Graphene Induced Formation of Nanostructures in Composites

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GRAPHENE INDUCED FORMATION OF NANOSTRUCTURES IN COMPOSITES

by

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A dissertation submitted in partial fulfillment of the requirements
for the degree of Doctor of Philosophy
in the Department of Materials Science and Engineering
in the College of Engineering and Computer Science
at the University of Central Florida
Orlando, Florida

Spring Term
2018

Major Professor: Lei Zhai
ABSTRACT

Graphene induced nanostructures in graphene-based composites and the performance of these composites have been explored in this study. For the metallic nanoparticles decorated graphene aerogels composites, the fabrication of hierarchically structured, reduced graphene oxide (rGO) aerogels with heavily metallic nanoparticles was realized. Higher loading of palladium nanoparticles in graphene aerogels leads to improved hydrogen gas sensing performance. For polymer derived ceramics (PDCs) composites with anisotropic electrical properties, the fabrication of composites was realized by embedding anisotropic reduced graphene oxide aerogels (rGOAs) into the PDCs matrix. Raman spectroscopy and X-ray diffraction studies of PDCs composites with and without graphene indicate that graphene facilitates the transition from amorphous carbon to graphitic carbon in the PDCs. For composites composed of PDCs and edge functionalized graphene oxide (EFGO), bulk PDCs based composites with embedded graphene networks show high electrical conductivity, high thermal stability, and low thermal conductivity. For the study of poly(3-hexylthiophene) (P3HT) crystallization on graphitic substrates (i.e. carbon nanotubes, carbon fibers and graphene), different types of P3HT nanocrystals (i.e. nanowires, nanoribbons, and nanowalls) were observed. The type of nanocrystals grown from graphitic substrates depends on the curvature of graphitic substrates, the molecular weight of P3HT molecules, and the concentration of P3HT marginal solutions. Besides, both specific surface area and curvature of graphitic substrates have major effects on P3HT crystallization processes.
for my dreams since childhood
ACKNOWLEDGMENTS

First of all, I would like to appreciate my parents for pushing me go abroad for study. I was kidding privately that I would definitely have kids if I decided not to go abroad. But I have to say I definitely experienced many things that could not happen if I did not leave my home country. Getting a PHD degree is not only about learning experimental skills, critical thinking, technical writing and professional presentation, but using these best years in my life to gain the wisdom for the future life. Now I can proudly say that I have become a quite different person who is mature, independent, and ready for the challenges in the future career. I hope my parents are satisfied with my performance now.

Secondly, I need to thank Dr. Zhai who offered me the chance to become a PHD. From strangers to now, we have experienced a lot. When I saw Acacia in the office, I realized that I have been here for so many years because she was even not born when I first came to UCF. Thank you for the guidance on analyzing problems, communication with people, and fully utilizing resources. Let’s see how these trainings can affect my future professional career.

Thirdly, I have to be grateful to my lab-mates for both the help on experiments and troubles made in the lab, although I guess the second part should much more than the first part. Let me list their names here. Binh, Astha, Jean, Matt are group members joined the group before me. Joe, Xiaoyan, Liz, David, Nilab, Zeyang are group members joined the group after me. Anyway, those troubles forced me to be a master in all experiments that can be performed in the lab and MCF. Besides, I had to manage the lab by myself to keep it in good conditions, and it made me to be able to remember the location of almost every tool in the lab.
Then, I need to appreciate all professors and staffs in NSTC, MCF, MSE and the graduate school for giving guidance and convenience to my life in the graduate school. I especially appreciate Kirk, Matt, and Karen in MCF because I met them every week while doing characterizations, and they answered my questions so nicely.

Also, I need to be thankful to my friends in United States and those friends I got when I was in China. Moving furniture together, arranging dinners together, chatting irrelevant issues together, the life at abroad is not that lonely with friends. On the other hand, for those friends who are not in the US, it is so fortunate that some of us are still chatting online. Gratitude from the bottom of my heart for a few sentences you said when I was experiencing several months of miserable life during my PHD career. What can I say now? You are friends for life. We stayed quite calm at our reunions when I came back to China, but we found that we can still talk in the way when we were in middle schools after the first eye contact. For their privacy, I am not going to reveal their names here.

Last but not the least, I need to say thanks to a person who even does not know me, Kobe Bryant. I became a Kobe fan since I first saw he played basketball in 2001 NBA finals. After watching about 200 matches he played, Kobe is like an old friend to me, and some of his personalities infiltrated into my soul. When I was facing tricky experiments that I could not operate well, I asked myself what Kobe would do after those failures. The answer was always “one more time”. As a rookie picked at the 13th place, a skinny boy who could not shoot well, and a player with small hands which could not grab the basketball, how many audiences can imagine him to be the point guard only worse than Michael Jordan, the 3rd all-time leading scorer, and a slam dunk champion. I guess the answer is hard working as he knew “how Los Angles looks like at 4 am everyday”.

vi
However, Kobe’s success is not only because of hard working. Here, I need to share one Kobe movement that inspired me during my PHD career, and I believe it will influence my whole life. It was April 11th, 2013, Kobe made a couple of free throws when his tender of the left ankle was broken, but no pain could be read from his face when he was making those two shots. For his loving team swaying in the midst of a raging storm, he played so many games with minimal rest only for wins and suddenly fell down. He devoted all his energy on the court because he promised Dr. Buss, who left the world in that season, and himself to bring Lakers to the playoffs. Thank you, Black Mamba.
# TABLE OF CONTENTS

LIST OF FIGURES ..................................................................................................................... xiii

LIST OF TABLES ..................................................................................................................... xxiii

LIST OF ABBREVIATIONS ..................................................................................................... xxiv

CHAPTER 1: BACKGROUND ..................................................................................................... 1

- Graphene ............................................................................................................................... 1
- Graphene Oxide ...................................................................................................................... 2
- Reduced Graphene Oxide ....................................................................................................... 3
- Edge Functionalized Graphene Oxide ................................................................................... 4
- Graphene Aerogel/metal Nanoparticles Composites ................................................................. 4
- Graphene/PDC Composites .................................................................................................... 5
- Graphene Induced P3HT Crystallizations ............................................................................ 7

Techniques ............................................................................................................................... 9

- Chemical Vapor Deposition ................................................................................................. 9
- Schlenk Lines ....................................................................................................................... 9
- Ball Milling .......................................................................................................................... 10

Characterizations ................................................................................................................... 10

- Scanning Electron Microscopy ........................................................................................... 10
- Energy-Dispersive X-Ray Spectroscopy ............................................................................. 11
- Transmission Electron Microscopy ..................................................................................... 11
- Selected Area Electron Diffraction ..................................................................................... 12
CHAPTER 3: ANISOTROPIC ELECTRICAL CONDUCTIVITY IN POLYMER DERIVED CERAMICS INDUCED GRAPHENE AEROGELS

Introduction
Experimental Procedures
Characterizations
Results and Discussion
Conclusions
Supporting Materials
References

CHAPTER 4: BULK POLYMER DERIVED CERAMIC COMPOSITES WITH EDGE FUNCTIONALIZEDGRAPHENE

Introduction
Experimental Procedures
Characterizations
Results and Discussion
Conclusions
Supporting Materials
References

CHAPTER 5: CRYSTALLIZATION OF P3HT ON GRAPHIITC SUBSTRATES WITH DIFFERENT CURVATURES

Supporting Materials
References
<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Introduction</td>
<td>158</td>
</tr>
<tr>
<td>Materials</td>
<td>160</td>
</tr>
<tr>
<td>Experimental Procedures</td>
<td>161</td>
</tr>
<tr>
<td>Characterizations</td>
<td>163</td>
</tr>
<tr>
<td>Results and Discussion</td>
<td>164</td>
</tr>
<tr>
<td>Crystallization of LM-P3HT on Graphitic Substrates</td>
<td>164</td>
</tr>
<tr>
<td>Crystallization of SM-P3HT on Graphitic Substrates by Using High Concentration Marginal Solutions</td>
<td>166</td>
</tr>
<tr>
<td>Crystallization of SM-P3HT on Graphitic Substrates by Using Low Concentration Marginal Solutions</td>
<td>177</td>
</tr>
<tr>
<td>Kinetic Study of LM-P3HT on Curved Graphitic Substrates</td>
<td>179</td>
</tr>
<tr>
<td>Kinetic Study of SM-P3HT on Curved Graphitic Substrates</td>
<td>184</td>
</tr>
<tr>
<td>Kinetic Study of LM-P3HT and SM-P3HT on Flat Graphene Substrates</td>
<td>187</td>
</tr>
<tr>
<td>Conclusions</td>
<td>188</td>
</tr>
<tr>
<td>Supporting Materials</td>
<td>190</td>
</tr>
<tr>
<td>References</td>
<td>199</td>
</tr>
<tr>
<td>CHAPTER 6: CONCLUSIONS AND FUTURE WORK</td>
<td>212</td>
</tr>
<tr>
<td>Conclusions</td>
<td>212</td>
</tr>
<tr>
<td>Future Work</td>
<td>215</td>
</tr>
<tr>
<td>References</td>
<td>216</td>
</tr>
<tr>
<td>APPENDIX A: LIST OF PUBLICATIONS</td>
<td>218</td>
</tr>
<tr>
<td>APPENDIX B: PERMISSIONS FOR COPYRIGHTED MATERIALS</td>
<td>220</td>
</tr>
</tbody>
</table>
Permission Request Policies from Multidisciplinary Digital Publishing Institute (MDPI)....... 221

Permission Request Policies from Royal Society of Chemistry ............................................. 223
LIST OF FIGURES

Figure 2-1. Schematic illustration of the formation of metal nanoparticles decorated rGO aerogels................................................................................................................................................................. 44

Figure 2-2. (a) SEM image of the cross-sectional area, (b) SEM image of the longitudinal section................................................................................................................................... 47

Figure 2-3. SEM images of the (a,e) Pd, (b,f) Pt, (c,g) Ni, and (d,h) Sn nanoparticles loaded aerogels formed after hydrogen reduction............................................................................ 48

Figure 2-4. SEM images of (a)Pd, (b)Pt, (c)Ni, and (d)Sn loaded rGO aerogels and the corresponding EDS spatial mapping images of loaded (e)Pd, (f)Pt, (g)Ni, and (h)Sn on rGO sheets. The scale bar is 20 µm. .............................................................................................. 49

Figure 2-5. EDS spectra of (a) palladium, (b) platinum, (c) nickel, and (d) tin loaded rGO aerogels after hydrogen reduction. ........................................................................................................................ 50

Figure 2-6. Deconvoluted XPS spectra of the loaded metal in the aerogels. Pd in Pd loaded aerogels (a) as prepared and (b) after reduction, Pt in Pt loaded aerogels (c) as prepared and (d) after reduction, Ni in Ni loaded aerogels (e) as prepared and (f) after reduction, Sn in Sn loaded aerogels (g) as prepared and (h) after reduction are shown. ............................................. 53

Figure 2-7. (a) The change of resistance of GA/Pd nanoparticle composites with different Pd loadings upon exposure to 1000 ppm hydrogen gas. (b) The change of resistance of GA/Pd nanoparticle composites upon hydrogen gas on/off cycles. ......................................................... 55

Figure 2-8. SEM images of Pd nanoparticles on GA surfaces made from (a) 30 mM and (b) 70 mM Pd ion in GO suspensions. .......................................................................................................................... 56
Figure 2-9. Deconvoluted XPS spectra of the carbon in the aerogels. C in Pd loaded aerogels (a) as prepared and (b) after reduction, C in Pt loaded aerogels (c) as prepared and (d) after reduction, C in Ni loaded aerogels (e) as prepared and (f) after reduction, C in Sn loaded aerogels (g) as prepared and (h) after reduction. ................................................................. 57

Figure 2-10. The change of current of a hydrogen sensor when exposed to 1000 ppm hydrogen gas. The responding time and recovery time are highlight in green and brown, respectively. ........................................................................................................................................... 58

Figure 3-1. Optical images of GO suspension (a), GO aerogel (b), free standing rGOAs (c), SEM images of rGOAs made from 20 mg/mL GO suspensions (d, e). .............................. 74

Figure 3-2. XPS spectra of the deconvoluted C 1s peaks of (a) GO aerogels and (b) rGOAs. ............................................................................................................................................ 74

Figure 3-3. Transversal section SEM images of SiCN/rGOA ceramic composites with (a,b) 10 mg/mL, (c,d) 20 mg/mL, (e,f) 30 mg/mL, and (g,h) 40 mg/mL rGOA. ......................... 76

Figure 3-4. Longitudinal section SEM images of SiCN/rGOA ceramic composites with (a) 10 mg/mL, (b) 20 mg/mL, (c) 30 mg/mL, and (d) 40 mg/mL rGO. .............................................. 78

Figure 3-5. Anisotropic electrical conductivity of SiCN/rGOA ceramic composites............ 79

Figure 3-6. Electrical conductivity change of SiCN/rGOA ceramic composites from room temperature to higher temperatures ................................................................. 79

Figure 3-7. Raman spectra of (a) SiCN and (b) SiCN/rGOA pyrolyzed at different temperatures. The G band in each spectrum is label by an asterisk. ................................. 82

Figure 3-8. XRD spectra of SiCN/rGOA composites pyrolyzed at different temperatures. 84

Figure 3-9. Young’s Modulus of SiCN/rGOA composites of different RGOA concentration. The inset is the picture of the cracked composite after the compression test.............. 85
Figure 3-10. SEM images of cracks formed during the compression test for SiCN/rGOA composites of (a,b) 10 mg/mL, (c,d) 20 mg/mL, (e,f) 30 mg/mL, and (g,h) 40 mg/mL rGOA.

Figure 3-11. A picture of bulk SiCN/rGOA composite.

Figure 3-12. Raman spectrum of single layer graphene transferred onto a quartz slide.

Figure 3-13. SEM images of longitudinal (A) and transversal (B) section of 30mg/mL rGO aerogel.

Figure 3-14. SEM images of SiCN ceramic surfaces at low (left) and high (right) magnification.

Figure 3-15. The SEM image of a SiCN film on graphene embedded between PDC and quartz slide.

Figure 3-16. Raman spectra of (a) PDC on graphene coated quartz slides after pyrolysis conducted at different temperatures (600 °C, 700 °C, 800 °C, 900 °C, and 1000 °C) and (b) PDC on quartz slides after pyrolysis conducted at different temperatures (600 °C, 700 °C, 800 °C, 900 °C, and 1000 °C). All G band positons are labeled by asterisks.

Figure 3-17. XRD spectra of GO.

Figure 3-18. XRD spectra of GO pyrolyzed at different temperatures.

Figure 3-19. Fitting the relationship between conductivity and temperature to the function of (a) $\sigma \propto T^{-1/2}$, (b) $\sigma \propto T^{-1/3}$, (c) $\sigma \propto T^{-1/4}$, respectively.

Figure 4-1. The schematic illustration of the preparation of EFGO network embedded PDC composites.
Figure 4-2. (a, b) TEM images of EFGO flakes. (c) The SAED pattern of EFGO flakes. Four sets of six-fold SAED pattern regarding the (1100) lattice fringe of graphitic structures are labeled in red, blue, green, and purple circles. ................................................................. 110

Figure 4-3. The AFM image of a EFGO flake on mica substrate. The scanning area is 2.5 μm×2.5 μm. The height profile beneath the AFM image reveals the height at the white sectioning line in the AFM image. ................................................................. 110

Figure 4-4. The Raman spectrum of EFGO flakes. The position of the G peak, the D peak and the 2D peak are at 1563.8 cm⁻¹, and 1343.9 cm⁻¹, and 2693.6 cm⁻¹, respectively. .............. 111

Figure 4-5. SEM images of EFGO attached PVA foams after the immersion of PVA foams in the EFGO dispersion. ........................................................................................................ 111

Figure 4-6. SEM images of PDC composites green bodies. ................................. 112

Figure 4-7. SEM images of PDC composites pyrolyzed at 1000 °C. ....................... 113

Figure 4-8. TGA curves of the PDC composite and each component in the composite. .... 114

Figure 4-9. Raman spectra of PDC composites pyrolyzed at different temperatures. .... 117

Figure 4-10. XPS spectra of PDC composites at (a) carbon region and (b) silicon region before pyrolysis (RT), at the transition state of pyrolysis (700 °C), and after pyrolysis (1000 °C). ................................................................................................................................. 118

Figure 4-11. Room temperature electrical conductivity of PDC composites pyrolyzed at different temperatures and the corresponding linear shrinkage after pyrolysis................. 122

Figure 4-12. Raman spectra of (a) pure SILRES 62C and (b) EFGO/SILRES 62C composites with 2 wt% EFGO pyrolyzed at different temperatures. ........................................................................ 123
Figure 4-13. Schematic illustration of graphitic domains evolution in (a) SILRES 62C, (b) EFGO/SILRES 62C, and (c) EFGO/SILRES 62C/PVA composites (PDC composites) during pyrolysis processes. ................................................................. 125

Figure 4-14. Electrical conductivity of PDC composites (EFGO/SILRES 62C/PVA composites) pyrolyzed at different temperatures. The testing temperature range is from 25 °C to 600 °C. ................................................................. 126

Figure 4-15. The particle size distribution of EFGO flakes from the DLS test. ................. 131

Figure 4-16. FTIR spectrum of SILRES 62C precursor before (black line) and after (red line) curing process. ................................................................. 131

Figure 4-17. 1H NMR spectrum of SILRES 62C preceramic polymer. The peak at 1.56 ppm is from water impurities. ................................................................. 132

Figure 4-18. The SEM image of bare PVA foams. ......................................................... 133

Figure 4-19. SEM images of the surface of PDC composites pyrolyzed at (a) 300 °C, (b) 400 °C, (c) 500 °C, (d) 600 °C, (e) 700 °C, (f) 800 °C, (g) 900 °C, and (h) 1000 °C. Scale bars are 50 µm. ................................................................. 133

Figure 4-20. SEM images of PDC composites pyrolyzed at (a) 300 °C, (b) 400 °C, (c) 500 °C, and (d) 600 °C without Au/Pd sputter coating. ................................................................. 134

Figure 4-21. Linear shrinkage of PDC composites after pyrolysis at different temperatures. ......................................................................................... 134

Figure 4-22. EDS spectra of PDC composites pyrolyzed at (a) 300 °C, (b) 400 °C, (c) 500 °C, (d) 600 °C, (e) 700 °C, (f) 800 °C, (g) 900 °C, and (h) 1000 °C. ................................................................. 135

Figure 4-23. The SEM image of PDC composites treated in air at 500 °C. ...................... 135
Figure 4-24. Electrical conductivity comparison of different composites with same pyrolysis conditions at the testing temperature from 25 °C to 600 °C. Composites are pyrolyzed at (a) 700 °C, (b) 800 °C, (c) 900 °C, and (d) 1000 °C, respectively. ......................................................... 136

Figure 4-25. Electrical conductivity of (a) EFGO/SILRES 62C/PVA, (b) EFGO/SILRES 62C, and (c) SILRES 62C pyrolyzed at different temperatures. The testing temperature range is from 25 °C to 600 °C. ........................................................................................................ 136

Figure 4-26. Specific heat capacity of (a) green bodies and (b) 1000 °C pyrolyzed PDC composites at different temperatures. ........................................................................................................ 137

Figure 4-27. Fabrication of ceramic composites, from starting materials to final products.142

Figure 4-28. Use a PDC composite pyrolyzed at 1000 °C to light up four white LED diodes with an output of 9 V. A propane gun is used to heat up the composite. The dimension of the composite is 5 mm×5 mm×40 mm................................................................. 143

Figure 5-1. Schematic illustrations of (a) nanowire crystals formation from extended P3HT chains, (b) nanowire crystals formation from folded P3HT chains, and (c) nanoribbon crystals formation from extended P3HT chains. .................................................................................. 160

Figure 5-2. TEM images of LM-P3HT crystallized on (a) SWCNTs, (b) MWCNTs, (c) CFs, and (d) graphene from 0.05 mg/mL marginal solutions. Scale bars are 250 nm...................... 164

Figure 5-3. Schematic illustrations of nanowires formation from LM-P3HT on graphitic substrates of (a) CNTs, (b) CFs, and (c) graphene................................................................. 165

Figure 5-4. (a) The TEM image of SM-P3HT crystallized from SWCNTs by using a 0.30 mg/mL LM-P3HT marginal solution. (b) The SAED pattern of nanowires in (a). ............. 167

Figure 5-5. The schematic illustration of a SM-P3HT nanowire grown coaxially from SWCNTs........................................................................................................ 167
Figure 5-6. (a) The TEM image of SM-P3HT crystallized on MWCNTs to form nanoribbons from a 0.30 mg/mL marginal solution. (b) The SAED pattern of nanoribbons in (a). 169

Figure 5-7. The Schematic illustration of SM-P3HT nanoribbons grown from MWCNTs with a confined orientation. 170

Figure 5-8. The AFM image of P3HT nanoribbons grown from MWCNTs. The scanning area is 2 µm × 2 µm. 170

Figure 5-9. (a) The TEM image of SM-P3HT crystallized on CFs from a 0.30 mg/mL marginal solution. (b) The SAED pattern of nanoribbons in (a). 171

Figure 5-10. (a) The SEM image of SM-P3HT crystallized on CFs, the scale bar is 1 µm. (b) The 3D image of SM-P3HT crystallized on CFs generated from AFM data (2 µm × 2 µm). 172

Figure 5-11. The schematic illustration of SM-P3HT nanoribbons grown from CFs with random radial and axial orientations. 173

Figure 5-12. The Raman spectrum of crystallized SM-P3HT on CFs surface. The optical image of crystallized SM-P3HTT on CFs is in the inset, and the red circled area is investigated by Raman spectroscopy. 174

Figure 5-13. (a) The TEM image of SM-P3HT crystallized on the surface graphene. Fell-down nanowalls are pointed out by arrows. (b) The SAED pattern of nanowalls in (a). Two sets of six-fold SAED patterns from the graphene substrate are circled in red and blue. 175

Figure 5-14. The illustration of SM-P3HT nanowalls grown vertically from graphene surface (top view) with random orientations in the plane of graphene surface. 176

Figure 5-15. The AFM image of SM-P3HT crystallized on graphene and height profiles of two lines labeled as 1 and 2. The scanning area is 1 µm × 1 µm. 176
Figure 5-16. TEM images of SM-P3HT crystallized on CFs from (a) 0.03 mg/mL, (b) 0.05 mg/mL marginal solutions. The thin film in (a) and nanoribbons in (b) are pointed by arrows.

Figure 5-17. The absorbance change at 600nm for P3HT crystallization on SWCNTs (triangle), MWCNTs (square), and CFs (diamond) graphitic surfaces.

Figure 5-18. Attached mass of LM-P3HT on unit area of SWCNTs (triangle), MWCNTs (square), and CFs (diamond) graphitic substrates. Diameters of MWCNTs and CFs are considered as 15 nm and 170 nm in calculations.

Figure 5-19. The absorbance change at 600nm for SM-P3HT crystallizations on SWCNTs (black line), MWCNTs (red line), and CFs (blue line) graphitic surfaces.

Figure 5-20. Attached mass of SM-P3HT on unit area of SWCNTs (black line), MWCNTs (red line), and CFs (blue line) graphitic substrates. Diameters of SWCNTs, MWCNTs and CFs are considered as 1.5 nm, 15 nm and 170 nm in calculations.

Figure 5-21. Attached mass of LM-P3HT (black line) and SM-P3HT (red line) on unit area of graphene surface in crystallization processes.

Figure 5-22. (a) The TEM image of dispersed SWCNTs. (b) The TEM image of dispersed MWCNTs. (c) The TEM image of CVD graphene transferred on a TEM grid. (d) The SAED pattern of graphene on TEM grids.

Figure 5-23. (a, b) TEM images of CFs. (c) The SEM image of CFs. (d) The AFM image of CFs. (e) The height profile of the line is shown in (d).

Figure 5-24. SAED patterns of LM-P3HT nanowires crystallized on (a) SWCNTs, (b) SWCNTs, (c) CFs, and (d) graphene. Two sets of six-fold SAED patterns from the graphene substrate are circled in red and blue in (d).
Figure 5-25. The AFM image of LM-P3HT crystallized on CFs and the height profiles of two lines labeled as 1-2. The scanning area of AFM imaging is 5 µm×2.5 µm. .......................... 192

Figure 5-26. UV-Vis spectra during processes of P3HT crystallization (a) SWCNTs, (b) MWCNTs, and (c) CFs. Need to label 2 peaks about loss of free P3HT and gain of crystallized P3HT.................................................................................................................................... 192

Figure 5-27. The TEM image of SM-P3HT crystallized in the dispersion contained MWCNT by rapid cooling. The concentration of MWCNTs and SM-P3HT are 0.005 mg/mL and 0.3 mg/mL, respectively................................................................. 193

Figure 5-28. The top view AFM image (2 µm×2 µm) and the height profiles of 4 lines labeled as 1-4. Line 1 reveals a tilted nanoribbon from CF. Line 2 reveals two nanoribbons parallel to the horizontal plane with the thickness of 105 nm and 10 nm. Line 3 reveals a nanoribbon with the length of 312 nm. Line 4 reveals a nanoribbon grown vertically respect to the horizontal plane with a width of 138 nm................................................................. 193

Figure 5-29. The Raman spectrum of graphene surface................................................. 194

Figure 5-30. The Raman spectrum of SM-P3HT powders.................................................. 194

Figure 5-31. The Raman spectrum of SM-P3HT crystallized on the graphene surface..... 194

Figure 5-32. TEM images of SM-P3HT crystallized on SWCNTs from (a) 0.05 mg/mL, and (b) 0.10 mg/mL marginal solutions........................................................................................................ 195

Figure 5-33. The TEM image of SM-P3HT crystallized on MWCNTs to form nanowires from a 0.05 mg/mL marginal solution. ................................................................. 195

Figure 5-34. The TEM image of SM-P3HT crystallized on graphene to form nanowalls composed on nanoribbons from a 0.05 mg/mL marginal solution................................. 195
Figure 5-35. (A) The figure of the optimized attachment of oligo(3-hexylthiophene) on SWCNT (13,0). (B) The attachment of oligo(3-hexylthiophene) on a MWCNT (310,0) at angles of 90°, 0°, and 30°. 197
LIST OF TABLES

Table 4-1. Elemental Compositions of PDC composites after pyrolysis at different temperatures. ................................................................................................................................................................................................................................. 116

Table 4-2. Summary of activation energy of different composites pyrolyzed at different temperatures............................................................................................................................................................................................................................................. 128

Table 4-3. Summary of pyrolysis processes details........................................................................................................................................................................................................................................................................... 137

Table 4-4. Normalized Mass change of ceramic composites in preparation processes........ 138

Table 4-5. Density of Pyrolyzed SiCO PDCs........................................................................................................................................................................................................................................................................... 138

Table 4-6. Density of Composites pyrolyzed at different temperatures............................ 139

Table 4-7. G peak positions of composites pyrolyzed composites........................................ 139

Table 4-8. Values of electrical conductivity increment from different pyrolyzed composites. . 140

Table 4-9. Young’s modulus of EFGO/SILRES 62C/PVA composites pyrolyzed at 1000 °C.. 140

Table 5-1. Curvature and specific surface area of different graphitic substrates. The diameter and specific surface area are from specifications given by manufacturers......................................................... 182

Table 5-2. Summary of nano-structures formation on different graphitic substrates from SM-P3HT and LM-P3HT molecules. Asterisks point out the formation of nanocrystals with a confined orientation. ........................................................................................................................................................................................................................................................................ 189

Table 5-3. The interaction energy of oligo(3-hexylthiophene) on different isomers of SWCNTs. ........................................................................................................................................................................................................................................................................ 197

Table 5-4. The interaction energy of oligo(3-hexylthiophene) on MWCNTs with different orientations respect to the axis of MWCNTs........................................................................................................... 197
# LIST OF ABBREVIATIONS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AFM</td>
<td>Atomic Force Microscopy</td>
</tr>
<tr>
<td>CF</td>
<td>Carbon Fiber</td>
</tr>
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<td>CNT</td>
<td>Carbon Nanotube</td>
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</tr>
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<td>Differential Scanning Calorimetry</td>
</tr>
<tr>
<td>DLS</td>
<td>Dynamic Light Scattering</td>
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<tr>
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<td>Energy-dispersive X-ray Spectroscopy</td>
</tr>
<tr>
<td>EFGO</td>
<td>Edge Functionalized Graphene Oxide</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier-transform Infrared Spectroscopy</td>
</tr>
<tr>
<td>GA</td>
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</tr>
<tr>
<td>GC-MS</td>
<td>Gas Chromatography-Mass Spectrometry</td>
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<tr>
<td>GIXRD</td>
<td>Grazing Incidence X-ray Diffraction</td>
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<tr>
<td>GO</td>
<td>Graphene Oxide</td>
</tr>
<tr>
<td>GPC</td>
<td>Gel Permeation Chromatography</td>
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<tr>
<td>LED</td>
<td>Light-emitting Diode</td>
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<tr>
<td>LM</td>
<td>Low Molecular weight</td>
</tr>
<tr>
<td>MWCNT</td>
<td>Multi-walled Carbon Nanotube</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear Magnetic Resonance</td>
</tr>
<tr>
<td>PDC</td>
<td>Polymer Derived Ceramic</td>
</tr>
<tr>
<td>P3HT</td>
<td>Poly (3-hexylthiophene)</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
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<tr>
<td>--------------</td>
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<tr>
<td>PVA</td>
<td>Poly (vinyl alcohol)</td>
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<tr>
<td>rGO</td>
<td>Reduced Graphene Oxide</td>
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<tr>
<td>rGOA</td>
<td>Reduced Graphene Oxide Aerogel</td>
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<td>Selected Area Electron Diffraction</td>
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<td>Small Angle X-ray Scattering</td>
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<tr>
<td>SiCN</td>
<td>Silicon Carbonitride</td>
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<td>Small Molecular Weight</td>
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<td>SiOC</td>
<td>Silicon Oxycarbide</td>
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<td>Single-walled Carbon Nanotube</td>
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<td>QCM</td>
<td>Quartz Crystal Micro-balance</td>
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<td>Ultraviolet-Visible</td>
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<td>X-ray Photoelectron Spectroscopy</td>
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<td>XRD</td>
<td>X-ray Diffraction</td>
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CHAPTER 1: BACKGROUND

Graphene

Graphene is a single layer of carbon atoms arranged in hexagonal lattices. Because of its unique structure, graphene has many unusual properties. For example, graphene has carrier mobility of about 20000 cm$^2$/V·s at 25°C, its specific surface area is more than 2500 m$^2$/g, and its Young’s modulus is 1.0 TPa. [1-7] Graphene was first got from a “scotch-tape” method. Graphite attached on silicon wafers was thinner into one-atom thick layer after many times of cleavages by using scotch tapes. Geim and Novoselov first performed the experiments to get single layer graphene, and their follow-up research on this new material led them to be the Nobel prize winners of physics in 2010. However, the “scotch-tape” method has several drawbacks such as impossible to get large area graphene, limitation of substrates (unavailable to deposit onto hollow substrate such as TEM grids), and difficult to handle without expertise. Chemical vapor deposition (CVD) method is a method which can overcome those drawbacks from the “scotch-tape” method. Gases of hydrogen and methane react at high temperature (~1000 °C) and then the deposited carbon on metal substrates such as copper and nickel to form graphene on substrates. After the etching of metal substrates, graphene can be transferred to required substrates for future experiments. Because graphene with the size of metal substrates can be prepared by using the CVD method, the synthesis of large area graphene (larger than 1 cm×1 cm) is available. In the CVD method, when the gas flow and temperature are well controlled, synthesizing graphene is similar to baking bread in an oven, which is more convenient comparing to the “scotch-tape” method. To date, graphene has been utilized in applications such as OPVs, [8-10] FETs, [11-15] GQD-LEDs, [16] batteries,
[17] sensors. [18-33] It is confident to believe that graphene will be a competitive candidate in more applications in the future.

