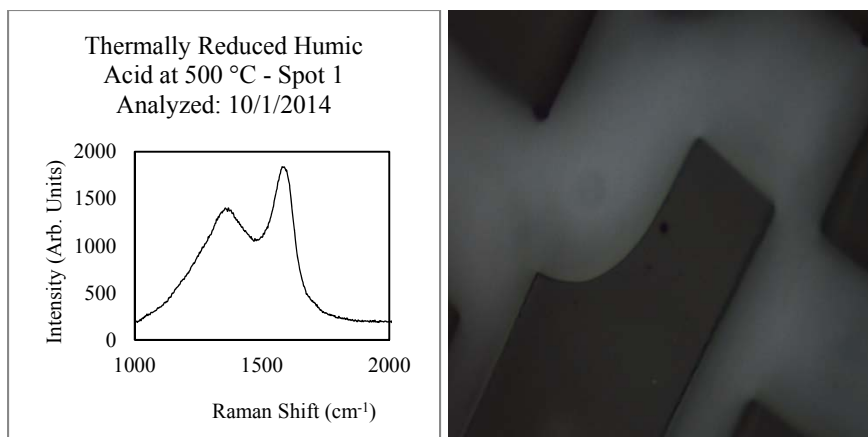


Figure A2-55. Thermally reduced humic acid at 500 °C – spot 1

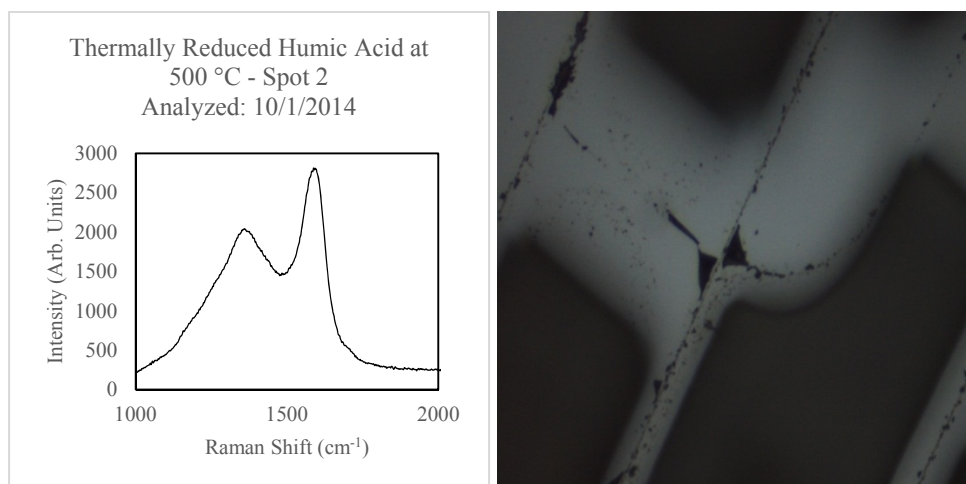


Figure A2-56. Thermally reduced humic acid at 500 °C – spot 2

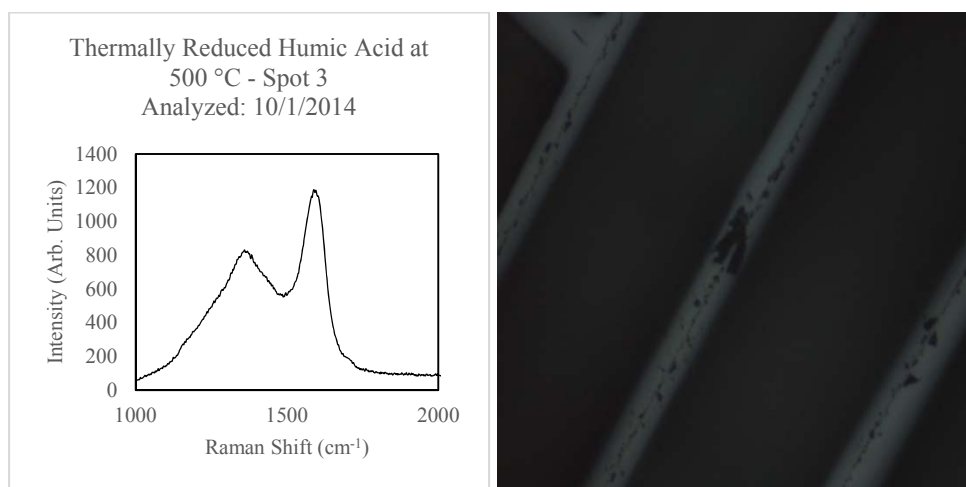


Figure A2-57. Thermally reduced humic acid at 500 °C – spot 3

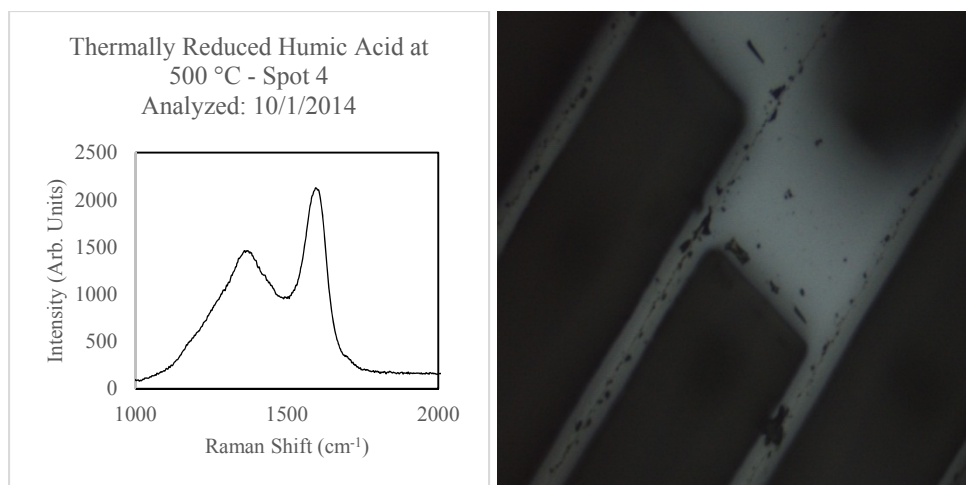


Figure A2-58. Thermally reduced humic acid at 500 °C – spot 4

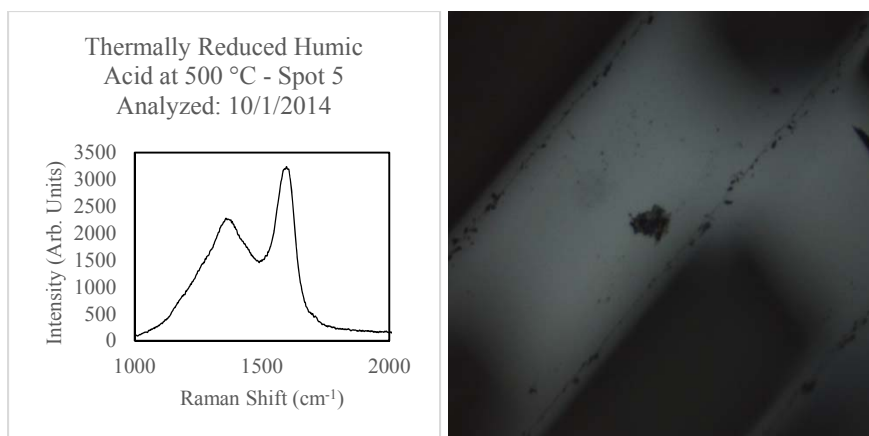


