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Application of Carbon Dioxide Towards the Development of Smart Materials, Green Reaction Schemes and Metallic Nanoparticle Synthesis

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APPLICATION OF CARBON DIOXIDE TOWARDS THE DEVELOPMENT OF 
SMART MATERIALS, GREEN REACTION SCHEMES AND 
METALLIC NANOPARTICLE SYNTHESIS

A Dissertation
Presented to
the Graduate School of
Clemson University

In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy
Chemical Engineering

by
Fiaz S. Mohammed
December 2012

Accepted by:
Dr. Christopher L. Kitchens, Committee Chair
Dr. David Bruce
Dr. Douglas E. Hirt
Dr. Thompson Mefford
ABSTRACT

Global carbon dioxide (CO\textsubscript{2}) emissions have steadily risen over the last 50 years, with 34 billion tons of CO\textsubscript{2} released in 2009 alone. Its potential as a greenhouse gas has negatively affected our lives and environment by the resulting ocean acidification and climate change. To mitigate atmospheric CO\textsubscript{2}, various strategies have been implemented for CO\textsubscript{2} separation, capture, storage and use as a chemical feedstock. The use of CO\textsubscript{2} in various chemical industries is attractive as its non-flammable, non-toxic, and relatively inert properties have made it an inherently safer alternative to traditional organic solvents, as well as, a greener carbon feedstock. Also, the accessible critical properties, appreciable critical density, high diffusivity and tunable thermophysical properties make liquid and supercritical CO\textsubscript{2} an attractive solvent for industrial applications.

In recent years, significant progress has been made in the field of tunable solvent media by employing the reversible reaction of CO\textsubscript{2} with amines to produce carbamates. This class of compounds possesses ionic properties that are significantly different from their amines resulting in a non-ionic to ionic switching mechanism that provides for switchable solvent properties, reversible surfactants, low molecular weight organogelators and stimuli responsive materials. The focus of this dissertation is therefore the implementation of the reversible CO\textsubscript{2} – amine reaction for the formation of smart surfaces, greener amine protection mechanisms, and cationic metallic nanoparticle synthesis. Chapter 2 of this dissertation demonstrates the reversible reaction of CO\textsubscript{2} with amine-containing self-assembled monolayers to yield “smart” surfaces that undergo a
reversible change in structure, charge, and wettability upon reaction with CO$_2$. The formation of carbamate esters are also a widely implemented mechanism for amine protection during organic synthesis. However, traditional methods of protection incur increased solvent use and energy consumption due to a separate deprotection reaction. To solve this dilemma, the reversible protection of amines using CO$_2$ induced carbamates was demonstrated in chapter 3; by reducing n-alkyl benzophenone imine and n-phenyl, n-alkylurea yields by up to 67% compared to non-protected amines. The applicability of this chemistry to these classes of nucleophilic substitution reactions and has significant potential to alter the way we approach amine protection in organic synthesis. Another research area that has grown popularity over the last decade is the development of metallic nanoparticles, specifically gold nanoparticles (GNPs), due to their size and shape dependent optical and catalytic properties. Chapter 4 of this dissertation demonstrates the successful application of polyethylene imine (PEI) in the synthesis of cationic GNPs, which are of significant interest for biomedical applications. In this work, we investigated the effect of pH, PEI concentration and reduction method on the size and stability of amine-stabilized gold and silver nanoparticles. Furthermore the potential of carbon dioxide as a stabilizing aid through reversible carbamate formation was explored, leading to a decrease in particle size at ambient temperature along with an increase in stability. In summary, this work has demonstrated the great potential of employing the reversible reaction of carbon dioxide with primary and secondary amines as an effective and greener alternative to conventional methods in a diversity of fields that include “smart” materials, organic chemistry, and functional nanomaterials.
DEDICATION

To my parents, Zai and Ozzie Mohammed.

Thank you for believing in me throughout this process and having the patience to see me finish and become the man you have always expected me to be.

I owe everything to you and I will never forget all you have sacrificed for me and my future. I love you both.
ACKNOWLEDGMENTS

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Secondly, I would like to acknowledge Dr. Thompson Mefford who has overseen my development as a graduate student through all of our joint symposiums and meetings over the last 4 years. I want to thank him for his input during these sessions and for always being very supportive.