**Graphene Oxide**

Graphene oxide (GO) is a kind of material which consists of graphene framework along with oxidized groups such as hydroxyl groups, carbonyl groups, and carboxylic acid groups. Hummer’s method is the most widely used method to prepare GO. [34-36] There are many recipes derived from Hummer’s method for GO preparation, and they are called modified Hummer’s methods. The main mechanism of these recipes is the same, which is oxidizing graphite into GO by applying strong oxidation agents. In our lab, we use concentrated sulfuric acid, potassium permanganate, and hydrogen peroxide as oxidation agents to convert graphite to graphene oxide. Due to the formation of functional groups on GO flakes, GO is dispersible in solvents such as water, tetrahydrofuran, dimethylformamide, and ethylene glycol from the affinity between functional groups and solvents. [37] The excellent dispersity of GO facilitates the solution-based processing of GO. Thus, GO can be applied in traditional processing methods such as drop casting, dip coating, and spraying. Also, GO can be converted to aerogels by extracting out the solvent in dispersions, and the process is called lyophilization. GO aqueous dispersions are first frozen, then the solvent was sublimated in a high vacuum, low temperature environment. GO Aerogels are ultra-light porous materials, and the density can be as low as 10 mg/mL. Also, the specific surface area of GO aerogels can be up to 1000 m²/g. [38,39] By controlling the direction of freezing, GO aerogels with anisotropic structures can be achieved after lyophilizations. [40] Due to their high specific surface area and porous structures, GO aerogels have outstanding efficiencies in absorbing...
substances, and they are excellent substrates for decorating active materials in applications of catalysis and sensing.

**Reduced Graphene Oxide**

GO can be reduced to form reduced graphene oxide (rGO) by thermal reductions or chemical reductions. In thermal reductions, oxidized functional groups are decomposed at high temperature (>300 °C), and the reductions are performed in inert atmosphere (N₂, Ar) to avoid oxidation of GO during heating processes. In chemical reductions, reducing agents such as hydrazine, ascorbic acid, and hydrogen are applied to chemical reduce oxidized functional groups on GO flakes. Also, it is found that combining thermal reduction and chemical reduction can more effectively reduce functional groups on GO flakes, reduction processes perform at elevated temperatures (>600 °C) in hydrogen/argon mixed atmosphere is usually used in this scenario.

rGO has better electrical conductivity at the range of 1 to 100 S/cm, [41-43] and it is much higher than that of GO which can be considered as an insulator. In rGO flakes, the abundance of functional groups is greatly diminished comparing to GO. Accordingly, the aromatic structure is partially recovered, and it can facilitate the transport of electrons through π bonds. In consequence, the electrical conductivity of rGO is dramatically higher than that of GO. Due to the good electrical conductivity of rGO, it has been widely used in electric devices. Also, researchers usually form GO composites with desired shapes then reduce them into rGO composites in these applications by taking advantages of both solution processable GO and electrical conductive rGO.
Edge Functionalized Graphene Oxide

Edge functionalized graphene oxide (EFGO) is a commercial product from Garmor Inc. EFGO flakes have unaffected aromatic graphene structures in the basal area and functional groups such as hydroxyl groups and carbonyl groups in the edge. The oxygen contents are between 5-10 wt%. Briefly speaking, EFGO is produced by applying oxidations agent of hydrogen peroxide during ball milling processes. The existence of functional groups only on edges of EFGO flakes leads to good dispersity of EFGO flakes in solvents (methanol, ethanol and acetone) and excellent electrical properties. Functional groups grant EFGO flakes with dispersity much better than that of graphite and rGO. The remaining graphitic structures in the basal area of flakes guarantees the availability of electron transport through intra-plane and inter-plane mechanisms. EFGO has been used in composites to increase the electrical conductivity and mechanical strength of composites.

Graphene Aerogel/metal Nanoparticles Composites

Graphene aerogels are cooperated with metal nanoparticles to form composites with sensing properties. Graphene aerogels (GAs) are attractive 3D graphene materials for sensing applications. [18-33] They are produced through freeze-drying of graphene oxide (GO) dispersions followed by thermal reductions. This method produces physical crosslinks between the graphene sheets that are oriented in the freezing direction, creating long, continuous open pores throughout the GAs. [33,44,45]

Graphene aerogels can be further functionalized with metal nanoparticles for sensing applications. Metallic and metal oxide nanoparticles have been deposited on the graphene surfaces using three general approaches. For the first approach, dispersed metallic nanoparticles are mixed with a GO
suspension and the aerogels are produced through the freeze-drying and reduction of the metal-GO mixture. [46] In the second approach, the aerogels are immersed in a salt solution followed by reduction. [31,33] In the third approach, the GO is mixed with a metal salt solution and then subsequently freeze-dried and reduced. [47,48] The third approach offers the most versatile and controllable method to load the metallic nanoparticles onto the GAs. However, the bridging effect of the metal cations on the negatively charged GO significantly hinders the loading capacity of metal ions onto the graphene surface. [47,49] To overcome this, chelating agents such as ethylenediaminetetraacetic acid (EDTA) and acetates can be used to screen the electrostatic interaction between the ions and GO and increase stability of dispersions. [50] In this dissertation, we demonstrate the successful fabrication of palladium, platinum, nickel, and tin decorated graphene aerogels. Also, a well-performed hydrogen gas sensor using palladium loaded GAs is assembled.

**Graphene/PDC Composites**

Graphene is cooperated with polymer derived ceramics (PDCs) to make composites with supreme properties from both graphene and PDCs. Composites with high electrical conductivity, excellent thermal-mechanical stability, and chemical inertness can be realized. Silicon-based Polymer Derived Ceramics (PDCs) have been synthesized from 1960s. [51] They keep the advantages of mechanical strength, thermal stability, and chemical inertness from traditional ceramics. [52-56] Unlike traditional ceramics obtained by sintering method, PDCs are synthesized by pyrolysis of liquid polymeric precursors in inert atmosphere thus directly convert polymers into ceramics. Liquid polymeric precursors provide the availability of various liquid-based processing techniques like casting, extrusion, spin-on coating, dip coating and spray coating. [57-61] These technologies
make PDCs capable to be processed into complex shapes such as fibers, [62,63] porous materials, [64-66] and membrane coatings, [67,68] which are difficult or even impossible to be obtain by conventional routes. Also, synthesis of ceramics at temperatures lower than those for traditional ceramics leads to energy-saving ceramics preparations. [69] These superior properties of PDCs mentioned above make them as a kind of materials widely used in applications such as MEMS, [70-72] energy storage, [61,73-75] and high temperature sensors. [76-79]

PDCs usually have low electrical conductivity $10^{-12}-10^{-7}$ S/cm, [80,81] and the fabrication of PDCs based composites is the way to increase their electrical conductivity. Adding conductive components such as CNTs, [82-85] carbon fibers, [86] carbon black, [87,88] graphite flakes, [89] reduced graphene oxide (rGO), [90,91] and metal salts like aluminum oxide and Molybdenum disilicide [92,93] into insulating PDCs matrix can effectively increase the electrical conductivity of PDCs based composites. In addition, introducing percolated networks of conductive materials into PDC composites is found to be a better method of increasing the electrical conductivity. [40,94,95] For example, additions of embedded graphene aerogels, which are conductive materials with inter-connected networks, were reported to be able to increase the electrical conductivity of composites to $1.57$ S/cm. [96] In consequence, it is believed that adding graphene materials into PDCs can also improve the electrical properties of PDC based materials.

During the investigation of the PDCs/graphene system, intriguing phenomena more than the improved electrical properties are observed.

In the anisotropic GO aerogels/PDC composites, the effect of carbon materials alignment on resulting composite properties is investigated. Graphene aerogels (GAs) prepared from directional freeze drying with anisotropic structures is used in this study. When such anisotropic structures
are embedded into a PDC matrix, the resulted composite is expected to offer anisotropic electrical conductivity since the electron transport along the graphene basal plane is much more efficient than the transport occurring through inter-plane hopping. [97-99] Bulk SiCN ceramics embedded with anisotropic reduced graphene oxide aerogels (rGOAs) were fabricated by filling anisotropic rGOAs with a preceramic polymer of SiCN ceramics, followed by crosslinking and pyrolysis. The morphology and electrical conductivity of SiCN/rGOA composites with different rGOA loadings were examined. The effect of rGOA on the transition of amorphous carbon to graphitic carbon in these composites was investigated by Raman spectroscopy and X-ray diffraction. In addition, the impact of rGOA on the mechanical properties of the composites was investigated.

In the EFGO/PDC composites, we report the introduction of conductive EFGO networks into bulk PDCs composites with a facile method different from embedding aerogels, and SiOC PDCs which can be prepared from nontoxic polymeric precursors are used. SiOC polymeric precursors are infiltrated into the highly porous EFGO attached PVA foams to form green bodies for pyrolysis. PVA foams are served as a sacrificial component and decomposes during pyrolysis, thus EFGO networks embedded SiOC PDC composites are prepared after pyrolysis. The electrical conductivity of such composites at a wide temperature (25 °C to 600 °C) is investigated. The role of percolated EFGO networks on the preparation of bulk PDC composites, graphitic domains formation in the nearby area, electrical conductivity improvement, and thermal conductivity is explored.

**Graphene Induced P3HT Crystallizations**

Conjugated polymer (CP) have numerous potential applications in solution processed organic electronics such as organic field-effect transistors (OFETs), [100-107] molecular electronics[108-
and bulk heterojunction organic photovoltaics (BHJ-OPVs). Charge transport characteristics in these devices is one of the determining factors to these organic electronic devices. The charge transport pathways in polycrystalline CP films include fast interchain and intrachain transport within crystals and slow inter-grain transport among CP crystals. A recent study of the relationship between the disorder, aggregation and charge transport of CP films suggests that the inter-grain charge transport is the rate determining step for charge transport. The key to improve the charge transport is eliminating the grain boundary. The understanding of charge transport mechanisms in CPs leads to much effort in producing CP crystals with controlled orientation and improving the active material/electrode interfacial properties.

P3HT is one of the most extensively studied CP due to its high charge mobility and tendency to assemble into crystals (i.e. nanowires and nanoribbons).

The investigation of P3HT crystallization process in solutions by changing molecular weight (Mn), crystallization temperature and polymer concentration suggested that P3HT polymer chains transit from extending to folding in nanowhiskers when the Mn is above a critical value (10 kDa), and extended P3HT chains can further grow into highly ordered two-dimensional (2D) nanoribbons by the combination of π-π interaction among polymer backbones and alkyl side chain Van der Waals interactions.

The formation of P3HT nanocrystals on substrates include carbon nanotubes and graphene has also been reported. However, the most reported P3HT superamolecular assemblies are nanowires, which are formed by π-π interactions among polymer backbones. No formation of P3HT nanoribbons on graphitic substrates is reported in any publications.
Here in, we report the formation of P3HT nanocrystals on graphitic substrates with different curvatures (i.e. SWCNTs, MWCNTs, carbon fibers, and graphene). The trend of P3HT nanocrystals formation on graphitic surfaces is studied by applying P3HT with $M_n$ below and above the folding threshold. Computational simulations of single P3HT molecule on carbon materials were used to justify the preferential orientation of P3HT nanocrystals on graphitic surfaces.

**Techniques**

The techniques used in samples preparations are briefly introduced in the following section.

*Chemical Vapor Deposition*

Chemical vapor deposition (CVD) is a chemical process used to prepare high quality solid materials with controllable thickness. In a typical CVD process, the substrate is exposed to gases or volatile precursors. Reactions or decompositions happen in the gas phase produce the desired substances on the substrate. In the meantime, by products in the gas phase are removed by gas flow through the reaction chamber.

*Schlenk Lines*

The Schlenk line is a commonly used chemistry apparatus developed by Wilhelm Schlenk. It consists of two separate gas supply lines with several ports. One gas supply line is connected to a source of inert gases such nitrogen and argon, while the other is connected to a vacuum pump. Schlenk lines are useful for safely manipulating air-sensitive reactions. The vacuum line is also often used to remove the air from reaction flasks, and the inert gas is backfilled through another
line. Also, more than one port on those two lines to make it possible for several reactions to be run simultaneously.

**Ball Milling**

Ball milling is a method used to grind and blend materials. The size reduction of materials is primary from the impact of balls drops from near the top of the shell of a ball mill machine. A ball mill machine consists of a hollow cylindrical shell, and it is partially filled with balls made of stainless steel, ceramic, or rubber, which are used as grinding media. Ball milling have several advantages over other grinding systems. 1. the cost of installation and grinding medium is low. 2. it is suitable for continuous operation. 3. It is applicable for materials in all degrees of hardness. [151-155]

**Characterizations**

All characterizations used to the investigations of samples and devices are briefly introduced in the following section.

**Scanning Electron Microscopy**

Scanning electron microscopy (SEM) produces images of a sample by scanning the surface with a focused beam of electrons. The electrons interact with atoms in the sample, producing various signals that contain information about the sample's surface morphologies. The most common SEM mode use the detection of secondary electrons emitted from the excitation of the electron beam. The number of secondary electrons that can be detected depends on specimen topography. Samples for SEM imaging have to be conductive to withstand the vacuum conditions and high energy beam
of electrons. Non-conductive specimens collect charges when scanned by the electron beam, and this causes image artifacts. Sputter coating the surface of non-conductive samples with conductive materials, such as gold, gold/palladium alloy, platinum, iridium, tungsten, is one effective method to image non-conductive specimens by SEM.

*Energy-Dispersive X-Ray Spectroscopy*

Energy-dispersive X-ray spectroscopy (EDS) is an analytical technique used for the analysis of a sample. It relies on an interaction of X-ray excitations and a sample. The characteristic X-rays emission is used to characterize atomic compositions in samples. To stimulate the emission of characteristic X-rays from a specimen, a high-energy beam of electrons is focused onto the surface of a sample. The incident electron beam can excite an electron in an inner shell, knocking out it from the shell while creating an electron hole where the electron once was. An electron from an outer, higher-energy shell then fills the hole, and the difference in energy between the higher-energy shell and the lower energy shell may be released in the form of an X-ray. The number and energy of the X-rays emitted from a specimen can be measured by detectors. As the energies of the X-rays are characteristic for each element, thus the elemental composition and the abundance of elements of the specimen can be measured.

*Transmission Electron Microscopy*

Transmission electron microscopy (TEM) is a kind of electron microscope technique which has a beam of electrons transmitted through a specimen to form an image. The specimen is most often an ultrathin section less than 200 nm thick or substances adhered on a grid. An image is formed from the interaction of the electrons with the sample. Transmission electron microscopes are
capable of imaging at a significantly high resolution (<0.1nm) owing to the small de Broglie wavelength of electrons used in the microscope. The high resolution of TEM makes it as a major analytical method in nanoscience. TEM specimens should be less than 200 nm in thickness for conventional TEM imaging.

Selected Area Electron Diffraction

Selected area electron diffraction (SAED) is a technique used to investigate the crystal structure of samples that can be performed inside a TEM. When a thin crystalline sample is subjected to a parallel beam of high energy electrons, some fractions of them will be scattered to particular angles, while others continue to pass through the sample without deflection. As a result, the image on the screen of the TEM will be a series of spots, and each spot corresponding to sample's crystal structure. During a SAED investigation, an aperture is used to block the image of the sample at the focal plane, and only diffractions of samples can be revealed.

Atomic Force Microscopy

Atomic force microscopy (AFM) is a very-high-resolution type of scanning probe microscopy with demonstrated resolution on the order of less than one nanometers. The AFM consists of a cantilever with a sharp tip at its end that is used to scan the specimen surface. The cantilever is typically silicon and silicon nitride, and the tip has a size of less than 10 nm. When the tip is brought into proximity of a sample surface, forces between the tip and the sample lead to a deflection of the cantilever, and it can be processed to get the morphological information of the sample. The AFM can be operated in a number of modes. In general, they can be classified into contact mode and tapping mode.
In the contact mode, the tip is literally dragged across the surface of the sample. The morphology of surface is measured either using the deflection of the cantilever directly or using the feedback signal required to keep the cantilever at a constant position which is commonly used in commercial AFM systems.

In the tapping mode, the cantilever is driven to oscillate up and down at or near its resonance frequency. This oscillation is commonly achieved with a small piezo element in the cantilever holder. In tapping mode, the frequency and amplitude of the driving signal are kept constant, leading to a constant amplitude of the cantilever oscillation as long as there is no drift or interaction with the surface. When the distance of the tip and the sample is closer, the amplitude of the tip will decrease, and the feedback signal loop adjust the height to make the cantilever go back to its original amplitude. As a result, a tapping AFM image with morphological information is creased during scanning.

AFM samples do not have specific preparation processes. AFM tests have to be done in a quiet environment, and the machine should be placed on a stable floating table.

*Raman Spectroscopy*

Raman spectroscopy is a spectroscopic technique used to observe vibrational, rotational, and other low-frequency modes in a system. Raman spectroscopy is commonly used in chemistry to identify chemicals by observing structural fingerprints. Also, the interactions of molecules can be revealed by the shift of Raman peaks. Raman signals rely on inelastic scattering of monochromatic laser. The laser light interacts with molecular vibrations, phonons or other excitations in the system, resulting in the energy of the laser photons being shifted up or down. The shift in energy gives
information about the vibrational modes in the system. There is no specific required sample preparation procedure for Raman spectroscopy.

**Fourier-Transform Infrared Spectroscopy**

Fourier-transform infrared spectroscopy (FTIR) is a technique used to obtain an infrared spectrum of a solid, liquid or gas. FTIR presents similar, but complementary, information comparing to Raman spectroscopy. There is no specific required sample preparation procedure for Raman spectroscopy.

**X-Ray Diffraction**

X-ray diffraction (XRD) is a technique used for determining the atomic and molecular structure of a crystal. By measuring the angles and intensities of these diffracted beams, the crystal structure of a sample can be obtained by comparing to databases. X-ray diffracts in crystals by following Bragg’s law. No specific sample preparation is needed for XRD tests, but powders used in tests need to be flattened for better results.

**X-Ray Photoelectron Spectroscopy**

X-ray photoelectron spectroscopy (XPS) is a surface-sensitive quantitative technique that measures the elemental composition of a material. XPS spectra are obtained by illuminating a material with a beam of X-ray and measuring the kinetic energy and number of electrons that escape from the top of the material simultaneously. About 10 nm of the top of materials can be analyzed. Each element produces a characteristic set of XPS peaks at characteristic binding energy values which can be used to identify the existence of elements in samples. These characteristic
spectral peaks correspond to the electron in different configuration, namely 1s, 2s, 2p, 3s, 3p, 3d, and so on. The number of detected electrons in each of the characteristic peaks is directly related to the amount of element in the sample. High vacuum of less than $10^{-8}$ mbar is required for XPS investigations, in consequence, dry samples are required for XPS investigations.

**Ultraviolet–Visible Spectroscopy**

Ultraviolet–visible spectroscopy (UV-Vis) is used to measure the absorbance of samples at the UV range of the visible range. The absorbance of light follows Beer-Lambert law in diluted solutions, or deviations may occur. Both solutions and thin films can be used in UV-Vis tests.

**Dynamic Light Scattering**

Dynamic light scattering (DLS) is a technique that can be used to determine the size distribution profile of small particles in suspensions. DLS is used to characterize size of various particles including proteins, polymers, micelles, nanoparticles, and cells. Dispersions are needed for DLS tests.

**Thermogravimetric Analysis**

Thermogravimetric analysis (TGA) is a method of thermal analysis in which the mass of a sample is measure as the temperature changes. This measurement provides information of thermal stability of samples. TGA can be used to evaluate the thermal stability of a material. The mass loss over temperature can tell when the decomposition happens and how much mass is lost at certain temperature. The atmosphere and ramping procedure need to be the same for the comparison of mass loss between different samples. Samples in powders are usually used in TGA tests.
**Differential Scanning Calorimetry**

Differential scanning calorimetry (DSC) is a thermal analytical technique in which the difference in the amount of heat required to increase the temperature of a sample and reference is measured as a function of temperature. Both the sample and reference are maintained at nearly the same temperature throughout the experiment. Generally, the temperature program for a DSC analysis is designed to be linearly increases as a function of time. The reference sample should have a well-defined heat capacity over the range of temperatures to be scanned. Differential scanning calorimetry can be used to measure a number of characteristic properties of a sample such as crystallization temperature and glass transition temperature. Also, specific heat can be calculated from the data of DSC tests. Powders are usually used in DSC tests.

**Gas Chromatography–Mass Spectrometry**

Gas chromatography–mass spectrometry (GC-MS) is an analytical method that combines gas-chromatography (GC) and mass-spectroscopy (MS) to identify different substances within a specimen. Gas chromatography utilizes a capillary column to separate molecules because of their different affinity to the column. Molecules are separated by different elution time. After that, the mass spectrometer detects the ionized fragments and their mass-to-charge ratio to identify molecules. By using these two components together, it is not possible to make an accurate identification of a particular molecule by gas chromatography or mass spectrometry alone. Combining the two processes reduces the possibility of error, as it is extremely unlikely that two different molecules will behave in the same way in both GC and MS. Diluted solutions are needed for GC-MS investigations.
Nuclear Magnetic Resonance

Nuclear magnetic resonance (NMR) is a technique usually used to identify molecules. NMR spectra usually have peaks at different chemical shift. By studying the peaks of nuclear magnetic resonance spectra, the structure of compounds can be determined. NMR a very selective technique, thus it is used to unambiguously identify known and novel compounds, and as such, is usually required by scientific journals for identity confirmation of synthesized new compounds. Solutions in deuterated solvents are needed for NMR tests.

Gel Permeation Chromatography

Gel permeation chromatography (GPC) is often used to determine the relative molecular weight of polymer samples as well as the distribution of molecular weight. GPC separates polymer molecules with different molecular weight based on the size. Separation of molecules occurs by the use of porous beads packed in a column. Smaller molecules can enter the pores more easily and therefore spend more time in these pores, thus increase their retention time. In the contrary, larger molecules spend less time in the column because there are less pores they are able to enter. Samples for GPC tests need to be diluted solutions.

Quartz Crystal Microbalance

The quartz crystal microbalance (QCM) measures a mass variation per unit area by measuring the change in frequency of a quartz crystal resonator. The resonance is disturbed by the addition or removal of a small mass. It is useful for monitoring the rate of deposition in thin film deposition systems under vacuum. In liquid, it is highly effective at determining the affinity of molecules to surfaces functionalized with recognition sites. Frequency measurements are easily leading to high
precision. It is easy to measure mass densities down to a level of below 1 μg/cm². Substances need to have interactions with QCM probes. If materials with no interaction need to be detected, QCM probes coated with substances that are interactive with materials can be used as useful probes.

*Four-probes Measurement*

Four-probes measurement is a measuring technique that uses separate pairs of current-carrying and voltage-sensing electrodes to make more accurate measurements than the simpler and more usual two-probes measurement. Separation of current and voltage electrodes eliminates the lead and contact resistance from the measurement. This is an advantage for precise measurement of low resistance values. Flat samples are required for normal four probe measurement machines because all four probes are integrated onto one flat chip. For the characterization itself, no specific sample requirement is required.

*Thermal Conductivity Measurements*

The laser flash method is used to measure thermal diffusivity of a variety of different materials. An energy pulse heats one side of a plane-parallel sample and the resulting time dependent temperature increment on another side due to the energy input is detected. The higher the thermal diffusivity of the sample, the faster the energy reaches the backside, and the higher increment of the temperature. Perfect conditions for the laser flash method are homogenous material, a homogenous energy input on the front side, and a short pulse. After the measurement of thermal diffusivity, the thermal conductivity of samples can be calculated by using the equation of $k = \alpha \cdot \frac{C_p \cdot \rho}{\rho}$, where $\alpha$ is the thermal diffusivity, $C_p$ is the specific heat capacity, and $\rho$ is the density. [156]
Disks coated with Pt and graphite aerosol are required for the measurement of thermal diffusivity when using the laser flash method.