Figure A2-59. Thermally reduced humic acid at 500 °C – spot 5

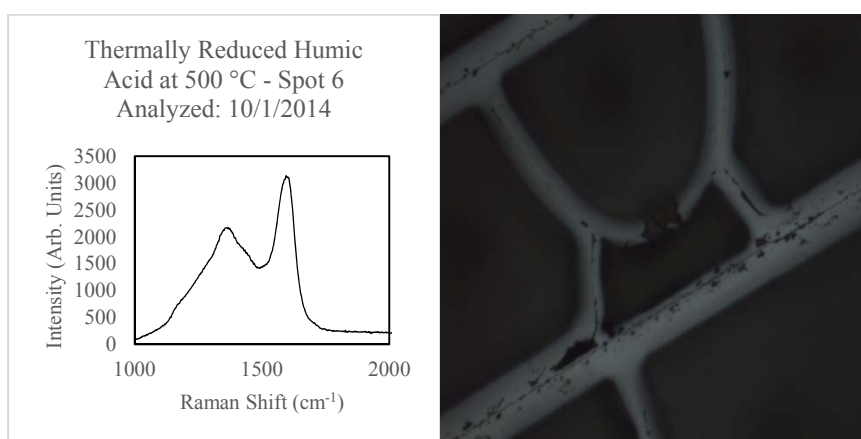


Figure A2-60. Thermally reduced humic acid at 500 °C – spot 6

C8. Raman spectral data for thermally reduced humic acid at 700 °C

Table A2-20. Raman spectral data for thermally reduced humic acid at 700 °C

Raman Analysis for Thermally Reduced Humic Acid at 700 °C					
Sample #	D Raman Shift (cm ⁻¹)	I _(D)	G Raman Shift (cm ⁻¹)	I _(G)	I _(D) /I _(G)
1	1339.72	900.97	1594.27	1052.68	0.86