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TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>CONTENT</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>TITLE PAGE</td>
<td>i</td>
</tr>
<tr>
<td>ABSTRACT</td>
<td>ii</td>
</tr>
<tr>
<td>DEDICATION</td>
<td>iv</td>
</tr>
<tr>
<td>ACKNOWLEDGMENTS</td>
<td>v</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>x</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>xi</td>
</tr>
<tr>
<td><strong>CHAPTER</strong></td>
<td></td>
</tr>
<tr>
<td><strong>I. INTRODUCTION AND BACKGROUND</strong></td>
<td>1</td>
</tr>
<tr>
<td>Significance of Carbon Dioxide</td>
<td>1</td>
</tr>
<tr>
<td>Carbon Dioxide as a Solvent</td>
<td>2</td>
</tr>
<tr>
<td>Chemical Usage of Carbon Dioxide</td>
<td>5</td>
</tr>
<tr>
<td>Carbamate Background</td>
<td>6</td>
</tr>
<tr>
<td>Application of Carbamate Chemistry</td>
<td>8</td>
</tr>
<tr>
<td>Climate Change</td>
<td>10</td>
</tr>
<tr>
<td>Trends in Atmospheric Carbon Dioxide</td>
<td>13</td>
</tr>
<tr>
<td>Scope of Dissertation</td>
<td>14</td>
</tr>
<tr>
<td><strong>II. INVESTIGATION OF AMINOSILANE CARBAMATES AND THE DEVELOPMENT OF STIMULI RESPONSIVE SELF ASSEMBLED MONOLAYERS</strong></td>
<td>16</td>
</tr>
<tr>
<td>Introduction</td>
<td>16</td>
</tr>
<tr>
<td>Materials and Methods</td>
<td>18</td>
</tr>
<tr>
<td>Materials</td>
<td>18</td>
</tr>
<tr>
<td>Carbamate Salt Isolation</td>
<td>18</td>
</tr>
<tr>
<td>Substrate Preparation</td>
<td>19</td>
</tr>
<tr>
<td>SAM Functionalization</td>
<td>20</td>
</tr>
<tr>
<td>Characterization</td>
<td>21</td>
</tr>
<tr>
<td>Results and Discussion</td>
<td>23</td>
</tr>
<tr>
<td>Carbamate Salt and Isolation</td>
<td>23</td>
</tr>
</tbody>
</table>
Table of Contents (Continued)

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAM Deposition</td>
<td>29</td>
</tr>
<tr>
<td>Effect of CO(_2) on SAMS</td>
<td>33</td>
</tr>
<tr>
<td>Conclusions</td>
<td>40</td>
</tr>
</tbody>
</table>

III. Employing Carbon Dioxide as a Protection/Deprotection Mechanism for Amines ................................................. 41

- Introduction .................................................................. 41
- General Procedures .................................................. 44
  - Amine Protection .................................................. 44
  - Typical Amine Deprotection .................................... 44
  - Characterization .................................................. 45
- Synthesis of n-alkyl n-phenyl urea ................................ 46
- Results and Discussion ............................................... 47
  - Proton NMR and FTIR .............................................. 47
  - DSC Analysis ...................................................... 51
  - Effect of Carbon Dioxide ....................................... 53
- Synthesis of n-propyl benzophenone imine ................................ 55
- Results and Discussion ............................................... 56
  - Effect of Carbon Dioxide on Imine Yield .................... 56
  - Imine Characterization and Quantification via FTIR ....... 57
  - Benzophenone imine synthesis in the absence
    Of Mechanical Stirring ........................................ 60
- Conclusions .............................................................. 63

IV. Direct Synthesis of Cationic Gold Nanoparticles Using Polyethyleneimine (PEI) and Carbon Dioxide ........................................... 64