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CHAPTER 2: FABRICATION OF GRAPHENE AEROGELS WITH HEAVILY LOADED METALLIC NANOPARTICLES


Introduction

Nature has produced remarkable materials possessing unique characteristics and behaviors that inspire scientists to replicate their structures synthetically. [1] Unlike synthetic materials, many natural biomaterials possess a hierarchical structure on many different size scales that have a complex interaction between each scale, leading to very unique behaviors. For example, the biomolecules in pollens self-assemble to form a connective, highly porous network that enables efficient mass transport. [2] Additionally, nanostructures on pollens possess a very large internal surface area, endowing many possible sites for surface reactions to occur. [3] In pollen grains, these two features enable a sensitive response of the pollen-stigma recognition and fertilization and the defense mechanism. [4-5] As such, the hierarchical porous network platform demonstrated in the pollen grain provides the possibility to manufacture a highly sensitive and efficient gas sensor. These possibilities have led to many researchers trying to fabricate biomimetic-sensing systems to advance today’s gas sensing technologies. [2-3, 6-10] For example, tin(IV) oxide (SnO₂) porous particles with large surface area have been produced using pollens as templates. [3] In this work, we demonstrate a strategy to achieve a similar hierarchical porous network for hydrogen sensing capabilities through the loading of metallic nanoparticles onto a graphene aerogel motif.
Graphene is a planar monolayer of carbon atoms arranged in a honeycomb lattice and has demonstrated very intriguing electrical properties, high strength, and a large in-plane electrical conductivity. Additionally, they have a very large surface-to-weight ratio, making them highly suitable sensor applications. For example, various metal nanoparticles have been attached on graphene to detect chemicals such as hydrogen peroxide [11-13] and hydrogen. [14] The hierarchical porous structure demonstrated in the pollen grains can be achieved in graphene through the creation of a graphene aerogel (GA) decorated with nanostructures [15] where aerogels provide a network for charge transport and nanostructures grant large surface area to interact with hydrogen gas. Graphene aerogels (GAs) are promising materials for gas sensing and energy storage applications. [16-31] Historically, GA is produced through freeze-drying a graphene oxide (GO) hydrogel, where the graphene oxide is synthesized via a modified Hummer’s method. The freeze-dried GO aerogel is then reduced to produce a reduced graphene oxide (rGO) aerogel. This method produces physical crosslinks between the graphene sheets that are oriented in the freezing direction, creating long, continuous open pores throughout the GA. [31-33] For use in gas sensing applications, GA is often functionalized with metallic nanoparticles like palladium, platinum, nickel, tin, and so on. [34]

Loading metallic nanoparticles onto a graphene surface requires mixing GO dispersion with a metal salt solution. The mixture was freeze-dried and then reduced to produce graphene/metallic nanoparticles composites. [35-36] However, the loading capacity of metallic nanoparticles on graphene sheets is limited by the bridging effect between GO and metal cations, and this effect diminishes the gas-sensing performance of the materials. [35, 37] To overcome this limitation, chelating agents such as ethylenediaminetetraacetic acid (EDTA) can be used to screen the
electrostatic interaction between metal cations and GO, thus increase the density of metallic nanoparticles exposed on the surface of GO sheets. [38]

Herein, we report an effective approach for loading a large number of metallic nanoparticles onto the surface of graphene aerogels using EDTA. These functionalized GO aerogels were fabricated by creating a metal salt solution containing EDTA prior to the introduction of the aqueous GO dispersion. The resulting GO aerogels loaded with metal ions were reduced to obtain the rGO (i.e. graphene) aerogels with nanoparticle. In this work, we demonstrate the successful preparation of palladium, platinum, nickel, and tin nanoparticle decorated graphene aerogels and the fabrication of a hydrogen gas sensor using palladium nanoparticles loaded graphene aerogels.

**Materials and Methods**

Sulfuric acid, potassium permanganate, hydrogen peroxide and 0.5 M ethylenediaminetetraacetic acid (EDTA) solution were purchased from Fisher Scientific. Tin chloride pentahydrate (SnCl₄·5H₂O), nickel chloride hexahydrate (NiCl₂·6H₂O), palladium chloride (PdCl₂) and chloroplatinic acid (H₂PtCl₆) were purchased from Alfa Aesar. Graphite powders (microfyne grade) were purchased from Dixon Inc. All chemicals were used as received without further purification.

Labconco freeze drying chamber (FreeZone 1) was used for the lyophilization of the graphene oxide hydrogels. The Labcono lyophilizer was operated at a temperature of -52 °C under a pressure of 0.02 mbar. VWR vacuum oven was used for the vacuum drying of GO powders. BRANSON digital horn-sonifier was used to disperse GO in water. Thermo Scientific tube furnace (Lindberg Blue M) was used for the hydrogen reduction of the freeze-dried graphene oxide aerogels.
Graphene Oxide (GO) was prepared by modified Hummers method using graphite powder. Typically, 1 gram of graphite powder was added to a 500 mL beaker that was immersed in an ice bath, followed by a slow addition of 50 mL concentrated sulfuric acid and 6 grams of potassium permanganate while stirring. The mixture was stirred for an additional hour at 30°C. 80 mL of deionized water (DI water) was added dropwise to the homogeneous mixture. After the addition of DI water, the beaker was then heated to 60 °C and maintained for 1 hour. 6 mL of 30% H_2O_2 was then added into the beaker. The heat was turned off after 5 minutes. After the mixture was cooled to room temperature, the crude products were washed with DI water followed by centrifugation to obtain the product. The washing was finished when the supernatant had a pH above 5. The wet GO was then dried in a vacuum oven at room temperature to avoid thermal reduction during the drying process. [39,40]

In a typical preparation, 1 mmol of a metal salt (i.e. Pd, Pt, Ni, or Sn salts) was added to a 10 mL 0.1 M EDTA solution. Thus, the molar ratio between the metal salt and EDTA was 1:1. Most solutions were prepared at room temperature. However, the PdCl_2/EDTA solution was heated at 90 °C for 15 minutes to fully dissolve the metal salt, and the solution was cooled to room temperature prior to the next step. An aqueous GO dispersion was prepared by using a horn-sonifier. A mixture of 200 mg of GO and 10 mL of DI water was sonicated for 30 minutes to form an aqueous GO dispersion. As shown in Figure 2-1a, the completely dissolved metal salt/EDTA solutions were mixed with 20 mg/mL GO dispersion with a volume ratio of 1:1 to form a metal salt/GO dispersion. The dispersion was then transferred to several 2 mL plastic cuvettes after vigorous mixing was applied. Dispersions in cuvettes were frozen by using dry ice for the following
lyophilization. After an overnight lyophilization, bulk metal salt loaded GO aerogels were formed as shown in Figure 2-1b.

The metal salt loaded GO aerogels shown in Figure 2-1b went through vapor phase reduction, and an atmosphere of hydrazine vapor mixed in nitrogen was used during this reaction. The reduction was conducted at 90 °C for one hour. Epoxide functional groups on the basal plane of GO were removed by hydrazine vapor to avoid potential structure destructions of aerogels in the next hydrogen reduction step. [39,41] Once the aerogels were cooled down from hydrazine reduction, they were further reduced by pure hydrogen gas in a pure hydrogen atmosphere at 400 °C for one hour and at 900 °C for 10 minutes. The hydrogen flow rate was kept at 30 SCCM. Such two steps reduction produced rGO aerogels decorated with metal nanoparticles as shown in Figure 2-1c, and the color of aerogels was converted from brown to black during the reduction process. To form tin decorated rGO aerogels, hydrogen reduction only needs to be conducted at 400 °C for one hour as tin nanoparticles would flow away if higher temperatures were applied.

Figure 2-1. Schematic illustration of the formation of metal nanoparticles decorated rGO aerogels.
Characterizations

The morphologies of the aerogels were characterized by using a scanning electron microscope operating at 10 keV (SEM, ZEISS ULTRA 55) and was coupled with Energy-Dispersive X-ray spectroscopy (EDS) to investigate the surface chemistry of the aerogels. The chemical states of elements were analyzed by X-ray photoelectron spectroscopy (XPS, PHI 5400).

In order to determine the influence of processing and experimental conditions of the aerogels on hydrogen sensing, rGO aerogels attached to electrical leads was inserted into a homemade flow chamber. The flow chamber was placed in a water bath with stable temperature, and a thermocouple was added to the interior of the flow chamber to diminish the affect from the exterior temperature. Conductometric response (i.e. resistance change of rGO aerogels) to hydrogen gas was carried out by monitoring the current through each aerogel under the condition of a steady flow of argon gas with periodic inclusion of 1000 ppm hydrogen gas into the stream. The relative change in resistivity \([\frac{(R_g-R_0)}{R} \%]\) was calculated from the current and the voltage applied. These values were plotted as a function of time after baseline correction.

Results and Discussion

The material fabrication started with a solution containing equal moles of a metal salt and a ligand, specifically EDTA, in this study. EDTA was crucial in order to successfully form GO aerogels during lyophilization. If a strong ligand like EDTA was not used, the strong electrostatic interactions between positively charged metal ions and the negatively charged functional groups on the edge of GO, usually the carboxylic acid groups caused the gelation of GO. [42] Such GO hydrogel would shrink significantly during the lyophilization. As a result, GO aerogels with porous
microstructures were not formed, leading to the loss of the advantages of the aerogels originated from this unique microstructure. On the other hand, if metal salts are mixed with EDTA before being added to the GO suspension, the formation of metal-EDTA complexes eliminated the electrostatic interactions between metal ions and GO. [43-45] Therefore, van der Waals interactions between the GO sheets became the major interactions in the mixtures, which is the same as when only GO was dispersed in water. As a result, nearly no shrinkage was observed after the lyophilization, and aerogels containing metal salts were successfully formed. After successfully creating the aerogels containing metal salts, the GO flakes and metal ions in the aerogels were converted to rGO sheets and metal nanoparticles during the high temperature hydrogen reduction.

The microstructure of a typical rGO aerogel decorated with metal nanoparticles was examined by SEM as shown in Figure 2-2. The stacking of the rGO sheets can be clearly seen from the cross-sectional image in Figure 2-2a. This structure indicates that the van der Waals interactions among the rGO sheets remained even after the hydrogen reduction process. Also, it is shown that the pore sizes in the aerogels are in the sub-millimeter range. The interconnected porous graphene framework with a significant directionality in the longitudinal direction was realized (Figure 2-2b). The well-defined 3D microstructure is due to the directional freezing resulted from placing dry ice beneath the cuvettes filled with metal salt/GO dispersions.
The loading of the metal nanoparticles was verified by the SEM under higher magnifications as shown in Figure 2-3. The morphologies of the aerogels loaded with palladium, platinum, nickel, and tin nanoparticles are shown in Figure (2-3a, 2-3e), Figure (2-3b, 2-3f), Figure (2-3c, 2-3g), and Figure (2-3d, 2-3h), respectively. The presence of ripples and wrinkles on the sheets verified the existence of rGO sheets. These features are typical in rGO sheets and are mainly resulted from the stress produced at elevated temperatures during hydrogen reduction process. After hydrogen reduction, metal ions chelated with EDTA on the rGO sheets were reduced into their metallic state. Thus, the nanoparticles located on rGO sheets can be seen on SEM images. The sizes of palladium, platinum, and nickel metal nanoparticles are comparable, which ranged from 10 to 120 nm in diameter. The tin nanoparticles loaded on rGO sheets have larger sizes when compared with other three metal nanoparticles. Particles as large as 400 nm in diameter were observed. However, small tin nanoparticles with diameters around 50 nm can still be observed.
To verify the distribution of metal nanoparticles on rGO sheets, the metal loaded aerogels were characterized by using EDS elemental mapping. The SEM images of metal loaded aerogels and the mapping of the loaded metal in the same area are shown Figure 2-4. The EDS mapping results of rGO aerogels loaded with palladium, platinum, nickel, and tin are shown in Figure (2-4a, 2-4e), Figure (2-4b, 2-4f), Figure (2-4c, 2-4g), and Figure (2-4d, 2-4h), respectively. Figure 2-4 (a-d) show SEM images of the area characterized for EDS elemental mapping. Uniform elemental
distribution of metals can be clearly seen on Figure 2-4 (e-h). Among them, Figure 2-4 (e-h) present the elemental mapping of palladium, platinum, nickel and tin on their corresponding rGO sheets in aerogels, respectively. These results confirm the successful loading of metal particles onto rGO aerogels with excellent uniformity.

Figure 2-4. SEM images of (a)Pd, (b)Pt, (c)Ni, and (d)Sn loaded rGO aerogels and the corresponding EDS spatial mapping images of loaded (e)Pd, (f)Pt, (g)Ni, and (h)Sn on rGO sheets. The scale bar is 20 µm.

The amount of loaded of metal nanoparticles in rGO aerogels after hydrogen reductions was also characterized by EDS. Based on the EDS spectra in Figure 2-5, carbon and the loaded metals are the predominant components of the aerogels after hydrogen reduction, which is to be expected. Oxygen in the palladium and platinum loaded aerogels are not detectable to give a reliable composition with the oxygen; however, small peaks at 0.525 eV can be seen for these two trials. Oxygen in the nickel and tin loaded aerogels were detected in quantifiable quantities and is likely attributed to the oxides formed on the surfaces of the aerogels, which will be discussed further in the XPS studies. For the aerogels containing tin, the excess oxygen content compared with the other samples is also due to the incomplete reduction of the rGO that occurred during reduction conducted at the significantly lower temperature of 400 °C. The loading efficiency of the metal
nanoparticles was evaluated by analyzing the EDS spectra in Figure 2-5, and the mass percentage of metal nanoparticles in rGO aerogels after hydrogen reduction was calculated to be 59 %, 67 %, 39 % and 46 % for Pd, Pt, Ni, and Sn nanoparticles, respectively. Compared with existing approaches of loading metal nanoparticles to graphene (around 10 %), [46,47] our method grants much higher loading efficiencies.

Figure 2-5. EDS spectra of (a) palladium, (b) platinum, (c) nickel, and (d) tin loaded rGO aerogels after hydrogen reduction.
The chemical states of the metal nanoparticles loaded onto the aerogels, before and after hydrogen reduction, were analyzed via XPS and the data is presented in Figure 2-6. The XPS spectra of palladium, platinum, nickel, and tin in aerogels before hydrogen reduction are presented in Figure 2-6a, 2-6c, 2-6e, and 2-6g, respectively. The XPS spectra of palladium, platinum, nickel, and tin in aerogels after hydrogen reduction are presented in Figure 2-6b, 2-6d, 2-6f, and 2-6h, respectively. The deconvoluted XPS spectra in Figure 2-6a and 2-6b show 3d peaks of palladium before and after hydrogen reduction. In Figure 2-6a, the deconvoluted XPS peaks are recognized as Pd$^{2+}$ 3d$_{5/2}$ peak (338.55 eV) of palladium (II) chloride (PdCl$_2$), Pd$^{2+}$ 3d$_{3/2}$ peak (344.71 eV) of PdCl$_2$, and Pd$^{2+}$ 3d$_{5/2}$ peak (337.19 eV) of palladium (II) oxide (PdO). [48] The presence of a small portion of PdO is most likely due to the hydrolysis of PdCl$_2$. In Figure 2-6b, the major deconvoluted XPS peaks are recognized as Pd$^0$ 3d$_{5/2}$ peak (335.20 eV) and Pd$^0$ 3d$_{3/2}$ peak (340.46 eV) of metallic palladium. These two major XPS peaks observed in palladium loaded aerogels after hydrogen reduction verifies the effective formation of metallic palladium during reduction. [49] Additionally, minimal deconvoluted XPS peaks correspond to PdO are observed in Figure 2-6b, namely Pd$^{2+}$ 3d$_{5/2}$ peak (337.20 eV) and Pd$^{2+}$ 3d$_{3/2}$ peak (342.50 eV) of PdO. [50] The PdO in the aerogels after hydrogen reduction is likely from the surface oxides. The deconvoluted XPS spectra in Figure 2-6c and 2-6d show 4f peaks of platinum before and after hydrogen reduction. The deconvoluted XPS peaks in Figure 2-6c are recognized as Pt$^{4+}$ 4f$_{7/2}$ peak (74.56 eV), Pt$^{4+}$ 4f$_{5/2}$ peak (77.87 eV), Pt$^{2+}$ 4f$_{7/2}$ peak (71.99 eV), and Pt$^{2+}$ 4f$_{5/2}$ peak (75.50 eV), respectively. [51-53] The existence of peaks for Pt$^{2+}$ is likely due to the reduction of Pt$^{4+}$ during the step of mixing Pt$^{4+}$ salts with EDTA. [51] Two major deconvoluted XPS peaks in Figure 2-6d are recognized as Pt$^0$ 4f$_{7/2}$ peak (70.81 eV) and Pt$^0$ 4f$_{5/2}$ peak (74.22 eV), respectively. [52-54] This result verifies the effective reduction to form metallic platinum. Besides, minimal deconvoluted XPS peaks
correspond to platinum (II) oxide (PtO) are observed in Figure 2-6d, namely Pt\(^{2+}\) 4f\(_{7/2}\) peak (71.98 eV) and Pt\(^{2+}\) 4f\(_{5/2}\) peak (75.45 eV). Similar to the case of palladium loaded aerogels, the PtO in the aerogels after hydrogen reduction is also likely from the surface oxides. The deconvoluted XPS spectra in Figure 2-6e and 2-6f show 2p peaks of nickel before and after hydrogen reduction. In Figure 2-6e, the single major peak is recognized as Ni\(^{2+}\) 2p\(_{3/2}\) peak (860.20 eV). [55,56] In Figure 2-6f, the deconvoluted XPS peaks are recognized as Ni\(^0\) 2p\(_{3/2}\) peak (858.63 eV), Ni\(^{2+}\) 2p\(_{3/2}\) peak (860.21 eV), and Ni\(^{3+}\) 2p\(_{3/2}\) peak (861.40 eV), respectively [57]. The Ni\(^0\) 2p\(_{3/2}\) peak (858.63 eV) is the major deconvoluted XPS peak, and this result verifies the effective reduction to form metallic nickel. Besides, the existence of Ni\(^{2+}\) and Ni\(^{3+}\) after hydrogen reduction is probably attributed to the formation of nickel (II) oxide (NiO) and nickel (III) oxide (Ni\(_2\)O\(_3\)) on the surface of aerogels. [51] The deconvoluted XPS spectra in Figure 2-6g and 2-6h show 3d peaks of tin before and after hydrogen reduction. In Figure 2-6g, the deconvoluted XPS peaks are recognized as Sn\(^{4+}\) 3d\(_{5/2}\) peak (487.09 eV) and Sn\(^0\) 3d\(_{5/2}\) peak (484.95 eV), respectively. [58-61] The presence of a small amount of metallic tin is likely due to the reduction by EDTA while mixing tin salts with EDTA. In Figure 2-6h, the single major peak is recognized as Sn\(^0\) 3d\(_{5/2}\) peak (484.96 eV), [61] and this result verifies the effective reduction to form metallic tin.

Overall, the effective reduction of metal salts during a hydrogen reduction process was confirmed by the comparison of the deconvoluted XPS peaks before and after reduction. The appearance of dominant XPS peaks, which correspond to the metals at their metallic state, indicates the highly effective reduction of the metal salts in this study. Additionally, only a small amount of metal oxides exists in the aerogels loaded with palladium, platinum, and nickel after hydrogen reduction, and the residual metal oxides are probably attributed to oxides formed on surface after hydrogen
reduction. Furthermore, no XPS peaks regarding tin oxides were seen while applying curve fitting, thus the reduction to form metallic tin nanoparticles is more effective than that of other three kinds of metals.

Figure 2-6. Deconvoluted XPS spectra of the loaded metal in the aerogels. Pd in Pd loaded aerogels (a) as prepared and (b) after reduction, Pt in Pt loaded aerogels (c) as prepared and (d) after reduction, Ni in Ni loaded aerogels (e) as prepared and (f) after reduction, Sn in Sn loaded aerogels (g) as prepared and (h) after reduction are shown.

The reduction of carbon in aerogels during hydrogen reduction was also confirmed by the XPS spectra of C 1s. The XPS images of carbon in aerogels loaded with four different kinds of metals are shown in Figure 2-8. The obvious shift of XPS peaks to the lower binding area proves the reduction of GO during the reduction. For aerogels loaded with palladium, platinum, and nickel, the presence of major deconvoluted peaks at the binding energy of 284.6 eV, which is the signature peak of graphitic C-C bonds, [25,37,62,63] indicates the effective reduction of carbon in hydrogen atmosphere at the temperature of 900°C. Besides, the dramatic decrease of the relative intensity for the XPS peaks which correspond to the oxidized carbons, namely peaks of hydroxyl groups
with binding energy around 286.5 eV, peaks of carbonyl C=O double bond with binding energy of around 288 eV, and peaks from O-C=O ester functional groups with binding energy around 289 eV, [25,37,62,63] further verifies the effective reduction of carbonyl and ester groups. For tin loaded aerogels, the appearance of the deconvoluted XPS peak at the binding energy of 284.6 eV, which is the characteristic peak of graphitic carbon, proves the effective reduction of carbon in hydrogen atmosphere. Because a much lower reduction temperature of 400°C was used for tin loaded aerogels, a much smaller fraction of graphitic carbon was formed. Additionally, the decrease of the relative intensity of the ester groups verifies the reduction of this functional group in aerogels. At last, deconvoluted peaks with the binding energies of 290.1 eV to 290.8 eV, which exist in all aerogel samples as prepared and after hydrogen reduction, are the characteristic π-π shakeup transition peaks in aromatic carbon compounds. [63,64]

Pd nanoparticles have been deposited on GO surfaces for hydrogen sensing because they have high affinity to hydrogen. Such affinity causes the electron density of the metal particle to be reduced, thereby increasing the work function of the graphene-metal-gas system, leading to a change of resistance. [47,65] The sensitivity of the sensors depends on the Pd nanoparticle/GO interfacial area and the response and recovery time is affected by the gas flow efficiency. The Pd nanoparticles on GAs offers large contact area between Pd nanoparticles and graphene and efficient gas flow due to the porous structures. In our study, different amount of Pd nanoparticles were loaded onto rGO aerogels (rGOAs) by adding different amount of PdCl₂/EDTA solutions to GO suspensions. In addition, PdCl₂ without EDTA was added to GO suspensions as a control. While the concentration of PdCl₂ can be as high as 70 mM with EDTA before GO is precipitated, more than 4mM pure PdCl₂ would precipitate GO. The produced rGOA composites were put
between two electrodes and subject to hydrogen sensing test as shown in Figure 2-7a inset. The resistance change of each rGOA/Pd nanoparticle composite upon the exposure to 1000 ppm hydrogen gas is shown in Figure 2-7a. First, heavy loading of Pd nanoparticles on rGOA using EDTA have much higher response to hydrogen gas than small loading of Pd nanoparticles using pure PdCl₂, suggesting that increased Pd nanoparticles on rGOA can increase sensitivity. Second, the sensor response increases with Pd nanoparticle loading, reach a peak at 30 mM Pd precursor concentration, and then decreases. With increasing Pd loading, the amount of nanoparticles increases, the resulted increased Pd nanoparticle surface area leads to a increase in sensitivity. However, the Pd nanoparticle size will increase with further increased Pd loading (Figure 2-9), which causes the reduction of Pd nanoparticle surface area. Figure 2-7 shows the change of resistance of rGOA/Pd nanoparticle composites versus time over four on-off cycles of 1000 ppm hydrogen gas. It clearly shows a fast response of hydrogen gas (25 seconds) and recovery (175 seconds) (Figure 2-10) that are attributed to porous structures of rGOAs.

Figure 2-7. (a) The change of resistance of GA/Pd nanoparticle composites with different Pd loadings upon exposure to 1000 ppm hydrogen gas. (b) The change of resistance of GA/Pd nanoparticle composites upon hydrogen gas on/off cycles.
Conclusions

In this paper, rGO aerogels loaded with four kinds of metallic nanoparticles were successfully prepared with excellent directionality and decent hieratical structures. The loading of 59 wt%, 67 wt%, 39 wt% and 46 wt% of metallic palladium, platinum, nickel, and tin in rGO/metal aerogels were achieved after hydrogen reduction at elevated temperatures. It is believed that other kind of metallic nanoparticles can also be loaded onto rGO aerogels with similar procedures. A hydrogel gas sensor was produced using Pd nanoparticle loaded rGO aerogels. The large surface area and porous structure of rGO aerogel offer high sensitivity and fast response/recovery time of the sensor. The metal nanoparticles decorated aerogels which have open-pores structure and large surface area are promising platforms for numerous applications, including energy storage, gas sensing and catalysts of vapor phase reactions.

Supporting Materials

Figure 2-8. SEM images of Pd nanoparticles on GA surfaces made from (a) 30 mM and (b) 70 mM Pd ion in GO suspensions.
Figure 2-9. Deconvoluted XPS spectra of the carbon in the aerogels. C in Pd loaded aerogels (a) as prepared and (b) after reduction, C in Pt loaded aerogels (c) as prepared and (d) after reduction, C in Ni loaded aerogels (e) as prepared and (f) after reduction, C in Sn loaded aerogels (g) as prepared and (h) after reduction.
Figure 2-10. The change of current of a hydrogen sensor when exposed to 1000 ppm hydrogen gas. The responding time and recovery time are highlight in green and brown, respectively.

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CHAPTER 3: ANISOTROPIC ELECTRICAL CONDUCTIVITY IN POLYMER DERIVED CERAMICS INDUCED GRAPHENE AEROGELS


Introduction

Polymer derived ceramics (PDCs), a class of silicon-based ceramics synthesized by the thermal decomposition of polymeric precursors, have various attractive properties such as excellent high-temperature thermo-mechanical properties, high piezoresistivity and chemical stability attributed to their unique nanostructures. [1-8] For example, SiCN ceramics produced from various preceramic polymers possess a unique nanostructure where Si3N4 domains of few nanometers are surrounded by carbon nanostructures, [8-10] This nanostructure grants SiCN interesting electrical properties as a semiconductor. [1,3,5,11,12] SiCN has a nitrogen content band gap ranging from 2.2 to 5.0 eV with charge carrier density of about 6.7x10^{17} /cm^{3} and a charge mobility around 0.6 cm^{2}/V∙s. SiCN ceramics also have an electrical conductivity around 10^{-7} S/m which can be further improved by increasing carbon content. [3] Additionally, the polymer-to-ceramic process enables the integration of various functional materials into the ceramics and promotes the fabrication of complex shaped composites and devices due to the hybrid processing/shaping technologies that are available to preceramic polymer. [13] These aforementioned properties have made PDCs a promising material for applications in energy storage, [14] electromagnetic energy absorption, [15,16] and high temperature sensors. [17,18]
On the other hand, the polymer-to-ceramic transformation involves the decomposition of organic molecules, the release of gases, and is usually accompanied with a shrinkage and possible breakage of the sample. [19] To mitigate the possible breakage, two types of fillers (i.e. inert or active filler) can be added to the preceramic polymers in order to reduce the amount of gas released. Inert fillers reduce the amount of gas released by diluting the polymers. [20-22] On the other hand, an active filler will react with the gases generated during the pyrolysis, thus reducing the amount of gases need to be released. [23] Nanoscale carbon materials such as carbon nanotubes (CNTs) are common inert fillers that are often used to improve the electrical and mechanical properties of PDCs, as well as their processability. [3,24,25] For example, multiwall carbon nanotubes (MWCNTs) have been added to oligosilazanes to produce SiCN/MWCNT electro-spun fibres, where the electrical conductivity is increased by 500 times with the addition of only 2 wt% MWCNTs. [3] Xu and co-workers have produced flexible SiCN/MWCNT composites with aligned carbon nanotube sheets through the infiltration and pyrolysis of liquid preceramic polymers. [26] Graphene is another intriguing inert filler, especially for energy storage applications [14,27] owing to its unique electrical properties (carrier mobility of about 20000 cm²/V·s at 25°C), large specific surface area (more than 2500 m²/g) and high mechanical strength (Young’s modulus of E = 1.0 TPa). [28-34]

To date, efforts to produce PDC composites have focused primarily on composites in the forms of fibers and thin films, and have yet to investigate the effect of carbon materials alignment on resulting composite properties. Given the anisotropic charge transport requirements of electronic materials, it is desirable to introduce anisotropic properties into bulk PDC composites. Embedding anisotropic graphene networks into polymer matrice becomes a common method for introducing
anisotropic properties into a composite. Graphene aerogels (GAs) prepared from directional freeze drying have anisotropic structures. [35,36] When such anisotropic structures are embedded into a PDC matrix, the resulted composite is expected to offer anisotropic electrical conductivity since the electron transport along the graphene basal plane is much more efficient than the transport occurring through inter-plane hopping. [37-39] Utilizing the unique open pore structure of GA along with the electrical and mechanical properties of graphene, GA has been used extensively in energy storage and polymer composite applications. [40-50] The question now becomes whether or not anisotropic GAs can introduce anisotropic electrical properties when embedded in PDCs and increase the electrical conductivity while simultaneously enabling the fabrication of crack-free bulk ceramic samples.

