SONOCHEMICAL SYNTHESIS AND CHARACTERIZATION OF METAL NANOPARTICLE-DECORATED CARBON SUPPORTS

Thesis

Submitted to

The School of Engineering of the University of Dayton

In Partial Fulfillment of the Requirements for

The Degree

Master of Science in Chemical Engineering

By

Nicholas D. McNamara

UNIVERSITY OF DAYTON

Dayton, Ohio

August, 2011
SONOCHEMICAL SYNTHESIS AND CHARACTERIZATION OF METAL
NANOPARTICLE-DECORATED CARBON SUPPORTS

Name: McNamara, Nicholas D.

APPROVED BY:

Elena A. Guliants, Ph.D.
Associate Professor
Electrical Engineering
Advisory Committee Chairperson

K. A. Shiral Fernando, Ph. D.
Research Scientist
UDRI
Technical Advisor

Scott Gold, Ph.D.
Associate Professor
Chemical and Materials Engineering
Committee Member

Khalid Lafdi, D.Sc., Ph.D.
Professor
Materials Engineering
Committee Member

John G. Weber, Ph.D.
Associate Dean
School of Engineering

Tony E. Saliba, Ph.D.
Dean, School of Engineering
& Wilke Distinguished Professor
ABSTRACT

SONOCHEMICAL SYNTHESIS AND CHARACTERIZATION OF METAL NANOPARTICLE-DECORATED CARBON SUPPORTS

Name: McNamara, Nicholas D.
University of Dayton

Research Advisor: Dr. Elena A. Guliants
Technical Advisor: Dr. K.A. Shiral Fernando
Academic Advisor: Dr. Kevin J. Myers

Of the wide variety of nanomaterials currently under study, metal nanoparticles have seen a large amount of research activity due to their unique and useful properties and applications. Nanoparticles of noble metals such as silver, gold, and platinum are of particular interest because of their resistance to oxidation in addition to their myriad possible applications including use in catalysis, biomedical devices, and sensing. While noble metal nanoparticles are relatively easy to synthesize initially, aggregation of metal particles is a problem that frequently occurs which prevents long term stability. When particles become agglomerated, the nano-sized regime of the particles is lost which inhibits access to properties that are only exhibited at the
nanoscale. Many research groups have employed the use of nanoscale carbon supports to template nanoparticle growth in order to prevent aggregation, impart long-term stability, and preserve the nanoscale properties. Sonochemistry is well suited for this task because it has the ability to combine the synthesis of various metal nanomaterials with the deposition process due to the unique conditions that acoustic cavitation initiates.

In this work, silver nanoparticles were synthesized via the reduction of silver acetate and subsequently decorated onto the surface of single-walled carbon nanotubes (SWNTs). This synthesis was performed in two different solvents, either N,N-dimethylformamide (DMF) or de-ionized (DI) water, using either sonochemistry or conventional thermal heating and the products were analyzed in order to determine the optimal procedure for decorating carbon supports. Through characterization data provided by TEM, XRD, FTIR, and DSC/TGA analysis, it was determined that the sonochemical reaction in DMF provided the optimal product. This synthetic procedure for sonochemically coating carbon nanostructures with silver nanoparticles was extended to include decoration of two additional supports in the form of graphene oxide (GO) and carbon nanoparticles (CNPs) and resulted in varying degrees of success. The same sonochemistry-in-DMF procedure was then utilized to reduce two additional metal salts, gold acetate and platinum chloride, to their respective zero-valent metal nanoparticles and subsequently decorate SWNTs with these nanoparticles. XRD results showed that in all synthetic methods face-centered-cubic metal was synthesized. FTIR analysis indicated that the metal salt precursors were either successfully reduced or washed from the final products. TGA/DSC data provided information on metal content of the sample as well as thermal response. In all cases, carbon combustion was shown to occur at earlier
temperatures after metal decoration. TEM was used to determine the morphology of the products and it was determined that the size of nanoparticles and extent of decoration depended upon the multiple synthetic parameters including type of solvent, energy input (thermal or sonochemical), carbon support, and metal used.
ACKNOWLEDGEMENTS

I would like to first thank God who has provided me with the necessary tools and circumstances I needed to succeed.

I would like to thank my family for their unending support and unwavering confidence in me. Special thanks to my mother, father, and grandmother for checking in with me and supplying me with a constant stream of care packages.

I would like to thank my advisors, Dr. Chris Bunker and Dr. Elena Guliants, for giving me the opportunity to pursue this advanced degree and their guidance in research.

I would like to give special thanks to Dr. Shiral Fernando who taught me how to perform research at a competitive level and for his continued support and faith in me. Without his guidance I would have undoubtedly failed in this endeavor.

I would like to thank Dr. Kevin Myers for his guidance both in academics and professional development.

I would also like to thank every member of the Bunker/Guliants group for their various types of support, especially Barb Miller for TEM work and insightful discussion and Dr. Will Lewis for insightful discussion.
Of course I have to thank all of my friends for keeping me sane during the most stressful of times. There are too many of you to name but pretty much every one of you has helped me in some way or another.

I would also like to thank Dr. Scott Gold and Dr. Khalid Lafdi for taking the time to be on my committee.
TABLE OF CONTENTS

ABSTRACT ........................................................................................................................................ iii

ACKNOWLEDGEMENTS ........................................................................................................ vi

TABLE OF CONTENTS ........................................................................................................ viii

LIST OF FIGURES ................................................................................................................ xi

LIST OF TABLES ................................................................................................................... xvi

CHAPTER 1: INTRODUCTION .............................................................................................. 1

1.1 Types of Metal Nanoparticles ................................................................................ 1

1.2 Synthetic Techniques .............................................................................................. 3

1.3 Sonochemistry .......................................................................................................... 13

1.3.1 Sonochemical Deposition onto Supports ....................................................... 17

CHAPTER 2: EXPERIMENTAL METHODS ...................................................................... 20

2.1 Materials .................................................................................................................. 20

2.2 Acid Treatment of Carbon Nanotubes and Carbon Nanoparticles .............. 20

2.3 Sonochemical Synthesis of Ag-SWNTs at Room Temperature (R-DMF) .... 21

2.4 Sonochemical Synthesis of Ag-SWNTs at Elevated Temperatures (S-DMF) .............................................................. 22

2.5 Thermal Synthesis of Ag-SWNTs (T-DMF) .......................................................... 23

2.6 Sonochemical/Thermal Synthesis of Ag-SWNTs in Water (S-H2O and T-H2O) ........................................................................ 24
2.7 Sonochemical Synthesis of Ag-GO .................................................. 25
2.8 Sonochemical Synthesis of Ag-CNPs ....................................... 25
2.9 Sonochemical Synthesis of Au-SWNTs .................................. 26
2.10 Sonochemical Synthesis of Pt-SWNTs .................................. 26
2.11 Measurements ......................................................................... 27

CHAPTER 3: SILVER-DECORATED SINGLE-WALLED CARBON
NANOTUBES ..................................................................................... 29

3.1 Background .................................................................................. 29
3.2 Characterization of R-DMF ........................................................ 31
3.3 Improved Method for Sonochemistry in DMF (S-DMF) ............. 38
3.3.1 Characterization of S-DMF ..................................................... 39
3.4 Sonochemistry in Water (S-H$_2$O) ............................................. 47
3.4.1 Characterization of S-H$_2$O .................................................. 48
3.5 Thermal Reactions (T-DMF and T-H$_2$O) ................................. 54
3.5.1 Characterization of T-DMF and T-H$_2$O ............................... 55
3.6 Summary ...................................................................................... 62

CHAPTER 4: SILVER-DECORATED GRAPHENE OXIDE AND CARBON
NANOPARTICLES ............................................................................... 71

4.1 Background .................................................................................. 71
4.2 Characterization of Ag-GO ........................................................ 73
4.3 Characterization of Ag-CNPs ..................................................... 82
4.4 Summary ...................................................................................... 88

CHAPTER 5: GOLD AND PLATINUM-DECORATED SINGLE-WALLED CARBON
NANOTUBES ..................................................................................... 97

5.1 Background .................................................................................. 97
5.2 Characterization of Au-SWNTs ................................................ 99
5.3 Characterization of Pt-SWNTs ......................................................... 107
5.4 Summary ....................................................................................... 113

CHAPTER 6: CONCLUSIONS ................................................................. 121

REFERENCES ....................................................................................... 123
LIST OF FIGURES

Figure 3.1: TEM images of acid-purified SWNTs before (top left) and after (top right, bottom) the Rangari reaction. The silver nanoparticles decorating the nanotubes had an average size of ~2.4 nm and a size distribution of ~0.5-4 nm. The nanoparticles on the globular structures had an average size of ~4.2 nm and a size distribution of ~1.5-8 nm. The scale bar shown for all three images indicates 20 nm……………………………... 32

Figure 3.2: XRD spectra for the R-DMF sample, neat silver acetate, and ICDD pattern for fcc silver (00-004-0783). The spectrum of the R-DMF sample close resembles the silver acetate spectrum with all silver acetate peaks present. No individual peaks in the R-DMF sample spectrum could be clearly matched to the card data for fcc silver……………... 34

Figure 3.3: FTIR spectra for the R-DMF sample (top) and neat silver acetate (bottom). The peaks centered at 1502 and 1432 cm\(^{-1}\) correspond to the C-C backbone vibration and C-O stretching respectively while the doublet at 1377 and 1342 cm\(^{-1}\) refers to C-H bending. The two spectra are identical indicating that the R-DMF sample contained silver acetate……………………………………………………………………….. 35

Figure 3.4: TEM image (top left), XRD data (bottom), and FTIR data (top right) for the R-DMF sample after the more thorough washing procedure. The TEM image shows that many of the globular structures were removed and a clear view of the nanotubes was visible. XRD data shows that fcc silver is present in the R-DMF sample and FTIR results indicate that most silver acetate has been removed…………………………………….. 37

Figure 3.5: TEM images of R-DMF (left) compared to S-DMF (right). The S-DMF sample nanoparticles have an average size of ~5.7 nm and a size distribution of 1-15 nm. The scale bars for both images represent 20 nm…………………………………………………………………………. 40

Figure 3.6: Size distribution graph of the nanoparticles decorating the SWNTs in the S-DMF sample. The nanoparticles had an average size of ~5.7 nm and a range of 1-15 nm……………………………………………………………………………………………………….. 42

Figure 3.7: XRD spectra for S-DMF (top) and ICDD pattern for silver (bottom) (00-004-0783). The peaks at 38.1°, 44.3°, 64.4°, 77.5°, and 81.5° correspond to the (111), (200), (220), (311) and (222) crystal planes of fcc silver respectively (ICDD 00-004-0783)... 43
Figure 3.8: TGA (top) and DSC (bottom) data for acid-treated SWNT (solid line) and S-DMF (dashed line). The TGA curves for the acid-treated SWNTs and the S-DMF sample show a difference in final mass percentages which was used to calculate the silver content and found to be ~35%. The DSC curve for the acid-treated SWNTs showed an intense peak centered at ~560 ºC which was attributed to carbon nanotube combustion closely followed by a shoulder which resulted from combustion of residual graphitic carbon. The DSC curve of the S-DMF sample showed the same pattern but a significantly earlier temperature (~415 ºC).

Figure 3.9: TEM images of the S-DMF (top left) sample compared to the S-H2O (bottom, top right) sample. The S-H2O sample nanoparticles have an average size of ~7.3 nm and a size range of 4-50 nm. The scale bars for the top left and bottom images represents 20 nm. The scale bar for the top right image indicates 100 nm.

Figure 3.10: Size distribution graph of the nanoparticles decorating the SWNTs in the S-H2O sample. The nanoparticles had an average size of ~7.3 nm and a range of 4-50 nm.

Figure 3.11: XRD spectra for S-H2O (top) and ICDD pattern for silver (bottom) (00-004-0783). The peaks at 38.1º, 44.3º, 64.4º, 77.5º, and 81.5º correspond to the (111), (200), (220), (311) and (222) crystal planes of fcc silver respectively (ICDD 00-004-0783).

Figure 3.12: TGA (top) and DSC (bottom) data for acid-treated SWNT (solid line) and S-H2O (dashed line). The TGA curves for the acid-treated SWNTs and the S-H2O sample show a difference in final mass percentages which was used to calculate the silver content and found to be ~35%. The DSC curve for the acid-treated SWNTs showed an intense peak centered at ~560 ºC which was attributed to carbon nanotube combustion closely followed by a shoulder which resulted from combustion of residual graphitic carbon. The DSC curve of the S-H2O sample showed the same pattern but a significantly earlier temperature (~415 ºC).

Figure 3.13: TEM images of T-DMF (top) and T-H2O (bottom) samples. The T-DMF sample nanoparticles have an average size of ~43.3 nm and a size range of 2-115 nm. The T-H2O sample nanoparticles have an average size of ~6.7 nm and a size range of 2-25 nm. The scale bars for all four images represent 100 nm.

Figure 3.14: Size distribution graphs of the nanoparticles decorating the S-DMF, S-H2O, T-DMF, and T-H2O samples. The S-DMF sample nanoparticles had an average size of ~5.7 nm and a range of 1-15 nm. The S-H2O sample nanoparticles had an average size of ~7.3 nm and a range of 4-50 nm. The T-DMF sample nanoparticles had an average size of ~43.3 nm and a range of 2-115 nm. The T-H2O sample nanoparticles had an average size of ~6.7 nm and a range of 2-25 nm. The insets show the majority of the nanoparticle populations occur in the range of 0-25 nm.
Figure 3.15: XRD spectra of S-DMF, S-H$_2$O, T-DMF, T-H$_2$O, and ICDD card data for fcc silver. The peaks at 38.1º, 44.3º, 64.4º, 77.5º, and 81.5º correspond to the (111), (200), (220), (311) and (222) crystal planes of fcc silver respectively (ICDD 00-004-0783). ................................................................. 59

Figure 3.16: TGA data for S-DMF, S-H$_2$O, T-DMF, T-H$_2$O, and acid-treated SWNTs. The final mass percentages of the samples compared with undecorated, acid-treated SWNTs were used to calculate the silver content of each sample. The silver content of the samples was found to be: 35% for S-DMF, 35% for S-H$_2$O, 30% for T-DMF, and 25% for T-H$_2$O. ................................................................. 61

Figure 3.17: Representative TEM images of Ag-SWNTs prepared using all four synthesis methods (S-DMF, S-H$_2$O, T-DMF, T-H$_2$O). The scale bars for all four images represent 100 nm. ................................................................. 63

Figure 4.1: TEM images of undecorated GO sheets. The image on the left shows a bird’s eye view of an entire sheet of GO while the image on the right is a GO sheet at a higher magnification. The scale bar for the left image represents 500 nm and the scale bar for the right image represents 100 nm. ................................................................. 74

Figure 4.2: TEM images of silver-decorated GO sheets. The image on the left shows a bird’s eye view of an entire sheet of GO while the image on the right is a GO sheet at a higher magnification. The Ag-GO sample nanoparticles have an average size of ~8 nm and a size range of 2-100 nm. The scale bar for the left image represents 500 nm and the scale bar for the right image represents 100 nm. ................................................................. 76

Figure 4.3: Size distribution graph of the silver nanoparticles decorating the GO via the sonochemical method in DMF. The nanoparticles had an average size of ~8 nm and a range of 2-100 nm. The inset represents the majority of the silver nanoparticle population. ................................................................. 77

Figure 4.4: XRD spectra of Ag-GO (top) and ICDD pattern for silver (bottom) (00-004-0783). The peaks at 38.1º, 44.3º, 64.4º, 77.5º, and 81.5º correspond to the (111), (200), (220), (311) and (222) crystal planes of fcc silver respectively (ICDD 00-004-0783). ................................................................. 79

Figure 4.5: TGA (top) and DSC (bottom) data for undecorated GO (solid line) and GO-Ag (dashed line). The TGA curves for the undecorated GO sheets and the Ag-GO sample show a difference in final mass percentages which was used to calculate the silver content and found to be ~40%. The DSC curve for the undecorated GO sheets showed an initial peak centered at ~200 ºC which was attributed to oxygen leaving groups and a second peak centered at ~550 ºC which was attributed to graphitic carbon combustion. The DSC curve of the Ag-GO sample showed the same pattern but a significantly earlier temperature (~415 ºC). ................................................................. 80
Figure 4.6: TEM images of CNPs before (left) and after (right) decoration with silver nanoparticles. The Ag-CNPs sample nanoparticles have an average size of ~7 nm and a size range of 3-15 nm. The scale bar for both images represents 20 nm.

Figure 4.7: Size distribution graph of the silver nanoparticles decorating the CNPs via the sonochemical method in DMF. The nanoparticles had an average size of ~7 nm and a range of 3-15 nm.

Figure 4.8: XRD spectra of Ag-CNP (top) and ICDD card data for fcc silver (bottom) (00-004-0783). The peaks at 38.1º, 44.3º, 64.4º, 77.5º, and 81.5º correspond to the (111), (200), (220), (311) and (222) crystal planes of fcc silver respectively (ICDD 00-004-0783).

Figure 4.9: TGA (top) and DSC (bottom) data for CNP (solid line) and Ag-CNPs (dashed line). The TGA curves for the undecorated CNPs and the Ag-CNPs sample show a difference in final mass percentages which was used to calculate the silver content and found to be ~14%. The DSC curve for the undecorated CNPs sheets showed a peak centered at ~580 ºC which was attributed to carbon combustion. The DSC curve of the Ag-CNPs sample showed the same peak but a significantly earlier temperature (~320 ºC).

Figure 4.10: TEM images of Ag-SWNTs (top left), Ag-GO (top right), and Ag-CNPs (bottom). The scale bar indicates 20 nm for all images.

Figure 5.1: TEM images of gold-decorated SWNTs. The Au-SWNTs sample nanoparticles have an average size of ~25 nm and a size range of 9-60 nm. The scale bar for the left image represents 500 nm and the scale bar for the right image represents 100 nm.

Figure 5.2: Size distribution graph of the gold nanoparticles decorating the SWNTs via the sonochemical method in DMF. The nanoparticles had an average size of ~25 nm and a range of 9-60 nm.

Figure 5.3: XRD spectra of Au-SWNT (top) and ICDD card data for fcc gold (bottom) (00-004-0784). The peaks at 38.2º, 44.4º, 64.6º, 77.5º, and 81.7º which correspond to the (111), (200), (220), (311) and (222) crystal planes of fcc gold, respectively.

Figure 5.4: FTIR spectra for the Au-SWNTs sample (top) and neat gold acetate (bottom).