2	1335.86	759.91	1596.20	888.09	0.86
3	1335.86	1195.39	1599.10	1445.77	0.83
4	1341.65	1204.71	1597.17	1503.06	0.80
5	1339.72	799.11	1599.10	930.75	0.86
6	1334.90	792.13	1595.24	922.36	0.86
7	1339.72	386.30	1601.02	461.84	0.84
Average	1338.20		1597.44		0.84
Standard Deviation	2.60		2.41		0.02

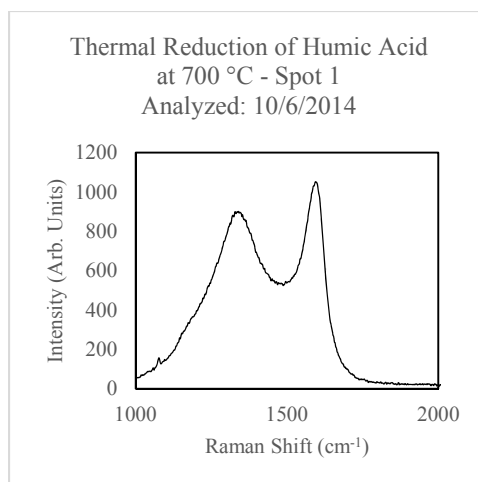


Figure A2-61. Thermally reduced humic acid at 700 °C – spot 1

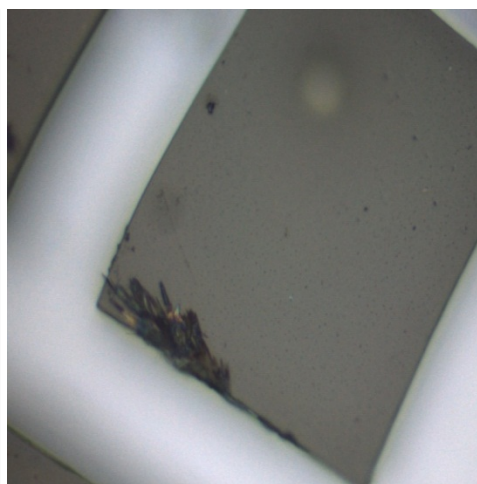
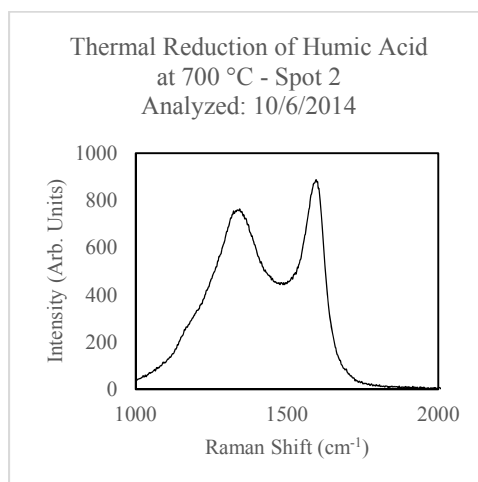