In the present study, bulk SiCN ceramics embedded with anisotropic reduced graphene oxide aerogels (rGOAs) were fabricated by filling anisotropic rGOAs with a preceramic polymer of SiCN ceramics, followed by crosslinking and pyrolysis. Anisotropic rGOAs in an amorphous SiCN matrix are expected to have multiple functions including: (1) a reinforcing frame to produce a bulk ceramic composite, (2) a conductive network to improve the charge transport efficiency, and (3) a filler to impart different electrical conductivity values in the highly aligned graphene sheets endowing different electrical conductivity in the longitudinal and transversal directions. The morphology and electrical conductivity of SiCN/rGOA composites with different rGOA loadings were examined. The effect of rGOA on the transition of amorphous carbon to graphitic carbon in these composites was investigated by Raman spectroscopy and X-ray diffraction. In addition, the impact of rGOA on the mechanical properties of the composites was investigated.
Experimental Procedures

Ceraset™ VL 20 (purchased from Kion Corporation, Charlotte, NC) was used as the preceramic polymer to prepare polymer derived SiCN based ceramics. Potassium permanganate, sulfuric acid (12M), hydrogen peroxide (30%), Azobisisobutyronitrile (AIBN), Iron Nitrate, and copper foil were purchased from Fisher and used as received. Poly (methyl methacrylate) (PMMA) with $M_n=35000$ was purchased from TCI and used as received. Quartz slides purchased from SPI were cleaned by subsequent sonications in methanol, acetone, and isopropanol before use. Hydrogen, methane, and argon were purchased from Air Liquide and used without further purifications.

Preparation of graphene oxide. GO was prepared by modified Hummers method starting from graphite powder. Briefly, graphite was oxidized by concentrated sulfuric acid and potassium permanganate. Deionized (DI) water was slowly added followed by 30% hydrogen peroxide. Graphene oxide was purified by washing with de-ionized water and subsequent centrifugation for several times until pH above 5 was obtained. Highly oxidized GO sheets are more stable than less oxidized GO when suspended in water.

Fabrication of Graphene Aerogels. Aqueous suspensions of graphene oxide (GO) at different concentrations of GO (10-40 mg/mL) were put into 1 cm x 1 cm plastic cuvettes. Each solution was then placed onto a block of dry ice until fully frozen (~20 minutes) before being lyophilized. Lyophilization was performed using a Labcono freeze drying chamber at 20 µbar with the collector temperature set at -52 °C. Subsequently, GO aerogels were reduced by hydrazine vapor at 90 °C for 1 hour. These partially reduced aerogels were further reduced by pyrolysis in an Argon atmosphere at 1000 °C for 2 hours to obtain reduced graphene oxide aerogels (rGOAs) which were used as the graphene aerogels (GA) in this study.
**Fabrication of SiCN/rGOA composites.** The pre-ceramic polymer, oligosilazane, was mixed with 0.25 wt% of AIBN and placed under vacuum for 2 hours. The degassed oligosilazane/AIBN solution was used to backfill the rGOAs with the aid of vacuum. Then, the backfilled rGOAs were heated to 60 °C for 48 hours in a nitrogen atmosphere to crosslink the preceramic polymer. The crosslinked oligosilazane/aerogel composites were pyrolyzed in a tube furnace under Argon. The ramping rate was 1°C/min in heat steps, and the temperature was halted at 400 °C, 600 °C and 1000 °C for 1 hour, 2 hours, and 2 hours, respectively. The slow ramping rate and the halting of temperature at 400 °C and 600 °C were used to ensure the release of gases. The picture of a bulk SiCN/rGOA composite is shown in Figure 3-11. The density of SiCN/rGOA composites was calculated to be 2.05 g/cm³. The filling of oligosilazane under vacuum and slow pyrolysis temperature increase ramp granted the production of high density composites. In addition, four composite samples of 40 mg/mL rGOA filled with oligosilazane were pyrolyzed at 600 °C, 700 °C, 800 °C, 900 °C, and 1000 °C along with crosslinked oligosilazanes. The samples were compared to evaluate the impact of rGO on the formation of crystalline carbon domains at different temperatures.

**Preparation and transfer of single layer graphene.** Graphene flakes were synthesized by using a chemical vapor deposition (CVD) method. At first, a quartz boat containing several copper foils (1 cm×1 cm) was placed into a quartz tube and mounted in a furnace. The quartz tube was then vacuumed by an oil pump until required vacuum level was reached. The pressure inside the quartz tube was less than 50 mTorr to meet the vacuum requirement. After that, hydrogen at a flow rate of 30 SCCM was introduced into the quartz tube. The furnace was then heated to 400 °C with a ramping rate of 10 °C/min, and it was halted at this temperature for 1 hour to eliminate copper
oxides residuals on copper foils. The furnace was further heated to 1000 °C and halted at the temperature for 30 minutes to anneal copper foils. After the annealing of copper foils, the furnace was kept at 1000 °C, and methane with a flow rate of 250 SCCM was introduced into the furnace. The reaction of mixed gases took 30 minutes. Then the quartz boat containing the copper foils was rapidly cooled down to room temperature by sliding the furnace away. Graphene flakes on copper foils were synthesized by the procedure mentioned above.

The as prepared graphene flakes on copper foils were transferred to quartz slides by a wet transfer process. Typically, PMMA was spin-coated onto copper foils as the protective layer of graphene. Copper foils were then etched by using iron nitrate aqueous solutions. After rinsed by deionized water several times, PMMA covered graphene flakes floating on water were transferred onto quartz slides for overnight drying. The PMMA covered graphene films on quartz slides were then annealed at 100 °C for 15 minutes in ambient atmosphere to flatten the films. At last, PMMA was washed away by using boiling acetone. Consequently, only graphene films were left on quartz slides. The Raman spectrum of graphene is shown in Figure 3-12.

**Preparation of PDC films on graphene coated quartz slides.** The preceramic polymer was spin-coated onto graphene coated quartz slides. Typically, 0.02 mL of preceramic polymer was dropped onto the center of the graphene film coated area, and spin coated immediately at 4000 rpm for 1 minute. The spin coated graphene/preceramic polymer films were cured in an oven at 160 °C for 16 hours to crosslink the preceramic polymer. After curing, the samples were pyrolyzed in argon at 600 °C, 700 °C, 800 °C, 900 °C, and 1000 °C. A ramping rate of 1 °C/min and a halting time of 2 hours at the final pyrolysis temperatures were used for all trials. As a control group, the
preceramic polymer was coated on a clean, non-graphene coated quartz slide and was crosslinked and pyrolyzed in following the same step as for the above graphene/preceramic polymer films.

Characterizations

The microstructures and surface morphologies of the ceramic/graphene bulk composites and ceramics on quartz slides were examined by Zeiss Ultra-55 field effect scanning electron microscope (SEM). Raman spectroscopy was performed using a Witec Raman spectrometer. A 532 nm laser with power of 0.175 mW was used in all Raman characterizations. The chemical compositions of aerogels were analyzed by X-ray photoelectron spectroscopy (XPS, PHI 5400). X-Ray diffraction (XRD) spectra were obtained using a PANalytical Empyrean X-ray diffractometer. The DC conductivity of SiCN/rGOA composites were obtained by measuring the current-voltage (I-V) curves (Keithley 2400, Keithley instruments Inc., Cleveland, USA) at room temperature. The surfaces of SiCN/rGOA composites were brushed with silver paste to form electrodes. The I-V curves of SiCN/rGOA composites were obtained using standard two-point measurements. The electric resistance (R) of samples was calculated by R=1/k, where k is the slope of I-V curve obtained from linear fitting. Then, the electric conductivity (σ) was calculated using the formula of σ=k·d/S, where d and S represent the length and cross-section area of samples, respectively. The specific surface area of aerogels was measured by nitrogen adsorption/desorption experiments carried out on a Quantachrome Nova 4200e analyzer. To measure the temperature-dependent conductivity of the SiCN/rGOA composite, the surfaces of the obtained SiCN/rGOA composite was cut to a 0.7 mm³ dimension. Electrodes of silver paint are applied to the composite edges perpendicular to the rGO sheet orientation in the sample. The temperature-dependent electrical conductivity of the samples was then measured in a tube furnace filled with high purity
nitrogen at temperatures range from 25 °C to 800 °C. The compression experiments were performed using a High Load Universal Testing: Instron 50kN Electromechanical Load Frame. All the compression experiments were performed at room temperature until sample breakage was detected with a crosshead speed ranging from 40 - 86 μm·min⁻¹. A constant starting height value of 10000 μm was set for every experiment, due to variation in sample height. Young’s modulus was calculated with the ratio of the stress or force applied per unit of area throughout an axis against the strain or the ratio of deformation over initial length of the sample throughout the same axis.

Results and Discussion

Figure 3-1. Optical images of GO suspension (a), GO aerogel (b), free standing rGOAs (c), SEM images of rGOAs made from 20 mg/mL GO suspensions (d, e).

Figure 3-2. XPS spectra of the deconvoluted C 1s peaks of (a) GO aerogels and (b) rGOAs.
Figure 3-1 (a-c) are the photographs of a GO suspension, a GO aerogel and an rGOA, respectively. Aerogels with different rGO densities have specific surface area in the range of 159 to 407 m²/g, which indicates the formation of highly porous structures from GO aerogels. Also, this value is less than the theoretical specific surface area for single graphene sheet (>2600 m²/g) likely due to stacking of graphene sheets within the composites. [51] The colour change from brown to black indicates the reduction of GO and restoration of the graphene network. [52] The scanning electron microscopy (SEM) images in Figure 3-1d and 1e demonstrate the alignment of GO sheets along the freezing direction. When the GO suspension was placed on a piece of dry ice, pseudo-steady-state growth of ice crystals took place and an array of micrometer-sized polygonal ice rods parallel to the freezing direction was obtained. [53-55] The ice rods acted as the templates for the directional growth of graphene sheets to produce GO aerogels with anisotropic structures (Figure 3-13). The chemical composition of the GO aerogels and rGOAs was monitored using X-ray photoelectron spectroscopy (XPS) (Figure 3-2). The deconvolution of C 1s spectra shows five peaks which correspond to the sp² C–C bonds of graphene at 284.6 eV, the alcohol, phenolic, and ether C–O bonds at 286.2 eV, the carbonyl C=O bonds at 287.2 eV; the carboxyl O=C–O bonds at 289.3 eV; and the carbonitride C–N bonds at 285.6 eV (Figure 3-2a). [56,57] The presence of C–N bonds is attributed to the hydrazine reduction process. The effective reduction of GO is confirmed by the XPS spectrum in Figure 3-2b. This spectrum indicates that the fraction of C–C signal makes up the majority of the total C 1s signal. The morphologies of the SiCN/rGOA composites with 10–40 mg/mL rGOAs were investigated using SEM. The weight percentage of rGO in the composites was estimated to be 0.5, 1, 1.5 and 2 percent, respectively, according to the mass reduction of GO upon reduction and the density of SiCN (~2.05 g/cm³). [58] Figure 3-3 and 3-4 show SEM images of the transversal section (perpendicular to rGO aligned direction) and the
longitudinal section (parallel to rGO aligned direction) of SiCN/rGOA composites, respectively. In Figure 3-3, rGO networks in the transversal section are clearly shown, and the density of rGO increases with higher loading of rGOAs. Additionally, the SEM images of pure SiCN ceramic powder (Figure 3-14) only show smooth interfaces, indicating the network features depicted in Figure 3-3 are indeed from the rGO. The longitudinal section SEM images of the SiCN/rGOA composites embedded with 10–30 mg/mL rGOAs (Figure 3-4 a–c) present decent SiCN/rGOA interfaces; however, the longitudinal section SEM image of SiCN/rGOA composite with 40 mg/mL rGOAs (Figure 3-4d) reveals the restacking of graphene sheets through the presence of multilayer rGO. The restacking of rGO is due to the inter-sheets van der Waals forces at high rGO loading. [59] Compared with wrinkle-free rGO flakes in pure rGOAs (Figure 3-1), all rGO flakes in the final ceramic composites are wrinkled due to the shrinkage of the samples (~17 %) during the pyrolysis. [60,61]

Figure 3-3. Transversal section SEM images of SiCN/rGOA ceramic composites with (a,b) 10 mg/mL, (c,d) 20 mg/mL, (e,f) 30 mg/mL, and (g,h) 40 mg/mL rGOA.
The electrical conductivities of the SiCN/rGOA composites, measured in the longitudinal and transversal directions are summarized in Figure 3-5. A small amount of rGOAs embedded in the PDC matrices can dramatically increase the electrical conductivity of the SiCN/rGOA ceramic composites. As shown in Figure 3-4, 20 mg/mL rGOAs, namely 1wt% of rGO, embedded in SiCN creates a composite with a conductivity of 157 S/m, which is more than $10^8$ higher than that of pure SiCN ceramics (4.15x10^{-7} S/m). [62] The high electrical conductivity is attributed to the embedded rGOAs which provide efficient charge transport paths in the ceramic matrices. The aligned rGO in SiCN lead to obvious anisotropic electrical properties. SiCN/rGOA ceramic composites with an rGO loading of 10, 20, 30 and 40 mg/mL have longitudinal electrical conductivities of 5 S/m, 157 S/m, 95 S/m, and 65 S/m, respectively. On the other hand, the transversal electrical conductivities of SiCN/rGOA composites are 0.8 S/m, 17 S/m, 28 S/m and 10 S/m, respectively. The longitudinal electrical conductivity of the SiCN/rGOA composite with 20 mg/mL rGOA is about 9 times higher than the transversal electrical conductivity. This huge difference confirms that the SiCN/rGOA composites have anisotropic electrical properties, and is attributed to the ease of electron transport along the graphene basal plane and the difficulty in transport between graphene sheets. The electrical conductivities in both directions share the same trend regardless of the degrees of rGO loading. Up to a critical loading value, the electrical conductivity increases with rGO loading content. Past this critical value, restacking of the graphene sheets occurs and disrupts the charge transport paths, thereby, lowering the observed electrical conductivity (Figure 3-4 c-d).
The electrical conductivity of SiCN is attributed to the main conducting phases (i.e. graphitic carbon) developed during pyrolysis. SiCN/rGOA ceramic composites have higher electrical conductivity than other polymer composites containing carbon nanotubes (CNTs) and rGO but with lower degree of electrical conductivity of matrix material. For example, Duong and co-workers have reported that a polydimthoxylsilane composite with 4.5 wt% CNT aerogel has an electrical conductivity of 33 S/m (with 16 orders of magnitude increase of electrical conductivity) [63] and a poly (methyl methacrylate) composite with 12 mg/mL rGO aerogels has an electrical conductivity of 0.9 S/m. [64] We believe that the lower degree of electrical conductivity over matrix materials is because SiCN has much higher electrical conductivity as a semiconductor than polymers as insulators. The high electrical conductivity of SiCN/rGOA ceramic composites is attributed to two facts, the alignment of rGO and the generation of graphitic (sp\(^2\)) carbon domains facilitated by embedded rGO.
Figure 3-5. Anisotropic electrical conductivity of SiCN/rGOA ceramic composites.

Figure 3-6. Electrical conductivity change of SiCN/rGOA ceramic composites from room temperature to higher temperatures.

In addition, electrical conductivity measurements of composites from 25 °C to 800 °C were performed. SiCN/rGOA ceramic composites with the highest electrical conductivity is used in this study. As shown in Figure 3-6, the electrical conductivity of the SiCN/rGOA ceramic composites increases 26.5% by increasing the testing temperature from 25 °C to 800°C. The positive temperature coefficient of the electrical conductivity indicates the SiCN/rGOA ceramic
The SiCN/rGOA composites generated in this work exhibit electrical conductivity greater than those of similar ceramic materials, and the semiconducting properties of this ceramic composite are believed to be attributed to the rGO matrix. The electrical conductivity of interconnected graphene sheets can be explained by mechanisms of hopping and tunnelling conduction. The relationship between electrical conductivity and temperature in Mott’s model can be expressed as $\sigma \propto T^{-1/n}$ in different mechanisms. In this model, the excellent linearity of curves when $n=2$, $n=3$, and $n=4$ can be used to indicate tunnelling conduction mechanism, 2D hopping mechanism, and 3D hopping mechanism for charge transport mechanism in materials. As shown in supporting materials (Figure 3-19), the curves of $\ln\sigma$ versus $T^{-1/n}$ are nearly linear when $n=2$, $n=3$, and $n=4$ as the coefficients of determination ($R^2$) are calculated to be 0.99587, 0.99742, and 0.99745, respectively. Therefore, the electron transport in the SiCN/rGOA ceramic composites follow hopping and tunnelling conduction mechanisms. Additionally, the 2D graphene sheets arranged 3D aerogels in composites could be the reason explains why both 2D and 3D hopping mechanisms are applicable to this composite. Because this kind of composites combine high thermal stability with high electrical conductivity, they have the potential to be used as conductive materials for fuel cells, high-temperature sensing, aerospace sciences, and other area where materials are required to be used in harsh environment with high electrical conductivity.

For pyrolysis temperatures at or below 1000 °C, the increase of conductivity results from the loss of residual hydrogen atoms that leads to the increase of the sp$^2$/sp$^3$ ratio of carbon atoms. It is very interesting to notice that rGO in oligosilazane matrices has significant impact on the formation of sp$^2$ carbon atoms (i.e. graphitic domains) during the pyrolysis. In our
study, four composite samples of 40 mg/mL rGOA filled with oligosilazane were pyrolyzed at 600°C, 700°C, 800°C, 900°C, and 1000°C along with crosslinked oligosilazanes. The obtained SiCN/rGOA composites and SiCN were examined using Raman spectroscopy and X-ray diffraction.

Raman spectra of SiCN/rGOA composites and SiCN pyrolyzed at different temperatures are shown in Figure 3-7. D peak (~1340 cm⁻¹) and G peak (~1580 cm⁻¹), characteristic peaks of graphitic materials, can be observed from SiCN/rGOA composites pyrolyzed at 700 °C and above and SiCN pyrolyzed at 800 °C and above. The G band is related to graphite lattices, and its shift toward higher frequency region (blue shift up to 1600 cm⁻¹) corresponds to the transition from amorphous carbon to graphitic domains. [71-74] The G band positions of SiCN/rGOA pyrolyzed at 700 °C, 800 °C, 900 °C and 1000 °C are 1571.9 cm⁻¹, 1574.2 cm⁻¹, 1583.5 cm⁻¹, and 1594.7 cm⁻¹, respectively. The blue shift of G band (22.8 cm⁻¹) indicates an effective transition from amorphous carbon to graphitic carbon in SiCN/rGOA composites. In contrast, the G band positions of pyrolyzed pure SiCN at 800 °C, 900 °C and 1000 °C are 1570.9 cm⁻¹, 1574.6 cm⁻¹, and 1578.8 cm⁻¹, respectively. The blue shift of G band (7.9 cm⁻¹) indicates the transition from amorphous carbon to graphitic carbon in SiCN, which agrees with previous reports. [9,75-77] Comparing the results of pyrolyzed SiCN with or without rGO, the lowest temperature of the appearance of the G band and the D band in SiCN with rGO is 100 °C lower than that of pyrolyzed SiCN without rGO. The difference of Raman spectra suggests that rGO plays a role in lowering the transition temperature of amorphous carbon to graphitic domains. In addition, rGO in SiCN leads to a much larger blue shift of G band in the composite, suggesting that rGO in PDCs grants a more effective
transition of amorphous carbons to graphitic domains probably due to the graphene domains on rGO.

Figure 3-7. Raman spectra of (a) SiCN and (b) SiCN/rGOA pyrolyzed at different temperatures. The G band in each spectrum is label by an asterisk.

Although a graphene-enhanced formation of crystalline carbon has not been reported before, surface-induced crystallization of liquids and soft materials has been investigated. [78,79] During the pyrolysis of preceramic polymers, carbon atoms are produced in bulk between Si$_3$N$_4$ domains
and crystalize into graphitic domains. If graphene is presented in the matrix, the transition of carbon atoms generated in the area close to graphene may have different values of the thermodynamic variables of state. The reduction of crystallization activation energy could need to lower crystallization temperature. In order to verify if graphene can enhance the formation of crystalline carbon during the pyrolysis, Raman spectroscopy was used to monitor the formation of $sp^2$ carbon atoms in the precursor samples with and without graphene at different pyrolysis temperatures. Preceramic polymer samples were produced by depositing polymers on bare quartz slides and graphene coated quartz slides followed by thermal crosslinking. The SEM image of the cross-section of preceramic polymer on a graphene coated quartz slide substrate shows a uniform polymer film with a thickness around 21 microns (Figure 3-15). After pyrolysis, brown or black PDC films were formed on substrates, and Raman spectroscopy was used to characterize the carbon contents in PDC films (Figure 3-16). The Raman spectra of SiCN with graphene are similar to those of SiCN with rGOA. PDCs with and without graphene exhibit different Raman spectra at different pyrolysis temperatures. The G band positions for the PDC films with graphene pyrolyzed at 700 °C, 800 °C, 900 °C and 1000 °C are 1581.9 cm$^{-1}$, 1582.2 cm$^{-1}$, 1586.3 cm$^{-1}$, and 1595.6 cm$^{-1}$, respectively. In contrast, the G band positions of the PDC films without graphene pyrolyzed at 800 °C, 900 °C and 1000 °C are at 1581.4 cm$^{-1}$, 1582.4 cm$^{-1}$, and 1583.8 cm$^{-1}$, respectively. The G band blue shift (13.7 cm$^{-1}$) of SiCN films with graphene is larger than that of SiCN films (2.4 cm$^{-1}$). The comparison of Raman studies of SiCN, SiCN with rGOA and SiCN with graphene suggests that graphene domains on rGO grant a more effective transition of amorphous carbons to graphene nanocrystals.
The structure evolution of SiCN/rGOA composites pyrolyzed at different temperatures was monitored by XRD (Figure 3-8). Pure SiCN remains amorphous under these pyrolysis temperatures. [8-10] XRD peaks at around 26.5 degree are observed from SiCN/rGOA composites pyrolyzed at 700°C and above. The presence of characteristic (002) XRD peak of graphite at 26.5 degree suggests the formation of graphite nanocrystals in these samples. [65,80-82] To verify that the XRD peaks observed at 26.5 degree are from rGO induced crystallization of graphite nanocrystals but not from rGO itself, the evolution of XRD peaks of rGO was examined. The characteristic XRD peak of GO at around 11 degrees can be clearly seen from the GO [65,80,83] synthesized through the modified Hummer’s method (Figure 3-17). The XRD spectra of GO after heat treatments at different temperatures are shown in Figure 3-18. The appearance of characteristic (002) XRD peaks of rGO around 25 degrees [80,83] in Figure 3-18 verifies the formation of rGO. The shift of XRD peak position of from 24.9 degree to 25.9 degree with increased heat treatment temperatures suggests the decrease of space between rGO sheets resulted
from the removal of functional groups (e.g. epoxide and hydroxyl) on rGO basal plane upon the reduction. We believe that the absence of rGO peaks at around 25 degrees in SiCN/rGOA samples is due to the low concentration of rGO. The occurrence of XRD peaks at 26.5 degree from pyrolyzed SiCN/rGOA composites is attributed to the rGO induced formation of graphite carbon domains.

Figure 3-9. Young’s Modulus of SiCN/rGOA composites of different RGOA concentration. The inset is the picture of the cracked composite after the compression test.

The impact of embedded rGOA on the mechanical properties of SiCN/rGOA composites was investigated through the compression testing of the composites made from 10 mg/mL, 20 mg/mL, 30 mg/mL, and 40 mg/mL rGOA. The correlation between the rGOA concentration and the Young’s modulus of SiCN/rGOA material is shown in Figure 3-9. The Young's modulus was calculated in GPa to determine the rigidity of an elastic material.

Figure 3-9 shows that SiCN/rGOA composites have a Young’s modulus ranging from 0.38 to 0.25 GPa depending on the rGOA concentrations. The Young’s modulus of the composite with rGOA
concentration of 10 and 20 mg/mL remains nearly constant at approximately 0.38 GPa. However, with increased rGOA concentrations, the Young’s modulus decreases to 0.25 GPa at 40 mg/mL. This reduction in Young’s modulus is due to the restacking of the graphene sheets, which is clearly demonstrated in the SEM studies.

Figure 3-10. SEM images of cracks formed during the compression test for SiCN/rGOA composites of (a,b) 10 mg/mL, (c,d) 20 mg/mL, (e,f) 30 mg/mL, and (g,h) 40 mg/mL rGOA.

The SEM images of the fractured samples (Figure 3-10) show breakage locations of SiCN/rGOA composites under compression. Figure 3-10 a-d shows that the cracks were formed in SiCN matrix for SiCN/rGOA composites with rGOA concentration of 10 and 20 mg/mL. Figure 3-10 a,b shows that the graphene sheets stop the crack propagation in SiCN matrix. In contrast, the breakage
occurs along the stacked graphene sheet interfaces when the rGOA concentration increases to 30 and 40 mg/mL (Figure 3-10 e-h). Combining the Young’s modulus of SiCN/rGOA composites, it is clear that stacked rGOs lower the strength of the composite. Lehmann and co-workers produced SiCN films with the thickness around several microns through ion-beam sputtering. The films have Young’s modulus of 260 and 85 GPa with the carbon content of 0% and 68%, respectively. Their results also show that the addition of carbon content decreases the Young’s modulus of the material.

[84] Jiang and co-workers have reported a method to make bulk SiCN ceramics using polyvinyl alcohol sponges as templates, the obtained bulk SiCN ceramics have a porosity of ~ 10% and a strength of about 80 MPa. [85] While our SiCN/rGOA composites have lower modulus than SiCN films, the strength is much higher than the porous SiCN samples.

Conclusions

Bulk SiCN ceramics embedded with anisotropic graphene aerogels have been fabricated through filling anisotropic graphene aerogels with a polymer precursor of SiCN ceramics (oligosilazane), followed by crosslinking and pyrolysis. The electrical conductivity of SiCN/rGOA composites increases from $10^{-7}$ S/m to about 157 S/m by embedding 1 wt% of anisotropic rGOA in SiCN ceramics. The electrical conductivity in longitudinal direction is ten times higher than that in transversal direction due to the aligned graphene. It is interesting to discover that graphene also facilitates the formation of graphitic domains in ceramics. Graphene embedded in ceramic precursors lowers the transition temperature of amorphous carbons to graphene nanocrystals. These results suggest that anisotropic graphene structures have great potential in creating anisotropic properties in PDCs.
Supporting Materials

Figure 3-11. A picture of bulk SiCN/rGOA composite.

Figure 3-12. Raman spectrum of single layer graphene transferred onto a quartz slide.

The quality of CVD graphene transferred onto quartz slides was verified by using Raman spectroscopy. The characteristic peaks of graphene, namely the G band (1587 cm\(^{-1}\)), the 2D band (2673 cm\(^{-1}\)), and the D band (1343 cm\(^{-1}\)) are labeled in Figure 3-15. The intensity ratio between
the 2D band and G band is 2.0. In addition, the D band which corresponds to defects in graphene only shows a small intensity, verifying the high quality of the graphene.

Figure 3-13. SEM images of longitudinal (A) and transversal (B) section of 30 mg/mL rGO aerogel.

Figure 3-14. SEM images of SiCN ceramic surfaces at low (left) and high (right) magnification.

Figure 3-15. The SEM image of a SiCN film on graphene embedded between PDC and quartz slide.
Figure 3-16. Raman spectra of (a) PDC on graphene coated quartz slides after pyrolysis conducted at different temperatures (600 °C, 700 °C, 800 °C, 900 °C, and 1000 °C) and (b) PDC on quartz slides after pyrolysis conducted at different temperatures (600 °C, 700 °C, 800 °C, 900 °C, and 1000 °C). All G band positons are labeled by asterisks.

Figure 3-17. XRD spectra of GO.
Figure 3-18. XRD spectra of GO pyrolyzed at different temperatures.

Figure 3-19. Fitting the relationship between conductivity and temperature to the function of (a) $\sigma \propto T^{-1/2}$, (b) $\sigma \propto T^{-1/3}$, (c) $\sigma \propto T^{-1/4}$, respectively.