Figure 5.5: TGA (top) and DSC (bottom) data for acid-treated SWNTs (solid line) and Au-SWNTs (dashed line). The TGA curves for the acid-treated SWNTs and the Au-SWNTs sample show a difference in final mass percentages which was used to calculate the silver content and found to be ~44%. The DSC curve for the acid-treated SWNTs...
showed an intense peak centered at ~560 °C which was attributed to carbon nanotube combustion closely followed by a shoulder which resulted from combustion of residual graphitic carbon. The DSC curve of the Au-SWNTs sample showed the same pattern but a significantly earlier temperature (~460 °C)………………………………………….. 106

Figure 5.6: TEM images of SWNTs before (left) and after (middle, right) decoration with platinum nanoparticles. The Pt-SWNTs sample nanoparticles have an average size of ~6 nm and a size range of 1-15 nm. The scale bar for the left image represents 100 nm and the scale bar for the right image represents 20 nm………………………………………….. 108

Figure 5.7: Size distribution graph of the platinum nanoparticles decorating the SWNTs via the sonochemical method in DMF. The nanoparticles had an average size of ~5.2 nm and a range of 1-15 nm………………………………………………………………... 109

Figure 5.8: XRD spectra of Pt-SWNT (top) and ICDD card data for fcc platinum (bottom) (ICDD 01-087-0646. The peaks at 39.8, 46.3°, 67.5°, and 81.3° correspond to the (111), (200), (220), and (311) crystal planes of fcc platinum respectively………….. 111

Figure 5.9: TGA (top) and DSC (bottom) data for acid-treated SWNTs (solid line) and Pt-SWNTs (dashed line). The TGA curves for the acid-treated SWNTs and the Pt-SWNTs sample show a difference in final mass percentages which was used to calculate the silver content and found to be ~24%. The DSC curve for the acid-treated SWNTs showed an intense peak centered at ~560 °C which was attributed to carbon nanotube combustion closely followed by a shoulder which resulted from combustion of residual graphitic carbon. The DSC curve of the Pt-SWNTs sample showed the same pattern but a significantly earlier temperature (~460 °C)………………………………………….. 112

Figure 5.10: TEM images of SWNTs before metal decoration along with SWNTs that are decorated with silver, gold, and platinum respectively. The scale bar for all images represents 20 nm…………………………………………………………………. 114
LIST OF TABLES

Table 3.1: Significant property values of Ag-SWNTs prepared using various methods................................................................. 65

Table 4.1. Significant property values of silver-decorated carbon supports........... 91

Table 5.1. Significant property values of metal-decorated SWNTs...................... 116
1.1 Types of Metal Nanoparticles

Of the wide variety of nanomaterials currently under study, metal nanoparticles have seen a large amount of research activity due to their unique and useful properties and applications. Nanoparticles of noble metals such as silver, gold, and platinum are of particular interest because of their resistance to oxidation in addition to their myriad possible applications such as catalysis, biomedical devices, and sensors. The strong antimicrobial effects for a wide variety of organisms (including bacteria, viruses, fungi) of silver nanoparticles has been well documented. This has quite naturally led to silver nanoparticles having uses in biomedical applications such as wound dressings, medical catheters, and bone prostheses (in addition to many others). Irradiating silver nanoparticles with visible light causes the oscillation of free electrons in the conduction band which causes surface plasmon resonance to occur. This phenomenon allows silver nanoparticles to be used in sensing applications such as detection of DNA sequences and laser desorption/ionization mass spectrometry. Silver nanoparticles have also found uses in catalysis. An example of this is that silver nanoparticles have been used to catalyze the oxidation of many species including carbon monoxide and methanol. Nanoparticles formed from gold have many of the same applications as
silver. A color change in gold nanoparticle aggregates has been exploited to distinguish complementary DNA sequences.\textsuperscript{16, 37} Gold nanoparticles have also been shown to have applications in catalysis including asymmetric dihydroxylation reactions, the oxidation of CO, and carboxylic ester cleavage.\textsuperscript{13-15, 37} Platinum nanoparticles have been used for numerous similar applications as well including but not limited to electro-catalytic oxidation of methanol, catalysis of chemiluminescence, and sensing.\textsuperscript{31, 32, 38}

In addition to pure noble metal nanoparticles, research efforts have also been focused on the properties and application of nanoalloys of metal nanoparticles. According to Munoz-Flores and co-workers, nanoalloys are metallic clusters composed of two or more metal elements.\textsuperscript{39} The physical and chemical properties of these nanoalloys are determined by size, type and degree of chemical ordering, and composition.\textsuperscript{39-41} As well as exhibiting unique properties different than the corresponding bulk material, nanoalloys often display properties distinct from those of pure metal element nanoparticles.\textsuperscript{40, 41} Furthermore, there are several examples of metals that are immiscible as bulk alloys but readily form alloys at the nanoscale (such as iron and silver).\textsuperscript{41} Nanoalloys have applications in a wide variety of fields including biomedicine, sensors, magnetic, optics, and filters among others but a predominant amount of recent reports are on the subject of catalysis.\textsuperscript{39-42} According to Ferrando and co-workers, some of the most important properties in determining catalytic activity are the surface structures, compositions, and segregation properties.\textsuperscript{41} Generally, nanoalloys of noble metals are the most effective in the field of catalysis.\textsuperscript{39} As an example, nanoalloys of PtRu have been used as catalysts for methanol oxidation.\textsuperscript{43} PtRu nanoparticles have even been shown to have enhanced catalytic activity and are less
likely to be poisoned by carbon monoxide. Nanoalloys have found use in sensing due to their magnetic properties. According to Sumiyama, ferromagnetic particles inside noble metal matrices (such as FeAg) exhibit the phenomenon known as giant magnetoresistance (GMR) which is a change in resistance upon the application of a magnetic field by as much as 50%. Thus, GMR materials show promise for applications as magnetic sensors and magnetic recordings. Bimetallic nanoalloys can be used as biodiagnostics agents as well due to their wide variety of tunable parameters. In fact, Mirkin and co-workers were able to use AgAu nanoalloys modified with biomolecules in order to impart biorecognition properties to the particles.

1.2 Synthetic Techniques

There are a large multitude of methods available for synthesizing metal nanoparticles. The research presented here focused on a bottom-up approach to synthesis and thus the works summarized here will all fall under this category. In a bottom-up synthesis technique, newly formed metal atoms are associated to form small clusters which eventually grow (through the association of additional atoms) into larger nanoparticles.

One of the most widespread methods for the production of metal nanoparticles is the wet chemical method. Generally in this method metal salts in solution dissociate to form metal ions. The metal ions are then reduced by a chemical reduction agent to form metal nanoparticles. Ions of noble metals in particular are often fairly easy to reduce. As an example, the monovalent silver ion has a large reduction potential (0.7996...
V) and thus can easily be reduced by a wide variety of both organic and inorganic compounds.\textsuperscript{51}

Many of these wet chemical techniques employ various modifications to the synthetic method used by J. Alan Creighton.\textsuperscript{50, 51} Creighton was using both silver and gold nanoparticles in the 1970s in order to study plasma resonance enhancement of Raman scattering.\textsuperscript{50} In the Creighton synthesis method, aqueous metal salt solutions (either AgNO\textsubscript{3} or HAuCl\textsubscript{4}) were prepared and the metal ions were subsequently reduced by NaBH\textsubscript{4} at room temperature using only simple mixing. The prepared nanoparticles were in the size range of 1-50 nm.

Lee and Meisel proposed several additional methods for the wet chemical synthesis of noble metal nanoparticles.\textsuperscript{52} Perhaps the most well known Lee-Meisel method is the reduction of metal ions using sodium citrate. In the silver synthesis method, AgNO\textsubscript{3} was dissolved in water and heated to boiling. A 1% sodium citrate solution was then added and the mixture was allowed to boil for an hour. In the gold synthesis method, an aqueous solution of HAuCl\textsubscript{4} was boiled and the gold ions were reduced by sodium citrate. In both cases, nanoparticles of \textasciitilde10 nm in diameter were formed.

While noble metal ions are relatively easy to reduce, aggregation of metal particles is a problem that frequently occurs. When particles become agglomerated, the size regime of the particles is lost which prevents access to properties that are only exhibited at the nanoscale. Many research groups have employed stabilizing agents in order to prevent aggregation, impart long-term stability, and preserve the nanoscale
properties.\textsuperscript{51, 53-58} Sondi et al. used Daxad 19 (a sodium salt of high-molecular-weight naphthalene sulfonate formaldehyde condensate) as a stabilizing agent in the production of silver nanoparticles.\textsuperscript{53} In their experiment, an aqueous solution of silver nitrate was reduced by ascorbic acid in the presence of Daxad 19. Sondi was able to prepare Daxad stabilized silver nanoparticles that were fully redispersible even after long-term storage. Furthermore, Sondi was able to show the size of the particles could be tuned by adjusting reaction parameters such as the reaction time and chemical concentrations.

Partoriza-Santos and Liz-Marzan were able to show the dependence of reduction rate and nanoparticle morphology on temperature.\textsuperscript{54} In this experiment, solutions containing 3-(aminopropyl) trimethoxy-silane (ASP) and AgNO\textsubscript{3} or AgClO\textsubscript{4} were added to DMF. The reduction of silver ions to silver metals was observed at varying temperatures and Ag to ASP ratios. It was discovered that at room temperature the reaction would take several weeks to reach completion but at reflux the reaction would be finished within seconds. They also observed that smaller nanoparticles were formed at room temperature but the particles became more monodisperse at higher temperatures.

One popular method for fabricating metal nanoparticles is photochemistry.\textsuperscript{49, 59-67} In the photochemical method, a metal atom is generated through the direct photoreduction of a metal precursor (such as a metal salt or metal complex) or through the reduction of metal ions using photochemically generated intermediates such as excited molecules or radicals (known as sensitizers).\textsuperscript{49} One of the main advantages to this method is that light-induced processing has high spatial resolution. Due to this advantage, the photochemical method can synthesize metal nanoparticles in selected microscopic regions. Photochemical synthesis also has the advantage of reaction
selectivity because light must be absorbed by a chemical substance in order for a reaction to take place. This allows light to trigger a reaction without affecting the external circumstances. Additional advantages include reaction controllability (due to light being the exclusive cause of the reaction) as well as offering the ability to tune the size and shape of the nanoparticles formed.\textsuperscript{49, 64-67}

Amidst the many advantageous aspects of photochemistry lie a few common glaring disadvantages in the form of long irradiation times and modest yields.\textsuperscript{61} To address these issues, McGilvray et al. studied the photochemical production of gold nanoparticles using I-2959, a water-soluble benzoin, as the reducing species.\textsuperscript{62} McGilvray found that the reason for the inefficient reaction process could be attributed to the quenching of the radicals by the transition metal ions. Benzoin triplet states have subnanosecond lifetimes and thus are not prone to quenching by transition metal ions which lead to a significantly shortened irradiation time necessary for the reaction to proceed. Marin et al. further expanded upon this concept by photochemically synthesizing gold nanoparticles using ketyl radicals derived from various benzoin sources as reducing agents.\textsuperscript{60} In these experiments, Marin and coworkers determined that the key to achieving reduced irradiation times lie in finding ways to minimize exited-state quenching by metals ions. This was accomplished by either using radical precursors with short triplet lifetimes or physically separating the radical generating reactions from the electron-transfer steps that lead to metal ion reduction.

Miranda et al. demonstrated an excellent example of one of the ways in which photochemistry could be used to tune the size and shape of the particles produced.\textsuperscript{63} Miranda studied the effect of wavelength and intensity of light on photochemical
synthesis processes. In this experiment, gold nanorods were produced by irradiating a solution containing \( \text{Au}^{+3} \) and \( \text{Au}^+ \) ions with varying wavelengths (254 nm and 300 nm) of light at various intensities. Gold nanorods of higher yields and longer lengths were produced with the 300 nm wavelength light as compared to 254 nm wavelength light. Higher intensities at shorter irradiation times lead to longer rods, but at excessively long times the rods began to dissociate into spherical nanoparticles. Thus, Miranda found that the length and shape of the gold nanostructures produced was dependent upon both the wavelength of light used and the intensity.

Similar to photochemistry, radiation chemistry employs the use of high energy radiation (\( X \)-radiation and \( \gamma \)-radiation, fast electrons, etc.) to initiate a chemical reaction.\(^{68-72} \) There are two approaches to this to of reaction: continuous irradiation (steady-state) and high intensity pulsed-radiation. Most applications of radiation chemistry primarily depend on the reactions of ions, atoms, free radicals, and excited states which are formed extremely rapidly upon absorption of the radiation. In the case of metal nanoparticle synthesis, generally high energy radiation is used to ionize a species which transfers electrons to metal ions thus forming zero valent metal. Pulse radiolysis in particular is a useful technique for generating and following the reactivities of molecular cations and anions. In addition, radiation chemistry can be performed at ambient temperature, does not introduce chemical impurities (because the solvent is usually the irradiated material), and the reactions proceed homogeneously (no local concentration gradients).\(^{69} \) An advantage of using radiation chemistry for the reduction of metal ions is that the initial concentration of the metal atoms can easily be varied and is known to a fairly accurate degree (within a few percent).\(^{70} \) One major drawback to
radiation chemistry is that in low dielectric constant liquids the ion recombination usually occurs rapidly.\textsuperscript{72} Thus, electron-capture or charge-transfer processes are frequently employed by adding solute to the system.

Arnim Henglein has been a pioneer in the field of metal nanoparticle synthesis using radiation chemistry. In the 1970s his group was able to successfully prepare silver nanoparticles using pulsed radiolysis.\textsuperscript{70} In another experiment, aqueous solutions containing $\text{Ag}_2\text{SO}_4$, methanol, and varying concentrations of $\text{CuSO}_4$ were irradiated with a high energy electron beam. The effect of the concentration of $\text{CuSO}_4$ on the formation of silver nanoparticles was studied. Henglein discovered that $\text{Ag}^+$ was reduced by $\text{Cu}^+$ at growing silver aggregates and the reaction required a certain size aggregate to proceed ($\text{Ag}^{+}/\text{Ag}_{10}$).

Biswal et al. performed in-depth studies on the size and shape tuning of gold nanoparticles synthesize using radiation chemistry.\textsuperscript{68} Gold nanoparticles were synthesized by irradiating an aqueous solution containing gold precursor ions, a stabilizing agent (cetyltrimethyl ammonium bromide), isopropanol, silver ions, and ascorbic acid. The effect of altering several reaction parameters (irradiation energy, concentrations, etc.) on the morphology of the gold nanoparticles was studied. They found that all of the reaction parameters had some sort of effect on the morphology. At low irradiation energies the size distribution of gold nanoparticles was narrow, while upon increasing the irradiation energy the size distribution became much wider. The concentrations of the various species had varying effects but the most notable was that at high gold ion concentrations spherical nanoparticles were formed but at lower concentrations nanorods were synthesized.
Biochemical methods have also been gaining notoriety in the field of metal nanoparticle synthesis. Biochemical synthesis employs the use of living organisms or biological chemicals in order to construct metal nanoparticles. In the former method, living organisms (often referred to as microbes) such as bacteria, fungi, or viruses are used to initiate and regulate chemical reactions. These microorganisms are resistant to toxic metal ions because they have adapted ways to reduce these ions to zero valent metal. This ability is exploited in order to synthesize metal nanoparticles. In the latter method, biological chemicals are used either as reducing agents or catalysts (frequently enzymes) that mediate the formation of growing crystals. Biochemical methods have the marked advantages of being biocompatible and environmentally friendly, both of which are growing concerns in recent times. Unfortunately, these methods have a number of disadvantages including a relatively narrow set of reaction conditions (neutral pH, ambient temperature and pressure, aqueous medium, etc.), time-consuming processes, and limited control over particle morphology.

One of the earlier works in using bacteria for metal nanoparticle synthesis was done by Beveridge et al. at the University of Guelph. In this experiment, the cell walls of Bacillus subtilis were used to reduce metal ions to metal nanoparticles. Beveridge discovered that the bacteria cell walls contained reactive sites that could bind watersoluble metal ions. These ions would then nucleate and form an inorganic deposition on the cell wall. Furthermore, these reactive sites could then be modified (e.g. amino functional groups could be reacted with an anhydride to change the electropositive charge to negative) to alter their chemical behavior. From these studies, it was determined that the majority of metal ion binding occurred at the highly reactive COO⁻ groups. In
addition to this, the metal deposits became less crystalline as the COO\(^-\) groups were neutralized or made positive.

While many biochemical processes lack the ability to effectively tune the size and shape of the synthesize nanostructures, some progress has been made in this field. One particular example was exhibited by Ma et al. in which different types of RNA were used to grow CdS nanocrystals.\(^7^6\) In this experiment, they used a folded wild-type tRNA and an unfolded mutant tRNA of identical lengths to mediate the formation of CdS nanocrystals. The nanocrystals mediated by the wild type tRNA were uniform in diameter at 6 nm while those mediated by the mutant tRNA had a bimodal distribution of 7 and 11.5 nm. With this work, Ma et al. were able to show that the nanocrystals sizes could be controlled by the type of folding present in the RNA that is used as a mediator.

Mechanochemical processes offer a solid-state method for the formation of metal nanoparticles, metal oxide nanoparticles, and bimetallic nanoparticles.\(^8^2\)\(^-\)\(^9^0\) Mechanochemical synthesis is different from standard ball milling, which is a top-down approach.\(^8^3\) Generally in standard ball milling, metal powders with large particle sizes are ground to roughly micron-sized particles with nanosized grains in an inert atmosphere. Mechanochemical synthesis is characterized by a solid-state displacement reaction that takes place during the balling process which can result in nanosized particles.\(^8^3\) In the case of metallic nanoparticle formation, a metal precursor can be reduced to metal nanoparticles by employing a reducing agent in conjunction with mechanical milling.\(^8^3\) Mechanochemical reactions for the formation of metal nanoparticles are advantageous because of their simplicity and low cost.\(^8^2\) Due to the solid-state nature of the reaction, the process does not require organic solvents which the
makes this method more environmentally sound.\textsuperscript{82} Because of the inherent nature of mechanochemical processes, repeated welding and fracturing of powder particles increases the area of contact between reaction particles which allows these processes to occur at lower temperatures than is normally necessary.\textsuperscript{85} In addition, the nature of the particles and the reaction kinetics can be controlled by adjusting several reactions parameters such as reactant ratios, milling time, ball-to-powder mass ratio, ball size, and milling temperature.\textsuperscript{83, 85} But this method does not come without drawbacks which can include long reaction times (up to several days in some cases).\textsuperscript{82}

McCormick et al. performed some of the earliest work in synthesizing metal nanoparticles with mechanochemical processes.\textsuperscript{84} In one experiment, a mixture of dried CuCl\textsubscript{2} powder and small Na pieces was loaded into a steel vial along with several steel balls. The mixture was then milled for 16 h in a high-purity argon filled glove box. By monitoring temperature during the milling, it was discovered that a solid-state combustion reaction occurred between the two materials. The combustion reaction resulted in the formation of a nanocrystalline mixture of Cu and NaCl. TEM and XRD studies showed the Cu particles had diameters in the range of 20-50 nm.