Figure A2-62. Thermally reduced humic acid at 700 °C – spot 2

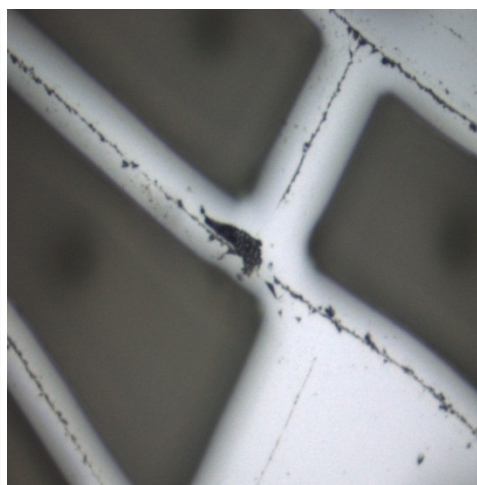
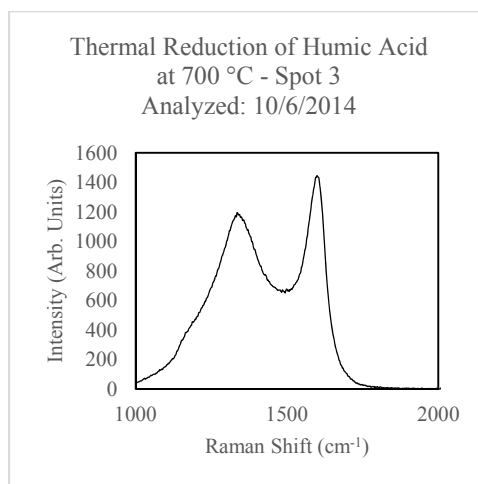


Figure A2-63. Thermally reduced humic acid at 700 °C – spot 3

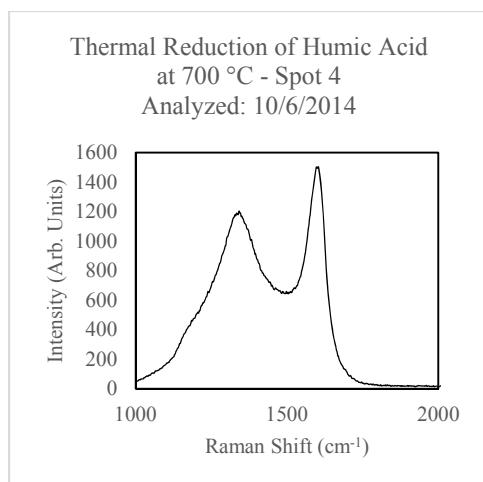


Figure A2-64. Thermally reduced humic acid at 700 °C – spot 4

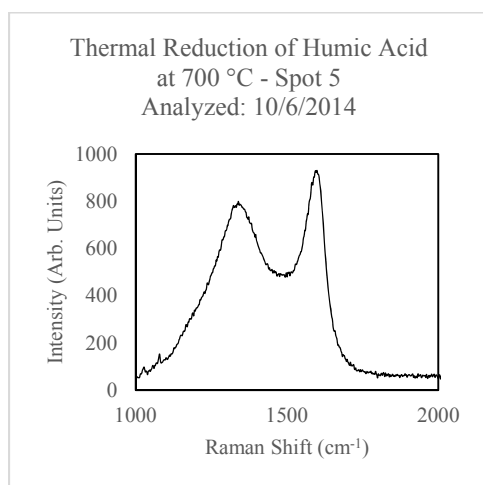


Figure A2-65. Thermally reduced humic acid at 700 °C – spot 5

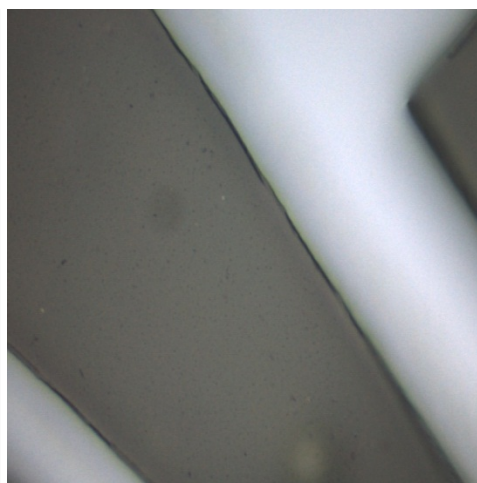
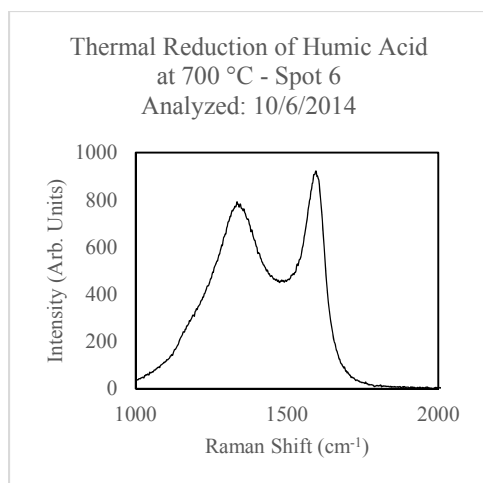