References


CHAPTER 4: BULK POLYMER DERIVED CERAMIC COMPOSITES WITH EDGE FUNCTIONALIZED GRAPHENE

Introduction

Silicon-based Polymer Derived Ceramics (PDCs) have been synthesized from 1960s. [1] They keep the advantages of mechanical strength, thermal stability, and chemical inertness from traditional ceramics. [2-6] Unlike traditional ceramics obtained by sintering method, PDCs are synthesized by pyrolysis of liquid polymeric precursors in inert atmosphere thus directly convert polymers into ceramics. Liquid polymeric precursors provide the availability of various liquid-based processing techniques like casting, extrusion, spin-on coating, dip coating and spray coating. [7-11] These technologies make PDCs able to be used in fabrications of ceramics and related devices with complex shapes such as fibers, [12,13] porous materials, [14-16] and membrane coatings, [17,18] which are difficult or even impossible to be obtain by conventional routes. Also, synthesis of PDCs at temperatures lower than those for traditional ceramics leads to energy-saving ceramics preparations. [19] These superior properties of PDCs mentioned above make them as a kind of materials widely used in applications such as MEMS, [20-22] energy storage, [11,23-25] and high temperature sensors. [26-29]

PDCs usually have low electrical conductivity $10^{-12}$-$10^{-7}$ S/cm, [30,31] and the fabrication of PDCs based composites is the way to increase their electrical conductivity. Adding conductive components such as CNTs, [32-35] carbon fibers, [36] carbon black, [37,38] graphite flakes, [39] reduced graphene oxide (rGO), [40,41] and metal salts like aluminum oxide and Molybdenum disilicide [42,43] into insulating PDCs matrix can effectively increase the electrical conductivity of PDCs based composites. Additionally, introducing percolated networks composed of
conductive materials into PDC composites is found to be a better method of increasing the
electrical conductivity. [44-46] For example, the addition of embedded graphene aerogels
composted of conductive materials with inter-connected networks was reported to increase the
electrical conductivity of composites to 1.57 S/cm. [47]

Edge functionalized graphene oxide (EFGO) is a commercial conductive material from Garmor
Inc. Functional groups such as hydroxyl groups, carbonyl groups, and carboxylic acid groups only
form on edges of graphene flakes. Those functional groups provide EFGO with a good dispersity
in solvents such as ethanol, acetone. Meanwhile, the electrical conductivity of EFGO (~10 S/cm)
is much higher that of graphene oxide synthesized from Hummer’s method. It is attributed to the
remaining graphitic structures in the basal area of EFGO flakes which facilitate the charge
transport by inter-plane hopping among EFGO flakes.

Here in, we report the introduction of conductive EFGO networks into bulk PDCs composites with
a facile method different from introducing embedded graphene aerogels. Meanwhile, nontoxic
polymeric precursors for the preparation of SiOC PDCs are used. [48] Polymeric precursors are
infiltrated into the highly porous PVA foams with an excellent EFGO attachment to form green
bodies for pyrolysis processes. PVA foams are served as a sacrificial component and decomposes
during pyrolysis. As a result, EFGO networks embedded SiOC PDC composites are prepared after
pyrolysis. The electrical conductivity of such composites at a wide temperature is investigated.
The role of percolated EFGO networks on the preparation of bulk PDC composites, graphitic
domains formation in the nearby area, electrical conductivity improvement, and thermal
conductivity is explored.
Experimental Procedures

Polysiloxane precursor (SILRES 62C, Wecker), poly (vinyl alcohol) (PVA) foam (Sponge King), Pyro-Duct 597-A conductive adhesive (Aremco), ethanol (Fisher) and copper wires (Fisher) were used as received. Argon was purchased from Air Liquide and used without further purifications. Edge functionalized graphene oxide (EFGO) with a few layers graphene was provided by Garmor Inc.

**Preparation of EFGO/SILRES 62C/PVA composites (PDC composites).** A mixture containing 700 mg EFGO and 100 mL ethanol was sonicated (Branson digital sonifer equipped with stainless steel tips) for 30 minutes, and a homogenous EFGO dispersion with a concentration of 7 mg/mL was obtained. Pre-shaped PVA foams were immersed into the EFGO dispersion for 2 hours, and the resulted EFGO attached PVA foams were placed into a vacuum oven set at 50 °C for 12 hours to completely evaporate the residual ethanol in PVA foams. Once the PVA foams were dried, they were immersed into the SILRES 62C precursor under vacuum for 12 hours to ensure that all voids were filled with SILRES 62C. The SILRES 62C filled samples were heated at 160 °C for 16 hours to crosslink the polysiloxane for subsequent pyrolysis. In a typical pyrolysis process, green bodies (i.e. crosslinked composites) were pyrolyzed at 300 °C, 400 °C, 600 °C, and 1000 °C for 2 hours, respectively. The ramping rate in all heating steps was 1 °C/min, and composites were naturally cooled down after pyrolysis. The whole pyrolysis process was conducted in argon atmosphere. To study the composition evolution of ceramic composites during pyrolysis processes, composites with different final pyrolysis temperatures (300 °C, 400 °C, 500 °C, 600 °C, 700 °C, 800 °C, and 900 °C) were obtained. The details of pyrolysis conditions are summarized in Table 4-3.
Preparation of EFGO/SILRES 62C ceramic composites. EFGO was first manually mixed with SILRES 62C precursor with the mass ratio of EFGO: SILRES 62C=2:100, and the mixture was then sonicated by a horn sonifier for 30 minutes. After sonication, the mixture was filled into cylinder shape molds made by aluminum foils. Filled molds were placed into an oven set at 160 °C for 16 hours to cure the precursor. After peeling aluminum foils off, cured samples were ready for pyrolysis. EFGO/SILRES 62C ceramic composites with different final pyrolysis temperatures (300 °C, 400 °C, 500 °C, 600 °C, 700 °C, 800 °C, 900 °C, and 1000 °C) were prepared by using the same pyrolysis conditions as those for preparations of PVA/SILRES 62C/EFGO ceramic composites.

Preparation of pure SILRES 62C ceramics. The liquid SILRES 62C precursor was put into molds made by aluminum foils and placed into the oven at 160 °C for 16 hours to crosslink the precursor. After removing aluminum foils, Pure crosslinked SILRES 62C samples were pyrolyzed at different temperatures (300 °C, 400 °C, 500 °C, 600 °C, 700 °C, 800 °C, 900 °C, and 1000 °C) by using the same pyrolysis conditions as those for preparations of EFGO/SILRES 62C/PVA ceramic composites.

Heat treatment to reveal networks embedded in pyrolyzed composites. Green bodies used for the preparation of EFGO/SILRES 62C/PVA composites were heated in air with the ramping rate of 1 °C/min. The furnace temperature was halted at 300 °C and 500 °C for 2 hours, respectively.

Measurement of electrical conductivity. Resistance on two ends of cylinder shape samples recorded using electrochemistry workstation (CH Instruments) was used to calculate the electrical conductivity. The resistance was measured in a furnace filled with argon from room temperature.
(25 °C) to 600 °C. Electrical conductivity of samples is calculated from the resistance. The resistance of each sample was measured at least 3 times.

**Measurement of thermal conductivity.** Thermal conductivity of samples was calculated by using the equation of \( k = \alpha \cdot C_p \cdot \rho \), where \( \alpha \) is the thermal diffusivity, \( C_p \) is the specific heat capacity, and \( \rho \) is the density. [49] FlashLine 5000 thermal diffusivity system (Anter Corporation, USA) was used to obtain heat diffusivities of composites. Round shape disks with 12.5 mm diameter and 1-2 mm thickness from PDC composites before and after pyrolysis at 1000 °C were used for the measurement. Both sides of these disks were coated with ~15 nm platinum (Pt) by sputter coating followed by a graphite aerosol spray. Standard pulse flash technique was used in measurement of heat diffusivities. Specific heat capacity was measured by using differential scanning calorimetry DSC (TA Instruments). About 10 mg PDC composites before and after pyrolysis at 1000 °C were used in DSC tests. Ramping rate applied was 5 °C/min, and the scanning temperature was 10 °C to 170 °C for green bodies and 10 °C to 350 °C for pyrolyzed PDC composites. Acquired endothermal curves were used to calculate heat capacities at specific temperatures (Figure 4-23).

**Measurement of linear shrinkage.** Linear shrinkage was obtained by measuring the change of dimension from multiple cylinder shape samples after pyrolysis processes at different temperatures.

**Measurement of Young’s modulus.** Young’s modulus of composites was acquired by an Instron 50 kN Electromechanical Load Frame Universal Testing Machine at room temperature. 20 mm×20 mm×20 mm EFGO/SILRES 62C/PVA composites pyrolyzed at 1000 °C were used in this series of tests. Every test was performed until sample breakage was observed with the starting height
value of 30 mm. Young’s modulus was calculated by the ratio between the force applied per unit of area and the strain of the sample.

**Characterizations**

The tests on size distribution of EFGO flakes is performed on a dynamic light scattering instrument (DLS, Malvern ns290). TEM images and selected area electron diffraction (SAED) patterns are obtained from a JEOL 1011 transmission electron microscope. Thickness of EFGO flakes is revealed by a Veeco Dimension 3100 atomic force microscope system. The proton nuclear magnetic resonance (¹H NMR) spectrum of SiOC polymeric precursor was obtained from a Bruker Avance III 400 (400 MHz). The Fourier-transform infrared (FTIR) spectrum of polysiloxane precursor was investigated by a Perkin Elmer Spectrum 100 spectrometer. Morphologies and elemental compositions of ceramic composites were examined by a scanning electron microscope (SEM, ZEISS Ultra 55) coupled with Energy-Dispersive X-ray spectroscopy (EDS).

Decomposition and mass loss of ceramic composites and starting materials were acquired by thermal gravimetric analysis (TGA) from TA Instruments. Raman spectra of ceramic composites were obtained from a WiTec Raman system, and a 532 nm laser with power of 0.175 mW was used in all Raman characterizations. Chemical states of elements in ceramic composites were tested by X-ray photoelectron spectroscopy (XPS, PHI 5400). Electrical conductivities of ceramic composites were measured by a chemical workstation from CH instruments with the aid of an argon filled tube furnace. Thermal diffusivities of composites were measured by a FlashLine 5000 thermal diffusivity system (Anter Corporation, USA). Heat capacities of ceramic composites were obtained from differential scanning calorimetry (DSC, TA Instruments).
Results and Discussion

Figure 4-1 illustrates the fabrication process of SiOC/EFGO composites. The graphene network was obtained by immersing the pre-shaped PVA foam into a EFGO ethanol dispersion where EFGO flakes were deposited onto PVA foam walls. The liquid SiOC precursor (SILRES 62C) was filled into the voids of the PVA foam and crosslinked to produce EFGO/SILRES 62C/PVA green bodies. The PVA foam was decomposed during the pyrolysis, which led to SiOC/EFGO composites with a continuous EFGO network.

Figure 4-1. The schematic illustration of the preparation of EFGO network embedded PDC composites.

EFGO is a kind of commercialized multi-layers graphene oxide, and it is produced by ball-milling with simultaneous hydrogen peroxide oxidation. Edges of EFGO flakes are functionalized with hydroxyl, carbonyl and carboxylate groups, and the oxygen contents is reported to be about 5 wt%. EFGO flakes have sizes of below 1 µm (Figure 4-2a), and the average size of them is 350 nm from
the DLS test (Figure 4-15). The multi-layer structure of EFGO can be clearly seen from Figure 4-2b. Additionally, four sets of six-fold SAED patterns circled in Figure 4-2c indicate the existence of stacked multi-layer graphitic structure in EFGO. [50-52] Also, arcs in the SAED image regarding the spacing of 2.10 nm and 1.23 nm is attributed to the (1100) and (1120) lattice fringes of graphitic structures randomly oriented in EFGO flakes. [53-55] The typical thickness of EFGO flakes is found to be around 8 nm from the AFM height profile (Figure 4-3), therefore EFGO flakes have around 8 layers of stacked graphene.

The Raman spectrum in Figure 4-4 verifies the existence of graphitic domains in EFGO flakes because characteristic G peak, D peak and 2D peak at 1563.8 cm\(^{-1}\), 1343.9 cm\(^{-1}\), and 2693.6 cm\(^{-1}\) are observed in the spectrum. The intensity ratio between the D peak and the G peak is 0.39, and it is much smaller than that for GO synthesized from Hummer’s method (0.9-1.9). [56-59] The intensity ratio of the D peak and the G peak relates to the ratio between sp\(^3\) carbon and sp\(^2\) carbon. Smaller value of the intensity ratio reflects higher percentage of sp\(^2\) carbon in samples, namely more ordered graphitic structure and fewer defects. Therefore, EFGO have more ordered structure than GO synthesized by the Hummer’s method. The graphitic structure in the basal area of EFGO flakes endow EFGO with electrical conductivity (~10 S/cm) dramatically higher than that of GO synthesized from Hummer’s method. Meanwhile, functional groups on edges facilitate the dispersity of EFGO in solvents such as ethanol, acetone, and water, thus makes EFGO as an excellent candidate in solution-based processing. It needs to be noted that ethanol is the best medium to disperse EFGO among common solvents, and it is believed to be attributed to the abundant hydroxyl groups on edges of EFGO flakes. Therefore, ethanol is used as the dispersant for EFGO in the preparation of composites.
Figure 4-2. (a, b) TEM images of EFGO flakes. (c) The SAED pattern of EFGO flakes. Four sets of six-fold SAED pattern regarding the (1100) lattice fringe of graphitic structures are labeled in red, blue, green, and purple circles.

Figure 4-3. The AFM image of a EFGO flake on mica substrate. The scanning area is 2.5 μm×2.5 μm. The height profile beneath the AFM image reveals the height at the white sectioning line in the AFM image.
Figure 4-4. The Raman spectrum of EFGO flakes. The position of the G peak, the D peak and the 2D peak are at 1563.8 cm$^{-1}$, and 1343.9 cm$^{-1}$, and 2693.6 cm$^{-1}$, respectively.

Figure 4-5. SEM images of EFGO attached PVA foams after the immersion of PVA foams in the EFGO dispersion.
EFGO flakes are attached on the surface of PVA networks after the immersion of PVA foams into the EFGO ethanol dispersion. The excellent coverage of EFGO on PVA foams is shown in Figure 4-5. EFGO flakes attach onto PVA networks by the Van der Waals interaction, and the high magnification SEM images (Figure 4-5 b-c) show no exposed PVA foams. Therefore, the immersion of PVA foams in the EFGO dispersion is an effective method to form EFGO flakes wrapped PVA networks.

![Figure 4-6](image)

Figure 4-6. SEM images of PDC composites green bodies.

The EFGO attached PVA foams were infiltrated by the SiOC polymeric precursor in a vacuum environment and cured at 160 °C to obtain green bodies for pyrolysis. The excellent infiltration of SiOC precursor is verified by the SEM image (Figure 4-6a) which shows the formation of nearly fully-dense green bodies. The vacuum assisted SiOC precursor infiltration nearly completely avoid the formation of voids in green bodies by facilitating the exclusion of trapped air between the PVA foam and the SiOC precursor. In addition, the thickness of EFGO wrapped PVA foam networks in green bodies is 10-25 µm from Figure 4-6b.
Figure 4-7. SEM images of PDC composites pyrolyzed at 1000 °C.

PDC composites pyrolyzed at 1000 °C are shown in Figure 4-7. The cross-section area of PDC composites shows the interface between EFGO component and SiOC matrix. The breakage of PDC composites happens at the interface because it is usually the weakest part in composites. Tiny gaps between these two components can be seen from the SEM images, and the aggregates of EFGO flakes at the interface are observed. The nearly fully-dense morphology of PDC composites and the presence of EFGO component within composites verify the successful fabrication of
EFGO embedded PDC composites. Also, the surface of pyrolyzed PDC composites are investigated, no cracks are seen from SEM images (Figure 4-19). For pyrolyzed PDCs from pure SiOC polymeric precursors, cracks can be clearly seen from the surface by naked eyes. Thus, the embedded EFGO helps the formation of nearly crack-free PDC composites. Additionally, PDC composites which pyrolyzed at 300 °C to 600 °C without Au/Pd sputter coating show strong charging during SEM imaging, and contents on the surface were burnt out in seconds (Figure 4-20), thus the poor electrical conductivity of ceramic composites pyrolyzed at 300 °C to 600 °C is revealed. No obvious charging is observed for PDC composites pyrolyzed above 600 °C without Au/PD sputter coating. Therefore, it is an evidence of huge electrical conductivity difference among composites pyrolyzed above or at and below 600 °C.

Figure 4-8. TGA curves of the PDC composite and each component in the composite.
The mass change of PDC composites and each component in PDC composites (PVA, SILRES 62C precursor, and EFGO) at elevated temperatures is monitored by TGA. TGA curves in Figure 4-8 show the mass loss of materials from room temperature to 1000 °C. PVA foam has a dramatic mass loss from 300-350 °C which is result from the decomposition of PVA, and only 4% of the original mass remains at 1000 °C. The mass of EFGO nearly keeps constant through the heating process. Its minimal mass loss at 100 °C to 150 °C is from the evaporation of residual moisture, and 96% of its original mass remains at 1000 °C. The major mass loss of SILRES 62C happens from 300 °C to 800 °C and around 75% of its original mass remains at 1000 °C. Its mass loss is primarily from the decomposition of organic components during the heat treatment. The breakage of Si-H bonds and Si-C bonds in polymeric precursors leads to major emitted gases such as methane and hydrogen. [60-64] The mass change of the PDC composites green body is also monitored by TGA, and it can be considered as a mass change superimposition of all components included. The major mass loss is at the temperature range from 200 °C to 800 °C, and about 63% of its original mass remains at 1000 °C. Additionally, the loading percentage of EFGO in PDC composites is calculated by the mass change of composites after each preparation step (Table 4-4). The loading percentage EFGO is calculated to be 1.4-1.9 wt% in pyrolyzed PDC composites, and consistent EFGO loading in composites is realized. The linear shrinkage of composites after the pyrolysis at 1000 °C is 22-24% comparing to green bodies (Figure 4-21). The density of composites pyrolyzed at different temperatures are logged in Table 4-5. The density of pyrolyzed composites increases with the increasing of pyrolysis temperatures, and it is attributed to both the mass loss from the organic component decomposition and the shrinkage of composites during pyrolysis. The faster volumetric shrinkage of composites than that of mass loss leads to denser composites pyrolyzed at higher temperatures. The density of composites pyrolyzed at 1000 °C is
~1.76 g/cm³ (Table 4-5), and it is close to the SiOC polymeric precursor pyrolyzed at 1000 °C (1.768 g/cm³, Table 4-6) thus verify the formation of nearly fully-dense ceramic composites. Also, the density of EFGO is 1.8 g/cm³, so its spatial density is 1.4-1.9% in pyrolyzed composites. Young’s modules of composites pyrolyzed at 1000 °C have the average value of 213.4 MPa (Table 4-9), which is comparable to previous reported PDC based composites. [47]

Table 4-1. Elemental Compositions of PDC composites after pyrolysis at different temperatures.

<table>
<thead>
<tr>
<th></th>
<th>300°C</th>
<th>400°C</th>
<th>500°C</th>
<th>600°C</th>
<th>700°C</th>
<th>800°C</th>
<th>900°C</th>
<th>1000°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon (%)</td>
<td>67.69</td>
<td>66.84</td>
<td>63.04</td>
<td>56.83</td>
<td>55.72</td>
<td>50.88</td>
<td>49.13</td>
<td>47.03</td>
</tr>
<tr>
<td>Oxygen (%)</td>
<td>21.11</td>
<td>21.23</td>
<td>22.86</td>
<td>28.60</td>
<td>29.12</td>
<td>32.67</td>
<td>33.41</td>
<td>35.54</td>
</tr>
<tr>
<td>Silicon (%)</td>
<td>11.09</td>
<td>11.93</td>
<td>14.10</td>
<td>14.56</td>
<td>15.16</td>
<td>16.45</td>
<td>17.45</td>
<td>17.43</td>
</tr>
</tbody>
</table>

The elemental composition of PDC composites after pyrolysis processes conducted at different temperatures is investigated by EDS, and the results are summarized in Table 4-1. All samples for EDS acquisitions were not sputter coated by Au/Pd to get authentic elemental compositions. The atomic percentage of carbon decreases with the increasing of pyrolysis temperatures, and it results from the decomposition of organic components in ceramics to form carbon containing gases such as methane and ethane. [65] In the meantime, the atomic ratio between silicon and oxygen keeps at nearly 0.5 after pyrolysis at different temperatures. It indicates the existence of SiO₂ clusters in SiOC ceramics, which is in accordance with the observation of structural evolution of PDCs in previous reports. [30,66,67] Si-O bond has a dissociation energy of 452 kJ/mol which is considerably higher than those of C-C bond (346 kJ/mol), Si-C bond (318 kJ/mol), and Si-H bond (319 kJ/mol) exist in composites, [68] and it is why Si-O bonds remain during pyrolysis processes.
Figure 4-9. Raman spectra of PDC composites pyrolyzed at different temperatures.

Raman study is performed to further study the chemical composition in PDC composites after pyrolysis at different temperatures. It is interesting to see the presence of the G peaks and D peaks, which are signature Raman peaks of graphitic domains, from PDC composites pyrolyzed at or above 700 °C (Figure 4-9). Also, there is no discernible peaks of graphitic domains from PDC composites pyrolyzed below 700 °C. However, EFGO itself has Raman signals from graphitic domains due to its graphitic structure in the basal area (Figure 4-4). Therefore, these signature Raman signals from graphitic domains observed from PDC composites pyrolyzed at or above 700 °C is not from the EFGO component. As EFGO is not the source for graphitic Raman signals, these Raman signals should be resulted from chemical change of other components during pyrolysis.

PVA foam is almost completely decomposed below 700 °C, so the Raman signals of graphitic carbon domains should be from the chemical evolution of SILRES 62C precursor. Furthermore, blue shift of G peaks is observed from ceramic composites with higher pyrolysis temperatures. With increased pyrolysis temperature from 700 °C to 1000 °C, G peaks shift from 1586.4 cm\(^{-1}\) to
1614.7 cm\(^{-1}\). The blue shift (28.3 cm\(^{-1}\)) of G peaks indicates the effective transition from amorphous carbon to graphitic domains in composites during pyrolysis. [69,70]

Figure 4-10. XPS spectra of PDC composites at (a) carbon region and (b) silicon region before pyrolysis (RT), at the transition state of pyrolysis (700 °C), and after pyrolysis (1000 °C).

Figure 4-10. XPS spectra of PDC composites at (a) carbon region and (b) silicon region before pyrolysis (RT), at the transition state of pyrolysis (700 °C), and after pyrolysis (1000 °C).
XPS study is conducted to investigate the switch of elemental chemical state in PDC composites before pyrolysis, pyrolyzed at the transition temperature, and pyrolyzed at 1000 °C. Because obvious transition stage for ceramic composites pyrolyzed at 700 °C is observed both from SEM imaging (lowest pyrolysis temperature to observe no charging in SEM imaging without Au/Pd sputter coating) and Raman spectroscopy study (lowest pyrolysis temperature to observe the presence of the G peak and the D peak from graphitic domains), this pyrolysis temperature is considered to be the transition stage. XPS curves at carbon and silicon binding energy regions are presented in Figure 4-10. Small shift of XPS peaks at the carbon region is observed from PDC composites pyrolyzed at 700 °C, which indicate the start of graphitic “free carbon” domain formation in composites. [71-73] Deconvoluted XPS spectrum at the carbon region for PDC composites pyrolyzed at 1000 °C shows a peak with the binding energy of 284.6 eV, indicating the formation of abundant graphitic domains. On the other hand, the XPS peak in silicon region shifts to the lower energy region when PDC composites are pyrolyzed at 700 °C, and the peak shifts more to the lower energy region when PDC composites are pyrolyzed at 1000 °C. The breakage of Si-C bond and Si-H bond decreases the valance of silicon element in composites and leads to the shift of silicon XPS peak to the lower energy region. Therefore, the shift of XPS peak at the silicon region indicates the decomposition of organic component.

After the investigation of morphologies and chemical composition of PDC composites, the electrical conductivity of pyrolyzed samples at room temperature (25 °C) is studied (Figure 4-11). Composites before pyrolysis shows electrical resistance beyond the measurement range, thus they can be considered as insulators at room temperature even with embedded conductive EFGO networks. After pyrolysis at 300 °C or higher, electrical conductivity is capable to be calculated
from the reading of electrical resistance, and composites pyrolyzed at higher temperature have higher electrical conductivity at room temperature. As known from the Raman study, the formation of conductive graphitic domains in the SILRES 62C precursor happens above 600 °C, thus the observed electrical conductivity of composites pyrolyzed at or below 600 °C should not be from the formation of graphitic domains in composites. In another aspect, composites shrink during pyrolysis processes, and the more compacted composites after pyrolysis could be the reason for the observable electrical conductivity of composites pyrolyzed at or below 600 °C. It can be explained that the shrinkage of composites during pyrolysis processes enhances the interactions of adjacent EFGO sheets, and the compact EFGO networks lead to improved electrical conductivity by facilitating the charge transport of inter-plane hopping among EFGO flakes. The embedded EFGO networks become more compact when higher pyrolysis temperature is applied, and the electrical conductivity of composites increases. Besides, the electrical conductivity of composites increases even after the increment of shrinkage is not obvious when the pyrolysis temperature is at or above 800 °C. The increasing electrical conductivity of PDC composites pyrolyzed at or above 800 °C is primarily due to the increasing abundance of graphitic domains in composites when higher pyrolysis temperatures are applied. The electrical conductivity of composites after pyrolysis at 1000 °C and 1100 °C are almost identical, thus the threshold of electrical conductivity is believed to be reached after the pyrolysis at 1000 °C.

To better understand the effect of each component to electrical conductivity properties, composites of control groups were prepared. To investigate the function of EFGO, pyrolyzed PVA/SILRES 62C composites were fabricated to compare with PDC composites (PVA/SILRES 62C/EFGO composites). However, only deformed composites with cracks from inside can be prepared at
pyrolysis temperatures at or above 400 °C. In contrary, intact PDC composites can be successfully prepared even when the pyrolysis temperature is much higher than 400 °C. Consequently, EFGO must play an important role in avoiding cracks and deformation during the pyrolysis. The main reason of cracks formation in PDCs based composites is the ineffective stress releasing from emitted gases during pyrolysis processes. [74-76] PVA foams embedded in composites is the major source of gas generation during pyrolysis, and it leads to severe problems of stress releasing from composites. When bare PVA foams with no attached EFGO are in the composite, the force from gas expansion directly acts onto cured SILRES 62C precursors, and cracks can be easily formed because of the high stiffness of cured precursor as well as no effective pathways for gas releasing in such binary system. However, when EFGO attached PVA foams are embedded in SILRES 62C precursors, the force from gas expansion acts onto EFGO first, and the loosely packed EFGO flakes act as cushions to partially absorb the stress applied onto cured SILRES 62C precursor. Also, the network of EFGO attached PVA foams provides effective pathways for gas releasing from composites. In consequence, EFGO flakes attached PVA foams help to release stress from gas formation during pyrolysis, and it is vital to the formation of intact pyrolyzed PDC composites.

Because no intact pyrolyzed SILRES 62C/PVA composites can be fabricated, the function of EFGO on improving electrical conductivity of composites needs to be compared by pyrolyzed EFGO/SILRES 62C composites and pyrolyzed SILRES 62C composites. It can be clearly seen from Figure 4-24 that pyrolyzed EFGO/SILRES composites have electrical conductivity higher than that of pyrolyzed SILRES both at room temperature and at elevated temperatures. The
improvement of electrical conductivity by having EFGO in composites is due to the introduction of more conductive component. [36,42,77,78]

Figure 4-11. Room temperature electrical conductivity of PDC composites pyrolyzed at different temperatures and the corresponding linear shrinkage after pyrolysis.

The function of PVA foams to electrical conductivity can be revealed by comparing the electrical conductivity of pyrolyzed PVA/SILRES 62C/EFGO composites (PDC composites) and pyrolyzed SILRES 62C/EFGO composites. It can be clearly seen from Figure 4-24 that pyrolyzed EFGO/SILRES/PVA composites have electrical conductivity several orders of magnitude higher than that of SILRES/PVA pyrolyzed both at room temperature and at elevated temperatures. When EFGO flakes attached PVA foams are embedded in composites, conductive EFGO networks after pyrolysis can facilitate the electron transport within pyrolyzed composites by the percolated
networks. However, conductive EFGO flakes can only randomly distribute in composites without the presence of PVA frameworks, and no effective networks for electron transport can be realized within composites in this case. Accordingly, the introduction of percolated networks for electron transport is the main reason to the improvement of electrical conductivity when PVA foams are included in green bodies. [32,79-82].