- Introduction .................................................................. 64
- Experimental Procedures ............................................. 66
  - Materials ................................................................ 66
  - \(\text{NaBH}_4\) Reduction ......................................... 66
  - Thermal Reduction .................................................. 67
  - Room Temperature Reduction .................................... 67
  - Characterization .................................................... 67
- Results and Discussion ............................................... 68
  - Effect of Reduction Method ...................................... 69
  - Effect of Concentration and pH ................................ 72
  - Effect of Carbon Dioxide ......................................... 80
Table of Contents (Continued)

| Effect of Boiling Time on the Thermal Reduction Method | 87 |
| Conclusions | 89 |
| V. CONCLUSIONS AND RECOMMENDATIONS | 90 |
| APPENDICES | 95 |

A: Effect of Post-Synthesis and Post-Ligand Exchanged Purification on Gold and Silver Nanoparticles | 96 |
| Introduction | 96 |
| Experimental | 98 |
| Citrate Capped NP Synthesis | 98 |
| Dodecanethiol exchanged GNPs and SNPs | 98 |
| Direct Synthesis of Alkane thiol capped SNPs | 99 |
| Results and Discussion | 101 |
| Effect of purification on Ligand Exchanged Nanoparticles | 101 |
| Effect of Purification on Dodecanethiol Capped SNPs via the Direct Method | 108 |
| Optimized Solvent: anti-solvent Volume Ratio for Dodecanethiol Capped SNPs | 113 |
| Conclusions | 118 |

B: Surface Plasmon Resonance (SPR) Background | 120 |
C: Variable Angle Ellipsometry Instrumentation | 123 |
D: Static Contact Angle Measurements | 125 |

REFERENCES | 131
# LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Table of the AEAPMDS, AHAPTS and PEI-Sil monolayer thicknesses, static water contact angles and calculated solid surface tensions before and after CO$_2$ exposure</td>
<td>34</td>
</tr>
<tr>
<td>3.1</td>
<td>n-phenyl, n-alkylurea melting points and crystallization temperatures determine from DSC</td>
<td>51</td>
</tr>
<tr>
<td>3.2</td>
<td>Percentage yields of the n-phenyl-n-alkylureas of for pure, protected and de-protected amine</td>
<td>54</td>
</tr>
<tr>
<td>3.3</td>
<td>Determined BP conversion from GC analysis compared to BP conversion calculated from IR spectral C=N:C=O absorbance ratio. * denotes a value that was estimated using figure 3.11</td>
<td>59</td>
</tr>
<tr>
<td>4.1</td>
<td>Table showing GNPs core size obtained from TEM, Zeta Potential and Hydrodynamic radius ($R_h$) from DLS</td>
<td>73</td>
</tr>
</tbody>
</table>
## LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Graph showing the density of Carbon dioxide vs. pressure isotherms</td>
<td>3</td>
</tr>
<tr>
<td>1.2</td>
<td>Reaction scheme showing the formation carbamic/carbonic acid intermediates from coupling of carbon dioxide with amines/water</td>
<td>6</td>
</tr>
<tr>
<td>1.3</td>
<td>Reaction scheme of reversible alkylammonium carbamate formation from coupling of carbon dioxide and a secondary amine</td>
<td>6</td>
</tr>
<tr>
<td>1.4</td>
<td>Depiction of the greenhouse effect</td>
<td>11</td>
</tr>
<tr>
<td>1.5</td>
<td>Schematic depiction of the Carbon Cycle highlighting the major pathways for movement between the atmosphere, ocean and land</td>
<td>12</td>
</tr>
<tr>
<td>2.1</td>
<td>Molecular structures of AEAPMDS (left), AHAPTS (middle) and PEI-sil (right) amino silanes</td>
<td>19</td>
</tr>
<tr>
<td>2.2</td>
<td>AEAPMDS and AHAPTS carbamate structures formed from the bubbling of CO₂ through 0.1Molar acetonitrile solutions</td>
<td>24</td>
</tr>
<tr>
<td>2.3</td>
<td>TGA spectra of pure AEAPMDS (solid) and isolated AEAPMDS carbamate salt (dashed)</td>
<td>25</td>
</tr>
<tr>
<td>2.4</td>
<td>TGA spectra of pure AHAPTS (solid) and isolated AHAPTS carbamate salt (dashed)</td>
<td>25</td>
</tr>
<tr>
<td>2.5</td>
<td>ATR FT-IR spectrum of AEAPMDS reaction cycle within a) Carbonyl Region (top)</td>
<td>27</td>
</tr>
<tr>
<td></td>
<td>b) N-H stretching region (bottom)</td>
<td></td>
</tr>
<tr>
<td>2.6</td>
<td>ATR FT-IR spectrum of pure AHAPTS and isolated AHAPTS carbamate salt</td>
<td>28</td>
</tr>
</tbody>
</table>
List of Figures (Continued)