Figure A2-66. Thermally reduced humic acid at 700 °C – spot 6

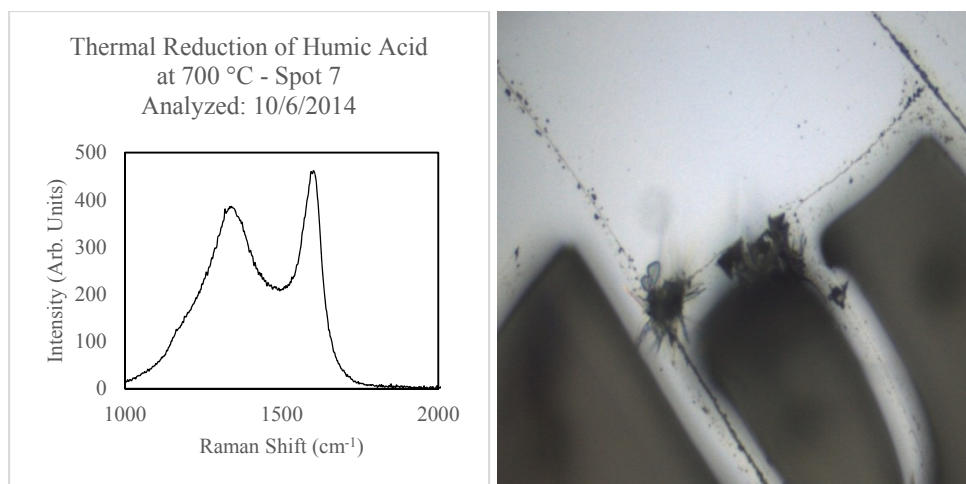


Figure A2-67. Thermally reduced humic acid at 700 °C – spot 7

Section C9. Raman spectral data for thermally reduced humic acid at 900 °C

Table A2-21. Raman spectral data for thermally reduced humic acid at 900 °C

Raman Analysis for Thermally Reduced Humic Acid at 900 °C					
Sample #	D Raman Shift (cm ⁻¹)	I _(D)	G Raman Shift (cm ⁻¹)	I _(G)	I _(D) /I _(G)
1	1334.90	560.81	1595.24	505.96	1.11
2	1332.97	577.26	1595.24	520.97	1.11
3	1337.79	555.48	1598.13	512.16	1.08
4	1332.97	565.44	1598.13	504.64	1.12
5	1340.68	512.83	1597.17	477.40	1.07
6	1334.90	555.21	1597.17	499.30	1.11
Average	1335.70		1596.85		1.10
Standard Deviations	3.01		1.32		0.02