The electrical conductivity data from PDC composites (EFGO/SILRES 62C/PVA composites) and pyrolyzed SILRES 62C composites is further analyzed to dig out more information about the mechanism of electrical conductivity improvement in ceramic composites. By extracting the electrical conductivity data of these two kinds of composites pyrolyzed at 1000 °C at room temperature, it is intriguing to notice that the value of PDC composites electrical conductivity is higher than that from classic models regarding the electrical conductivity of composites.[83-86] Here in, SILRES 62C pyrolyzed at 1000 °C is considered as the less conductive continuous matrix, and EFGO is considered as the more conductive component. The detailed calculations are presented in the supplementary materials.

![Raman spectra of (a) pure SILRES 62C and (b) EFGO/SILRES 62C composites with 2 wt% EFGO pyrolyzed at different temperatures.](image)

Figure 4-12. Raman spectra of (a) pure SILRES 62C and (b) EFGO/SILRES 62C composites with 2 wt% EFGO pyrolyzed at different temperatures.
Two possible reasons can be attributed to the exceeding electrical conductivity compared to classic models. (1) excellent connectivity of the more conductive EFGO phase, and (2) the formation of more conductive components during pyrolysis. To investigate the formation of EFGO networks buried in the composites, green bodies for the preparation of PDC composites were heated in air at 500 °C to completely decompose PVA foam, and 3D inter-connected channels can be observed within composites (Figure 4-23). Also, EFGO flakes are observed on edges of those void channels. This morphology indicates that EFGO networks exist in pyrolyzed PDC composites. On the other hand, Raman spectroscopy is used to find out the effect of embedded EFGO on chemical change during pyrolysis processes. Raman spectra of pyrolyzed SILRES 62C in Figure 4-25a shows the presence of the G peak and the D peak from graphitic domains when the pyrolysis temperature is at or above 800 °C. By comparing the results to the Raman spectra of pyrolyzed PDC composites (Figure 4-9), the temperature to the appearance of graphitic domain signals is 100 °C higher. Also, the blue shift of G band (3.9 cm⁻¹) is much smaller than that of PDC composites (28.3 cm⁻¹) from Table 4-7. Therefore, EFGO attached PVA foams facilitate the formation of graphitic domains in composites. To further verify the promoted formation of graphitic domains is from the addition of EFGO, Raman spectra of pyrolyzed EFGO/SILRES 62C composites are acquired (Figure 4-12b). By having well dispersed EFGO in composites, the temperature for the presence of D band and G band is lower than that of pure SILRES 62C ceramics, and it appears at 700 °C which is the same as that of PDC composites. Also, the blue shift of G band and D band (23.1 cm⁻¹) is larger than that of pyrolyzed pure SILRES 62C (3.9 cm⁻¹) from Table 4-7. Consequently, the embedded EFGO is the primary reason of accelerated formation of graphitic in composites. This result is in accordance with the phenomenon observed in the previous report that reduced graphene oxide and single layer graphene can induce the crystallization of graphitic domains from carbon nearby their
surfaces, [47] and it is believed due to the graphitic structures, which are resembled to reduced graphene oxide and graphene, in the basal area of EFGO flakes.

Figure 4-13. Schematic illustration of graphitic domains evolution in (a) SILRES 62C, (b) EFGO/SILRES 62C, and (c) EFGO/SILRES 62C/PVA composites (PDC composites) during pyrolysis processes.

From the discussion above, schematic illustrations of graphitic domains formation in composites during pyrolysis processes are summarized in Figure 4-13. The formation of graphitic domains in composites have two kinds of mechanisms, namely self-crystallization and EFGO induced crystallization. In pyrolyzed SILRES 62C composites, only the self-crystallization is available to form graphitic domains in composites (Figure 4-13a). The abundance of graphitic domains increases with increasing pyrolysis temperatures, and it is proved by the analysis from Raman spectroscopy that characteristic peaks from graphitic domains have higher intensity when applying higher pyrolysis temperatures. In pyrolyzed EFGO/SILRES 62C composites, self-crystallization
and EFGO induced crystallization are both available to form graphitic domains (Figure 4-13b). The abundance of graphitic domains in matrix increases with increasing pyrolysis temperatures. Besides, EFGO induces the formation of graphitic domains from the surface of EFGO flakes. In pyrolyzed EFGO/SILRES 62C/PVA composites (PDC composites), self-crystallization and EFGO induced crystallization are also both available to form graphitic domains (Figure 4-13c). Other than the increment of graphitic domains abundance in matrix with increased pyrolysis temperatures, EFGO induces the formation of graphitic domains from the surface of embedded EFGO networks.

Figure 4-14. Electrical conductivity of PDC composites (EFGO/SILRES 62C/PVA composites) pyrolyzed at different temperatures. The testing temperature range is from 25 °C to 600 °C.
The electrical conductivity of PDC (EFGO/SILRES 62C/PVA composites) composites at elevated temperatures is further studied, and the results are presented in Figure 4-14. Composites pyrolyzed at higher temperatures have higher electrical conductivity through the whole measurement range. Also, the increment of conductivity from room temperature to 600 °C decreases with increased pyrolysis temperatures (Table 4-8). To better understand the mechanism of electrical conductivity change from room temperature to elevated temperatures, electrical conductivity of pyrolyzed EFGO/SILRES 62C composites and pyrolyzed SILRES 62C composites are also investigated (Figure 4-7). Like pyrolyzed PDC composites, the increment of electrical conductivity from room temperature to 600 °C decreases with increased pyrolysis temperature for these two kinds of composites (Table 4-8). In addition, the times of electrical conductivity improvement from room temperature to 600 °C have the trend of EFGO/SILRES 62C/PVA> EFGO/SILRES 62C> SILRES among composites pyrolyzed at the same temperature.

The average activation energy of composites is the prominent parameter of electron transport. [30,65,87-90] The classical equation of \( \sigma_T \sim \exp \left( \frac{\Delta E}{k_B T} \right) \) is used to calculate the average activation energy, where \( \sigma_T \) is electrical conductivity, \( k_B \) is Boltzmann constant, and \( \Delta E \) activation energy. This equation is considering the electrical conductivity of semi-conductors in the intrinsic temperature range. Within this temperature range, the activation energy equals to one-half of the band gap between the conduction band and the valence band. [87] The average activation energies of composites pyrolyzed at different temperatures are calculated by curve fittings and are summarized in Table 4-2.

For pyrolyzed EFGO/SILRES 62C composites and pyrolyzed SILRES 62C composites, the electrical conductivity is primarily from the electron transport in matrix, the overall activation
energy of pyrolyzed EFGO/SILRES 62C and pyrolyzed SILRES 62C decreases with increasing pyrolysis temperature. Also, the overall activation energy of pyrolyzed EFGO/SILRES 62C is smaller than that of pyrolyzed SILRES 62C when same pyrolysis conditions are applied. Filled EFGO in composites by sonication have band gap much smaller than that of SILRES 62C, thus the overall activation energy decreases. Besides, based on the observation in Raman spectra regarding pyrolyzed EFGO/SILRES 62C and SILRES 62C, the formation of graphitic domains is induced by EFGO particles in the nearby area. The formation of graphitic domains which are more conductive than the SiOC matrix further decreases the overall activation energy.

Table 4-2. Summary of activation energy of different composites pyrolyzed at different temperatures.

<table>
<thead>
<tr>
<th>Pyrolysis Temperature (°C)</th>
<th>Activation Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>EFGO/SILRES 62C/PVA</td>
</tr>
<tr>
<td>600</td>
<td>0.0287</td>
</tr>
<tr>
<td>700</td>
<td>0.0265</td>
</tr>
<tr>
<td>800</td>
<td>0.0224</td>
</tr>
<tr>
<td>900</td>
<td>0.0192</td>
</tr>
<tr>
<td>1000</td>
<td>0.0107</td>
</tr>
</tbody>
</table>

Compare pyrolyzed EFGO/SILRES 62C/PVA composites (PDC composites) to pyrolyzed EFGO/SILRES 62C composites, the calculated activation energy of pyrolyzed PDC composites is smaller than that of pyrolyzed EFGO/SILRES 62C when same pyrolysis conditions are applied (Table 4-2). PDC composites and EFGO/SILRES 62C composites have almost identical mass percentage of conductive EFGO component in composites before pyrolysis, so the arrangement of EFGO flakes in composites is crucial to the electrical properties of composites. Percolated EFGO
networks in pyrolyzed EFGO/SILRES 62C/PVA composites provide effective pathways for electrons, thus electrical conductivity of PDC composites is primarily from these networks. [30,91,92] With the increasing of pyrolysis temperature, the number and size of graphitic domains in SILRES 62C matrix increases, the electrical conductivity from SILRES matrix component thus increases. Also, the formation of graphitic domains from the surfaces of EFGO networks helps to build better pathways for electron transport. Meanwhile, the distance from graphitic domains in SILRES 62C matrix to EFGO networks decreases when applying higher pyrolysis temperatures, and it further facilitates the transport of electrons from matrix to effective pathways composed of EFGO networks from hopping mechanism. It can be analogous to the case that closer distance from rural area (SILRES 62C matrix) to highway networks (EFGO networks) leads to more convenient travel from the rural area.

At last, the thermal conductivity of PDC composites is investigated. The thermal conductivity of PDC composites pyrolyzed at 1000 °C is 0.7654±0.1091 W·m⁻¹·K⁻¹ and 0.8676±0.1289 W·m⁻¹·K⁻¹ at room temperature (25 °C) and at 300 °C, respectively. Therefore, the thermal conductivity of pyrolyzed PDC composites at room temperature and at elevated temperature are quite close. Besides, the thermal conductivity of PDC composites is much lower than the reported thermal conductivity of pure SiOC matrix (1.5-3 W·m⁻¹·K⁻¹). [93,94] It is probably due to the embedded EFGO networks impede the phonon scattering through composites by the strong phonon-boundary scattering at interfaces between EFGO and matrix. [95] In addition, the thermal conductivity of PDC composites before pyrolysis, namely green bodies, is 0.1459±0.0428 W·m⁻¹·K⁻¹ at 25 °C. Therefore, the thermal conductivity increases from green bodies to pyrolyzed PDC composites. It is believed to be attributed to the formation of graphitic domains during pyrolysis processes.
Graphitic “free-carbon” domains have higher thermal conductivity than the SiOC matrix, based on the common estimation method for the thermal conductivity of amorphous mixtures which is the superimposition of different components, the overall thermal conductivity of composites increases with the formation of components which are more thermal conductive than the matrix. [96,97] In conclusion, the thermal conductivity of pyrolyzed composites keeps low and its increment after pyrolysis is dramatically less than that of electrical conductivity.

Conclusions

EFGO embedded PDC composites are successfully fabricated. SiOC polymeric precursor is infiltrated into EFGO attached PVA foams, and it is then cured and pyrolyzed to form composites. This facile method is suitable to prepared composites with different shapes because only the shaping of PVA foams into desired dimensions is needed. The introduction of EFGO networks greatly increases the electrical conductivity of PDC based composites, and it is resulted from (1) the effective pathways for the transport of electrons provided by embedded EFGO networks, and (2) the induced formation of conductive graphitic domains in PDC matrix nearby embedded EFGO networks. By only applying less than 2 wt% of EFGO, the electrical conductivity of composites is 0.95 S/cm at 25 °C and 1.8 S/cm at 600 °C. The times of electrical conductivity increment of PDC composites from room temperature to 600 °C is much lower than that of pyrolyzed SiOC polymeric precursor due to the percolation of embedded EFGO networks. Also, the increment of electrical conductivity from room temperature to 600 °C decreases when PDC composites are pyrolyzed at higher temperature. More abundant graphitic domains in SiOC matrix after pyrolysis performed at higher temperature lead to smaller energy needed for the transport of electrons from SiOC matrix to EFGO networks, and the increment of electrical conductivity thus decreases based on the classic
equation of semi-conductor electrical conductivity. Furthermore, the thermal conductivity of pyrolyzed PDC composites almost keeps the same at different testing temperatures and is quite low (<1 W·m⁻¹·K⁻¹). Such thermally stable materials with high electrical conductivity and low thermal conductivity have great potentials in applications such as thermal insulator, energy sources, and high temperature sensors. [98-100]

Supporting Materials

Figure 4-15. The particle size distribution of EFGO flakes from the DLS test.

Figure 4-16. FTIR spectrum of SILRES 62C precursor before (black line) and after (red line) curing process.
Figure 4-17. $^1$H NMR spectrum of SILRES 62C preceramic polymer. The peak at 1.56 ppm is from water impurities.

FTIR spectra of SILRES 62C precursor before and after curing in Figure 4-16 shows the chemical bond change during curing process. The FTIR spectrum of SILRES 62C precursor before curing (black line) shows the stretching vibrations of Si-O bonds ($1000-1150 \text{ cm}^{-1}$), Si-H bonds ($\approx 2100 \text{ cm}^{-1}$), C-O bonds ($\approx 1260 \text{ cm}^{-1}$), C-H bonds in alkanes ($2900-3000 \text{ cm}^{-1}$), C-H bonds in alkenes ($3000-3100 \text{ cm}^{-1}$), and aromatic C-H bonds ($\approx 1700 \text{ cm}^{-1}$), as well as the bending vibrations of alkyl C-H bonds ($\approx 1500 \text{ cm}^{-1}$). For cured SILRES 62C precursor (red line), the absence of stretching vibrations of Si-H bonds at around 2100 cm$^{-1}$ is observed, and it is due to the hydrosilylation reactions

$$R-Si-H + H_2C = CH-Si-R' \xrightarrow{\text{heat}} R-Si-H_2C-CH_2-Si-R'$$

happened during cross-linking process. [101-103] In another aspect, the $^1$HNMR spectrum shown in Figure 4-17 reveals the chemical composition of the liquid SiCO precursor. The broad peak from -0.3 ppm to 0.5 ppm is the resonance of H in Si-CH$_3$, Si-CH$_2$, the peak at around 1.1ppm corresponds to the resonance of H in Si-CH, the broad peaks at around 4.8 ppm and 3.8 ppm are attributed to the resonance of H in vinyl groups, the broad peak at around 5.9 ppm is from the resonance of H in aromatic Si-H, and the broad peak at 7-8 ppm is assigned to the resonance of H in aromatic C-H. [104-108]
Figure 4-18. The SEM image of bare PVA foams.

Figure 4-19. SEM images of the surface of PDC composites pyrolyzed at (a) 300 °C, (b) 400 °C, (c) 500 °C, (d) 600 °C, (e) 700 °C, (f) 800 °C, (g) 900 °C, and (h) 1000 °C. Scale bars are 50 µm.
Figure 4-20. SEM images of PDC composites pyrolyzed at (a) 300 °C, (b) 400 °C, (c) 500 °C, and (d) 600 °C without Au/Pd sputter coating.

Figure 4-21. Linear shrinkage of PDC composites after pyrolysis at different temperatures.
Figure 4-22. EDS spectra of PDC composites pyrolyzed at (a) 300 °C, (b) 400 °C, (c) 500 °C, (d) 600 °C, (e) 700 °C, (f) 800 °C, (g) 900 °C, and (h) 1000 °C.

Figure 4-23. The SEM image of PDC composites treated in air at 500 °C.
Figure 4-24. Electrical conductivity comparison of different composites with same pyrolysis conditions at the testing temperature from 25 °C to 600 °C. Composites are pyrolyzed at (a) 700 °C, (b) 800 °C, (c) 900 °C, and (d) 1000 °C, respectively.

Figure 4-25. Electrical conductivity of (a) EFGO/SILRES 62C/PVA, (b) EFGO/SILRES 62C, and (c) SILRES 62C pyrolyzed at different temperatures. The testing temperature range is from 25 °C to 600 °C.
Figure 4-26. Specific heat capacity of (a) green bodies and (b) 1000 °C pyrolyzed PDC composites at different temperatures.

Table 4-3. Summary of pyrolysis processes details.

<table>
<thead>
<tr>
<th>Final Pyrolysis Temperature of Samples (°C)</th>
<th>Halting Temperature 1 (°C)</th>
<th>Halting Temperature 2 (°C)</th>
<th>Halting Temperature 3 (°C)</th>
<th>Halting Temperature 4 (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>300</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>400</td>
<td>300</td>
<td>400</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>500</td>
<td>300</td>
<td>400</td>
<td>500</td>
<td>N/A</td>
</tr>
<tr>
<td>600</td>
<td>300</td>
<td>400</td>
<td>600</td>
<td>N/A</td>
</tr>
<tr>
<td>700</td>
<td>300</td>
<td>400</td>
<td>600</td>
<td>700</td>
</tr>
<tr>
<td>800</td>
<td>300</td>
<td>400</td>
<td>600</td>
<td>800</td>
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<tr>
<td>900</td>
<td>300</td>
<td>400</td>
<td>600</td>
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<tr>
<td>1000</td>
<td>300</td>
<td>400</td>
<td>600</td>
<td>1000</td>
</tr>
</tbody>
</table>
Table 4-4. Normalized Mass change of ceramic composites in preparation processes.

<table>
<thead>
<tr>
<th>Batch Number</th>
<th>PVA Foam (g)</th>
<th>After EFGO infiltration (g)</th>
<th>After SILRES 62C infiltration (g)</th>
<th>After pyrolysis at 1000°C (g)</th>
<th>EFGO in PDC after Pyrolysis at 1000°C (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>26.19</td>
<td>27.63</td>
<td>160.78</td>
<td>100</td>
<td>1.44</td>
</tr>
<tr>
<td>2</td>
<td>27.59</td>
<td>29.17</td>
<td>161.96</td>
<td>100</td>
<td>1.58</td>
</tr>
<tr>
<td>3</td>
<td>25.57</td>
<td>27.07</td>
<td>161.41</td>
<td>100</td>
<td>1.50</td>
</tr>
<tr>
<td>4</td>
<td>26.72</td>
<td>28.45</td>
<td>161.57</td>
<td>100</td>
<td>1.73</td>
</tr>
<tr>
<td>5</td>
<td>27.09</td>
<td>28.63</td>
<td>160.97</td>
<td>100</td>
<td>1.55</td>
</tr>
<tr>
<td>6</td>
<td>26.41</td>
<td>28.29</td>
<td>161.20</td>
<td>100</td>
<td>1.89</td>
</tr>
<tr>
<td>7</td>
<td>26.36</td>
<td>28.25</td>
<td>163.74</td>
<td>100</td>
<td>1.90</td>
</tr>
<tr>
<td>8</td>
<td>26.60</td>
<td>28.17</td>
<td>161.97</td>
<td>100</td>
<td>1.56</td>
</tr>
<tr>
<td>9</td>
<td>26.37</td>
<td>27.73</td>
<td>161.33</td>
<td>100</td>
<td>1.37</td>
</tr>
<tr>
<td>10</td>
<td>26.76</td>
<td>28.25</td>
<td>161.34</td>
<td>100</td>
<td>1.49</td>
</tr>
<tr>
<td>Average</td>
<td>26.57</td>
<td>28.17</td>
<td>161.63</td>
<td>100</td>
<td>1.60</td>
</tr>
</tbody>
</table>

Table 4-5. Density of Pyrolyzed SiCO PDCs.

<table>
<thead>
<tr>
<th>Pyrolysis Temperature (°C)</th>
<th>Density of SiCO PDCs (g/cm³)</th>
<th>Average Density of SiCO PDCs (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>1.762</td>
<td>1.768</td>
</tr>
<tr>
<td></td>
<td>1.775</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.769</td>
<td></td>
</tr>
</tbody>
</table>
Table 4-6. Density of Composites pyrolyzed at different temperatures.

<table>
<thead>
<tr>
<th>Pyrolysis Temperature (°C)</th>
<th>Density of Composites (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>1.22</td>
</tr>
<tr>
<td>400</td>
<td>1.24</td>
</tr>
<tr>
<td>500</td>
<td>1.28</td>
</tr>
<tr>
<td>600</td>
<td>1.32</td>
</tr>
<tr>
<td>700</td>
<td>1.52</td>
</tr>
<tr>
<td>800</td>
<td>1.65</td>
</tr>
<tr>
<td>900</td>
<td>1.73</td>
</tr>
<tr>
<td>1000</td>
<td>1.76</td>
</tr>
</tbody>
</table>

Table 4-7. G peak positions of composites pyrolyzed composites.

<table>
<thead>
<tr>
<th>Pyrolysis Temperature (°C)</th>
<th>G Peak Position of Pyrolyzed Composites (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>EFGO/SILRES 62C/PVA</td>
</tr>
<tr>
<td>700</td>
<td>1586.4</td>
</tr>
<tr>
<td>800</td>
<td>1593.7</td>
</tr>
<tr>
<td>900</td>
<td>1601.5</td>
</tr>
<tr>
<td>1000</td>
<td>1614.7</td>
</tr>
<tr>
<td>Blue Shift</td>
<td>28.3</td>
</tr>
</tbody>
</table>
Table 4-8. Values of electrical conductivity increment from different pyrolyzed composites.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Pyrolysis Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>600</td>
</tr>
<tr>
<td>Pure SILRES</td>
<td>N/A</td>
</tr>
<tr>
<td>2%EFGO in SILRES</td>
<td>N/A</td>
</tr>
<tr>
<td>SILRES/EFGO/PVA</td>
<td>5.4</td>
</tr>
</tbody>
</table>

Table 4-9. Young’s modulus of EFGO/SILRES 62C/PVA composites pyrolyzed at 1000 °C.

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Young's Modulus (Mpa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>205.2</td>
</tr>
<tr>
<td>2</td>
<td>234.8</td>
</tr>
<tr>
<td>3</td>
<td>198.6</td>
</tr>
<tr>
<td>4</td>
<td>224.9</td>
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<tr>
<td>5</td>
<td>203.5</td>
</tr>
<tr>
<td>Average</td>
<td>213.4</td>
</tr>
<tr>
<td>Standard Deviation</td>
<td>15.6</td>
</tr>
</tbody>
</table>

Calculations of PDC composites (EFGO/SILRES 62C/PVA composites) electrical conductivity at room temperature by applying different models for the electrical conductivity of composites.

Consider SILRES 62C pyrolyzed at 1000 °C and embedded EFGO networks as two phases in pyrolyzed composites. The volume fraction of EFGO is 1.4-1.9%, so the volume fraction of SILRES 62C matrix is 98.1-98.6%. The electrical conductivity of EFGO and pyrolyzed SILRES
62C (SiOC matrix) at room temperature are \(\sim 10\ \text{S/cm}\) and \(1.8 \times 10^{-5}\ \text{S/cm}\), respectively. Effective electrical conductivity is denoted as \(\sigma_{\text{eff}}\), electrical conductivity of components in composites is denoted as \(\sigma_i\), and volume fraction of components in composites is denoted as \(X_i\).

Alternating parallel layers. [84]

EFGO networks arrange parallel to applied external current flow.

\[
\sigma_{\text{eff}} = \sum_{i=0}^{n} X_i \sigma_i = X_{\text{EFGO}} \sigma_{\text{EFGO}} + X_{\text{matrix}} \sigma_{\text{matrix}} \tag{4-1}
\]

So, the effective electrical conductivity of composites is between 0.14 S/cm to 0.19 S/cm by applying this model.

EFGO networks arrange axially to external current flow.

\[
\frac{1}{\sigma_{\text{eff}}} = \sum_{i=0}^{n} \frac{X_i}{\sigma_i} = \frac{X_{\text{EFGO}}}{\sigma_{\text{EFGO}}} + \frac{X_{\text{matrix}}}{\sigma_{\text{matrix}}} \tag{4-2}
\]

So, the effective electrical conductivity of composites is between \(1.81 \times 10^{-5}\ \text{S/cm}\) to \(1.83 \times 10^{-5}\ \text{S/cm}\) by applying this model.

Effective conductivity of the random model. [83]

\[
\sigma_{\text{eff}} = \prod_{i=1}^{n} \sigma_i^X_i = \sigma_{\text{EFGO}} X_{\text{EFGO}} \times \sigma_{\text{matrix}}^X_{\text{matrix}} \tag{4-3}
\]

So, the effective electrical conductivity of composites is between \(2.17 \times 10^{-5}\ \text{S/cm}\) to \(2.31 \times 10^{-5}\ \text{S/cm}\) by applying this model.
Effective conductivity of mixed media. [86] Because the equation is symmetric, consider EFGO as phase 1 and SiOC matrix as phase 2.

\[
\sigma_{\text{eff}} = \frac{1}{4} \left[ (3X_1 - 1)\sigma_1 + (3X_2 - 1)\sigma_2 + \sqrt{((3X_1 - 1)\sigma_1 + (3X_2 - 1)\sigma_2)^2 + 8\sigma_1\sigma_2} \right] \tag{4-4}
\]

So, the effective electrical conductivity of composites is between \(1.84 \times 10^{-5}\) S/cm to \(1.86 \times 10^{-5}\) S/cm by applying this model.

Archies’s law. [85] \(m\) and \(p\) is connectivity exponents. Larger value of connectivity exponent corresponds to less effective connectivity. In usual cases, the phase with more volume fraction phase has \(0 < m < 1\) (SiOC matrix), and the phase with less volume fraction has \(1 < p < 2.5\) (EFGO).

\[
\sigma_{\text{eff}} = \sigma_1 X_1^m + \sigma_2 X_2^p \tag{4-5}
\]

So, the effective electrical conductivity of composites is between \(2.5 \times 10^{-4}\) S/cm to \(0.19\) S/cm by applying this model.

![Image of fabrication process](image)

Figure 4-27. Fabrication of ceramic composites, from starting materials to final products.
Figure 4-28. Use a PDC composite pyrolyzed at 1000 °C to light up four white LED diodes with an output of 9 V. A propane gun is used to heat up the composite. The dimension of the composite is 5 mm×5 mm×40 mm.

References


CHAPTER 5: CRYSTALLIZATION OF P3HT ON GRAPHITIC SUBSTRATES WITH DIFFERENT CURVATURES

Introduction

Solution processed organic devices are of great interest for their potential applications in low cost electronics, optoelectronics and clean energy harvest because of their ease of processing, cost effective fabrication, light weight, flexibility, ability to cover large areas as well as their potential of constructing desired device using rationally designed molecules. [1-3] Conjugated polymers (CPs), containing conjugated chains with π-electrons delocalized along the polymer backbones, have numerous potential applications in solution processed organic electronics such as organic field-effect transistors (OFETs), [4-11] molecular electronics [12-14] and bulk heterojunction organic photovoltaics (BHJ-OPVs). [15-30] The performance of CP based organic electronic devices is determined by two factors: the morphology of CPs and the interface between CPs and electrodes due to the anisotropic charge transport characteristics in these devices. The charge transport pathways in polycrystalline CP films include fast interchain and intrachain transport within crystals and slow inter-grain transport among CP crystals. [31] A recent study of the relationship between the disorder, aggregation and charge transport of CP films suggests that the inter-grain charge transport is the rate determining step for charge transport. The key to improve the charge transport is eliminating the grain boundary. [32] The understanding of charge transport mechanisms in CPs leads to much effort in producing CP crystals with controlled orientation and improving the active material/electrode interfacial properties. [33-39] Regioregular poly(3-hexyl thiophene) (P3HT) is one of the most extensively studied CPs due to its high charge mobility and tendency to assemble into crystals (i.e. nanowires and nanoribbons). [34-37,40-47] The research
has been focused on the formation of P3HT crystals in solutions and on substrates include carbon nanotubes [8,37,40,48], graphene [49] and derivatives [50-54], and polymer assemblies. [55,56] The most reported P3HT superamolecular assemblies are nanowires, which are formed by π-π interaction among polymer backbones. [44-47,54,57-60] The investigation of P3HT crystallization process in solutions by changing molecular weight (Mn), crystallization temperature and polymer concentration suggested that P3HT polymer chains transit from extending to folding in nanowhiskers when the Mn is above a critical value (10 kDa). The folding length can be controlled by crystallization temperature, and extended P3HT chains can further grow into highly ordered two-dimensional (2D) nanoribbons by the combination of π-π interaction among polymer backbones and alkyl side chain Van der Waals interactions. [34]

CNTs and graphene have been used as electrodes in organic electronic devices in OFETs and for replacing indium tin oxide (ITO) transparent OFETs. [61] CNT electrodes are known to have superior charge injection than metal electrodes in OFETs.[62-66] Graphene has extraordinary room-temperature carrier mobility (20000 cm²/Vs), [67-72] conductivity, and high optical transmittance (97.7 % at 550 nm), making it a viable candidate for electrodes π-bonded surfaces CNTs and graphene are ideal for guiding the assembly of CPs to improve charge transport and providing optimum CP/electrode interfaces for efficient charge injection. The π-π intermolecular interactions between graphitic surfaces (i.e. CNT and graphene) and CPs such as poly(3-hexylthiophene) (P3HT) have been used to guide the growth of CP supramolecular assemblies (i.e. nanowires) on graphitic surfaces, [35,40,49] and fabricate efficient organicelectronics with optimized CP assembly orientation and CP assembly/electrode interfacial contact.
Here in, we report the formation of P3HT nanocrystals on graphitic substrates with different curvatures (i.e. SWCNTs, MWCNTs, carbon fibers, and graphene). P3HT with $M_n$ below and above the folding threshold were used in this study to investigate the assembly of P3HT from graphitic surfaces. Computational simulations of single P3HT molecule on carbon materials were used to justify the preferential orientation of P3HT nanocrystals on graphitic surfaces.