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.7</td>
<td>ATR FT-IR spectrum of ethylene diamine in ambient air at time = 0 minutes (solid) and time = 1 hr (dashed)</td>
<td>29</td>
</tr>
<tr>
<td>2.8</td>
<td>Representation of the dip coating mechanism for SAM production</td>
<td>30</td>
</tr>
<tr>
<td>2.9</td>
<td>Drawing representing the various modes of attachment that can occur during the dip coating procedure</td>
<td>31</td>
</tr>
<tr>
<td>2.10</td>
<td>Graph of AEAPMDS SAM thickness vs. time of deposition</td>
<td>32</td>
</tr>
<tr>
<td>2.11</td>
<td>Scheme showing the deposition of the coupling agents onto Si substrate followed by the reversible reaction with CO$_2$ leading to the formation of the carbamate structures.</td>
<td>33</td>
</tr>
<tr>
<td>2.12</td>
<td>Average ellipsometry measurements of AEAPMDS SAM demonstrating the reversible switch in surface property</td>
<td>36</td>
</tr>
<tr>
<td>2.13</td>
<td>Average static water contact angle measurements of the AEAPMDS and AHAPTS SAMs demonstrating the reversible switch surface property</td>
<td>37</td>
</tr>
<tr>
<td>2.14</td>
<td>AFM images of AEAPMDS SAM a) before and b) after CO$_2$ exposure</td>
<td>39</td>
</tr>
<tr>
<td>3.1</td>
<td>Reaction scheme displaying imine and urea products along with alkylammonium carbamate for amine protection</td>
<td>43</td>
</tr>
<tr>
<td>3.2</td>
<td>Reaction scheme for n-phenyl, n-alkylurea synthesis using: A) non-protected amines, B) carbamates induced from CO$_2$ and C) deprotected amines obtained from the thermal treatment of carbamates</td>
<td>46</td>
</tr>
<tr>
<td>3.3</td>
<td>ATR-FTIR of n-phenyl, n-alkylureas showing the similar absorption spectra and characteristic carbonyl and secondary amine peak</td>
<td>48</td>
</tr>
</tbody>
</table>
List of Figures (Continued)

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.4</td>
<td>$^1$H NMR of n-phenyl, n-propylurea&lt;br&gt;$\delta = 1.0$ (t,3H), 1.6 (m,2H), 3.3 (t,2H), 4.9 (s,1H), 6.4 (s,1H), 7.1-7.5 (5H)</td>
<td>49</td>
</tr>
<tr>
<td>3.5</td>
<td>$^1$H NMR of n-phenyl, n-decylurea</td>
<td>50</td>
</tr>
<tr>
<td>3.6</td>
<td>DSC spectra of n-propyl urea isolated from all three amine starting materials. Ramp rate = 5°C per minute to 140°C followed by equilibration to 60°C and repeated heating</td>
<td>52</td>
</tr>
<tr>
<td>3.7</td>
<td>DSC spectra of n-propyl urea at ramp rate 5°C per minute to 140°C followed by equilibration to 60°C and repeated heating</td>
<td>53</td>
</tr>
<tr>
<td>3.8</td>
<td>Reaction scheme for benzophenoneimine synthesis in Methanol using A) non-protected amines, B) carbamates induced from CO$_2$ and C) deprotected amines obtained from the thermal treatment of carbamates</td>
<td>55</td>
</tr>
<tr>
<td>3.9</td>
<td>Plot of BP concentration determined via GC for the non-protected, protected and de-protected propylamine reactions at 3, 6 and 24hrs</td>
<td>56</td>
</tr>
<tr>
<td>3.10</td>
<td>FTIR of pure BP (dashed) compared to isolated BP imine product (solid)</td>
<td>57</td>
</tr>
<tr>
<td>3.11</td>
<td>ATR-FTIR spectra of non-protected BP reactions at 3hrs (A) and at 12 hrs (B). ATR-FTIR of protected BP reaction at 3hrs (C) and at 12hrs (D)</td>
<td>58</td>
</tr>
<tr>
<td>3.12</td>
<td>BP conversion % of Non-protected (left), Protected (middle) and De-protected (right) reactions monitored in-situ from 4reaction vials</td>
<td>61</td>
</tr>
<tr>
<td>4.1</td>
<td>TEM image of PEI-GNPs along with the corresponding particle size distribution histogram and UV-vis absorption spectrum. Particles were synthesized via thermal reduction with a boiling time of 1 minute. The sizes of the particles were determined using Image J software</td>
<td>69</td>
</tr>
</tbody>
</table>
List of Figures (Continued)