Furthermore, McCormick was able to show the size tunability of mechanically formed ZrO\textsubscript{2} particles.\textsuperscript{86} Powders containing nanosized particles and crystallites of ZrO\textsubscript{2} were synthesized by mechanically induced reduction of anhydrous ZrCl\textsubscript{4}. In these experiments, the effects of varying several reaction parameters were studied. When MgO was used as a reduction agent, the milling time significantly affected the end particle and crystallite size. By increasing the milling time from 10 minutes to 6 hours the average particle size decreased from 11 nm to 5 nm. When Li\textsubscript{2}O was used as a reducing agent,
particle and crystallite size was strongly affected by both the milling time and the presence of the inert LiCl diluent agent. For a given milling time, the addition of the diluent decreased the average crystallite size and increased the proportion of single crystal particles. The crystallite size of the ZrO$_2$ product formed by the undiluted reactant system was found to be independent of the milling time. But increasing the milling time of the diluted reactant mixture yielded ZrO$_2$ powders with a reduced crystallite size. The difference in behavior between the MgO and Li$_2$O systems was attributed to the significantly higher enthalpy change associated with the Li$_2$O system, which allowed crystal growth during reaction.

Electrochemistry offers a versatile method for synthesizing and depositing metal nanoparticles onto conductive substrates.\textsuperscript{91-100} In electrochemistry, metal ions are reduced to metal atoms by electrons provided from an electrode. In this way, either thin films or individual metal nanoparticles can be synthesized by potential regulation. The electrode potential controls the particle formation rate and, in turn, affects morphology. At lower formation rates the particles will be smooth while at higher rates a rougher surface is formed. Potential also affects the size of particles because the ratio of nucleation rate to growth rate of the nuclei depends on the applied potential. Another advantage of electrochemical synthesis is that metal salts are quickly reduced to metal nanoparticles under applied potential which results in short reaction times.\textsuperscript{92} Unfortunately, a major disadvantage of electrochemistry is that it is difficult to produce bulk quantities of synthesized materials.

While nanocrystallites of metals had previously been observed, Reetz and Helbig were the first to use electrochemistry to synthesize transition metal nanoparticles and tune
the particle size. In this experiment, palladium ions in a solution of acetonitrile/tetrahydrofuran were reduced to palladium colloid particles at a platinum electrode by applying a current and voltage to the system. Tetraalkylammonium salts were used as both the supporting electrolytes and stabilizers for the metal clusters. Thus, bulk metal was oxidized at the palladium anode, the metal cations migrated to the cathode, and reduction took place at the platinum cathode where agglomeration was prevented by the ammonium stabilizers. Palladium nanoparticles having diameters in the 1-10 nm range were formed and the size could be controlled by adjusting the current density. At a higher current density, smaller nanoparticles were synthesized.

Zoval et al. further demonstrated that electrochemistry could be used to deposit nanoparticles directly onto a cathode. Zoval was able to synthesize and deposit silver nanoparticles directly onto the atomically smooth basal plane of a graphite cathode. In his experiment, the potential of a graphite surface immersed in a dilute solution containing silver ions was pulsed with overpotentials. Silver nanoparticles with diameters in the range of 20-60 nm were electrochemically deposited onto the graphite surface. Zoval found that the number density of the silver nuclei did not increase with deposition time but the nuclei did grow in size.

1.3 Sonochemistry

Sonochemistry is a method for the synthesis of metal nanoparticles that has been gaining increased attention because of the extreme conditions that can be achieved which can result in unique mechanisms and reaction pathways. In sonochemistry, energy is supplied to the system by irradiating a liquid with high intensity ultrasonic waves in
Ultrasound uses these extreme conditions because acoustic wavelengths are much larger than molecular dimensions and thus no direct molecular level interaction between ultrasound and a chemical species takes place. Rather, ultrasound creates acoustic cavitation which is the formation, growth, and implosive collapse of bubbles in the liquid. When a liquid is irradiated with ultrasonic waves, it is subjected to alternating expansive and compressive acoustic waves. During the negative pressure cycle, the liquid is pulled apart at “weak spots” to form voids. The “weak spots” in the liquid are those locations which contain some form of gaseous impurity. Thus, chemical effects due to ultrasound are not observed when there are no dissolved gases in the system. The alternating pressure waves cause this newly formed void to oscillate between expansion and contraction cycles. In certain conditions, the bubble will grow at a greater rate during the expansion cycle than it shrinks during the compression cycle. The bubble can accumulate ultrasonic energy until it grows to a certain size (typically on the order of tens of micrometers). Eventually, the bubble may reach a size where it can no longer efficiently absorb energy and collapse. The collapse of the bubble can be assumed to occur adiabatically because it happens in such a small amount of time. At this point, the accumulated energy stored in the bubble will be released within a very short amount of time in a very localized spot leading to extreme conditions such as a temperature of ~5000 K and a pressure of ~1000 bar. These localized “hot spots” undergo very high heating and cooling rates on the order of > \(10^{10}\) K s\(^{-1}\). These high cooling rates hinder the organization and crystallization of products. Thus, in any case where volatile precursors enter the gas phase amorphous materials will be produced. In
addition to the gaseous collapsing bubble, there is also a thin liquid layer that surrounds the core.\textsuperscript{103, 104} This liquid layer is exposed to less extreme pressures and temperatures (a temperature of \(~1900\) K has been proposed by Suslick).\textsuperscript{103} Due to the milder conditions in the liquid layer, non-volatile precursors can react in this region and produce either amorphous or crystalline materials.\textsuperscript{104}

In producing metal nanoparticles, sonochemical synthesis has several advantages.\textsuperscript{101-104} No chemical reducing agent is necessary when using sonochemistry. Sonochemical irradiation of both water and organic solvents produces radicals which can act as reducing agents. Also due to the extreme conditions, reaction rates are reasonably fast and very small metal nanoparticles are typically formed. Sonochemistry, however, generally only produces spherical metal nanoparticles which limits its use in applications that require shape tuning.

Suslick and coworkers were the first to prepare nanostructured metals using sonochemistry.\textsuperscript{105} Suslick studied the effects of cavitation conditions on amorphous iron synthesis. He was able to show that by changing experimental parameters that control the conditions of bubble collapse, different chemical environments could be created. In this experiment a decane solution of iron pentacarbonyl was sonochemically irradiated under varying conditions (temperature, vapor pressure, atmosphere gas, etc.). Under weak cavitation conditions, ligand substitution and cluster formation reactions would occur. But when conditions were altered to maximize the cavitation heating, metal powder with an amorphous nanostructure was formed. The product was found to be \(>96\)% pure iron using elemental analysis. Suslick used microscopy techniques to determine the bulk material was a composite of many smaller iron particles. After long
exposure to heating from an electron beam, partial crystallization occurred and the crystallites had an average size of ~40 nm.

While sonochemical synthesis usually produces spherical particles, several groups have recently had some success in shape tuning. Jiang et al. were able to alter the shape of both gold and silver nanostructures using a seeded growth strategy. Spherical silver nanoparticles (2-5 nm) were first prepared using a reduction reaction. These particles were then employed as seeds for the sonochemically-assisted formation of silver nanoplates using PVP as a selective growth agent. The nanoplates were formed via an Ostwald ripening process in which the nanoparticles first rapidly grew to larger crystals and then slowly grew to uniform silver nanoplates. Acoustic cavitation was shown to increase the rate of Ostwald ripening. The silver nanoplates could then be used as a growth template for the formation of gold ring-like structures via a displacement reaction route.

Our group specializes in sonochemistry and has also had success in the field of sonochemically synthesized metal nanostructures. We were able to synthesize iron nanoparticles that contained an organic capping agent. This was accomplished by sonicating iron pentacarbonyl in deoxygenated dodecane that contained either dioctyl sulfosuccinate sodium salt or oleic acid. This reaction resulted in iron nanoparticles with an organic shell which protected the iron from oxidation at lower temperatures. The particles were ~7 nm and were stable for several months. Further studies yielded methods of shape tuning of the iron nanoparticles. In this experiment, we studied the sonochemical decomposition of iron pentacarbonyl in the presence of bovine serum albumen. Iron pentacarbonyl was sonicated in water with varying degrees of BSA
concentrations. It was found that the shape of the iron oxide nanostructures could be altered from spherical nanoparticles with no BSA, to nanoneedles or nanofibers depending on the BSA concentration.

We have also had success in sonochemically synthesizing organically capped aluminum nanoparticles.\textsuperscript{108, 109} In this method, alane N, N-dimethylamine was thermally decomposed with the catalyst titanium isopropoxide using sonochemistry in the presence of oleic acid. Characterization data showed that spherical aluminum nanoparticles were formed with average sizes of either 5 nm or 30 nm depending on the oleic acid concentration. The aluminum nanoparticles were air-stable at room temperature and it was found that the oleic acid layer was attached via an Al-O-C bond where the carbon atom was formerly involved in the carboxylic acid group.

1.3.1 Sonochemical Deposition onto Supports

Sonochemical techniques have also been used to deposit metal nanoparticles onto various substrates.\textsuperscript{111-126} Metal nanoparticle decoration of supports is of special interest because it allows for a fine dispersion and stabilization of small nanoparticles.\textsuperscript{113} This in turn leads to large number of chemically active atoms for processes to take place. Sonochemistry is well suited for this task because it has the ability to combine the synthesis of various metal nanomaterials with the deposition process.\textsuperscript{111} Also, the physical effects that result from ultrasound are particularly useful in depositing nanoparticles onto the surface of substrates.\textsuperscript{101} Acoustic cavitation generates regions with extreme conditions (high temperature, pressure, etc.) and creates shockwaves and
microjets that travel at high speeds. These unique conditions could lead to surface damage, high-speed collisions, and fragmentation of materials which all aid in the deposition process.

Gedanken and coworkers have done a large amount of research in the field of sonochemical deposition of in-situ generated metal nanoparticles. In one work, they showed that sonochemistry could be used to deposit air-stable iron nanoparticles onto carbon spheres. Slurry of carbon spheres and iron pentacarbonyl in dephenylmethane were irradiated with ultrasound under an argon atmosphere. The as-prepared amorphous material was then annealed in argon at 700 °C which led to the formation of air-stable iron nanoparticles. The iron nanoparticles were ~10 nm in size and deposited onto the surface of the carbon spheres.

Gedanken was also able sonochemically deposit silver and gold nanoparticles onto silica spheres. In the preparation of gold coated silica, slurry of silica submicrospheres, HAuCl4, and ammonia in an aqueous environment was subjected to ultrasonic irradiation under an argon atmosphere at room temperature. Various reaction conditions (temperature, pressure, concentrations, atmosphere, etc.) had to be carefully controlled in order for deposition to take place. The final product consisted of submicron sized silica spheres that contained uniform depositions of ~5 nm gold particles.

Taking it one step further, noble metal nanoparticles were synthesized and anchored to polystyrene spheres by Gedanken’s group. In this experiment, precursors of noble metals (Ag, Au, Pd, and Pt) were dispersed in an aqueous medium containing polystyrene spheres. Argon gas was bubbled through the mixture to expel any dissolved
oxygen/nitrogen. Then the solution was sonicated while ammonia was added dropwise and an argon/hydrogen gas mixture was bubbled through the solution. This reaction resulted in polystyrene spheres (with diameters of either 600 or 900 nm) which were uniformly coated with nanoparticles in the range of 5-10 nm for all the noble metal precursors used (Ag, Au, Pd, and Pt).

Rangari et al. used a sonochemical method in the preparation of silver decorated multi-walled carbon nanotubes (Ag-MWNTs) for antimicrobial applications. Rangari and coworkers sonochemically irradiated a solution of dimethylformamide (DMF) containing silver acetate and MWNTs while externally cooling the reaction vessel in order to avoid a temperature increase in the bulk solution. The Ag-MWNTs were then incorporated into a nylon polymer to form a nanocomposite material by an extrusion process. XRD and TEM studies showed the carbon nanotubes were uniformly coated with face-centered-cubic (fcc) silver nanoparticles with a particle size range of ~5-10 nm in diameter. The nylon-Ag-MWNTs composite material was found to have improved tensile strength, elastic modulus, thermal stability, and antimicrobial activity.

While it is clear that sonochemical methods can be used to synthesize metal nanoparticles and decorate different supports in-situ, the roles of the various reaction parameters are still not fully understood.
CHAPTER 2
EXPERIMENTAL METHODS

2.1 Materials

N,N-dimethylformamide (99.8%), silver acetate (99.99%), gold acetate (99.99%), PtCl$_2$ (99.99%), 13.3 M nitric acid (>69%), and carbon nanopowder (<50 nm, 99%) were all obtained from Aldrich and used as received. Reagent ethanol (90%) was obtained from Fisher Scientific and single-walled carbon nanotubes (SWNTs) were obtained from Carbon Solutions, Inc. Graphene oxide (GO) was obtained from Dr. Sun’s group at Clemson University where it was synthesized using a modified Hummers method.

2.2 Acid Treatment of Carbon Nanotubes and Carbon Nanoparticles

Most of the pristine single-walled carbon nanotubes generally contain impurities in the form of amorphous carbon and metal particles which are relics of nanotube synthesis.$^{127-135}$ In order to remove these impurities, the SWNTs were subjected to a nitric acid treatment. In a typical procedure to purify carbon nanotubes, 500 mg of SWNTs were added to a 2.6 M solution of 250 mL of nitric acid and heated to reflux temperature (~120 °C). The solution was left to reflux with stirring for 24 hours. Upon completion of refluxing, the mixture was cooled to room temperature before performing
the washing procedure. The solution was then centrifuged to accumulate the SWNTs and washed with de-ionized (DI) water. This process was repeated many times until the supernatant came to a neutral pH upon centrifugation. Then the nanotube sample was washed with acetone several times to remove the water. Nitrogen was blown over the sample to remove the acetone and the final product was recovered as a dried black powder.

Carbon nanoparticle (CNP) samples are composed of amorphous carbon, polycrystalline carbon structures, and metal nanoparticles (relics of nanoparticle synthesis).\(^{136-138}\) The nitric acid treatment for a CNP sample was performed in a fashion similar to the aforementioned SWNT purification. The procedure is briefly described as follows. 500 mg of CNPs was mixed with 100 mL of 2.6 M nitric acid and refluxed (\(~120\, ^\circ\text{C}\)) with stirring for 24 hours. Upon completion of the refluxing procedure, the CNPs were subjected to the same washing procedure as the SWNTs.

2.3 Sonochemical Synthesis of Ag-SWNTs at Room Temperature (R-DMF)

Similar to the method published by Rangari and co-workers, 50 mg of SWNTs were added to 100 mL of DMF in a 150 mL beaker and magnetically stirred for half an hour at room temperature. 500 mg of solid silver acetate was then added to the solution (for a concentration of 5 mg/mL and a silver acetate to SWNTs ratio of 10:1) and stirred for an additional half hour at room temperature. The solution was then subjected to high intensity sonochemical irradiation at 50% amplitude for 3 hours total time following a 1-second-on, 1-second-off pulsed procedure. The sonication instrument (Sonics Inc. Vibra...
Cell) consisted of a 0.5 in. diameter solid titanium horn operated at 20 kHz. The reaction vessel was externally cooled at 30 °C using an icy water bath in order to avoid a bulk solution temperature increase caused by the sonication process. Upon completion of the sonication process, the solution was transferred to a centrifuge tube and centrifuged to accumulate the product. The supernatant was removed and the product was then washed with ethanol and centrifuged. This washing procedure was repeated 4-5 times to remove excess silver acetate and reaction byproducts. The residual ethanol was then evaporated by blowing nitrogen across the surface of the sample.

2.4 Sonochemical Synthesis of Ag-SWNTs at Elevated Temperatures (S-DMF)

In this sonochemical method a solution composed of 50 mg of SWNTs in 15 mL of DMF was prepared in a sonication flask (Sonics Inc., Suslick flask). 25 mg silver acetate was added to the solution resulting in a concentration of ~1.67 mg/mL and a silver acetate to SWNTs ratio of 1:2. The solution was then sonicated in this flask using a pulsed (1-s-on, 1-s-off) procedure at 37% amplitude for 20 minutes total time. Upon sonication, the reaction solution turned black. The bulk solution reached a temperature of ~90 °C upon completion of the reaction and was left to cool to room temperature. Eventually, a black powder precipitated at the bottom of the flask if the solution was left to stand.

The product of the reaction was purified in the following manner. The mixture was first transferred to a tear drop flask and the DMF was removed using a rotary evaporator. The remaining solid material was transferred to a centrifuge tube where it
was washed with DI water and centrifuged to separate the product from the solution. This process was repeated five times with DI water as the wash to remove unreacted species, reaction by-products, and any remaining DMF. The process was then repeated five additional times with ethanol as the wash to remove any remaining unreacted species, by-products, and excess water. The ethanol was dried by blowing nitrogen across the surface of the solution. The final product for the silver decorated SWNTs was recovered as a black powder and the yield was ~56 mg.

**2.5 Thermal Synthesis of Ag-SWNTs (T-DMF)**

To synthesize Ag-SWNTs using the thermal method, a solution of 50 mg of acid treated SWNTs and 15 mL of DMF was prepared in a 2-neck 25 mL round bottom flask. The solution was refluxed (~153 °C) with magnetic stirring. Once the solution began refluxing, 25 mg silver acetate was added resulting in a concentration of ~1.67 mg/mL and a silver acetate to SWNTs ratio of 1:2. The solution was allowed to reflux for 20 minutes and then air cooled to room temperature. Upon completion of the refluxing time, the solution turned black. Eventually, a black powder precipitated at the bottom of the flask if the solution was left to stand. The product was recovered and purified in the same manner as described in Section 2.4 (Sonochemical Synthesis of Ag-SWNTs at Elevated Temperatures). The final product was recovered as a black powder and the yield was ~47.5 mg.
2.6 Sonochemical/Thermal Synthesis of Ag-SWNTs in Water (S-H$_2$O and T-H$_2$O)

The sonochemical and thermal reactions in water were performed in the same way as described in Sections 2.4 and 2.5, respectively. The sole difference was that in these reactions DI water was used as the solvent instead of DMF. In the sonochemical method, 50 mg of SWNTs and 25 mg of silver acetate (silver acetate to SWNTs ratio of 1:2) were added to 15 mL of DI water (which lead to a ~1.67 mg/mL concentration of silver acetate) in a Suslick flask. The mixture was sonicated in this flask using a pulsed (1-s-on, 1-s-off) procedure at 37% amplitude for 20 minutes total time. The solution darkened to an opaque black color during the course of the sonication time. If left to stand for a long period of time (~24 hours), the product would precipitate to the bottom of the flask. The product was purified in the same manner as described in Section 2.4. The final product was recovered as a black powder and the yield was ~46.3 mg.