![Figure 5-1](image)

Figure 5-1. Schematic illustrations of (a) nanowire crystals formation from extended P3HT chains, (b) nanowire crystals formation from folded P3HT chains, and (c) nanoribbon crystals formation from extended P3HT chains.

**Materials**

Poly(3-hexylthiophene) (P3HT) molecules with vinyl end groups were synthesized in our lab using a procedure which has been previously reported. [73] P3HT molecules with different molecular weight were synthesized by using different polymerization time, and their molecular weight was determined by Gel permeation chromatography (GPC). P3HT with molecular weight larger than
the chain folding threshold was denoted as “LM-P3HT” \( (M_n=13.8 \text{ kDa}, \text{PDI}=1.51) \), and P3HT with molecular weight smaller than the chain folding threshold was denoted as “SM-P3HT” \( (M_n=4.8 \text{ kDa}, \text{PDI}=1.70) \).

Graphene flakes were synthesized by a chemical vapor deposition (CVD) method similar to previous reports. [74-76] Mixed gases of hydrogen and methane were reacted at 1000 °C, and graphene flakes were formed on copper foils. After etching copper foils by the iron nitrate aqueous solution, graphene flakes were transferred onto desired substrates (TEM grids and QCM probes) by a wet transfer process.

Single-walled carbon nanotubes (SWCNTs) with 1.5 nm diameters and Multi-walled carbon nanotubes (MWCNTs) with 10-20 nm diameters were purchased from NanoLab Inc. Carbon fibers (CFs) with 160-180 nm diameters were purchased from Sigma Aldrich. Highly Ordered Pyrolytic Graphic (HOPG) and silicon wafers were purchased from SPI. Anisole (HPLC grade) and dimethylformamide (DMF) (HPLC grade) were purchased from Fisher. Hydrogen and Methane were purchased from Air Liquide. All materials were used as received without further purifications.

**Experimental Procedures**

For crystallizations of P3HT on SWCNTs, MWCNTs and CFs, these graphitic carbon materials were added into 95 °C P3HT marginal solutions with required mass. After that, mixtures contained graphitic carbon materials and P3HT were sonicated for 30 minutes by a horn sonifier, and uniform bright yellow dispersions were formed after sonications. Dispersions were then heated back to 95 °C, and the crystallizations of P3HT on graphitic substrates were started by cooling down the P3HT/graphitic carbon materials dispersions. After several hours (usually 6 hours) of
crystallizations, dispersions were drop-casted onto carbon film supported TEM grids for TEM study and were drop-casted onto silicon wafers for characterizations of SEM and AFM.

For crystallizations of P3HT on graphene, TEM grids coated with graphene and exfoliated HOPG flakes on silicon wafers were used as substrates. In crystallization processes, TEM grids or silicon wafers were vertically immersed into 95 °C P3HT marginal solutions. Marginal solutions were cooled down in ambient atmosphere to induce crystallizations of P3HT on graphene. After crystallizations, TEM grids and silicon wafers were directly dried for further characterizations.

In all crystallization processes conducted in this paper, the marginal solvent for LM-P3HT crystallization is anisole, and the marginal solvent for SM-P3HT crystallization is the mixed solvent of anisole and DMF with a volume ratio of 2:1.

In the study on crystallization kinetics, 0.05 mg/mL LM-P3HT solutions in anisole at 95 °C were mixed with SWCNTs, MWCNTs, and CFs, respectively. In these mixtures, a mass ratio of 10:1 between LM-P3HT and graphitic carbon materials was applied in all trials. Consequently, the concentration of P3HT and graphitic carbon materials in each dispersion were 0.05 mg/mL and 0.005 mg/mL, respectively. Mixtures were sonicated by a horn sonifier for 30 minutes to form uniform dispersions, and then they were heated back to 95 °C. Dispersions at 95 °C were transferred to quartz cuvettes for UV-Vis spectroscopy study. Quartz cuvettes were placed in the sample chamber at room temperature (20 °C), and UV-Vis spectra at different crystallization time were obtained from a UV-Vis spectrometer.

In the study for SM-P3HT, Details of the crystallization study of SM-P3HT are the same as those of LM-P3HT except a marginal solvent of anisole: DMF= 2:1 (v: v) was applied in this series of
experiments. The concentration of graphitic substrates in dispersions is 0.005 mg/mL, and the concentration of SM-P3HT is 0.05 mg/mL.

In the Quartz Crystal Microbalance (QCM) study, QCM probes coated with graphene were used. Graphene flakes on the QCM probes have a dimension of 1 cm×1 cm. The probe was vertically immersed into a 100 mL 0.05 mg/mL LM-P3HT or SM-P3HT marginal solution at 95 °C, and the point of immersion was considered as the time to start crystallization processes. The deposited mass of P3HT on graphene during crystallization processes was recorded by the built-in microbalance.

Characterizations

The number-average molecular weight ($M_n$) and polydispersity index (PDI) of P3HT were determined by gel permeation chromatography (GPC) using a JASCO LC2000 HPLC system. Polystyrene was used as standards, and tetrahydrofuran was used as the eluent. TEM images and the corresponding selected area electron diffraction (SAED) patterns were obtained on a JEOL 1011 electron microscopy operated at 100 kV. SEM images were got from a ZEISS ULTRA55 scanning electron microscope. AFM images were acquired from a Veeco Dimension 3100 scanning probe microscope in tapping mode. UV-Vis spectra were recorded on a Varian 300 Bio UV-Visible spectrophotometer. Raman Spectroscopy was conducted on a Raman confocal spectroscopy (Witec Alpha300RA) spectrometer system. The deposited mass of P3HT on graphene was monitored by a Matrex Quartz Crystal Microbalance (QCM) probe coated with a 1 cm×1 cm graphene film.
Results and Discussion

Crystallization of LM-P3HT on Graphitic Substrates

Figure 5-2. TEM images of LM-P3HT crystallized on (a) SWCNTs, (b) MWCNTs, (c) CFs, and (d) graphene from 0.05 mg/mL marginal solutions. Scale bars are 250 nm.

For LM-P3HTs with Mₙ>10 kDa, their molecular chains are folded. [34] It has been reported that LM-P3HT form nanowires from the surface of graphitic substrates such as SWCNTs and MWCNTs. [40,77] P3HT nanowires with widths of 14 nm are found on surfaces of these graphitic
substrates, and the width is almost identical to that of nanowires crystallized from marginal solutions without graphitic substrates. Here in, it is not surprising to see P3HT nanowires with similar widths grown from the surface of CFs (Figure 5-2c) and graphene (Figure 5-2d). The assembly of LM-P3HT molecules can only be from $\pi-\pi$ stacking among thiophene rings in their backbones, and it is the reason for the only formation of nanowire crystals from LM-P3HT.

The orientation of LM-P3HT nanowires grown from surfaces of graphitic substrates is also explored. It has been reported that P3HT molecules tend to interact coaxially with the surface of SWCNTs and MWCNTs to get a conformation with the lowest energy. [77] For the formation of P3HT nanowires on CFs, the overlapping of P3HT nanowires at different height positions is observed in the AFM image (Figure 5-25). Such results reveal the formation of P3HT nanowires on different area of CFs and thus indicates their random radial orientations on CFs. The crystallization of LM-P3HT on graphene leads to randomly oriented nanowires, and it is because of the minimal curvature of graphene that grants LM-P3HT molecules with the freedom in arrangement orientations on the nearly flat graphene surface. Schematic illustrations of LM-P3HT nanowires grown from different graphitic substrates are presented in Figure 5-3.

![Figure 5-3. Schematic illustrations of nanowires formation from LM-P3HT on graphitic substrates of (a) CNTs, (b) CFs, and (c) graphene.](image-url)
P3HT molecules with Mₙ<10 kDa have extended molecular chains. Previous report has addressed the formation of nanoribbon crystals from SM-P3HT in marginal solutions. [34] Here in, the crystallization behavior of it on graphitic substrates is explored.

For the crystallization of SM-P3HT on SWCNTs, it is intriguing that no nanoribbons are observed from the surface of SWCNTs even by applying SM-P3HT marginal solution with the concentration (0.3mg/mL) higher than the threshold (0.2 mg/mL) for SM-P3HT nanoribbons formation. Only Nanowires with widths of around 7-8 nm are observed from Figure 5-4a, and the widths of nanowires are in agreement with the length of SM-P3HT backbones with Mₙ= 4.8 kDa. Besides, the SAED signal from P3HT nanowires is shown in Figure 5-4b. The spacing in the SAED image is the reciprocal of the spacing in the real world. The ring with the spacing of 2.56 \( \frac{1}{nm} \) in the SAED image is corresponding to the spacing of 3.9 Å (010) in P3HT nanowires crystals. The spacing of 3.9 Å verifies the formation of nanowire crystals because it reflects the distance between two adjacent P3HT molecules interacted by π-π stacking. Based on our previous studies using Molecular Dynamics (MD) simulations, P3HT chains are found attached along the axis of SWCNTs with alkyl chains wrapping around the carbon nanotube to achieve minimal interaction energy. [77] Here, additional simulations about P3HT oligomer arrangements on different types of SWCNTs, namely chiral (9, 0), armchair (8, 8) and zigzag (13, 0) are operated. Results in Table 5-3 suggest that the coaxial wrapping of P3HT is favored on surfaces of all types of SWCNTs because of the large negative interaction energy. With such coaxial arrangement on SWCNTs, the growth of P3HT nanocrystals from alkyl side chain interactions among extended P3HT chains is
inhibited. It is attributed to the huge curvature of SWCNTs surface which leads to the incapability of providing ground to support P3HT chains interacted by alkyl side chains. Therefore, the growth of P3HT nanocrystals can only be from the $\pi$-$\pi$ stacking among thiophene rings in P3HT backbones. In consequence, only nanowires can be formed with a confined orientation coaxial to SWCNTs (Figure 5-5), and the formation of nanoribbons on SWCNTs is unavailable.

Figure 5-4. (a) The TEM image of SM-P3HT crystallized from SWCNTs by using a 0.30 mg/mL-P3HT marginal solution. (b) The SAED pattern of nanowires in (a).

Figure 5-5. The schematic illustration of a SM-P3HT nanowire grown coaxially from SWCNTs.
Different from the crystallization of SM-P3HT on the surface of SWCNTs, the formation of nanoribbons is observed from the surface of MWCNTs. P3HT crystals grown from the surface of MWCNTs by using SM-P3HT molecules are shown in Figure 5-6. In this study, the concentration of SM-P3HT is 0.3 mg/mL. In Figure 5-6a, P3HT nanoribbons with widths of 70-120 nm and lengths of 50-150 nm are observed from the surface of MWCNTs. SAED rings regarding the spacing of 16.6 Å (100) and 3.9 Å (010) in crystals are seen from the SAED image (Figure 5-6b) by getting reciprocals of the spacing shown in the SAED image. 16.6 Å and 3.9 Å are in accordance with distances of two adjacent P3HT chains interacted by alkyl side chains and π–π stacking, respectively. Thus, the formation of nanoribbon crystals on MWCNTs is verified. The assembly of SM-P3HT nanoribbons on MWCNTs is schematically illustrated in Figure 5-7 based on results from TEM and SAED images. P3HT nanoribbons grown from the surface of MWCNTs have the orientation that backbones of SM-P3HT within nanoribbons arrange perpendicular to the axis of MWCNTs. To verify the availability of this arrangement of SM-P3HT on MWCNTs, Molecular Dynamics (MD) simulation regarding the interactions between P3HT chains and MWCNTs is performed. The length of P3HT chain used in this simulation is much smaller than the diameter of MWCNTs. According to the values of interaction energy shown in Table 5-4, P3HT molecules can take different orientations such as parallel (0°), perpendicular (90°) and have an angle of 30° to the axis of MWCNTs with minimal energy differences in this scenario. In consequence, not only the arrangement of SM-P3HT with backbones parallel to the axis of MWCNTs is available, but also arrangements with other orientations are eligible. When P3HT backbones arrange perpendicular to the axis of MWCNTs, the surface of MWCNTs can provide the ground to support follow-up P3HT chains interacted by Van de Waals alkyl side chain interactions, and the arrangement of P3HT chains by this interaction extends along the axis of MWCNTs. Besides,
P3HT molecules on MWCNTs can surely interact with follow-up P3HT molecules by $\pi$-$\pi$ stacking to have the vertical growth from MWCNTs surface. Therefore, P3HT nanoribbons are formed by both $\pi$-$\pi$ stacking and alkyl side chain interactions among SM-P3HT molecules. However, if P3HT chains attach on the surface of MWCNTs with other orientations, no ground will be given by MWCNTs to support the extension from follow-up P3HT molecules interacted by their alkyl side chains due to the heavily curved surface of MWCNTs. As a result, SM-P3HT can only form nanoribbons on the surface of MWCNTs with a confined orientation. Furthermore, it needs to be mentioned that nanoribbons grown from MWCNTs are only able to be realized by using a slow cooling rate (15 °C/hour). P3HT nanoribbons prefer to be formed in the solution (Figure 5-27) instead of the surface of MWCNTs if rapid cooling processes are applied. Additionally, no nanowires on MWCNTs are observed in crystallizations using rapid cooling. It is probably attributed to the additional alkyl side chain interactions among P3HT molecules in P3HT nanoribbons which reduce the total entropy by assembling more ordered P3HT crystals. Thus, the formation of P3HT nanoribbons in the solution is more favored than the formation of P3HT nanowires on MWCNTs in crystallizations applying rapid cooling.

Figure 5-6. (a) The TEM image of SM-P3HT crystallized on MWCNTs to form nanoribbons from a 0.30 mg/mL marginal solution. (b) The SAED pattern of nanoribbons in (a).
Figure 5-7. The Schematic illustration of SM-P3HT nanoribbons grown from MWCNTs with a confined orientation.

Figure 5-8. The AFM image of P3HT nanoribbons grown from MWCNTs. The scanning area is 2 µm×2 µm.

Figure 5-8. The AFM image of P3HT nanoribbons grown from MWCNTs. The scanning area is 2 µm×2 µm.
The typical AFM image of nanoribbons composed of SM-P3HT on MWCNTs is shown in Figure 5-8. P3HT nanoribbons grown from the surface of MWCNTs can be clearly seen in this image. The height profile of the section line shows the thickness of nanoribbons to be 7.5 nm, and it is almost identical to the length of the unfolded SM-P3HT backbone. Therefore, nanoribbons composed of one layer of SM-P3HT are grown from the surface of MWCNTs. In addition, widths and lengths of P3HT nanoribbons observed from the AFM image are in accordance with the results from the TEM image.

For the crystallization of SM-P3HT on CFs, nanoribbons with lengths of 150-300 nm are observed (Figure 5-9a) from the surface of CFs, and the SAED pattern of nanoribbons is shown Figure 5-9b. SAED rings regarding the spacing of 16.8 Å (100) and 3.9 Å (010) in crystals are obtained by getting reciprocals of the spacing shown in the SAED image. 16.8 Å and 3.9 Å reflect the distance of two adjacent P3HT chains interacted by side alkyl chains and P3HT π–π stacking, respectively. Therefore, the crystallinity of P3HT nanoribbons formed on CFs is verified.

Figure 5-9. (a) The TEM image of SM-P3HT crystallized on CFs from a 0.30 mg/mL marginal solution. (b) The SAED pattern of nanoribbons in (a).
To investigate the orientation of nanoribbons on CFs, P3HT nanocrystals grown from CFs are characterized by SEM and AFM. The SEM image of SM-P3HT nanoribbons grown from CFs is shown in Figure 5-10a. P3HT nanoribbons are vertically grown from the surface of CFs in different regions, so they have different radial orientations. Also, they have different orientations respect to the longitude axis of CFs, which can be clearly seen from the image. AFM imaging are further applied to reveal detailed information regarding the arrangement of P3HT nanoribbons on CFs. As shown in the 3D image generated from AFM imaging (Figure 5-10b), P3HT nanoribbons with different orientations to the longitude axis of CFs are clearly seen. their planes can be (I) perpendicular, (II) parallel or (III) non-parallel to the longitude axis of CFs as labeled in Figure 5-10b. By analyzing the height profiles of several section lines, the thickness of about 100-150 nm and the lengths of about 300 nm are found (Figure 5-28). The thickness of P3HT nanoribbons formed on CFs (~100 nm) is much larger than the thickness of single layer SM-P3HT nanoribbons formed on MWCNTs (7.5 nm), thus it indicates multi-layers of P3HT are stacked in one P3HT nanoribbons crystal. The arrangement of SM-P3HT ribbons on CFs is schematically shown in Figure 5-11. P3HT nanoribbons are grown from CFs with random radial orientations as well as different angles respect to the longitude axis of CFs.

Figure 5-10. (a) The SEM image of SM-P3HT crystallized on CFs, the scale bar is 1µm. (b) The 3D image of SM-P3HT crystallized on CFs generated from AFM data (2 µm×2 µm).
Localized Raman spectroscopy is used to verify nanocrystals on CFs are from P3HT. The optical image in the inset of Figure 5-12 is a CF wrapped by crystalized SM-P3HT, and the Raman spectrum of the red circled area on is shown in Figure 5-12. Signature Raman peaks of P3HT at 1369.6 cm\(^{-1}\) and 1451.2 cm\(^{-1}\) are seen from the spectrum, and they are characteristic peaks to the C=C (in thiophene rings) skeletal stretching vibration and the C–C (in thiophene rings) skeletal stretching vibration, \cite{78} respectively. Thus, the existence of P3HT on CFs is verified. Also, the redshift (12 cm\(^{-1}\)) of the peak regarding the stretching in thiophene rings from 1381.6 cm\(^{-1}\) (SM-P3HT powders) to 1369.6 cm\(^{-1}\) (SM-P3HT nanocrystals on CF) is obtained by the comparison between Figure 5-30 and Figure 5-12. It indicates the increase of conjugation length from the formation of ordered P3HT nanoribbon crystals on CFs. \cite{79-82}
Figure 5-12. The Raman spectrum of crystallized SM-P3HT on CFs surface. The optical image of crystallized SM-P3HTT on CFs is in the inset, and the red circled area is investigated by Raman spectroscopy.

At last, the crystallization of SM-P3HT on graphene is explored. TEM images of P3HT grown from graphene by using 0.30 mg/mL SM-P3HT in marginal solvents are shown in Figure 5-13a. P3HT nanoribbons are seen on the TEM image with widths of between 40-70 nm and lengths between 40-110 nm. In Figure 5-13b, strong SAED ring corresponding to the spacing of 16.7 Å (100) from alkyl side chain interactions and the weak SAED ring corresponding to the spacing of 3.9 Å (010) from $\pi$-$\pi$ stacking can be obtained by getting reciprocals of spacing shown in the SAED image. The results from SAED images suggest P3HT “nanowalls” grow vertically from the surface of graphene, and they are composed of P3HT nanoribbons with random orientations in the graphene plane. When P3HT nanowalls grow vertically from the surface of graphene, the SAED pattern with spacing of 3.9 Å from $\pi$-$\pi$ stacking cannot be seen from them. Therefore, the as seen SAED ring corresponding to the spacing of 3.9 Å from $\pi$-$\pi$ stacking is attributed to be fell-down
P3HT nanoribbons in the TEM image. When the vertical growth of P3HT is too fast in some regions, nanowalls fall down because of their large aspect ratio. They inhibit the further vertical growth of nanowalls on graphene and become the top layer of P3HT crystallized from graphene surface. Besides, circled 6-fold patterns from graphene substrates in the SAED image (Figure 5-13b) is consistent with a hexagonal lattice and indicates the high degree of crystallinity of graphene substrates. [83-86] The AFM image after the SM-P3HT crystallization on graphene surface is presented in Figure 5-15. The fell down nanowalls have the thickness of around 50-100 nm, and it indicates these nanowalls are composed of multi-layer nanoribbons from SM-P3HT molecules. From the discussion above, SM-P3HT nanowalls crystallized on graphitic substrates by using SM-P3HT are illustrated in Figure 5-14. Nanowalls grow vertically from the surface of graphene with random orientations in the plane of graphene surface.

Figure 5-13. (a) The TEM image of SM-P3HT crystallized on the surface graphene. Fell-down nanowalls are pointed out by arrows. (b) The SAED pattern of nanowalls in (a). Two sets of six-fold SAED patterns from the graphene substrate are circled in red and blue.
Figure 5-14. The illustration of SM-P3HT nanowalls grown vertically from graphene surface (top view) with random orientations in the plane of graphene surface.

Figure 5-15. The AFM image of SM-P3HT crystallized on graphene and height profiles of two lines labeled as 1 and 2. The scanning area is 1 µm×1 µm.
The interactions between SM-P3HT and graphene was investigated by examining graphene surface, SM-P3HT, and SM-P3HT nanocrystals on graphene surface using Raman spectroscopy (Figure 5-29 to 5-31). The G peak from graphene redshifts 1 wavenumber from 1585.6 cm\(^{-1}\) to 1584.6 cm\(^{-1}\) after the growth of P3HT nanocrystals on its surface (Figure 5-31). The redshift of G peak is due to the interaction of electron donor with graphite. When graphene is contacting with an electron donor, the Fermi level of graphene increases, which leads to the decrease of the energy difference between the incident laser photons and the photons from Raman scattering, and G peak will have a redshift. [87,88] P3HT is a typical organic electron donor material, thus the interaction between P3HT and graphene surface is verified. In addition, the Raman shift regarding the peaks from P3HT is investigated. For the Raman peak around 1380 cm\(^{-1}\) which is assigned to the stretching vibration of C–C on thiophene rings, it redshifts 4.9 wavenumber from 1381.6 cm\(^{-1}\) to 1376.7 cm\(^{-1}\). The redshift indicates the increase of conjugation length which is believed to be attributed to the formation of P3HT nanowall crystals.

**Crystallization of SM-P3HT on Graphitic Substrates by Using Low Concentration Marginal Solutions**

Crystallization of SM-P3HT on graphitic surfaces by using solutions with concentration higher than the threshold of nanoribbons formation has been studied above. On the other hand, interesting phenomena are observed when solutions with concentration lower than the threshold of nanoribbons formation are applied. By using low concentration of SM-P3HT solutions, nanowires are formed from the surface of SWCNTs (Figure 5-32) and MWCNTs (Figure 5-33), and average length of nanowires increases with increasing concentration of SM-P3HT solutions used in crystallization processes. However, different kinds of nanocrystals are observed from the surface of CFs and graphene.
The results of SM-P3HT crystallization on CFs surface from low concentration marginal solutions are shown in Figure 5-16. Thin films are formed when the concentration of SM-P3HT is extremely low (0.03 mg/mL). Sparsely distributed nanoribbons are observed when the concentration of SM-P3HT increases to (0.05 mg/mL). In addition, the TEM image of SM-P3HT crystallized on graphene surface by applying a marginal solution with low concentration (0.05 mg/mL) is shown in Figure 5-34. Similar results are observed compared to applying high concentration of SM-P3HT marginal solutions (Figure 5-13).

Figure 5-16. TEM images of SM-P3HT crystallized on CFs from (a) 0.03 mg/mL, (b) 0.05 mg/mL marginal solutions. The thin film in (a) and nanoribbons in (b) are pointed by arrows.

It has been previously reported that SM-P3HT solutions with low concentrations leads to the formation of nanowires during crystallization processes without graphitic carbon substrates, [34] then why nanowires are formed on the surface of CNTs and SM-P3HT nanocrystals in other types are observed from the surface of CFs and graphene when applying low concentration marginal solutions? For the crystallization of SM-P3HT on CNTs by using low concentration marginal
solutions, one of the reason of not forming large 2D nanocrystals is the lack of molecules. However, the large curvature of CNTs graphitic substrates is believed to be the primary reason. When SM-P3HT molecules wrap on the surface of SWCNTs and MWCNTs by the interaction of alkyl side chains, the follow-up stacking of SM-P3HT molecules are unable to keep both interactions from π-π stacking and alkyl side chain integrations which are necessary to the formation of P3HT 2D structures. It is because large curvatures of CNTs will lead to significant distortions among follow-up stacked P3HT molecules arranged by alkyl side chain interactions. Such distortion increases with the stacking of more layers of P3HT molecules and will finally deassociates P3HT molecules interacted by alkyl side chains. As a result, no thin films composed of P3HT can be formed on surfaces of CNTs. For the crystallization of SM-P3HT on CFs, the much smaller curvature of CFs compared to CNTs leads to the capability of thin film formation due to much less distortion among P3HT interacted by alkyl side chains. However, when films become too thick, P3HT molecules interacted by alkyl side chains in the outer area will have the distortion large enough to dessociate these P3HT molecules and only the formation of nanoribbons in different regions can be realized. For the crystallization of SM-P3HT on graphene, the minimal curvature of the graphitic surface resulted in the formation of P3HT nanowalls by both π-π stackings and alkyl side chain interactions, and minimal distortion will exist within P3HT nanowalls ctystals. In some regions with faster vertical growth of SM-P3HT, nanowalls fall down and sparsely distributed on the top of P3HT crystals.

*Kinetic Study of LM-P3HT on Curved Graphitic Substrates*

In addition, in-situ UV-Vis spectroscopy studies are performed to investigate P3HT crystallizations on graphitic substrates with different curvatures. UV-Vis spectra during P3HT
crystallization processes are shown in Figure 5-26. The absorbance at around 455 nm decreases and the absorbance at around 600 nm increases during P3HT crystallization on SWCNTs, MWCNTs, and CFs. The absorbance with peak at 455 nm is assigned to individual P3HT molecules in the solution, and the absorption with peak at 600 nm is attributed to a combination of $\pi-\pi$ electronic transitions and strong lattice vibrations in P3HT crystalline domains. [89] Thus, the formation of P3HT nanowire crystals from individual P3HT molecules in verified. Besides, obvious isosbestic points at around 482 nm in these UV–Vis spectra suggest a direct transformation from dissolved individual P3HT molecules to ordered nanowires crystals on graphitic substrates. [90,91] The increment of UV-Vis absorbance at 600 nm during crystallization processes is plotted in Figure 5-17. The increment is calculated as subtracting the absorbance at 600 nm during crystallization processes by the absorbance at 600 nm before crystallization processes. It can be clearly seen from Figure 5-17 that the absorbance increment for three P3HT crystallization processes is MWCNTs>SWCNTs>CFs through the whole range of crystallization time. Therefore, the crystallization rate on graphitic substrates has the trend of MWCNTs>SWCNTs>CFs. Besides, the absorbance at 600 nm does not increase after 3 hours, 4 hours, and 8 hours for P3HT crystallizations on MWCNTs, SWCNTs, and CFs, respectively. Therefore, the crystallization completion time of P3HT on graphitic substrates are shorter that needed in the marginal solution (40 hours), [40] and graphitic substrates greatly accelerate P3HT crystallizations.
Figure 5-17. The absorbance change at 600nm for P3HT crystallization on SWCNTs (triangle), MWCNTs (square), and CFs (diamond) graphitic surfaces.

It is intriguing to find that the crystallization rate of P3HT on graphitic substrates have the trend of MWCNTs>SWCNTs>CFs. If the difference of total graphitic surface is the only parameter that affects the crystallization rate, the expected crystallization rate on graphitic substrates would be SWCNTs>MWCNTs>CFs. It is because the same concentration of graphitic substrates is applied in this series of experiments and their specific surface area has the trend of SWCNTs>MWCNTs>CFs from Table 5-1. However, this projected conclusion is different from the experimental results. Therefore, there must be other parameters that can affect P3HT crystallization rate on graphitic substrates.
Table 5-1. Curvature and specific surface area of different graphitic substrates. The diameter and specific surface area are from specifications given by manufacturers.