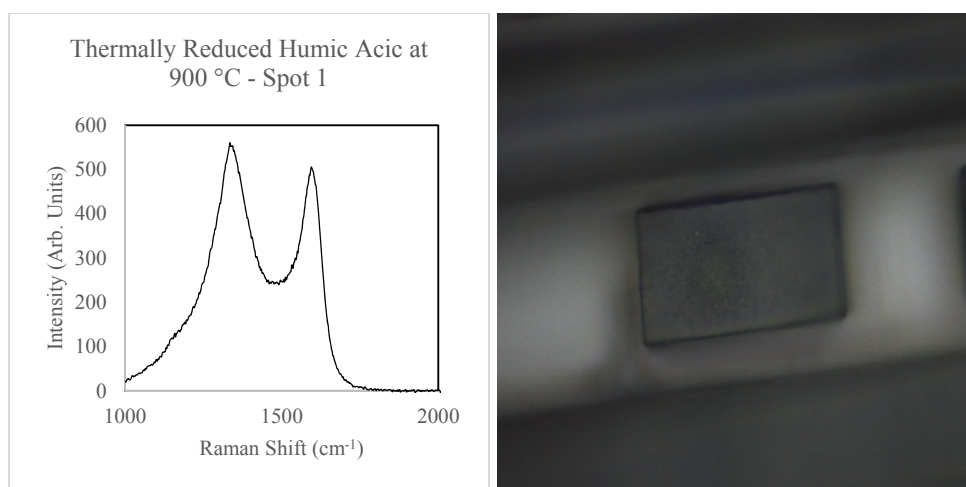


Figure A2-68. Thermally reduced humic acid at 900 °C – spot 1

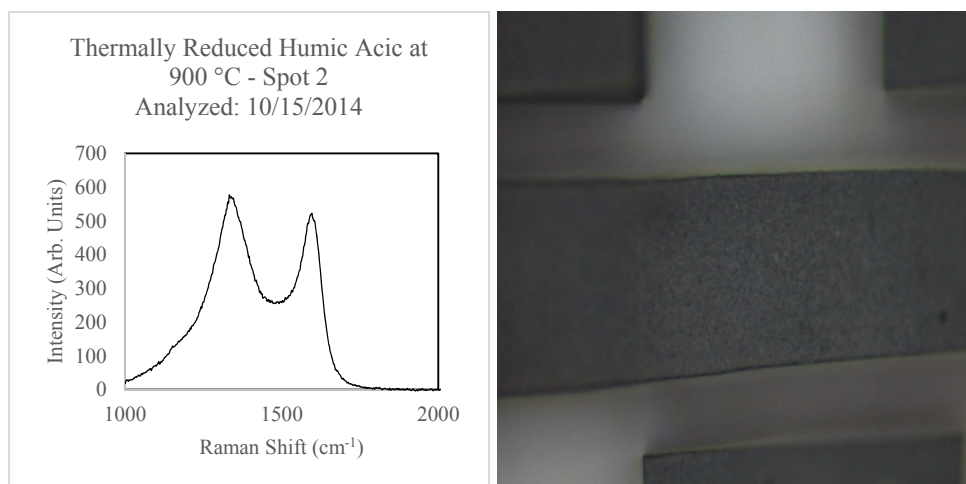


Figure A2-69. Thermally reduced humic acid at 900 °C – spot 2

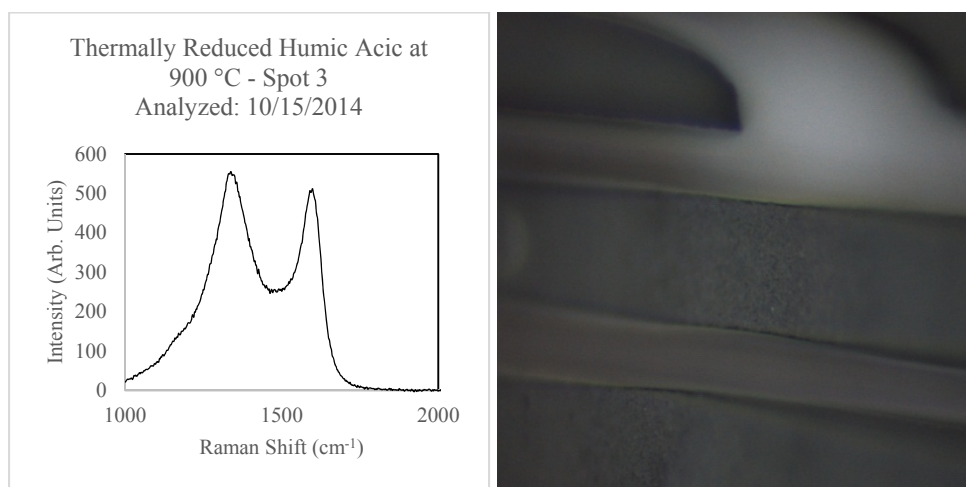


Figure A2-70. Thermally reduced humic acid at 900 °C – spot 3

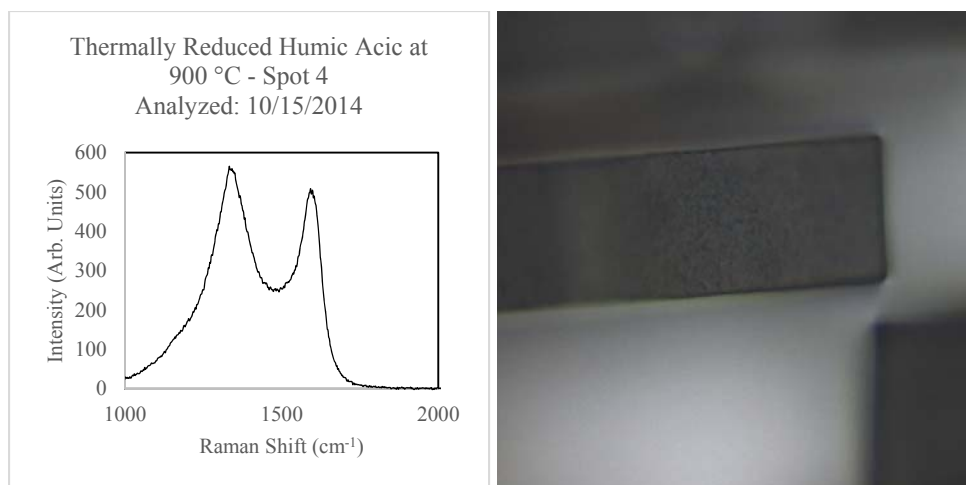