In the thermal method, 50 mg of acid treated SWNTs was added to 15 mL of DI water in a 2-neck 25 mL round bottom flask. The mixture was magnetically stirred and heated until reflux (~100 °C). Upon reaching the reflux temperature, 25 mg silver acetate was added resulting in a concentration of ~1.67 mg/mL and a silver acetate to SWNTs ratio of 1:2. The solution was refluxed for 20 minutes and then air cooled to room temperature. The solution turned black in color during the course of the reaction. The solid product would fall out of solution and collect at the bottom of the flask if it was left to stand for more than 24 hours. As was previously stated in Section 2.4, the solvent was removed using a rotary evaporator and the product was subjected to many washing cycles with both water and ethanol. The final product was recovered as a black powder and the yield was ~36 mg.
2.7 Sonochemical Synthesis of Ag-GO

The sonochemical synthesis of silver decorated graphene oxide (Ag-GO) was similar to the synthesis of Ag-SWNTs method described in Section 2.4. A mixture of 50 mg of GO, 25 mg silver acetate, and 15 mL of DMF was prepared. The silver acetate concentration in DMF was ~1.67 mg/mL and the silver acetate to GO ratio was 1:2. The solution was sonicated in a Suslick flask at 37% amplitude for 20 minutes using a pulsed (1-s-on, 1-s-off) procedure. The product was purified in the same manner as described in Section 2.4. The final product was recovered as a flaky, black powder and the yield was ~33 mg.

2.8 Sonochemical Synthesis of Ag-CNPs

The sonochemical synthesis of silver-decorated CNPs (Ag-CNPs) was nearly identical to the method described in Section 2.4 with the sole difference being that CNPs were used as the support material instead of SWNTs. In this synthesis, 50 mg of CNPs in 15 mL of DMF was prepared in a sonication flask. 25 mg silver acetate was added to the solution resulting in a concentration of ~1.67 mg/mL and a silver acetate to CNPs ratio of 1:2. The mixture was subjected to sonochemical irradiating using a pulsed (1-s-on, 1-s-off) procedure at 37% amplitude for 20 minutes. The Ag-CNPs were separated from the solvent and other impurities using the manner described in Section 2.4. The final product was recovered as a black powder and the yield was ~51 mg.
2.9 Sonochemical Synthesis of Au-SWNTs

SWNTs were decorated with gold nanoparticles in much the same way as its silver decorated counterpart. 25 mg of gold acetate and 50 mg of SWNTs were added to 15 mL of DMF for a final gold acetate concentration of ~1.67 mg/mL and a gold acetate to SWNTs ratio of 1:2. High intensity ultrasound was delivered to the mixture in a Suslick flask using a pulsed (1-s-on, 1-s-off) procedure at 37% amplitude for 20 minutes. The product was purified in the same manner as described in Section 2.4. The final product, gold decorated SWNTs (Au-SWNTs), was recovered as a black powder and the yield was ~52 mg.

2.10 Sonochemical Synthesis of Pt-SWNTs

The synthesis of platinum nanoparticle-decorated SWNTs (Pt-SWNTs) was performed in the same manner as the Ag-SWNTs and Au-SWNTs found in Sections 2.4 and 2.7 respectively. 50 mg of SWNTs was added to 15 mL of DMF in a Suslick flask. A mixture with a concentration of ~1.67 mg/mL metal precursor was prepared by adding 25 mg PtCl₂ (resulting in a PtCl₂ to SWNTs ratio of 1:2). The solution was then sonicated in this flask using a pulsed (1-s-on, 1-s-off) procedure at 37% amplitude for 20 minutes. Unreacted PtCl₂, reaction by-products, and excess DMF were removed with a rotary evaporator and centrifugation following the purification procedure used in Section 2.4. The final product was recovered as a black powder and the yield was ~51.5 mg.
2.11 Measurements

A Hitachi H-7600 operated at 100 kV was used to record transmission electron microscopy (TEM) images via a charge-coupled device (CCD) camera. Samples were prepared by diluting a small amount of powdered sample in isopropyl alcohol, sonicating in solution, and drip-spotting onto 400 mesh copper grids (obtained from SPI Supplies).

The crystal structure of the samples was analyzed by x-ray powder diffraction (XRD) using Bruker D8-Advanced equipped with a Cu α source, monochromator, and a Sol-X detector. Solid samples were placed on a Si zero-background holder for characterization. In a typical analysis, scans were run over a 2T range for 5 to 85 degrees with an angle increment of 0.1 degrees and a collection time of 1 sec/step. Observed XRD patterns were identified by comparison with patterns from the International Centre for Diffraction Data (ICDDS) crystallographic database.

A Perkin-Elmer L100 FTIR (Fourier-transform infrared) absorption spectrophotometer equipped with a universal attenuated total reflectance sample attachment was used to record infrared absorption spectra. Solid samples were placed directly on the diamond/ZnSe crystal plate with an applied pressure for analysis. Spectra were obtained over a wavenumber range from 4000 to 650 cm\(^{-1}\) with each spectrum being the average of 3 scans with a 4 cm\(^{-1}\) spectral resolution.

A TA instruments STD Q600 dual DSC/TGA (differential scanning calorimetry/thermal gravimetric analysis) with open pan alumina sample cups was used to analyze the mass content and energetic behavior of the samples as a function of
temperature. The samples were heated at a rate of 10 ºC/min from room temperature to 800 ºC under a constant 100 mL/min flow of air.
CHAPTER 3
SILVER-DECORATED SINGLE-WALLED CARBON NANOTUBES

3.1 Background

The purpose of this research is to determine the optimal synthesis procedure for preparing silver-decorated single-walled carbon nanotubes (Ag-SWNTs). The optimal product in this case is defined as well-dispersed single-walled carbon nanotubes homogeneously decorated with high silver content in the form of small, uniformly sized silver nanoparticles. Ag-SWNTs present an interesting and practical case study due to their myriad possible applications. They have been shown to have potential uses as photocatalysts, sensors, biomedical devices, etc. Many different synthesis methods have been established in the literature for the preparation of silver decorated carbon nanostructures including electrodeposition, mechanochemical ball milling, and sonochemistry. More specifically, Rangari et al. previously published a method for decorating multi-walled carbon nanotubes (MWNTs) with silver nanoparticles using sonochemistry in DMF. Because our group has previously utilized sonochemistry for the synthesis of metal nanoparticles with success, Rangari’s method served as an excellent entrance point for synthesis exploration.

In the Rangari method, the authors added 50 mg of MWNTs to 100 mL of DMF and stirred for half an hour at room temperature. They then added 500 mg of solid silver
acetate (5 mg/mL concentration) to the solution (yielding a silver acetate to MWNTs ratio of 10:1) and stirred for an additional half hour at room temperature. The solution was then subjected to high intensity sonochemical irradiation at an amplitude of 50% (~27 W) and a frequency of 20 kHz for 3 hours. The authors externally cooled the reaction vessel at 30 °C in order to prevent a bulk solution temperature increase caused by the sonication process. They then repeatedly washed and centrifuged the product solution using ethanol as a solvent. Rangari et al.’s TEM analysis showed MWNTs that were coated with small (~5-10 nm in diameter) spherical nanoparticles. Their XRD analysis showed the spectrum of the nanoparticle-decorated MWNTs matched with the spectrum of fcc silver.

We repeated Rangari’s preparation method in order to establish a baseline reaction for synthesis exploration. In this synthesis, SWNTs were used in place of the MWNTs while all other reaction parameters remained unchanged. Upon completion of the sonication process, the reaction product (R-DMF) was a viscous, black solution. The increase in the viscosity of the product solution over the initial DMF/SWNTs solution was due to the formation of a stable SWNT suspension. After repeated washing with ethanol, the sample was dried under nitrogen. Once dried, the final product was a black and white powder.
3.2 Characterization of R-DMF

TEM images of the R-DMF sample were taken to determine the morphology, extent of decoration, and size distribution of the nanoparticles decorating the SWNTs. TEM images of the R-DMF sample are shown in Figure 3.1 along with an image of undecorated, acid-purified SWNTs. The analysis of the acid-purified SWNTs clearly showed a network of nanotubes composed of thin tube bundles. The bundles were clear of most amorphous carbon and metal catalysts particles. It should be noted here that while amorphous carbon and metal catalyst particles are not visible in the image, these materials are still present in the sample but in lower quantities. The images of the nanotubes after silver decoration revealed mostly agglomerations of large globule-like structures. These globules were decorated with smaller nanoparticles of widely varying sizes. The nanoparticles can be indentified in the TEM images as the darker spheres. From the bottom TEM image in Figure 3.1, the average size of the nanoparticles decorating the globules was ~4.2 nm and varied from 1.5 to 8 nm. A few examples of individual SWNT bundles could be seen emerging from the globules; however, the majority of the material appeared to consist of the globules. These SWNTs were decorated with much smaller nanoparticles of variable sizes. From the middle image in Figure 3.1, the estimated average size of the nanoparticles decorating the nanotubes was ~2.4 nm and varied from 0.5 to 4 nm. Although very few SWNT bundles were seen throughout the TEM images, it is believed the bundles are present but obscured by the large, globular structures. Silver acetate is fairly insoluble in DMF and was used in
Figure 3.1: TEM images of acid-purified SWNTs before (top left) and after (top right, bottom) the Rangari reaction. The silver nanoparticles decorating the nanotubes had an average size of ~2.4 nm and a size distribution of ~0.5-4 nm. The nanoparticles on the globular structures had an average size of ~4.2 nm and a size distribution of ~1.5-8 nm. The scale bar shown for all three images indicates 20 nm.
excess in this reaction. These factors may have combined to produce the observed globules in this example.

XRD analysis was performed to confirm the presence of silver in the sample. The XRD results for the R-DMF reaction are displayed in conjunction with pristine silver acetate and card data for face-centered cubic (fcc) silver (ICDD 00-004-0783) (Figure 3.2). The spectrum of the R-DMF sample closely resembled the silver acetate spectrum with all silver acetate peaks present. No individual peaks in the R-DMF sample spectrum could be clearly matched to the card data for fcc silver. The XRD data indicated the R-DMF sample was composed of unreacted silver acetate.

FTIR analysis was performed in order to determine organic functionality present in the samples. The spectrum of the R-DMF sample is depicted with the spectrum for neat silver acetate in Figure 3.3. Neat silver acetate exhibited four distinct peaks. The peaks centered at 1502 and 1432 cm\(^{-1}\) correspond to the C-C backbone vibration and C-O stretching respectively while the peaks at 1377 and 1342 cm\(^{-1}\) refer to C-H bending.\(^{148}\) The R-DMF sample spectrum was identical to that of neat silver acetate, indicating the sample was composed of unreacted silver acetate.

The TEM images for this sample showed large globular structures that covered most of the sample with few visible nanotube bundles. XRD and FTIR analysis showed strong silver acetate signals with no evidence of fcc silver metal. From these characterization results it is clear that unreacted silver acetate was present in the sample. The purification process in this synthesis employed the use of ethanol as a washing agent for removing unreacted silver acetate. It should be noted that the solubility of silver
Figure 3.2: XRD spectra for the R-DMF sample, neat silver acetate, and ICDD pattern for fcc silver (00-004-0783). The spectrum of the R-DMF sample closely resembles the silver acetate spectrum with all silver acetate peaks present. No individual peaks in the R-DMF sample spectrum could be clearly matched to the card data for fcc silver.
Figure 3.3: FTIR spectra for the R-DMF sample (top) and neat silver acetate (bottom). The peaks centered at 1502 and 1432 cm\(^{-1}\) correspond to the C-C backbone vibration and C-O stretching respectively while the doublet at 1377 and 1342 cm\(^{-1}\) refers to C-H bending. The two spectra are identical indicating that the R-DMF sample contained silver acetate.
acetate in ethanol is poor. Therefore, we performed a secondary washing with water. While silver acetate is only slightly soluble in water as well, it does float to the top of the solvent while carbon nanotubes sink to the bottom which makes water a useful medium for separating the two components. After further washing with water, the R-DMF sample was characterized again using TEM, XRD, and FTIR and the data is shown in Figure 3.4. TEM images showed that while there appeared to be less of the globular structures, many still remained in the sample. The depicted TEM image shows that carbon nanotubes decorated with nanoparticles could be more easily seen. XRD data indicated that the sample contained all fcc silver peaks but also a few peaks associated with silver acetate. FTIR data showed very weak peaks which may be attributed to silver acetate. From this characterization data it was clear that the choice of solvent for washing the product sample was important. Because this newly collected data was in better agreement with the data Rangari et al. obtained, it is possible they may have not mentioned additional washing used in the sonochemical preparation of Ag-SWNTs. We were able to use the Rangari method to synthesize Ag-SWNTs but the reaction procedure and product were less than optimal; therefore, we made changes in attempt to optimize the reaction and final product.
Figure 3.4: TEM image (top left), XRD data (bottom), and FTIR data (top right) for the R-DMF sample after the more thorough washing procedure. The TEM image shows that many of the globular structures were removed and a clear view of the nanotubes was visible. XRD data shows that fcc silver is present in the R-DMF sample and FTIR results indicate that most silver acetate has been removed.
3.3 Improved Method for Sonochemistry in DMF (S-DMF)

Based on the analysis of the R-DMF sample, we modified the reaction in an attempt to obtain a more optimized product which will be referred to as S-DMF. Because previous characterization results showed such a great amount of unreacted silver acetate, the first modification of the new synthesis procedure was to reduce the amount of silver acetate. The second modification consisted of utilizing a more effective washing procedure with water. In addition to these changes, three other modifications were made to the procedure. (1) The cooling mechanism was removed which allowed the solution to be heated to ~90 °C. This is due to the fact that acoustic cavitation leads to extreme temperature regions which will dissipate and heat the bulk solution. The higher temperature can improve the solubility of silver acetate in DMF, and can improve DMF’s ability to reduce silver acetate.54 Pastoriza-Santos et al. conducted a series of experiments to determine the effect of temperature on the reduction rate of silver acetate in DMF.54 It was determined that silver acetate would be reduced to silver metal in DMF at room temperature but the reaction would take weeks to reach completion. At higher temperatures, the reaction proceeded much faster with the reaction reaching completion in seconds at reflux temperature (~153 °C). (2) The volume of the solvent was reduced. Decreasing the volume allowed for a greater bulk solution temperature to be achieved and increased the importance of acoustic cavitation in the reaction. Acoustic cavitation only occurs in the localized area around where the sonochemical horn is located in the solution. By reducing the volume, a greater percentage of the solution was directly subjected to acoustic cavitation. (3) A 1-s-on 1-s-off pulsed procedure was used to attain better coupling of the sonochemical energy with the solution. Continuous sonication
tends to create a void at the tip of the horn whereas pulsed sonication allows the solution to regain contact with the horn ensuring that each pulse is directly coupled with the solvent. Several other parameters were altered based on our group’s past experience with sonochemical synthesis of other metal nanoparticles. We did not believe that the sonication amplitude and reaction time needed to have such values to synthesize the desired product thus the sonication amplitude was reduced from 50% to 37% and the sonication time was reduced from 3 hours to 20 minutes.

These changes from the Rangari method resulted in the following procedure: a solution composed of 50 mg SWNTs and 25 mg silver acetate in 15 mL DMF was sonicated at 37% (~22 W) amplitude and 20 kHz for 20 minutes using a pulsed (1-s-on, 1-s-off) procedure. Upon completion of the sonication time, the bulk solution typically reached a temperature of ~90 ºC. The product was a viscous, black solution. The solution was placed in a rotary evaporator to remove the solvent then washed and centrifuged with water 5 times and ethanol 5 times. Nitrogen was blown across the surface of the solution to remove the remaining ethanol. After drying, the product was obtained in the form of a black powder.

3.3.1 Characterization of S-DMF

TEM images were taken to determine the effects of the altered synthesis method on the decoration of the SWNTs. A representative TEM image of the S-DMF sample is depicted along with the R-DMF sample image in Figure 3.5. The morphology of S-DMF
Figure 3.5: TEM images of R-DMF (left) compared to S-DMF (right). The S-DMF sample nanoparticles have an average size of ~5.7 nm and a size distribution of 1-15 nm. The scale bars for both images represent 20 nm.
vastly differed from that of the R-DMF sample. The globule agglomerations in the R-DMF sample were not present in S-DMF and a clear view of the SWNT bundles was visible. The nanotube bundles were well-dispersed and created an inter-woven network of SWNT bundles with clearly defined edges and little agglomeration. Note that individual SWNTs are extremely difficult to see with TEM and all nanotubes seen in the images are bundled. These SWNT bundles were decorated with spherical nanoparticles. The nanoparticles were deposited on the SWNTs fairly homogeneously decorating thin nanotube bundles uniformly well with little to no nanoparticle agglomeration. There was also evidence of what appeared to be amorphous carbon but it occurred in a much lower relative amount to the carbon nanotubes. This amorphous carbon was also decorated in a similar way to the SWNT bundles. Size distribution characterization was performed on the TEM images in order to determine average nanoparticle size and range and is shown in Figure 3.6. The particles were small with an average diameter of ~5.7 nm and did not vary widely in size with an estimated range of ~2-15 nm.

XRD data of the S-DMF sample was taken and analyzed in order to determine the nature of the nanoparticles. The results for the S-DMF reaction are displayed in conjunction with ICDD card data for face-centered cubic (fcc) silver (ICDD 00-004-0783) in Figure 3.7. The S-DMF spectrum showed peaks at 38.1°, 44.3°, 64.4°, 77.5°, and 81.5° which correspond to the (111), (200), (220), (311) and (222) crystal planes of fcc silver respectively. The small, barely-visible, broad peak centered at 26.6° was attributed to the acid-treated SWNTs. Consistent with this assignment, this peak was present in an XRD spectrum of the undecorated acid-treated SWNTs. Its identity was further demonstrated when the peak disappeared in the S-DMF after the sample was heated to
Figure 3.6: Size distribution graph of the nanoparticles decorating the SWNTs in the S-DMF sample. The nanoparticles had an average size of ~5.7 nm and a range of 1-15 nm.
Figure 3.7: XRD spectra for S-DMF (top) and ICDD pattern for silver (bottom) (00-004-0783). The peaks at 38.1°, 44.3°, 64.4°, 77.5°, and 81.5° correspond to the (111), (200), (220), (311) and (222) crystal planes of fcc silver respectively (ICDD 00-004-0783).
800 °C in air (past the carbon combustion temperatures of ~500-700 °C). The results of the XRD analysis indicated that fcc silver was present in the S-DMF sample.

FTIR analysis was performed on the S-DMF sample to determine if any unreacted silver acetate was present. The FTIR spectrum of S-DMF (not shown in figures) did not show any of the strong silver acetate peaks that were seen in the R-DMF reaction sample. The absence of silver acetate peaks in the S-DMF spectrum indicated that most of the silver acetate was either reduced to silver metal or washed from the sample.