<table>
<thead>
<tr>
<th>Graphitic Substrates</th>
<th>Diameter (nm)</th>
<th>Curvature (nm(^{-1}))</th>
<th>Specific Surface Area (m(^2/g))</th>
</tr>
</thead>
<tbody>
<tr>
<td>SWCNT</td>
<td>1.5</td>
<td>0.67</td>
<td>1000</td>
</tr>
<tr>
<td>MWCNT</td>
<td>10-20</td>
<td>0.05-0.1</td>
<td>200-400</td>
</tr>
<tr>
<td>CF</td>
<td>160-180</td>
<td>0.005-0.006</td>
<td>13-15</td>
</tr>
</tbody>
</table>

Because curvature is the major structural difference among those graphitic substrates, it is assumed as a vital parameter to P3HT crystallizations. The attached mass of P3HT on unit area graphitic substrates during crystallization processes is shown in Figure 5-18. The attached mass of P3HT on unit area of graphitic substrates is calculated as follows. The increment of absorbance at 600nm is divided by the absorbance at 455 nm before crystallization, then the value is multiplied by the concentration and the volume of marginal solution to get the total mass of attached P3HT. Attached mass of P3HT per unit area of graphitic substrates is obtained after dividing the total attached mass of P3HT by the total graphitic surface area from graphitic substrates. From Figure 5-18, the attached mass of P3HT on unit area of graphitic substrates has the trend of SWCNTs<MWCNTs<CFs throughout the crystallization process, which is the same as that of reciprocals of graphitic substrates curvatures. The interaction energy of P3HT on CNTs graphitic surface with larger diameter (smaller curvature) is smaller by comparing values in Table 5-3 and Table 5-4, so the attachment of P3HT on graphitic substrates with larger diameter (smaller curvature) is more stable. The more stable attachment of P3HT molecules on graphitic substrates will result in a higher possibility of P3HT nanowires formation from this area by interactions of follow-up P3HT molecules, thus higher utilization of graphitic surface for the formation of...
nanowire crystals will be realized. Therefore, graphitic substrates with smaller curvatures will lead to higher utilization of graphitic surface for P3HT nanowires growth, and the attached mass of P3HT on unit area of graphitic substrates will be higher in the meantime. In conclusion, both total surface area and the curvature of graphitic surface can affect the rate of P3HT crystallization on graphitic substrates.

Figure 5-18. Attached mass of LM-P3HT on unit area of SWCNTs (triangle), MWCNTs (square), and CFs (diamond) graphitic substrates. Diameters of MWCNTs and CFs are considered as 15 nm and 170 nm in calculations.

Avrami Equation 5-1 is used to examine the dimensionality of P3HT nanocrystals from graphitic substrates aided crystallization. Because hot P3HT/graphitic substrates dispersions can rapidly cool down to room temperature in ambient atmosphere, P3HT crystallization processes are able to be considered as quasi-isothermal crystallization processes. \( \varphi_c \) is the degree of crystallinity, \( K \) is the overall rate constant that generally depends on temperature, \( t \) is the crystallization time, and

\[
1 - \varphi_c = exp(-Kt^n)
\]  

(5-1)
\( n \) is the Avrami exponent. The value of \( n \) for crystallization processes of P3HT on SWCNTs, MWCNTs, and CFs are calculated to be 0.67, 0.68, and 0.57, respectively. Thus, the one-dimensional growth of P3HT crystals on graphitic carbon materials by using LM-P3HT is verified. Additionally, the order of crystallization reactions is also investigated. Typically, the reaction rate of a crystallization reaction is able to be expressed in Equation 5-2.[92,93] In the case of

\[
G = -\frac{dc}{dt} = kc^n
\]  

(5-2)

P3HT crystallization, \( G \) is crystallization rate of P3HT, \( c \) is the concentration of isolated P3HT in solutions, \( t \) is the crystallization time, \( k \) is the reaction coefficient, and \( n \) is the reaction order. First order reactions for these crystallization processes after the curve fitting method mentioned in the supplementary materials.

**Kinetic Study of SM-P3HT on Curved Graphitic Substrates**

The kinetic study of SM-P3HT crystallization on SWCNTs, MWCNTs, and CFs is performed by using the in-situ UV-Vis spectroscopy. Same as the analysis regarding crystallizations of LM-P3HT on graphitic substrates, the increments of absorbance at 600 nm from the start of crystallization processes are used to determine the amount of crystallized SM-P3HT on graphitic substrates, and the results are presented in Figure 5-19. The increment of absorbance at 600 nm for the crystallization of SM-P3HT on CFs is larger than that on SWCNTs and MWCNTs. Also, the increments of absorbance at 600 nm for SM-P3HT crystallizations on SWCNTs and MWCNTs are close, and the increment regarding the SM-P3HT crystallization on MWCNTs is a little bit faster. Thus, the rate of SM-P3HT crystallizations on graphitic substrates has the trend of CFs>MWCNTs\( \cong \)SWCNTs. The formation of 2D structures such as thin films and sparsely
dispersed nanoribbons is believed to be the reason of faster crystallization rate on CFs than that on SWCNTs and MWCNTs. Besides, the absorbance intensity at 600 nm keeps nearly unchanged in less than 2 hours of crystallization processes, which indicates no further formation of crystallized SM-P3HT molecules on graphitic substrates. As a result, the time takes to reach the plateau of absorbance intensity at 600 nm for SM-P3HT crystallizations on graphitic substrates is much shorter than that for LM-P3HT (4 hours, 3 hours, and 8 hours for crystallizations of LM-P3HT on SWCNTs, MWCNTs, and CFs, respectively), thus the SM-P3HT crystallizations on graphitic substrates completes much faster than that of LM-P3HT. An insight into their backbone structures can provide a plausible explanation on crystallization rate differences. The SM-P3HT molecule has an extended backbone (Figure 5-1a) instead of the folded backbone contains “turning points” and multiple segments of backbone separated by turning points (Figure 5-1b) from a LM-P3HT molecule. These “turning points” structures in LM-P3HT molecules can easily introduce defects into P3HT nanocrystals formed from LM-P3HT and thus weaken the stability of these P3HT nanocrystals. As a result, it will lead to a higher tendency of LM-P3HT molecules detachment in such dynamic crystallization processes and slow down the overall crystallization rate. Furthermore, the Avrami exponents regarding the crystallizations of SM-P3HT on SWCNTs, MWCNTs, and CFs are calculated by the same method as mentioned in the discussion of LM-P3HT crystallizations on graphitic substrates. The Avrami exponents of SM-P3HT crystallizations on SWCNTs, MWCNTs, and CFs are 0.65, 0.71, and 0.93, respectively. The larger Avramic exponent from the crystallization of SM-P3HT on CFs verifies the formation of 2D P3HT nanocrystals on CFs, and the smaller Avrami exponents from crystallizations of SM-P3HT on SWCNTs and MWCNTs verifies the formation of 1D P3HT nanowires on SWCNTs and MWCNTs.
Figure 5-19. The absorbance change at 600nm for SM-P3HT crystallizations on SWCNTs (black line), MWCNTs (red line), and CFs (blue line) graphitic surfaces.

Figure 5-20. Attached mass of SM-P3HT on unit area of SWCNTs (black line), MWCNTs (red line), and CFs (blue line) graphitic substrates. Diameters of SWCNTs, MWCNTs and CFs are considered as 1.5 nm, 15 nm and 170 nm in calculations.

Crystallized SM-P3HT per unit area through crystallizations process is plotted in Figure 5-20. The calculation method is the same as that for the analysis of crystallized LM-P3HT on graphitic
substrates. The mass of crystallized P3HT molecules on unit area of graphitic substrates still has the same trend of CFs>MWCNTs>SWCNTs. However, the difference between crystallized P3HT molecules on CFs and on other two kinds of graphitic substrates becomes more evident, and it is believed to be attributed to the formation of 2D SM-P3HT nanocrystals from the surface of CFs.

At last, all crystallization processes are first order reactions after the curve fitting method mentioned in the supplementary materials. From the results of TEM imaging, SM-P3HT molecules form nanowires from the surface of SWCNTs and MWCNTs when its concentration in the marginal solution is 0.05 mg/mL, but they form thin films and nanoribbons, which are 2D structures, from the surface of CFs at such concentration. The availability of forming 2D structures on CFs leads to a higher crystallization rate. Also, the Avrami exponent regarding the crystallization of SM-P3HT on CFs is larger than that of crystallizations of SM-P3HT on SWCNTs and MWCNTs, it suggests the formation of 2D structures from the surface of CFs and the formation of 1D nanowires from the surface of SWCNTs and MWCNTs.

Kinetic Study of LM-P3HT and SM-P3HT on Flat Graphene Substrates

Kinetic studies regarding the comparison of SM-P3HT and LM-P3HT crystallizations on graphene is monitored by the QCM technique, and crystallization processes are performed by using graphene coated QCM probes. The attached mass of LM-P3HT and SM-P3HT onto unit area of vertically placed QCM probe is recorded by the built-in microbalance and is presented in Figure 5-21. The attached mass of SM-P3HT is higher than that of LM-P3HT throughout the whole range of crystallization time. 25 µg/cm² and 52 µg/cm² of attached P3HT are found after 19 hours of LM-P3HT and SM-P3HT crystallizations, respectively. In addition, the attached mass of LM-P3HT is almost constant after 6 hours, and the attached mass of SM-P3HT keeps increasing with
longer crystallization time. Avrami equation is applied to study the crystallization of P3HT on graphene. The Avrami exponent of P3HT crystallization on graphene is calculated to be 0.81 for LM-P3HT and 1.05 for SM-P3HT. The larger value of Avrami exponent from the crystallization of SM-P3HT on graphene indicates the formation of nanocrystals with higher dimensions, namely the vertically grown 2D nanowalls, from the graphene surface.

![Graph showing attached mass of LM-P3HT and SM-P3HT on graphene surface](image)

Figure 5-21. Attached mass of LM-P3HT (black line) and SM-P3HT (red line) on unit area of graphene surface in crystallization processes.

Conclusions

The crystallization behavior of P3HT molecules on graphitic substrates with different curvatures is investigated. The type of P3HT nanocrystals grown from graphitic substrates is summarized in Table 5-2. LM-P3HT molecules are only able to form nanowires on graphitic substrates, while the formation of nanocrystals from SM-P3HT is relying on both the concentration of marginal solutions and the curvature of graphitic substrates. The crystallization of SM-P3HT on SWCNTs
only form nanowires on SWCNTs which have a huge surface curvature. SM-P3HT nanocrystals formed on MWCNTs switch from nanowires to nanoribbons by increasing the concentration of SM-P3HT in marginal solutions. The crystallization of SM-P3HT on CFs which have a small curvature only form nanoribbons. On the surface of graphene with a minimal curvature, vertically grown nanowalls are obtained. Besides, the orientation of nanocrystals differs on graphitic surfaces with different curvatures. Nanowires arrange coaxially on SWCNTs. Nanoribbons formed on MWCNTs have a confined orientation, and random oriented nanoribbons or nanowalls are formed on the surface of CFs and graphene. Studies of crystallization kinetics reveal that the rate of P3HT crystallization on graphitic substrates has a trend of MWCNTs>SWCNTs>CFs, and it results from both the specific surface area and curvature of graphitic substrates. Also, growth rate of SM-P3HT on graphene surface is much faster than that LM-P3HT which is believed from the capability of forming more ordered 2D P3HT nanowalls crystals.

Table 5-2. Summary of nano-structures formation on different graphitic substrates from SM-P3HT and LM-P3HT molecules. Asterisks point out the formation of nanocrystals with a confined orientation.

<table>
<thead>
<tr>
<th></th>
<th>Small M_n P3HT</th>
<th>Large M_n P3HT</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Low Concentration</td>
<td>High Concentration</td>
</tr>
<tr>
<td>SWCNT</td>
<td>Nanowires*</td>
<td>Nanowires*</td>
</tr>
<tr>
<td>MWCNT</td>
<td>Nanowires*</td>
<td>Nanoribbons*</td>
</tr>
<tr>
<td>CF</td>
<td>Nanoribbons</td>
<td>Nanoribbons</td>
</tr>
<tr>
<td>Graphene</td>
<td>Nanowalls</td>
<td>Nanowalls</td>
</tr>
<tr>
<td>No Substrates</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(In Solution)</td>
<td>Nanowires</td>
<td>Nanoribbons</td>
</tr>
</tbody>
</table>
Supporting Materials

Figure 5-22. (a) The TEM image of dispersed SWCNTs. (b) The TEM image of dispersed MWCNTs. (c) The TEM image of CVD graphene transferred on a TEM grid. (d) The SAED pattern of graphene on TEM grids.

Figure 5-23. (a, b) TEM images of CFs. (c) The SEM image of CFs. (d) The AFM image of CFs. (e) The height profile of the line is shown in (d).
Figure 5-24. SAED patterns of LM-P3HT nanowires crystallized on (a) SWCNTs, (b) SWCNTs, (c) CFs, and (d) graphene. Two sets of six-fold SAED patterns from the graphene substrate are circled in red and blue in (d).

Calculation of spacing reflected in the crystal is as follows. The spacing reflected in the real world is the reciprocal of the value get from the SAED image. The spacing in the SAED image should be measured from the center electron beam spot to the desired position. If the center electron beam spot is blocked by the tip, find at least 3 points in diffraction signals from the same plane and generate a circle. The radius of the circle is the spacing in the SAED image, and its reciprocal is the spacing in the real world. For these SAED rings with spacing of 2.52-2.58 \( \frac{1}{nm} \) in SAED images above, their spacing in the real world is 3.88-3.97 Å. So, they reflect the distance between two adjacent P3HT molecules interacted by \( \pi-\pi \) stacking. In addition, the circled 6-fold SAED patterns from graphene substrates is consistent with a hexagonal lattice and indicates high degree of crystallinity of graphene substrates applied in this crystallization process.
Figure 5-25. The AFM image of LM-P3HT crystallized on CFs and the height profiles of two lines labeled as 1-2. The scanning area of AFM imaging is 5 µm×2.5 µm.

Figure 5-26. UV-Vis spectra during processes of P3HT crystallization (a) SWCNTs, (b) MWCNTs, and (c) CFs. Need to label 2 peaks about loss of free P3HT and gain of crystallized P3HT.
Figure 5-27. The TEM image of SM-P3HT crystallized in the dispersion contained MWCNT by rapid cooling. The concentration of MWCNTs and SM-P3HT are 0.005 mg/mL and 0.3 mg/mL, respectively.

Figure 5-28. The top view AFM image (2 µm×2 µm) and the height profiles of 4 lines labeled as 1-4. Line 1 reveals a tilted nanoribbon from CF. Line 2 reveals two nanoribbons parallel to the horizontal plane with the thickness of 105 nm and 10 nm. Line 3 reveals a nanoribbon with the length of 312 nm. Line 4 reveals a nanoribbon grown vertically respect to the horizontal plane with a width of 138 nm.
Figure 5-29. The Raman spectrum of graphene surface.

Figure 5-30. The Raman spectrum of SM-P3HT powders.

Figure 5-31. The Raman spectrum of SM-P3HT crystallized on the graphene surface.
Figure 5-32. TEM images of SM-P3HT crystallized on SWCNTs from (a) 0.05 mg/mL, and (b) 0.10 mg/mL marginal solutions.

Figure 5-33. The TEM image of SM-P3HT crystallized on MWCNTs to form nanowires from a 0.05 mg/mL marginal solution.

Figure 5-34. The TEM image of SM-P3HT crystallized on graphene to form nanowalls composed on nanoribbons from a 0.05 mg/mL marginal solution.
Molecular Dynamics (MD) simulation was performed to investigate the interaction between the polymers and CNTs. [94] Three SWCNTs isomers: chiral (9, 0), armchair (8, 8) and zigzag (13, 0), and two types of MWCNTs: (150, 150) and (310, 0) were used to study the interaction between CNTs and the model oligomers. The steepest decent method and the NAMD Molecular Dynamic simulation are chosen to perform the optimization and the Amber Force Field was used in all the calculations. The model oligomers and the CNTs were constructed in VMD and optimized in NAMD. In the simulation, a model oligomer was put in the vicinity of a CNT, and the system energy will be optimized. The internal energy of nanotubes was not considered since it did not contribute to the interaction energy between the oligomer and the CNT. The interaction energy was obtained by subtracting the internal energy of the oligomer from the optimized energy of the oligomer/CNT system. Theoretical simulation was performed to study the orientation of 3-hexylthiophene oligomer with six repeating units on SWCNTs and MWCNTs by examining the interaction between oligomers and CNTs. In the studies, the oligomers were added to the optimized structures of CNTs in the vacuum system. The energy of the system was minimized, and the binding energy between the two parts was calculated. The interaction energy between the oligomers and three types of SWCNTs, and the interaction energy of the oligomers on MWCNTs (310, 0) at three angles were studied. As shown in Figure 5-35, the oligomer attaches along the SWCNTs axis with the alkyl chains wrapping around the tube after the energy minimization. The interaction energy values listed in Table 5-3 suggest that SWCNTs structures have trivial effect on the oligomer orientation on the SWCNTs surfaces. Also, the interaction energy values listed in Table 5-4 indicate the oligomer can take different orientation on the MWCNTs surfaces without causing much energy difference. Such theoretical simulation was in good agreement with our experimental observation of P3HT nanowires and nanoribbon formation on CNTs.
Figure 5-35. (A) The figure of the optimized attachment of oligo(3-hexylthiophene) on SWCNT (13,0). (B) The attachment of oligo(3-hexylthiophene) on a MWCNT (310,0) at angles of 90°, 0°, and 30°.

Table 5-3. The interaction energy of oligo(3-hexylthiophene) on different isomers of SWCNTs.

<table>
<thead>
<tr>
<th>Isomer of SWCNTs</th>
<th>Interaction Energy (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chiral (9,0)</td>
<td>-80.35</td>
</tr>
<tr>
<td>Armchair (8,8)</td>
<td>-81.70</td>
</tr>
<tr>
<td>Zigzag (13,0)</td>
<td>-80.15</td>
</tr>
</tbody>
</table>

Table 5-4. The interaction energy of oligo(3-hexylthiophene) on MWCNTs with different orientations respect to the axis of MWCNTs.

<table>
<thead>
<tr>
<th>Angle to the Axis of MWCNTs</th>
<th>Interaction Energy (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0°</td>
<td>-112.65</td>
</tr>
<tr>
<td>30°</td>
<td>-111.70</td>
</tr>
<tr>
<td>90°</td>
<td>-111.51</td>
</tr>
</tbody>
</table>
Because hot P3HT/carbon materials dispersions can rapidly cool down to room temperature in ambient atmosphere, P3HT crystallization processes are able to be considered as quasi-isothermal crystallization processes. Derive Equation 5-1 to get Equation 5-3 and Equation 5-4.

\[ \ln(1 - \varphi_c) = -Kt^n \]  

(5-3)

\[ \ln[-\ln(1 - \varphi_c)] = \ln K + n\ln t \]  

(5-4)

The value of \( \varphi_c \) in each trial was calculated by dividing the absorbance change at 600nm to the original absorbance at 454nm. After that, data from UV-Vis spectra was substituted in Equation 5-4. \( \ln[-\ln(1 - \varphi_c)] \) versus \( \ln t \) was plotted for each trial, and a linear correction was conducted. The value of \( n \), which is the slope of corrected line, was got after the linear correction.

For the calculation of reaction order, the presence of an obvious isosbestic point at around 488 nm in the UV-Vis spectra (Figure 5-26) suggests a direct transformation from dissolved individual polymer chains to ordered nanowires without any intermediate state, [90,91] so \( \frac{dx}{dt} = -\frac{dc}{dt} \), \( c \) is the concentration of isolated P3HT in solutions and \( x \) is the concentration of crystallized P3HT. As a result, Equation 5-2 can be derived to Equation 5-5 for this crystallization study.

\[ G = \frac{dx}{dt} = -\frac{dc}{dt} = kc^n \]  

(5-5)

Besides, the effective area on graphitic carbon materials for P3HT crystallizations is reasonable to be considered as a constant during crystallization processes. It is because the area stacked with P3HT by \( \pi-\pi \) interactions is still effective for further P3HT stackings. Therefore, the concentration of individual P3HT molecules is the only variable in crystallization processes. Equation 5-5 was derived to Equation 5-6 by considering the starting condition as \( c = c_0, t = 0 \). Equation 5-5
was integrated to get Equation 5-7 and Equation 5-8. Values of absorbance at 454nm were extracted to get curves of crystallinity ($c$) versus crystallization time ($t$). Then, values of $c_0$, $c$, and $t$ were substituted into Equation 5-7 and 5-8 to find out integral $n$ with the best fitting, and the value of $n$ turned out to be 1 for all three trials. First order reactions for these crystallization processes are revealed after data processing mentioned above.

$$\int_{c_0}^{c_t} \frac{1}{c^n} dc = \int_0^t -k \, dt$$ \hspace{1cm} (5-6)

$$\frac{1}{c_t^{n-1}} = \frac{1}{c_0^{n-1}} + (n-1)kt \hspace{.5cm} (n \neq 1)$$ \hspace{1cm} (5-7)

$$\ln c_t = \ln c_0 - kt \hspace{.5cm} (n = 1)$$ \hspace{1cm} (5-8)

References


202


82. Khlaifia, D.; Ewels, C.P.; Massuyeau, F.; Chemek, M.; Faulques, E.; Duvail, J.-L.; Alimi, K. Unraveling the real structures of solution-based and surface-bound poly(3-


CHAPTER 6: CONCLUSIONS AND FUTURE WORK

This dissertation focuses on graphene induced nanostructures in composites. Graphene aerogels with large surface area are great substrates for the decoration of metallic nanoparticles. Embedded graphene aerogels and EFGO in PDC composites dramatically increase the electrical conductivity of composites and induce the crystallization of graphitic domains in the area nearby the embedded graphitic materials. Graphitic surfaces can guide the formation of highly ordered one dimensional (nanowires) or two dimensional (nanoribbons and nanowalls) P3HT nanocrystals on these substrates. Conclusions of each chapter and the prospective work of each project are summarized as below.

Conclusions

In chapter 2, rGO aerogels loaded with four kinds of metallic nanoparticles were successfully prepared with excellent directionality and decent hieratical structures. The loading of 59 wt%, 67 wt%, 39 wt% and 46 wt% of metallic palladium, platinum, nickel, and tin in rGO/metal aerogels were achieved after hydrogen reduction at elevated temperatures. It is believed that other kind of metallic nanoparticles can also be loaded onto rGO aerogels with similar procedures. A hydrogel gas sensor was produced using Pd nanoparticle loaded rGO aerogels. The large surface area and porous structure of rGO aerogel offer high sensitivity and fast response/recovery time of the sensor. The metal nanoparticles decorated aerogels which have open-pores structure and large surface area are promising platforms for numerous applications, including energy storage, gas sensing and catalysts of vapor phase reactions.
In chapter 3, Bulk SiCN ceramics embedded with anisotropic graphene aerogels have been fabricated through filling anisotropic graphene aerogels with a polymer precursor of SiCN ceramics (oligosilazane), followed by crosslinking and pyrolysis. The electrical conductivity of SiCN/rGOA composites increases from $10^{-7}$ S/m to about 157 S/m by embedding 1 wt% of anisotropic rGOA in SiCN ceramics. The electrical conductivity in longitudinal direction is ten times higher than that in transversal direction due to the aligned graphene. It is interesting to discover that graphene also facilitates the formation of graphitic domains in ceramics. Graphene embedded in ceramic precursors lowers the transition temperature of amorphous carbons to graphene nanocrystals. These results suggest that anisotropic graphene structures have great potential in creating anisotropic properties in PDCs.

In chapter 4, EFGO embedded PDC composites are successfully fabricated. SiOC polymeric precursor is infiltrated into EFGO attached PVA foams, and it is then cured and pyrolyzed to form composites. This facile method is suitable to prepare composites with different shapes because only the shaping of PVA foams is desirable. The introduction of EFGO networks greatly increases the electrical conductivity of PDC based composites, and it results from (1) the effective pathways for the transport of electrons provided by embedded EFGO networks, and (2) the induced formation of conductive graphitic domains in PDC matrix nearby embedded EFGO networks. By only applying less than 2 wt% of EFGO, the electrical conductivity of composites is 0.95 S/cm at 25 °C and 1.8 S/cm at 600 °C. The times of electrical conductivity increment of PDC composites from room temperature to 600 °C is much lower than that of pyrolyzed SiOC polymeric precursor due to the percolation of embedded EFGO networks. Also, the increment of electrical conductivity from room temperature to 600 °C decreases when PDC composites are pyrolyzed at higher
temperatures. More abundant graphitic domains in SiOC matrix after pyrolysis performed at higher temperatures lead to smaller energy needed for the transport of electrons from SiOC matrix to EFGO networks, and the increment of electrical conductivity thus decreases based on the classic equation of semi-conductor electrical conductivity. Furthermore, the thermal conductivity of pyrolyzed PDC composites almost keeps the same at different testing temperatures and is quite low (<1 W·m⁻¹·K⁻¹). Such thermally stable materials with high electrical conductivity and low thermal conductivity have great potentials in applications such as thermal insulator, energy sources, and high temperature sensors.

In chapter 5, The crystallization behavior of P3HT molecules on graphitic substrates with different curvatures is investigated. LM-P3HT molecules are only able to form nanowires on graphitic substrates, while the formation of nanocrystals from SM-P3HT is relying on both the concentration of marginal solutions and the curvature of graphitic substrates. The crystallization of SM-P3HT on SWCNTs only form nanowires because of the huge curvature of SWCNTs surface. SM-P3HT nanocrystals formed on MWCNTs switch from nanowires to nanoribbons by increasing the concentration of SM-P3HT in marginal solutions. The crystallization of SM-P3HT on CFs which have a small curvature only form nanoribbons. On the surface of graphene, which has a minimal curvature, vertically grown P3HT nanowalls are obtained. Besides, the orientation of nanocrystals differs on graphitic surfaces with different curvatures. Nanowires arrange coaxially on SWCNTs. Nanoribbons formed on MWCNTs have a confined orientation, and random oriented nanoribbons or nanowalls are formed on the surface of CFs and graphene. Studies of crystallization kinetics reveal that the rate of LM-P3HT crystallization on CNTs has a trend of MWCNTs>SWCNTs>CFs, and it results from both the specific surface area and curvature of graphitic substrates. Besides, the
growth rate of SM-P3HT on graphene surface is much faster than that of LM-P3HT which is believed due to the capability of forming more ordered 2D P3HT nanowalls crystals from SM-P3HT molecules.

**Future Work**

For graphene embedded PDC composites, the mechanism of graphene induced formation of graphitic domains needs more experiments to explore. In-situ TEM is a good candidate for this study. [1] The electrical conductivity of graphene embedded PDC composites at temperature higher than 600 °C and lower than room temperature needs to be systematically investigated to better understand the charge transport mechanism in PDCs in a wider temperature range. Also, the thermal conductivity of PDC composites needs to be systematically studied to find out its trend of change at a wide range of temperature to guide the designing for thermo-electrics.

For graphitic surface guided crystallization of P3HT, more experiments such as small angle X-ray scattering (SAXS), [2-4] grazing incidence X-ray diffraction (GIXRD) [5,6] need to be done to further verify the vertical growth of P3HT on graphene. High resolution TEM or scanning tunneling microscopy (STM) needs to be done to reveal the arrangements of P3HT molecules in nanocrystals. Also, techniques like conductive AFM [7,8] and Kevin Probe force microscope (KPFM) [9] need to be performed to further study the electrical conductivity and work function of P3HT in nanocrystals. Thus, the electrical properties to the behavior of P3HT arrangements can be more closely related.
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APPENDIX A: LIST OF PUBLICATIONS

2. Limin Guo, Kun liang, Kyle Marcus, Zhao Li, Prabhu Doss Mani, Hao Chen, Chen Shen, Yajie Dong, Lei Zhai, Kevin R. Coffey, Nina Orlovskaya, Yong-Ho Sohn, Yang Yang, Enhanced Photoelectrocatalytic Reduction of Oxygen Using Au@TiO₂ Plasmonic Film, *ACS Applied Materials & Interfaces* 2016, 8(51), 34970–34977.


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