Figure A2-71. Thermally reduced humic acid at 900 °C – spot 4

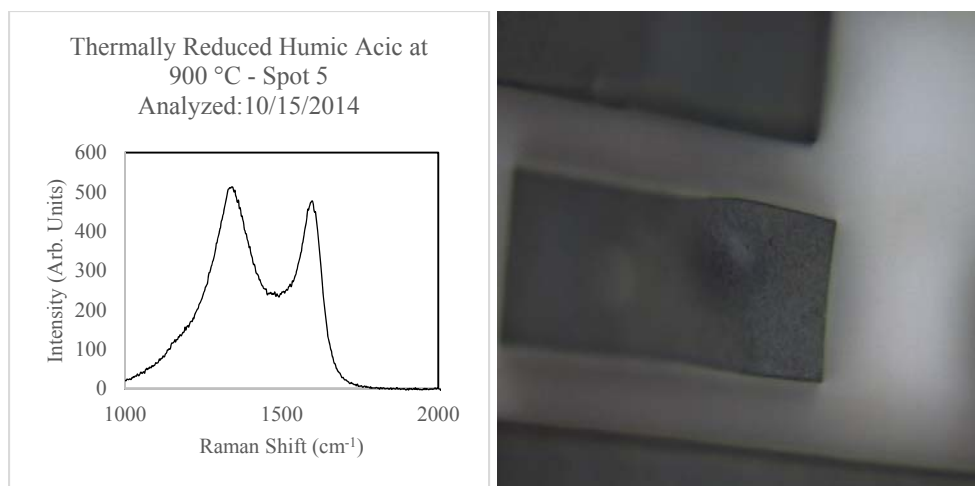


Figure A2-72. Thermally reduced humic acid at 900 °C – spot 5

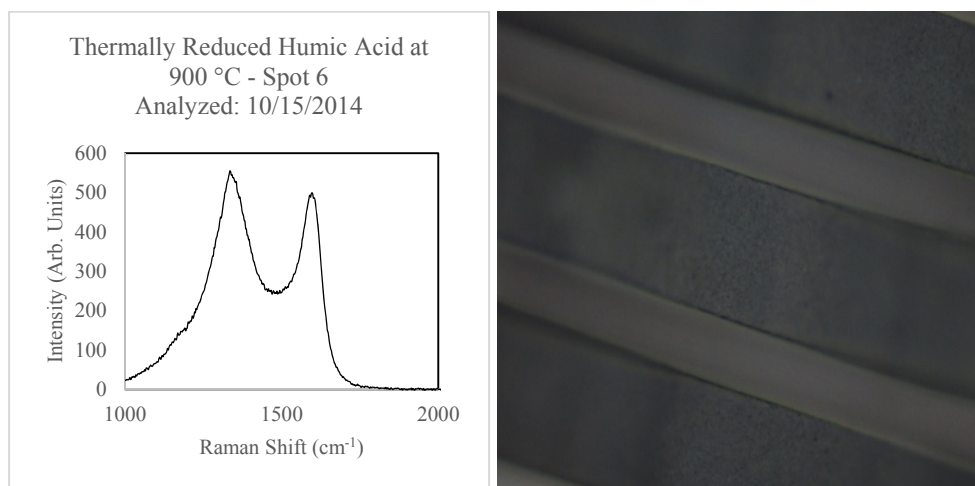


Figure A2-73. Thermally reduced humic acid at 900 °C – spot 6

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