The mass content and energetic behavior of the S-DMF sample and acid-treated SWNTs were analyzed using simultaneous DSC/TGA and the results are displayed in Figure 3.8. Samples were analyzed under a constant 100 mL/min flow of air for a temperature range of 25 °C to 800 °C at a heating rate of 10 °C/min. Commercially available carbon nanotubes have been previously determined to be a mixture of carbon nanotubes, amorphous carbon, graphitic carbon, and residual metal catalyst particles. The TGA of acid-treated SWNTs showed a decrease in mass around 560 °C which corresponded with the combustion of carbon nanotubes including amorphous and graphitic carbon. Because 800 °C is well past the carbon combustion temperature, the remaining mass was taken to be residual metal catalysts. The TGA curve of the S-DMF sample showed a similar mass loss due to carbon nanotube combustion but at ~410 °C, a temperature that was ~150 °C lower than the purified SWNTs. The difference in final weight percentages at 800 °C between S-DMF and the neat acid-treated SWNTs can
Figure 3.8: TGA (top) and DSC (bottom) data for acid-treated SWNT (solid line) and S-DMF (dashed line). The TGA curves for the acid-treated SWNTs and the S-DMF sample show a difference in final mass percentages which was used to calculate the silver content and found to be ~35%. The DSC curve for the acid-treated SWNTs showed an intense peak centered at ~560 ºC which was attributed to carbon nanotube combustion closely followed by a shoulder which resulted from combustion of residual graphitic carbon. The DSC curve of the S-DMF sample showed the same pattern but a significantly earlier temperature (~415 ºC).
be attributed to silver mass because silver metal does not oxidize under the conditions employed here.\textsuperscript{1-3} This was confirmed by XRD analysis of the S-DMF sample after the TGA/DSC treatment (heating to 800 °C) which showed only silver metal. The residual masses of the S-DMF and undecorated carbon nanotubes were 33% and 3%, respectively. Thus the silver content of the S-DMF sample was determined to be ~30%.

The DSC characterization data for the pristine SWNTs contained two peaks (Figure 3.8). The first intense peak, centered at ~560 °C, corresponded with carbon nanotube combustion.\textsuperscript{131, 132, 149} A second, less intense peak closely followed the first peak. The smaller peak, centered at ~660 °C, has been attributed to the combustion of residual graphitic carbon.\textsuperscript{131, 132} As expected from the TGA results, the DSC results of the S-DMF sample showed a similar two-peak pattern but at significantly lower temperatures (415 °C and 470 °C respectively) than the acid-treated SWNTs. Because these samples were analyzed using an open pan configuration, the DSC results are qualitative in nature. No intra-sample comparisons of the peak energies were made.

As was shown in the characterization results, the changes made from the R-DMF reaction to the S-DMF reaction yielded a product that was closer to the desired optimal product than what was seen in the Rangari method. As a reminder, the optimal product has been defined as well-dispersed SWNTs homogeneously decorated with a high silver content in the form of small, uniformly-sized silver nanoparticles. TEM images showed well-dispersed nanotubes with a uniform decoration of nanoparticles. XRD results demonstrated these nanoparticles were fcc silver metal. FTIR results further indicated that no residual silver acetate was present in the sample. By following the modified procedure we have shown that sonochemistry coupled with DMF reduction can produce
well-decorated SWNT samples; however, because small changes in the procedure resulted in apparent significant changes in the sample it would be of great value to further investigate this reaction and work toward better optimization. To accomplish this, we repeated the reaction that produced S-DMF by varying the means for heating the sample (via sonochemistry or direct heat) and the solvent (DMF or water) one parameter at a time.

3.4 Sonochemistry in Water (S-H₂O)

The purpose of this experiment was to gain a better understanding of the role of solvent in the synthesis of Ag-SWNTs. Because both acoustic cavitation and the solvent DMF have the potential to produce silver nanoparticles, we desired to separate these two processes. Water as a non-reducing solvent will allow us to examine just the effect of acoustic cavitation. In this experiment silver decoration on SWNTs was done in a similar fashion to the previous S-DMF method but with DI water used as the solvent. The product of this reaction will be named S-H₂O. In this reaction a solution composed of 50 mg SWNTs, 25 mg silver acetate, and 15 mL DI water was sonicated at 37% amplitude and 20 kHz for 20 minutes using a pulsed procedure. Upon completion of the reaction, the product was a viscous, black solution. The product of this reaction after the washing and drying was different from the S-DMF sample in appearance. The final product was a powder composed of both black and silver particles.
3.4.1 Characterization of S-H$_2$O

The TEM images of S-H$_2$O sample revealed distinctly different results from the S-DMF sample. Representative images of the S-H$_2$O sample as compared to the S-DMF sample are shown in Figure 3.9. While both samples showed the formation of nanoparticles, morphological differences were present. The most notable difference between the two samples was the widespread presence of agglomerated material in the S-H$_2$O sample. While bearing some similarities to the globules observed in the R-DMF sample, further analysis will show the agglomerations seen in Figure 3.9 are not due to silver acetate but likely due to amorphous carbon. Although a fair number of carbon nanotubes were still visible, these agglomerations appeared in localized pockets which covered a large portion of the nanotube network. The vast majority of the nanoparticles were contained within these agglomerations. While some nanoparticles did decorate the individual nanotube bundles the decoration was inhomogeneous. Large portions of carbon nanotubes were clear of any decoration. Size distribution characterization (shown in Figure 3.10) showed the nanoparticles were similar in average size (~7.3 nm) but had a wider range (4-49 nm) than those of the S-DMF reaction.
Figure 3.9: TEM images of the S-DMF (top left) sample compared to the S-H$_2$O (bottom, top right) sample. The S-H$_2$O sample nanoparticles have an average size of ~7.3 nm and a size range of 4-50 nm. The scale bars for the top left and bottom images represents 20 nm. The scale bar for the top right image indicates 100 nm.
Figure 3.10: Size distribution graph of the nanoparticles decorating the SWNTs in the S-H₂O sample. The nanoparticles had an average size of ~7.3 nm and a range of 4-50 nm.
Again, just as with the S-DMF sample, the XRD spectrum showed silver peaks and did not contain any evidence of silver acetate. The S-H$_2$O spectrum is shown with fcc silver card data in Figure 3.11. The S-H$_2$O spectrum showed peaks at 38.1º, 44.3º, 64.4º, 77.5º, and 81.5º which correspond to the (111), (200), (220), (311) and (222) crystal planes of fcc silver respectively (ICDD 00-004-0783). As in the S-DMF sample, this spectrum showed silver was formed and no silver acetate was in the sample. The lack of new peaks due to the presence of the agglomerations seemed to indicate that the agglomerations were either fcc silver or amorphous in nature.

The FTIR results for the S-H$_2$O sample are the same as those of the S-DMF sample. The FTIR spectrum of S-H$_2$O did not show any strong features consistent with silver acetate peaks. These results indicated the sample was not composed of silver acetate.

The weight loss and energetic behavior of the S-H$_2$O sample are shown in Figure 3.12 alongside acid-treated SWNTs for comparison purposes. The TGA curve of the S-H$_2$O sample showed a weight loss because of the carbon nanotube combustion with the same shift (by ~150 ºC) to a lower temperature that was seen in the S-DMF sample. The residual mass of the S-H$_2$O sample was ~33% and thus the silver content of the sample was found to be ~30%. As expected from the TGA data, the DSC curve of the S-H$_2$O showed both carbon combustion peaks occurring at lower temperatures than pristine, undecorated SWNTs.

By changing the reaction solvent from DMF to water we have removed solvent reduction as a means to make silver nanoparticles and yet the reaction effectively
Figure 3.11: XRD spectra for S-H$_2$O (top) and ICDD pattern for silver (bottom) (00-004-0783). The peaks at 38.1°, 44.3°, 64.4°, 77.5°, and 81.5° correspond to the (111), (200), (220), (311) and (222) crystal planes of fcc silver respectively (ICDD 00-004-0783).
Figure 3.12: TGA (top) and DSC (bottom) data for acid-treated SWNT (solid line) and S-H$_2$O (dashed line). The TGA curves for the acid-treated SWNTs and the S-H$_2$O sample show a difference in final mass percentages which was used to calculate the silver content and found to be ~30%. The DSC curve for the acid-treated SWNTs showed an intense peak centered at ~560 °C which was attributed to carbon nanotube combustion closely followed by a shoulder which resulted from combustion of residual graphitic carbon. The DSC curve of the S-H$_2$O sample showed the same pattern but a significantly earlier temperature (~415 °C).
produced silver nanoparticles with approximately the same diameter. The major
difference was the appearance of agglomerations which we attributed to amorphous
carbon because no silver acetate was seen in XRD and FTIR analyses. Further, it
appeared that in water the nanoparticles preferentially decorate the agglomerations. It is
therefore likely that DMF reduction is important in obtaining silver-decorated SWNTs.
These results showed that sonochemistry was still capable of producing silver
nanoparticles, but because sonochemistry produces two processes capable of reduction
(acoustic cavitation and bulk heating) it would be worthwhile to examine the outcome
when sonochemistry is removed and heat is applied in a traditional manner.

3.5 Thermal reactions (T-DMF and T-H₂O)

The next two reactions were designed to determine the importance of
sonochemistry in the preparation of Ag-SWNTs, specifically to examine the role of
acoustic cavitation versus simple bulk heating of the solution. In the following two
experiments, Ag-SWNTs were synthesized using a thermal heating method in place of
sonochemistry. The thermal heating method was completed in both DMF and water and
the products of these reactions will be referred to as T-DMF and T-H₂O, respectively. In
these reactions, a solution of 50 mg SWNTs and 15 mL of solvent (DMF or water) was
prepared and heated to reflux (~153 or 100 °C, respectively). Once at reflux temperature,
25 mg of silver acetate was added and the solution was allowed to reflux for 20 minutes
then air cooled to room temperature. Upon washing and drying, both the T-DMF and T-
H$_2$O samples were recovered as powders. The appearance of the products was similar to the S-H$_2$O sample in which a mix of black and silver powder was obtained.

3.5.1 Characterization of T-DMF and T-H$_2$O

The TEM images of the T-DMF and T-H$_2$O samples are shown and compared in Figure 3.13. The TEM images of the T-DMF sample showed that the final product was much different in morphology than the desired optimal products. The nanotubes seemed to have become more agglomerated after the reaction. In the acid-purified SWNT sample (Figure 3.1), networks of well-dispersed individual nanotube bundles could be seen. After the T-DMF reaction, the nanotubes had become more tightly bunched creating a denser network of nanotubes than what was previously seen. The T-DMF reaction did produce some discrete spherical nanoparticles, but most nanoparticles tended to group together in localized clusters or agglomerations. While these clusters did appear in multiple locations throughout the sample, the majority of the nanotubes were completely untouched by nanoparticles. The nanoparticles did not appear to decorate individual nanotube bundles, but rather seemed to be entirely separate species. Particle size characterization data (seen in Figure 3.14 for all samples) shows that the T-DMF nanoparticles were very large in size (avg. $\sim$43.3 nm) with a wide range of diameters (2-115 nm).
Figure 3.13: TEM images of T-DMF (top) and T-H\textsubscript{2}O (bottom) samples. The T-DMF sample nanoparticles have an average size of ~43.3 nm and a size range of 2-115 nm. The T-H\textsubscript{2}O sample nanoparticles have an average size of ~6.7 nm and a size range of 2-25 nm. The scale bars for all four images represent 100 nm.
Figure 3.14: Size distribution graphs of the nanoparticles decorating the S-DMF, S-H$_2$O, T-DMF, and T-H$_2$O samples. The S-DMF sample nanoparticles had an average size of ~5.7 nm and a range of 1-15 nm. The S-H$_2$O sample nanoparticles had an average size of ~7.3 nm and a range of 4-50 nm. The T-DMF sample nanoparticles had an average size of ~43.3 nm and a range of 2-115 nm. The T-H$_2$O sample nanoparticles had an average size of ~6.7 nm and a range of 2-25 nm. The insets show the majority of the nanoparticle populations occur in the range of 0-25 nm.
The TEM images of the T-H$_2$O sample are shown in Figure 3.13. T-H$_2$O sample was surprisingly similar in morphology to the S-H$_2$O sample. As was seen in the S-H$_2$O sample, the carbon nanotube network contained multiple agglomerations. Spherical nanoparticles were formed and nanoparticles did occasionally decorate thin nanotube bundles, but the majority of the decoration was once again located on this amorphous material. As seen in Figure 3.14, small nanoparticles (avg. ~6.7 nm) with a relatively narrow size distribution (range of ~2-25 nm) were formed.

The XRD spectra for all samples are shown in Figure 3.15. The XRD spectra for the thermal samples had small differences when compared to the other reactions. The spectra for both thermal samples showed peaks at 38.1°, 44.3°, 64.4°, 77.5°, and 81.5° which correspond to the (111), (200), (220), (311) and (222) crystal planes of fcc silver respectively (ICDD 00-004-0783). The small, sharp peaks at ~29° and 33° in the T-DMF sample were assigned to unreacted silver acetate that was not successfully removed in the washing procedure. The small, broad peak at 26.6° in the samples was attributed to the SWNTs. The XRD spectra for both samples indicated that fcc silver metal was present.

The FTIR results of the thermal samples were identical to the spectrum for the S-DMF sample. The FTIR spectrum of samples did not show any strong features consistent with silver acetate peaks. These results in conjunction with XRD data demonstrated most silver acetate had been reduced to silver metal or the washing procedure removed most of the unreacted silver acetate from the sample, thus any agglomerations observed in the TEM images not clearly composed of silver nanoparticles were likely due to amorphous carbon.
Figure 3.15: XRD spectra of S-DMF, S-H\textsubscript{2}O, T-DMF, T-H\textsubscript{2}O, and ICDD card data for fcc silver. The peaks at 38.1\(^\circ\), 44.3\(^\circ\), 64.4\(^\circ\), 77.5\(^\circ\), and 81.5\(^\circ\) correspond to the (111), (200), (220), (311) and (222) crystal planes of fcc silver respectively (ICDD 00-004-0783).
The TGA curve of all four samples are shown in Figure 3.16. The TGA data for both thermal samples showed a mass loss due to carbon combustion with the same shift to a lower temperature (by \(~150 \, ^\circ\text{C}\)) that was seen in the other samples. The final residual masses for the T-DMF and T-H_2O samples were found to be \(~33\%\) and \(~28\%\), respectively. Accounting for the residual mass of 3\% that was found in the pristine SWNTs, the silver content of the T-DMF and T-H_2O samples were found to be \(~30\%\) and 25\%, respectively. While the value of 30\% for the T-DMF was similar to the silver content for the S-DMF and S-H_2O, the value of 25\% for the T-H_2O sample was significantly lower again suggesting the importance of the DMF reduction process in the production of silver nanoparticles. As expected, the DSC results (not shown) of the thermal samples showed that the carbon combustion peaks occurred at temperatures of \(~150 \, ^\circ\text{C}\) lower than the carbon combustion peaks of undecorated SWNTs.
Figure 3.16: TGA data for S-DMF, S-H$_2$O, T-DMF, T-H$_2$O, and acid-treated SWNTs. The final mass percentages of the samples compared with undecorated, acid-treated SWNTs were used to calculate the silver content of each sample. The silver content of the samples was found to be: 35% for S-DMF, 30% for S-H$_2$O, 30% for T-DMF, and 25% for T-H$_2$O.
3.6 Summary

As previously stated, the goal of this work was to determine the optimal process for producing Ag-SWNTs. The best product was defined as well-dispersed single-walled carbon nanotubes homogeneously decorated with a high content of small, uniformly sized silver nanoparticles. Four different synthesis procedures which employed a combination of sonochemical energy, thermal energy, and different solvent environments (DMF and water) were used to prepare Ag-SWNTs via the reduction of silver acetate in the presence of SWNTs. XRD analysis showed that all four synthesis procedures reduced silver acetate to fcc silver metal and no unreacted silver acetate was present (a trivial amount may have been present in the T-DMF sample). FTIR analyses further confirmed that most of the silver acetate was successfully reduced or washed away from the final product in all four samples.

TEM images for all four samples are again displayed in Figure 3.17. These images showed that while all four samples contained nanoparticles, the morphology and decoration were different in each sample. To review, the S-DMF reaction produced small (avg. size ~5.7 nm) nanoparticles that were the most homogeneous in both size (range of 1-14 nm) and decoration of nanotubes. The S-H₂O sample also contained small nanoparticles (avg. size ~7.3 nm) but with a broader size distribution (4-50 nm) and demonstrated a tendency to decorate the amorphous material as opposed to the carbon nanotube bundles. The T-DMF reaction produced relatively larger nanoparticles (avg. size ~43.3 nm) with a wide size range (2-115 nm). The nanoparticles grouped together in
Figure 3.17: Representative TEM images of Ag-SWNTs prepared using all four synthesis methods (S-DMF, S-H₂O, T-DMF, T-H₂O). The scale bars for all four images represent 100 nm.
localized clusters and did not appear to decorate the nanotube bundles. Finally, the images of the T-H$_2$O sample again showed small nanoparticles (avg. ~6.7 nm) with a narrow size range (2-25 nm), also with a tendency to decorate the amorphous agglomerations instead of the carbon nanotube bundles.

Side-by-side comparison of the morphologies and product properties of the four samples provides some insight into the mechanisms of the reduction and decoration processes occurring in the preparation of Ag-SWNTs. A summary of important property values for all four samples is given in Table 3.1. Sonication with the DMF reducing solvent produced silver nanoparticles which decorated thin SWNT bundles. Going from S-DMF to S-H$_2$O (removing the reducing DMF solvent), several notable observations were made. (1) Silver nanoparticles were formed in both cases. (2) The average particle sizes and size distributions were similar. (3) The silver content of both samples was similar. (4) The S-DMF sample showed decoration of SWNT bundles while the S-H$_2$O sample showed preferential decoration of amorphous carbon. Observations 1-3 suggested that solvent was not important in the synthesis procedure, but this was contradicted by observation 4. This may be the result of the statistics of available carbon surface area in each solvent. While amorphous carbon was present in all samples, carbon nanotubes were present in a much greater relative amount due to the acid purification procedure.\textsuperscript{127, 128, 134, 135} But Haddon and co-workers showed that the amorphous carbon contained a higher density of oxygen functional groups and thus had a higher zeta potential in water making it more easily dispersed than SWNTs.\textsuperscript{127} Numerous reports showed that in DMF, however, both SWNTs and amorphous carbon can be easily dispersed to form stable solutions.\textsuperscript{128-130} Thus it logically follows that there was a greater
<table>
<thead>
<tr>
<th>Sample</th>
<th>Ag content</th>
<th>Count</th>
<th>Ave. size</th>
<th>Range</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>S-DMF</td>
<td>35%</td>
<td>530</td>
<td>5.7 nm</td>
<td>1-15 nm</td>
<td>86%</td>
</tr>
<tr>
<td>S-H$_2$O</td>
<td>30%</td>
<td>500</td>
<td>7.3 nm</td>
<td>4-50 nm</td>
<td>69%</td>
</tr>
<tr>
<td>T-DMF</td>
<td>30%</td>
<td>214</td>
<td>43.3 nm</td>
<td>2-115 nm</td>
<td>72%</td>
</tr>
<tr>
<td>T-H$_2$O</td>
<td>25%</td>
<td>500</td>
<td>6.7 nm</td>
<td>2-25 nm</td>
<td>54%</td>
</tr>
</tbody>
</table>

Table 3.1: Significant property values of Ag-SWNTs prepared using various methods.
amount of SWNTs dispersed in DMF (and hence more surface area of SWNTs) and a
greater amount of amorphous carbon dispersed in water. This in turn suggested the
nature of the carbon decorated by silver nanoparticles was determined by the relative
surface area of materials that were dispersed in the solvent. Further, in going from S-
H₂O to T-H₂O (removing the process of acoustic cavitation) (1) both syntheses formed
silver nanoparticles, (2) both samples contained similar average sized particles and size
distributions, (3) both samples had similar silver content, and (4) both samples showed
preferential decoration of amorphous carbon. These results seemed to indicate that
sonochemistry was not a factor in the synthesis of Ag-SWNTs. However, heat was
generated in both sonochemical and thermal reactions. These results suggested that these
syntheses produced silver nanoparticles via thermal reduction. In going from T-H₂O to
T-DMF (1) silver nanoparticles were formed, (2) the samples contained vastly different
average sized particles and size distributions, (3) both samples contained similar silver
content, and (4) the T-DMF sample did not show any decoration of carbon with silver
nanoparticles. The increase in nanoparticle size (observation 2) may be due to
temperature effects. In the S-DMF, S-H₂O, and T-H₂O reactions the bulk solution
generally reached temperatures of ~90-100 °C but in the T-DMF reaction the solution
was refluxed at ~153 °C. It has been previously shown by Pastoriza-Santos and co-
workers that an increase in temperature in the DMF reduction of silver acetate reaction
can lead to increased nanoparticle sizes and Ostwald ripening. The lack of decoration
(observation 4) may have arisen from a combination of the loss of
nanoparticle/amorphous carbon interactions and the increased reduction rate (due to
higher temperatures). As previously stated, it is not unreasonable to assume a greater
amount of SWNTs are present in the DMF than amorphous carbon which would lead to greater nanoparticle/nanotube interactions over nanoparticle/amorphous carbon interactions. If the nanoparticle formation and decoration steps were competing processes, an increase in the temperature and loss of nanoparticle/amorphous carbon interactions would lead to larger nanoparticles and less decoration. Furthermore once the nanoparticles were attached, the carbon supports may have been acting as a templating agent by limiting the growth of the silver nanoparticles. In going from S-DMF to T-DMF (maintaining the reductive solvent but eliminating acoustic cavitation) (1) silver nanoparticles were formed, (2) the average sizes and size distributions were different, (3) silver content was similar, and (4) extent of decoration was significantly different. The difference in nanoparticle sizes (observation 2) may have been due to several different reasons but two possibilities are discussed here. (1) As previously stated, the particle sizes may have been influenced by temperature effects and Ostwald ripening. (2) Due to a loss of decoration, the carbon support may have no longer acted as a templating agent to limit particle growth. The lack of decoration on the SWNTs (observation 4) in the T-DMF sample may have been due to the loss of the hot spots and microjetting that occur in acoustic cavitation. Carbon nanotubes are composed of highly stable sp² bonded networks. But acoustic cavitation creates hot spots and microjetting which could cause defects (such as oxygen functional groups) on the surface of the nanotubes. These defects are believed to act as active sites for nanoparticle attachment. Based on the changes observed in going from S-DMF to S-H₂O to T-H₂O, the morphology of the T-DMF sample did not fit the pattern. We expected the T-DMF sample to be nearly identical to the S-DMF sample and we could thus conclude that sonochemistry did not
play a role in the reaction other than providing a bulk temperature increase. But these seemingly contradictory results seemed to indicate multiple underlying factors affect the reduction mechanism, particle growth process, and decoration process. The factors affecting the final product have not been isolated in these four reactions. These factors could include (but are not limited to) the solvent properties, analyte concentration, reaction time, temperature, presence of carbonaceous impurities, and presence/absence of acoustic cavitation.

Further studies are needed in order to more effectively characterize the roles of both the solvent and sonochemistry due to the myriad possible factors affecting morphology. (1) These studies could include solvent experiments. As previously mentioned, DMF and water differ in more than one single property (reducing ability, polarity, heat capacity, etc.). A series of experiments in which the silver decoration reaction is performed using a mixture of DMF and water at various volumetric ratios could lead to observations that help better determine the role of solvent. In addition, other organic solvents which are similar to DMF could be used in order to isolate variables in solvent properties. (2) The concentration of the silver acetate could also be varied to study the effects on final product properties. Several research groups have shown initial metal precursor concentration affects final nanoparticle morphology for a number of different synthetic techniques.\textsuperscript{53, 68, 70, 83, 85, 96} (3) The effect of reaction time on product properties could be characterized as well. Samples of the reaction mixture could be taken at various time intervals in order to study these effects. Numerous reports determined reaction time affects the morphology of the metal nanoparticles.\textsuperscript{53, 85, 86, 96} (4) Reactions could also be carried out isothermally at varying temperatures in order to
determine temperature effects on product morphology. Previous studies by Pastoriza-Santos and co-workers have shown that the nanoparticle size can be affected by temperature in the reduction of silver acetate.\(^{54}\) Our results also suggested that temperature may play a role in product formation. (5) Experiments involving further carbon nanotube purification may yield important results. As previously discussed, amorphous carbon was present in all samples and was preferentially decorated when water was used as a solvent. Repeated washing and centrifugation with water may eventually lead to the removal of most carbonaceous impurities and carbon nanotubes of high purity as these impurities are more easily dispersed than carbon nanotubes.\(^{127}\) The experiments in this chapter can be repeated with higher purity SWNTs in order to better isolate and determine the role of the solvent in the reduction and decoration mechanisms. (6) All the previously discussed studies could be extended by performing the reactions both sonochemically and thermally as well in order to create a matrix of data which could better characterize the system and help explain observed discrepancies.

While not of the greatest importance, a notable observation seen in the DSC data (and summarized in Table 3.1) was that once the SWNTs were decorated with silver nanoparticles in all cases (sonochemical, thermal, DMF, water), both carbon combustion peaks shifted to a temperature \(~150 \, ^\circ C\) earlier in the spectra. Several possible reasons can explain this shift in the peaks. (1) Silver has been shown to act as a catalyst in the oxidation of various hydrocarbons.\(^{4,5}\) Silver could have functioned in the same way in this instance by catalyzing the combustion of carbon nanotubes and graphitic carbon. (2) Silver is a metal with high thermal conductivity \((429 \, \text{W m}^{-1} \, \text{K}^{-1} \, \text{at} \, 300 \, \text{K})\). The presence
of silver on the surface of the SWNTs could be increasing the heat transfer rate from the pan to the sample which results in combustion at what appears to be a lower temperature.

The Ag-SWNTs prepared by the sonochemistry-in-DMF synthesis (S-DMF) showed characteristics most in agreement with the defined optimal product. The sample morphology showed well-dispersed carbon nanotubes that were fairly evenly decorated with small (~5.7 nm) silver nanoparticles. The silver content was also the highest of any of the samples at ~35%. TEM and TGA data indicated that while the combination of sonochemistry and DMF produced the most optimal results, several more underlying factors were involved that were not isolated in the individual synthesis procedures. While the individual roles of each (sonochemistry and DMF) are still unknown and further studies are needed to elucidate, it was determined that both of these reaction parameters were needed in order to attain the optimal product. Thus, both sonochemistry and DMF played critical roles in synthesizing Ag-SWNTs. In this chapter, we studied the reaction only using SWNTs but other carbon nanostructures are available and have been used as supporting material for metal nanoparticles. In the following chapter two additional carbon supports, graphene oxide and carbon nanoparticles, were studied.
CHAPTER 4
SILVER-DECORATED GRAPHENE OXIDE AND CARBON NANOPARTICLES

4.1 Background

The purpose of this section was to determine a method for the silver decoration of additional carbon supports. In Chapter 3, we showed that SWNTs could be decorated with silver nanoparticles using a sonochemistry-in-DMF synthetic procedure. The reaction resulted in SWNTs that were well-decorated with small (average diameter of \(~5.7\) nm) silver nanoparticles. We wanted to determine if this method could be extended to include the decoration of two additional carbon supports, graphene oxide (GO) and carbon nanoparticles (CNPs). Both GO and CNPs are composed of carbon nanostructures that are distinctly different from SWNTs and both have unique properties and applications which make them attractive in the field of research. Graphite oxide is composed of stacked sheets of 6-membered carbon rings arranged in a honeycomb lattice.\textsuperscript{152,153} While some of these rings are aromatic in character, a portion of the sp\textsuperscript{2} bonded network is disrupted by oxygen functional groups predominantly in the form of alcohols and epoxides.\textsuperscript{152,153} While graphite oxide has some attractive properties including high mechanical strength, one of its strongest attributes is that it can easily be completely exfoliated to single-layered GO by sonication and stirring.\textsuperscript{152,153}
Thus, the single-layered sheets of GO were used in this experiment. It is important to note that graphene oxide is the oxidized form of graphene and the un-oxidized form was not used in the following experiments. Exfoliation of graphite oxide to GO is an important step in the process of achieving graphene. Graphene is used to refer to the single-layered and un-oxidized form of graphite which exhibits remarkable properties including a high Young’s modulus, fracture strength, thermal conductivity, and mobility of charge carriers which allows it to be used in such applications as energy-storage materials, ‘paper-like’ materials, polymer composites, liquid crystal devices, and mechanical resonators.\textsuperscript{154} Carbon nanoparticles (CNPs), typically referred to as glassy carbon, are solid spheres composed of a combination of amorphous carbon, graphitic carbon, and metal catalyst.\textsuperscript{136-138} While CNPs are frequently referred to as amorphous, this is not necessarily true as a majority of the surface has been shown to be composed of sp\textsuperscript{2} hybridized graphitic carbon similar to the structure of carbon nanotubes or graphene.\textsuperscript{136-138} Oxygen functionality was added to the surface of these CNPs using the previously discussed nitric acid treatment (Chapter 2). Some of the useful properties of CNPs include a high surface area, high thermal stability, unique electronic properties, low density, and a highly tailorable structure.\textsuperscript{137} These properties have allowed CNPs to have applications in lithium batteries, as a catalyst support, in drug delivery, and magnetic data storage.\textsuperscript{137}

It was determined in the previous section that the sonochemical reaction in DMF produced the best Ag-SWNTs. The method for decorating the two additional carbon supports was kept as similar as possible to the sonochemistry-in-DMF reaction for preparing Ag-SWNTs in order to minimize reaction variables. No changes were made to
the synthesis method for producing Ag-SWNTs in extending the procedure to prepare silver-decorated graphene oxide (Ag-GO) and silver-decorated carbon nanoparticles (Ag-CNPs). The only difference in these syntheses was that the 50 mg of SWNTs used in the previous reactions were replaced with 50 mg of GO or CNPs. In summary, a solution composed of 15 mL DMF, 50 mg of carbon support (GO or CNP), and 25 mg silver acetate was sonicated for 20 minutes at 37% amplitude (~22 W) and 20 kHz using a pulsed (1-s-on, 1-s-off) procedure. After sonication, both products (Ag-GO and Ag-CNP) were viscous, black solutions. The solution was placed in a rotary evaporator to remove the solvent. The product was then transferred to a centrifuge tube where it was washed and centrifuged with water 5 times and ethanol 5 times. The sample was then dried under nitrogen. Once dried the Ag-GO product was composed of black flakes and the Ag-CNP product was composed of a black powder.

4.2 Characterization of Ag-GO

TEM images were taken to determine the morphology, size distribution of the silver nanoparticles, and extent of silver decoration on the GO sheets. TEM images of the undecorated GO sheets are shown in Figure 4.1. The left image in Figure 4.1 shows a bird’s eye view of a large sheet of GO and the right image shows a more magnified view of a GO sheet. The sheet in the left image appeared to be darker because it is likely composed of more stacked layers of carbon than the sheet shown on the right. The darkened lines which can be seen branching across the sheets were attributed to folds and
Figure 4.1: TEM images of undecorated GO sheets. The image on the left shows a bird’s eye view of an entire sheet of GO while the image on the right is a GO sheet at a higher magnification. The scale bar for the left image represents 500 nm and the scale bar for the right image represents 100 nm.
creases. The thinner (less stacked) sheets of GO are difficult to see in TEM due to the low amount of contrast between the sample and the grid. This was particularly exhibited near the edges of the sheets which were often difficult to discern from the grid. TEM images are shown in Figure 4.2 for the Ag-GO sample. The first observation of note is that the Ag-GO sheets appeared to be lighter in shade than the undecorated sample. GO can be easily dispersed in DMF and the decorated GO sheets were likely exfoliated into single layers during the sonication period. Spherical nanoparticles were present in the sample but nanoparticle decoration was inconsistent with certain areas of the sheet having a concentrated supply of particles and other areas having a sparse amount of particles at uneven intervals. While the decoration of the GO sheets was irregular, the TEM image on the left in Figure 4.2 paints a clearer picture of the area of the GO sheet that the nanoparticles occupy and it can be seen that there is an extensive amount of sheet coverage. Furthermore, the nanoparticles provide a much greater contrast with the grid and thus the edges of the GO sheets could be more easily identified. The nanoparticle sizes also varied widely with an average of ~8 nm but a range of 2-100 nm (Figure 4.3).
Figure 4.2: TEM images of silver-decorated GO sheets. The image on the left shows a bird’s eye view of an entire sheet of GO while the image on the right is a GO sheet at a higher magnification. The Ag-GO sample nanoparticles have an average size of ~8 nm and a size range of 2-100 nm. The scale bar for the left image represents 500 nm and the scale bar for the right image represents 100 nm.
Figure 4.3: Size distribution graph of the silver nanoparticles decorating the GO via the sonochemical method in DMF. The nanoparticles had an average size of ~8 nm and a range of 2-100 nm. The inset represents the full range of sizes of the silver nanoparticle population.
XRD data of the Ag-GO sample was taken and analyzed in order to determine the nature of the crystal structures present in the nanoparticles. The results for the Ag-GO reaction are displayed in conjunction with ICDD card data for fcc silver (ICDD 00-004-0783) in Figure 4.4. The Ag-GO spectrum closely matched the peaks seen in the fcc silver spectrum which indicated the nanoparticles were composed of silver metal. These results indicated that the Ag-GO sample contained fcc silver metal.

After the cleaning procedure, the FTIR spectrum of the Ag-GO sample did not show any strong features consistent with silver acetate peaks. GO has very weak features in FTIR and thus the spectrum did not have any characteristic peaks and is not depicted. These results further indicated that most silver acetate was reduced or washed from the sample.

The mass content and energetic behavior of the Ag-GO sample and undecorated GO were analyzed using a simultaneous TGA/DSC and the results are shown in Figure 4.5. The GO samples were analyzed in the same way as the SWNT samples (under a constant 100 mL/min flow of air for a temperature range of 25 ºC to 800 ºC at a heating rate of 10 ºC/min). The TGA results of undecorated GO exhibited two distinct regions of weight loss. The first region of weight loss, which began at ~150 ºC, was attributed to the loss of oxygen functional groups in the form of CO and CO$_2$.\textsuperscript{155,156} The second region of weight loss, beginning at ~500 ºC, corresponded with the combustion of GO.\textsuperscript{131}\textsuperscript{132} The TGA curve of the Ag-GO sample showed a similar mass decrease region due to oxygen functionality loss at the same temperature (~150 ºC) but this mass loss percentage was smaller than undecorated GO. The mass loss region attributed to
Figure 4.4: XRD spectra of Ag-GO (top) and ICDD pattern for silver (bottom) (00-004-0783). The peaks at 38.1°, 44.3°, 64.4°, 77.5°, and 81.5° correspond to the (111), (200), (220), (311) and (222) crystal planes of fcc silver respectively (ICDD 00-004-0783).
Figure 4.5: TGA (top) and DSC (bottom) data for undecorated GO (solid line) and GO-Ag (dashed line). The TGA curves for the undecorated GO sheets and the Ag-GO sample show a difference in final mass percentages which was used to calculate the silver content and found to be \(~40\%\). The DSC curve for the undecorated GO sheets showed an initial peak centered at \(~200\degree C\) which was attributed to oxygen leaving groups and a second peak centered at \(~550\degree C\) which was attributed to graphitic carbon combustion. The DSC curve of the Ag-GO sample showed the same second peak occurred at a significantly earlier temperature (\(~415\degree C\)).
carbon combustion in the Ag-GO sample came at a temperature (~350 °C) that was ~150 °C earlier than the undecorated GO sample. The difference in final weight percentages at 800 °C between Ag-GO and undecorated GO was used to calculate the silver content in the silver decorated sample. As previously stated (in Chapter 3), the residual mass only arose from silver metal because silver does not oxidize at these temperatures under normal conditions.\(^1\)\(^-\)\(^3\) This was confirmed by XRD analysis of the Ag-GO sample after the TGA/DSC treatment (heating to 800 °C) which showed only silver metal. The residual masses of the undecorated GO and the Ag-GO samples were found to be ~1% and 41%, respectively. The silver content of the Ag-GO sample determined from this method was found to be ~40%.

The DSC analysis of undecorated GO was characterized by two exothermic peaks centered at ~200 °C and ~550 °C. These peaks corresponded with the two weight loss regions seen in the TGA spectra and were due to oxygen leaving groups and carbon combustion, respectively. As expected from the TGA results, the DSC results of the Ag-GO sample showed a similar two-peak pattern but with a significantly altered shape as compared to the undecorated GO sample. The peak attributed to the oxygen leaving group decreased in intensity after silver decoration which may possibly be due to silver displacing oxygen groups after decoration. The peak corresponding with carbon combustion occurred at a temperature ~150 °C earlier in the Ag-GO sample as opposed to the undecorated GO.
4.3 Characterization of Ag-CNPs

TEM images of the undecorated, acid-treated CNPs were compared with images of the Ag-CNPs in order to characterize nanoparticle size and extent of decoration. The TEM images are shown in Figure 4.6 for the Ag-CNP sample and undecorated CNPs. The TEM image of the acid-treated CNPs revealed large nanoparticles in the size range of ~40-50 nm. Most particles were roughly spherical in shape but frequently diverged from this pattern and became more ellipsoid in character. The edges of the individual CNP spheres were easily distinguished but the particles did tend to form agglomerated collections of particles due to their attraction to each other through van der Waals forces. After decoration, the TEM images showed that the CNPs were decorated with smaller nanoparticles. While the CNPs tended to form agglomerated structures (including but not limited to rings like that seen in the TEM), the silver nanoparticles did not form agglomerations and were mostly dispersed evenly on the surface of the CNPs. As well as being consistent in decoration, the particles were small in size with an average of ~7 nm and had a narrow size distribution of ~3-15 nm as shown in Figure 4.7.
Figure 4.6: TEM images of CNPs before (left) and after (right) decoration with silver nanoparticles. The Ag-CNPs sample nanoparticles have an average size of ~7 nm and a size range of 3-15 nm. The scale bar for both images represents 20 nm.
Figure 4.7: Size distribution graph of the silver nanoparticles decorating the CNPs via the sonochemical method in DMF. The nanoparticles had an average size of ~7 nm and a range of 3-15 nm.
The XRD results for the Ag-CNPs reaction are displayed in conjunction with ICDD card data for fcc silver (ICDD 00-004-0783) in Figure 4.8. The peaks of the Ag-CNPs sample closely matched those of the fcc silver card data. The peaks seen in the range of 20° to 30° were attributed to the graphitic nature of CNPs. This was confirmed when these peaks matched the XRD spectrum of undecorated acid-treated CNPs. XRD data indicated that the sample contained fcc silver metal.

The FTIR spectrum of the Ag-CNPs sample did not show any strong features consistent with silver acetate peaks. Undecorated acid-treated CNPs do not have strong signals in FTIR and thus its spectrum is not shown. These results further indicated that most silver acetate was reduced or washed from the sample.

The TGA/DSC data for the Ag-CNPs and undecorated CNPs is shown in Figure 4.9. The TGA spectrum for undecorated acid-treated CNPs showed one region of weight loss beginning at ~450 °C which corresponded with carbon combustion and left a remaining relative weight percent of 38%. As was expected from previous data, the TGA of the Ag-CNPs also showed one region of weight loss but it began at a significantly lower temperature at ~300 °C (lower by ~150 °C). The remaining relative weight percent in the Ag-CNPs was also higher (at ~52%) than what was seen in the undecorated sample. From the remaining relative weights the silver content of the Ag-CNPs was calculated and found to be ~14%. The DSC spectrum for undecorated CNPs exhibited a peak centered at ~580 °C for carbon combustion which matched the weight loss region seen in TGA. The spectrum for Ag-CNPs exhibited the same carbon combustion at a significantly reduced temperature (~320 °C) which was 250 °C lower than that of the undecorated sample.
Figure 4.8: XRD spectra of Ag-CNP (top) and ICDD card data for fcc silver (bottom) (00-004-0783). The peaks at 38.1°, 44.3°, 64.4°, 77.5°, and 81.5° correspond to the (111), (200), (220), (311) and (222) crystal planes of fcc silver respectively (ICDD 00-004-0783).
Figure 4.9: TGA (top) and DSC (bottom) data for CNP (solid line) and Ag-CNPs (dashed line). The TGA curves for the undecorated CNPs and the Ag-CNPs sample show a difference in final mass percentages which was used to calculate the silver content and found to be ~14%. The DSC curve for the undecorated CNPs sheets showed a peak centered at ~580 °C which was attributed to carbon combustion. The DSC curve of the Ag-CNPs sample showed the same peak but a significantly earlier temperature (~320 °C).
4.4 Summary

The purpose of this chapter was to determine if the previously established (Chapter 3) sonochemical method for preparing Ag-SWNTs could be extended to decorate additional carbon supports. In this chapter, silver acetate was reduced to silver metal via sonochemistry in DMF and the resulting nanoparticles were used to decorate two additional carbon supports, GO and CNPs. XRD analysis showed that both synthesis procedures produced fcc silver metal. FTIR analyses confirmed that most of the silver acetate was either reduced or washed away from the final product in both samples. TEM images showed that all three carbon supports were successfully decorated with silver nanoparticles.

The TEM images for Ag-SWNTs, Ag-GO, and Ag-CNPs are shown in Figure 4.10. TEM characterization revealed all carbon supports were decorated with silver nanoparticles which for the most part were spheroid in shape but the size of the nanoparticle and nature of the decoration depended on the type of support. The silver nanoparticles attached to the SWNT supports were small in diameter (avg. ~5.7 nm) and narrow in distribution (1-14 nm). The nanoparticles decorated the nanotubes fairly evenly with little agglomeration of silver. The Ag-SWNTs sample contained ~35% silver content. Silver decoration of GO produced nanoparticles that varied widely in size (avg. ~8 nm, range ~2-100 nm) and while the presence of nanoparticles on the sheets was widespread, the decoration was somewhat less evenly dispersed. The Ag-GO sample contained ~40% silver content. The nanoparticles decorating CNPs were small in size
Figure 4.10: TEM images of Ag-SWNTs (top left), Ag-GO (top right), and Ag-CNPs (bottom). The scale bar indicates 20 nm for all images.
(avg. ~7 nm) with a narrow size distribution (range ~3-15 nm). The CNPs were well-decorated with silver nanoparticles. The Ag-CNPs sample contained ~14% silver content.

The differences in morphology and product properties of the various silver-decorated supports yielded some insight into the function of the carbon support. A summary of important property values for all three silver-decorated carbon supports (Ag-SWNTs, Ag-GO, and Ag-CNPs) is given in Table 4.1. Silver decoration of SWNTs compared to GO showed (1) both samples contained silver nanoparticles, (2) differences in average nanoparticle size and size distribution, (3) similar silver content, and (4) both supports were decorated. The differences in nanoparticle morphology (observation 2) may have stemmed from the differences in the nature and density of defect sites present on the surface of each carbon nanostructure. Pastoriza-Santos et al. reported that silver nanoparticles will form in DMF solution via the reduction of Ag$^+$ ions without the use of a stabilizer.$^{54}$ Furthermore, it has been reported that the surface of these silver nanoparticles may contain a slight positive charge due to the adsorption of unreacted Ag$^+$ ions which gives the particles the tendency to stick to surfaces.$^{54, 76}$ A widespread theory in literature espoused by many research groups states that metal nanoparticles attach to defect sites (such as oxygen moieties) on carbon nanostructures.$^{36, 150, 151}$ However, the oxygen functional groups present on SWNTs and GO are different in both identity and density. According to Haddon and co-workers (in addition to multiple other reports), the majority of the oxygen functional groups present on 2.6 M nitric-acid treated SWNTs are composed of aldehydes/ketones and carboxylic acids, although other groups (such as alcohols and epoxides) are present.$^{127, 129-131, 133}$ Furthermore, several sources (including
<table>
<thead>
<tr>
<th>Sample</th>
<th>Ag content</th>
<th>Count</th>
<th>Ave. size</th>
<th>Range</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag-SWNTs</td>
<td>35%</td>
<td>530</td>
<td>5.7 nm</td>
<td>1-15 nm</td>
<td>86%</td>
</tr>
<tr>
<td>Ag-GO</td>
<td>40%</td>
<td>690</td>
<td>7 nm</td>
<td>3-15 nm</td>
<td>50%</td>
</tr>
<tr>
<td>Ag-CNPs</td>
<td>14%</td>
<td>500</td>
<td>9 nm</td>
<td>2-100 nm</td>
<td>77%</td>
</tr>
</tbody>
</table>

Table 4.1. Significant property values of silver-decorated carbon supports.
Haddon) have measured the oxygen functionality on 2.6 M nitric acid-treated SWNTs and have determined about \(~5-6\%\) oxygen-containing groups.\textsuperscript{131,133} Numerous reports state the functional groups present on the surface of GO can be any oxygen containing group (carboxylic acid, aldehyde/ketone, alcohol, ether, epoxide) but the majority are composed of alcohols or epoxides.\textsuperscript{152-154} GO generally has a higher density of oxygen functional groups than SWNTs. The density of oxygen functional groups depends on the oxidative treatments used to synthesize GO and is still being debated in literature but it is generally agreed that GO has about \(~33\%\) oxygen functionality.\textsuperscript{152,154} It is possible that, due to their slight positive surface charge, silver nanoparticles are more likely to attach at certain oxygen functional groups rather than others and thus cease the nanoparticle growth process that is occurring in solution. The density of these oxygen groups on the surface of the carbon support would also influence this process as well. While the silver contents of the two samples were not significantly different (\(~35\%\) for SWNTs and \(~40\%\) for GO), it may have arisen from several possibilities. One such possibility is presented in the discussion below. GO is composed of flat sheets of carbon while SWNTs are composed of these same sheets of carbon rolled into hollow tube structures. Therefore, rationally GO should have double the amount of exposed surface available compared to SWNTs. This is not necessarily true because of several varying factors in morphology. GO may be composed of stacked sheets of carbon which would decrease the available surface area. Also, individual nanotubes are usually bundled together which reduces available surface area. Therefore, differences in morphology could alter the available surface area to weight ratio of these carbon nanostructures. If GO had more surface area
available, and thus more defect sites, it would logically follow that GO could contain a higher content of silver.

In comparing the Ag-SWNTs with the Ag-CNPs sample, once again (1) silver nanoparticles were formed, (2) the nanoparticle size and distribution was similar, (3) silver content was significantly different, and (4) both carbon supports were successfully decorated. In order to discuss possible reasons for the differences in silver content (observation 3), a brief review of the chemistry present on the surface of the CNPs is presented here. As previously reported by several authors (including Suda, Deshmukh, and Inagaki), CNPs are solid spheres composed of both amorphous carbon and graphitic carbon.\textsuperscript{136-138} The surface of the nanoparticles is composed of mostly graphitic carbon.\textsuperscript{136-138} Thus, the surface of the CNPs has a similar structure to carbon nanotubes and GO but the core is composed of additional carbon atoms. While the exact value for extent of oxidation and type of oxygen moieties present on the surface of CNPs are unknown, it is not unreasonable to assume these values are similar to that which is present on SWNTs (5\% and primarily composed of ketones/aldehydes and carboxylic acids, respectively) because the CNPs were subjected to the same acid treatment as the SWNTs. If the SWNTs and CNPs have similar oxygen functionality, the differences in the size of nanoparticles decorating the two structures could have possibly arose due to the difference in surface area to weight ratio between the two nanostructures. While the surface chemistry of the SWNTs and CNPs may be similar, SWNTs are composed of hollow tubes while CNPs are spheres which contain a solid core of carbon atoms. SWNTs form bundles which reduce surface area, but CNPs also form agglomerations through van der Waals forces which reduce available surface area. If, through a
combination of density and agglomeration issues, SWNTs have a higher surface area to weight ratio than CNPs, the ratio of silver salt to active sites for nanoparticle attachment will be less in the CNPs sample and thus result in less silver content. Following a similar analysis as was stated in the above discussion of the Ag-SWNTs/Ag-GO TEM images, the differences in nanoparticle size and decoration between CNPs and GO can possibly be attributed to the differences in surface area as well as density and nature of oxygen moieties.

These differences in average nanoparticle sizes, size distributions, and silver content between the three samples indicated that the nature of the carbon support affected the final properties of the silver-decorated structure. As was seen in Chapter 3, this synthesis procedure involves many underlying factors and the study of three different supports was not extensive enough to isolate all variables. Further studies on the varying factors involved in this synthesis would be needed to determine a clearer view of the role of the carbon support. These factors include (but are not limited to) carbon support-to-silver acetate ratio, surface functionality, and type of support. (1) A study on the carbon support-to-silver acetate ratio could be performed which may yield clarifying data. A theory in the literature suggests that metal nanoparticles will only attach to carbon supports at defect sites and thus a limited number of spaces for nanoparticle attachment are present. Studying the effects of altering the carbon support-to-silver acetate ratio may further probe the method of nanoparticle attachment. (2) Studies could also be extended to altering the functionalities present on the surface of the carbon nanostructure. One such study would be to alter the nitric acid treatment (increase/decrease acid concentration, extend reflux times, etc.) of the SWNTs or CNPs and observe what effects
this alteration had on the final product of the silver decoration reactions. Another study would be to functionalize the carbon surface with other surface functionalities not limited to oxygen-containing groups. This could give insight into how the surface functionality affects the silver decoration. (3) Further studies could include the use of additional supporting materials such as MWNTs or even non-carbon based supports which may yield useful information pertaining to the affect of surface area-to-density ratio.

As was seen in all the Ag-SWNTs samples in Chapter 3, the DSC data for both additional silver-decorated supports (GO and CNPs) showed the onset of carbon combustion at earlier temperatures (~150-250 ºC) than that of their undecorated carbon supports. Several possible sources may have been the cause of this shift in the carbon combustion peaks and three possible reasons were discussed in Chapter 3. In brief (1) silver may have acted as a catalyst for carbon combustion or (2) worked to increase the heat transfer rate to the sample during heating.

Characterization data of the Ag-SWNTs, Ag-GO, and Ag-CNPs demonstrated that the sonochemical method in DMF could be used to decorate multiple carbon supports with silver nanoparticles. Several differences in the characterization between the three samples suggested the carbon support was not a passive observer in the silver decoration reactions but rather played an important role in the synthesis. Each sample contained different morphologies and silver content which may have been due to multiple factors including the number and functionality of available defect sites for nanoparticle attachment. The exact role of the carbon support is still unknown but the subject has been somewhat clarified due to the experiments in this chapter and it is believed that the nature of the carbon support affects the growth process of the nanoparticles. Having
previously performed studies on the roles of the energy input mechanism, solvent, and carbon support the next logical study was on the type of metal used. We have shown that multiple types of carbon supports could be decorated with silver nanoparticles using the sonochemistry-in-DMF synthesis method. In the next chapter, we will perform studies on decorating carbon supports with various metals, more specifically gold and platinum decorated SWNTs.
CHAPTER 5

GOLD AND PLATINUM-DECORATED SINGLE-WALLED CARBON NANOTUBES

5.1 Background

In the previous chapters, carbon supports were decorated with silver nanoparticles. Both gold and platinum are similar in nature to silver in that all of these elements are noble metals (stable and do not oxidize easily).\textsuperscript{1-3, 17-19, 33-35} Both metals have also seen increased research activity due to the unique properties their nanoparticles exhibit. Gold nanoparticles have been used in a wide variety of fields including optics, electronics, sensors, catalysis, and medicine.\textsuperscript{20-22} Platinum nanoparticles have been shown to have high catalytic activity in a wide variety of reactions including hydrogenation, photo-induced hydrogen production, electro-oxidation of formic acid or methanol, and catalytic reduction of oxygen.\textsuperscript{31, 32, 36} Carbon nanotubes are currently being considered as ideal supports for these noble metal nanoparticles because of their unique electrical properties, high chemical stability, and high surface-area-to-volume ratios.\textsuperscript{157} Gold-decorated and platinum-decorated carbon nanotubes have been synthesized through various techniques such as wet-chemistry, sonication-assisted deposition, mechanochemistry, electrodeposition, and solid-state heating.\textsuperscript{137, 139, 140, 157, 158}
The purpose of this chapter was to determine if the sonochemistry-in-DMF method of synthesizing silver-decorated carbon supports could be used in decorating SWNTs with other metal nanoparticles. In Chapters 3 and 4, we have previously shown that this method was versatile in that it could be used to decorate multiple types of carbon supports (SWNTs, GO, and CNPs) with silver nanoparticles. Two additional metal precursors, gold acetate and platinum (II) chloride, were used in an effort to prepare metal-decorated (gold and platinum respectively) SWNTs.

The method for preparing gold-decorated SWNTs (Au-SWNTs) and platinum-decorated SWNTs (Pt-SWNTs) was kept the same as the sonochemistry-in-DMF reaction for preparing silver-decorated carbon supports seen in the previous sections in order to minimize reaction variables. The only reaction variable in these syntheses was the type of metal precursor used. It should be noted here that the metal precursor weights were the same but this resulted in different molar concentrations depending on the metal used. At this point, we were unconcerned with concentration effects and wanted to determine if the synthesis would work. Future studies will address concentration issues. In summary a solution composed of 15 mL DMF, 50 mg of SWNTs, and 25 mg metal salt precursor (gold acetate or platinum (II) chloride) was sonicated for 20 minutes at 37% amplitude (~22 W) and 20 kHz using a pulsed (1-s-on, 1-s-off) procedure. Both products, Au-SWNTs and Pt-SWNTs, were a viscous, black solution at this point. The solution was placed in a rotary evaporator to remove the solvent then washed and centrifuged with water 5 times and ethanol 5 times. The samples were then dried under nitrogen. Once dried, both products were composed of black powder.
5.2 Characterization of Au-SWNTs

TEM images were taken to determine the morphology, size distribution, and extent of gold decoration on the SWNTs. The TEM images are shown in Figure 5.1 for the Au-SWNTs in comparison with undecorated, acid-treated SWNTs. The acid-treated SWNTs have been seen and described previously (Chapter 3) so an in depth analysis will not be presented here. The TEM image of the SWNTs after gold decoration revealed nanotube bundles with limited spherical nanoparticle decoration. The nanoparticle decoration was inconsistent. Nanoparticles would agglomerate in certain areas in large groups while other areas of the nanotube network were free of any decoration at all. Furthermore, the nanoparticles seemed to preferentially decorate agglomerated material rather than deposit along thin nanotube bundles. This agglomerated material was previously seen in the synthesis of Ag-SWNTs in water (S-H₂O and T-H₂O). In addition to poor decoration, the nanoparticles were also large in diameter with an average size of ~25 nm and a range of 9-60 nm (shown in Figure 5.3).
Figure 5.1: TEM images of gold-decorated SWNTs. The Au-SWNTs sample nanoparticles have an average size of ~25 nm and a size range of 9-60 nm. The scale bar for the left image represents 500 nm and the scale bar for the right image represents 100 nm.
Figure 5.2: Size distribution graph of the gold nanoparticles decorating the SWNTs via the sonochemical method in DMF. The nanoparticles had an average size of ~25 nm and a range of 9-60 nm.
An XRD spectrum of the Au-SWNTs sample was taken and analyzed in order to characterize the crystal structure of the nanoparticles. The results for the Au-SWNTs are displayed in conjunction with ICDD card data for face-centered cubic (fcc) gold (ICDD 00-004-0784) in Figure 5.3. The Au-SWNTs spectrum showed peaks at 38.2°, 44.4°, 64.6°, 77.5°, and 81.7° which correspond to the (111), (200), (220), (311) and (222) crystal planes of fcc gold respectively. As previously stated, the broad peak centered at 26.6° was attributed to the graphitic nature of acid-treated SWNTs and was removed once the sample was heated to 800 °C. It should be noted at this point that a spectrum of neat gold acetate was taken and none of these peaks were discernable in the Au-SWNTs sample. These results indicated fcc gold was present in the sample.

FTIR analysis was performed on the Au-SWNTs to determine if any remaining gold acetate was in the sample and the data is shown in Figure 5.4. The FTIR spectrum of the Au-SWNTs did not show any strong peaks consistent with gold acetate. While neat gold acetate exhibited strong peaks, the FTIR features of gold and SWNTs are very weak. The absence of gold acetate peaks in the spectrum indicated that most of the gold acetate was either reduced to gold metal and/or washed from the sample.
Figure 5.3: XRD spectra of Au-SWNT (top) and ICDD card data for fcc gold (bottom) (00-004-0784). The peaks at 38.2°, 44.4°, 64.6°, 77.5°, and 81.7° which correspond to the (111), (200), (220), (311) and (222) crystal planes of fcc gold, respectively.
Figure 5.4: FTIR spectra for the Au-SWNTs sample (top) and neat gold acetate (bottom).
Simultaneous TGA/DSC characterization was used in order to investigate the mass content and thermal stability of the Au-SWNTs and this data is shown in Figure 5.5. The TGA spectrum of Au-SWNTs was compared to undecorated SWNTs in order to determine the gold content of the sample. The TGA of acid-treated SWNTs showed a decrease in mass beginning at ~480 °C which corresponded with carbon combustion and had a residual mass of ~3%. The Au-SWNTs showed a similar behavior but at a temperature that was ~80 °C lower (T = ~400 °C) and a higher residual mass at ~44%. Gold is an extremely stable metal and resists oxidation at the temperatures seen in this experiment (T < 800 °C).\textsuperscript{17,19} This was confirmed when an XRD spectrum of the residual mass from the Au-SWNTs showed fcc gold peaks. The same procedure used to calculate silver content was employed here and the gold content was found to be ~41%.

The DSC analysis of acid-treated SWNTs, as described in previous sections, was characterized by an intense exothermic peak closely followed by a second, less intense peak. The first intense peak, centered at ~560 °C, corresponded with carbon nanotube combustion while the second peak, centered at ~660 °C, was attributed to residual graphitic carbon combustion.\textsuperscript{131,132,149} As expected from the TGA results, the DSC results of the Au-SWNTs sample showed the same carbon combustion peaks but centered at a much earlier temperature of ~460 °C.
Figure 5.5: TGA (top) and DSC (bottom) data for acid-treated SWNTs (solid line) and Au-SWNTs (dashed line). The TGA curves for the acid-treated SWNTs and the Au-SWNTs sample show a difference in final mass percentages which was used to calculate the gold content and found to be ~41%. The DSC curve for the acid-treated SWNTs showed an intense peak centered at ~560 °C which was attributed to carbon nanotube combustion closely followed by a shoulder which resulted from combustion of residual graphitic carbon. The DSC curve of the Au-SWNTs sample showed the same pattern but a significantly earlier temperature (~460 °C).
5.3 Characterization of Pt-SWNTs

TEM analysis was performed on the SWNTs subjected to the platinum decoration reaction in order to characterize the morphology of the product sample. The TEM images are shown in Figure 5.6 for the Pt-SWNTs in conjunction with undecorated SWNTs. The images of the SWNTs after the platinum reaction revealed thin nanotube bundles decorated with spherical nanoparticles. The decoration was relatively well dispersed with nanoparticles anchored onto the nanotubes. The decoration was also widespread and there were no large areas of nanotubes free of nanoparticles. As seen in previous samples, there was also evidence of what appeared to be amorphous carbon but it occurred in a much lower relative amount to the carbon nanotubes. The nanoparticles decorated the amorphous material as equally well as the carbon nanotubes. The nanoparticles were small in size with an average diameter of ~5.2 nm and narrow in distribution with a range of ~1-15 nm as shown in Figure 5.7.
Figure 5.6: TEM images of SWNTs before (left) and after (middle, right) decoration with platinum nanoparticles. The Pt-SWNTs sample nanoparticles have an average size of ~6 nm and a size range of 1-15 nm. The scale bar for the left image represents 100 nm and the scale bar for the right image represents 20 nm.
Figure 5.7: Size distribution graph of the platinum nanoparticles decorating the SWNTS via the sonochemical method in DMF. The nanoparticles had an average size of ~5.2 nm and a range of 1-15 nm.
The results for the Pt-SWNTs are displayed in conjunction with ICDD card data for face-centered cubic (fcc) platinum (ICDD 01-087-0646) in Figure 5.8. The Pt-SWNTs spectrum showed peaks at 39.8, 46.3°, 67.5°, and 81.3° which corresponded to the (111), (200), (220), and (311) crystal planes of fcc platinum respectively. An XRD analysis was also performed on neat platinum (II) chloride and it was found that none of these peaks appeared in the spectrum of Pt-SWNTs. These results indicated fcc platinum was present in the sample.

The DSC-TGA spectrum of Pt-SWNTs was analyzed in conjunction with the spectrum of undecorated SWNTs in order to determine the platinum content and energetic response of the sample. The DSC-TGA spectra are shown in Figure 5.9. The Pt-SWNTs showed a mass loss at a temperature of ~360 °C (which was ~100 °C less than acid-treated SWNTs) and a residual mass at ~25%. Platinum is a relatively stable metal in air and will not oxidize easily even at the DSC/TGA final temperature of 800 °C.\textsuperscript{33, 34} This was confirmed with XRD data of the residual mass after DSC/TGA treatment which showed fcc platinum. Thus the residual mass from the TGA/DSC experiment only arose from platinum and residual metal catalysts (relics of SWNT synthesis). The same procedure used to calculate silver and gold content was employed here and the platinum content was found to be ~22%.

As expected from all previous DSC sample data and the TGA results, the DSC results of the Pt-SWNTs sample showed similar characteristics to all other SWNT samples. The intense carbon nanotube combustion peak was centered at ~460 °C, which was similar to the gold and silver behavior, and was ~100 °C earlier in temperature than undecorated SWNTs.
Figure 5.8: XRD spectra of SWNT-Pt (top) and ICDD card data for fcc platinum (bottom) (ICDD 01-087-0646. The peaks at 39.8°, 46.3°, 67.5°, and 81.3° correspond to the (111), (200), (220), and (311) crystal planes of fcc platinum respectively.
Figure 5.9: TGA (top) and DSC (bottom) data for acid-treated SWNTs (solid line) and Pt-SWNTs (dashed line). The TGA curves for the acid-treated SWNTs and the Pt-SWNTs sample show a difference in final mass percentages which was used to calculate the platinum content and found to be ~22%. The DSC curve for the acid-treated SWNTs showed an intense peak centered at ~560 °C which was attributed to carbon nanotube combustion closely followed by a shoulder which resulted from combustion of residual graphitic carbon. The DSC curve of the Pt-SWNTs sample showed the same pattern but a significantly earlier temperature (~460 °C).
5.4 Summary

The purpose of this chapter was to determine if the sonochemical method in DMF for decorating carbon supports with silver could be extended to include additional noble metals. In Chapter 3, it was shown that acid-treated SWNTs could be used as a support for synthesizing silver nanoparticles. The optimal synthesis was determined to be silver acetate reduction in the presence of SWNTs via sonochemistry with DMF as the solvent. The results of Chapter 4 further showed that the sonochemical method in DMF could be used to decorate additional carbon supports (such as GO and CNPs) with silver nanoparticles. In this chapter, two additional metal precursors, gold acetate and platinum (II) chloride, were used in an attempt to synthesize metal-decorated SWNTs. XRD analysis showed that both synthesis procedures produced fcc zero-valent metal. Furthermore in the gold sample, FTIR analyses confirmed that the gold acetate was either reduced to metallic gold or washed away from the final product during the cleaning process.

The TEM images for Ag-SWNTs, Au-SWNTs, and Pt-SWNTs are shown in Figure 5.10. TEM characterization revealed the synthesis formed spherical nanoparticles in all three cases but the size of the nanoparticle and nature of the decoration depended on the type of metal precursor. The silver nanoparticles attached to the SWNT supports were small in diameter (avg. ~5.7 nm) and narrow in distribution (1-14 nm). The nanoparticles decorated the nanotubes fairly evenly with little agglomeration of silver. The Ag-SWNTs sample contained ~35% silver content. The gold-decorated sample
Figure 5.10: TEM images of SWNTs before metal decoration along with SWNTs that are decorated with silver, gold, and platinum respectively. The scale bar for all images represents 20 nm.
contained large nanoparticles (~26 nm) with a wide size distribution (9-60 nm). Furthermore, the gold nanoparticles appeared to preferentially decorate the amorphous material over the SWNTs and the gold content was found to be ~41%. The Pt-SWNTs sample was composed of relatively smaller nanoparticles (~5.2 nm) with a narrow size distribution (1-15 nm). The nanoparticles were fairly evenly dispersed along the thin SWNT bundles and the sample contained a platinum content of ~22%.

Analysis of the morphology and properties of the three metal-decorated sample values yielded important insight on the role of the metal in this synthetic process. A summary of important property values for all three metal-decorated SWNTs (Ag-SWNTs, Au-SWNTs, and Pt-SWNTs) is given in Table 5.1. Synthesis with all three metal precursors yielded spherical nanoparticles but the size of the particles and extent of decoration depended on the metal. In changing the metal from silver to gold, (1) spherical metal nanoparticles were formed, (2) the average size and size distributions were significantly different, (3) the metal content was similar, and (4) gold did not decorate SWNT bundles. In regard to the average nanoparticle size and size distributions (observation 2), it was previously postulated in Chapter 3 that the SWNTs may have possibly acted as a templating agent that limited nanoparticle growth. The larger sized gold nanoparticles in this reaction seemed to further support this theory as the nanoparticle growth was not limited by attachment to the SWNTs. The lack of decoration on the nanotubes bundles (observation 4) may possibly be attributed to the surface functionality on the SWNTs. It was previously stated in Chapter 3 that we believed the silver nanoparticles would attach to the oxygen functional groups (predominantly in the form of carboxylic acids and ketones) of SWNTs. There are also
<table>
<thead>
<tr>
<th>Sample</th>
<th>Metal content</th>
<th>Count</th>
<th>Ave. size</th>
<th>Range</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag-SWNTs</td>
<td>35%</td>
<td>530</td>
<td>5.7 nm</td>
<td>1-15 nm</td>
<td>86%</td>
</tr>
<tr>
<td>Au-SWNTs</td>
<td>41%</td>
<td>208</td>
<td>25 nm</td>
<td>9-60 nm</td>
<td>83%</td>
</tr>
<tr>
<td>Pt-SWNTs</td>
<td>22%</td>
<td>501</td>
<td>5.2 nm</td>
<td>1-15 nm</td>
<td>74%</td>
</tr>
</tbody>
</table>

Table 5.1. Significant property values of metal-decorated SWNTs.
many examples in literature of silver and platinum nanoparticles attached to carbon nanotubes at what are believed to be oxygen functionalities. However, gold nanoparticles are typically stabilized with organic molecules by interactions through thiol functionalities. In fact, Azamian et al. were able to attach gold nanoparticles to SWNTs by first treating the nanotubes with nitric acid to attain carboxylic acid functionality and then converting the carboxylic acids to thiol linkers using 2-aminoethanethiol. Furthermore, when they attempted to attach gold without converting the carboxylic acids to thiols, the reaction failed and no decoration of the nanotubes was achieved. These results suggested that gold nanoparticles possibly will not attach to carboxylic acid groups but need other functionalities. In changing the metal from silver to platinum, once again the morphology of the final product was altered though in a much less significant way.

In changing the metal from silver to platinum, (1) spherical metal nanoparticles were formed, (2) the average nanoparticle size and size distributions were similar, (3) the metal content was lower in the platinum sample, and (4) both types of metal nanoparticles decorated SWNT bundles. The metal content (observation 3) discrepancy between the silver and platinum samples may possibly be due to concentration issues. The procedures employed in this chapter used the same metal precursor weights (25 mg) for the different metals but this translates to different molar concentrations (0.596 M silver ions compared to 0.375 M platinum ions). Thus it would logically follow the platinum sample would contain a lower metal content than the silver sample.

The differences in average nanoparticle size, size distribution, and decoration between the three samples indicated that the nature of the metal affected the final
properties of the metal-decorated SWNTs. As was previously discussed in both Chapters 3 and 4, the metal-decoration of SWNTs via sonochemistry in DMF involves many underlying factors and the study of three different metal precursors still leaves room for additional work. Further studies involving the metals may lead to enlightening results pertaining to the role of the metal in these sonochemical reactions. These further studies could include using different metal precursors (of silver, gold, and platinum) of the same oxidation states, using metal precursors with different oxidations states ($\text{Au}^+$, $\text{Au}^{+3}$, etc.), using additional metals (both noble and non-noble), and also (as previously discussed in Chapter 4) altering the chemical functionality present on the SWNTs. (1) There are many different precursors available for the same metal with the same oxidation state (such as silver acetate and silver nitrate both contain $\text{Ag}^+$). The chemistry of the metal precursor may have significant effects on the kinetics of the reduction rate and thus affect the final product morphology. Also it has been shown in literature that there is a relationship between crystallite size of the metal precursor and the size of the metal nanoparticles produced.\(^{29}\) This type of study could possibly yield useful information regarding the role of the metal precursor. (2) Many metal ions can have multiple oxidation states ($\text{Au}^+$, $\text{Au}^{+3}$, etc). In our synthesis each metal ion had a different oxidation state ($\text{Ag}^+$, $\text{Au}^{+3}$, and $\text{Pt}^{+2}$). It has been shown in the literature that these metal ions are reduced through different reaction pathways during sonochemistry.\(^{11,30}\) Performing metal-decoration of SWNTs with various metal precursors containing ions of different oxidation states may possibly lead to new insights pertaining to the role of the oxidation state of the metal in this synthetic procedure. (3) Further studies using additional metals not limited to gold, silver, and platinum could be performed. There are
many examples in the literature of synthesis of carbon nanotubes decorated with other metals such as palladium, cobalt, or nickel.\textsuperscript{139-142, 157, 160} These studies may further elucidate the role of the metal in the decoration of carbon nanotubes. (4) The functional groups on the SWNTs could be altered in additional studies. The functional groups present in this study were predominantly in the form of carboxylic acids and ketones. As was previously discussed, Azamian et al. decorated SWNTs with gold nanoparticles by first altering the carboxylic acid functional groups to thiol groups.\textsuperscript{159} Thus, altering functionalities may produce results pertaining to how specific metals attach to SWNTs.

As was seen in all previous samples in both Chapter 3 (Ag-SWNT) and Chapter 4 (Ag-GO, Ag-CNP), the DSC data for two additional metal-decorated SWNTs (Au-SNWTs and Pt-SWNTs) showed the onset of carbon combustion at earlier temperatures (~100-150 °C) than that of undecorated SWNTs. Several possible sources may have been the cause of this shift in the carbon combustion peaks and three possible reasons were discussed in Chapter 3. In brief the metals possibly may (1) have acted as a catalyst for carbon combustion or (2) worked to increase the heat transfer rate to the sample during heating.

Characterization data of the Au-SWNTs, and Pt-SWNTs showed that the sonochemical method in DMF for the synthesis Ag-SWNTs could be extended to synthesize additional metal-decorated SWNTs with varying degrees of success. Key morphological differences indicated that the type of metal used for synthesis affected the final product properties. While silver and platinum-decorated samples showed SWNTs that were well decorated with small nanoparticles, the gold reaction produced large nanoparticles which did not efficiently decorate the SWNTs. This may have possibly
been due to incompatible chemistry of gold nanoparticles with carboxylic acid groups which did not interact strongly. It is clear from these results that the type of metal has a role in the synthesis of metal-decorated SWNTs and while the precise role of the metal is unclear, it is believed that the type of metal affects how the nanoparticle interacts with the defects sites on the SWNTs.
CHAPTER 6

CONCLUSIONS

In the course of this study we have successfully demonstrated the ability to synthesize several noble metal nanoparticles and deposit these nanoparticles in-situ onto several different carbon supports. Ag-SWNTs were synthesized using several different reaction parameters. It was found that the Ag-SWNTs prepared by the sonochemistry-in-DMF synthesis (S-DMF) showed characteristics most in agreement with the defined optimal product. The sample morphology showed well-dispersed carbon nanotubes that were fairly evenly decorated with small (~5.7 nm) silver nanoparticles. The silver content was also the highest of any of the samples at ~35%. While the individual roles of both sonochemistry and DMF are still unknown, it was determined that both of these reaction parameters were needed in order to attain the optimal product. Thus, both sonochemistry and DMF played critical roles in synthesizing Ag-SWNTs.

The sonochemistry-in-DMF synthesis procedure was then successfully used to decorate additional carbon supports, in the form of graphene oxide and carbon nanoparticles, with silver nanoparticles. Each type of silver-decorated carbon supports (SWNTs, GO, CNPs) contained different morphologies and silver content which may have been due to multiple factors including the number and functionality of available defect sites for nanoparticle attachment. The exact role of the carbon support in the metal
decoration process is still unknown but it is believed that the nature of the carbon support affects the growth and decoration process of the metal nanoparticles.

The sonochemical method in DMF was also successfully used to synthesize gold and platinum nanoparticles but these particles decorated SWNTs only in the case of platinum. While silver and platinum-decorated samples showed well decorated SWNTs with small nanoparticles, the gold reaction produced large nanoparticles which did not efficiently decorate the SWNTs. This may have possibly been due to incompatible chemistry of gold nanoparticles with carboxylic acid groups which did not interact strongly. These results indicated that the type of metal had a role in the synthesis of metal-decorated SWNTs and while the precise role of the metal is unclear, it is believed that the type of metal affects how the nanoparticle interacts with the surface of the SWNTs.

Our future research in this field should include studies on additional solvents, concentration effects, reaction times, reaction temperatures, altering surface functionality of carbon supports, additional types of support, and additional metals. While clear mechanisms of particle formation and decoration are still unclear, the studies in this work have enhanced our understanding of the roles of sonochemistry, solvent, carbon support, and metal in the synthesis of metal nanoparticle decorated carbon supports. The knowledge gained from this work will lead us to more precise tuning in the synthesis of metal nanoparticle-decorated carbon supports and, to a certain extent, allow for a better understanding of the metal-decoration mechanism.
REFERENCES


5. Guo, D.J.; Li, H.L. *Carbon* 2004, 43, 1259-1264


50. Creighton, J.A.; Blatchford, C.G.; Albrecht, M.G. *Faraday Trans.* 2 **1979**, *75*, 790-798


53. Sondi, I.; Goia, D.V.; Matijevic, E.; *J. Colloid Interf. Sci.* **2003**, *260*, 75-81