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.2</td>
<td>GNP mean core size for each reduction method using 0.01 wt %PEI with varying solvent conditions. The error bars represent the standard deviation of the particle size distribution for each sample population. Thermal boiling time = 1 min.</td>
<td>70</td>
</tr>
<tr>
<td>4.3</td>
<td>TEM images of PEI capped GNPs synthesized using NaBH4, thermal and room temperature reductions. Average core size and zeta potential determined</td>
<td>71</td>
</tr>
<tr>
<td>4.4</td>
<td>Image of NaBH4 reduced GNPs core sizes from TEM analysis</td>
<td>74</td>
</tr>
<tr>
<td>4.5</td>
<td>UV–Vis absorption spectra of NaBH4 reduced GNPs using 0.005 – 0.02 wt % PEI solutions in pure DI- H2O and in 1mM HCl.</td>
<td>76</td>
</tr>
<tr>
<td>4.6</td>
<td>UV-Vis absorption spectra of GNPs reduced using the Thermal method using 0.005 -0.02 wt % PEI in 1mM HCl and DI-H2O.</td>
<td>77</td>
</tr>
<tr>
<td>4.7</td>
<td>Graph of the core diameter (TEM) and hydrodynamic diameter (DLS) of thermally reduced GNPs using 0.005 -0.02 wt % PEI in 1mM HCl and DI-H2O</td>
<td>78</td>
</tr>
<tr>
<td>4.8</td>
<td>UV-Vis absorption spectra of GNPs reduced at room temperature and pressure using various concentrations of PEI after A) 2 hrs and B) 2 weeks</td>
<td>79</td>
</tr>
<tr>
<td>4.9</td>
<td>Reaction scheme of PEI with Carbon dioxide forming carbamic acid. This acid forms a carbonate in the presence of water (a) or a carbamate salt in the presence of another amine (b). In the presence of an acid the amine is protonated(c)</td>
<td>81</td>
</tr>
<tr>
<td>4.10</td>
<td>Image showing the pH of a 0.01wt% PEI solution vs. the carbon dioxide bubbling time (left) and the respective GNPs synthesized using the NaBH₄ reduction method at the specific pH’s.</td>
<td>81</td>
</tr>
</tbody>
</table>
List of Figures (Continued)

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.11</td>
<td>UV-vis absorption spectra of NaBH$_4$ reduced GNPs obtained while varying the sequence of CO$_2$ exposure with reagent addition.</td>
</tr>
<tr>
<td>4.12</td>
<td>UV–vis absorption spectra of NaBH$_4$ reduced Gold nanoparticles with increasing CO$_2$ exposure at a PEI concentration of 0.01 wt%</td>
</tr>
<tr>
<td>4.13</td>
<td>Image of GNPs synthesized from a NaBH$_4$ reduction utilizing PEI and the PEI+CO$_2$ solutions</td>
</tr>
<tr>
<td>4.14</td>
<td>UV-Vis absorption spectra of thermally reduced GNPs using 0.01wt% PEI and 0.01wt% PEI-CO$_2$ at 1, 5 and 15 minutes boiling times along with an image of the thermally reduced 0.01wt% PEI GNPs at various boiling times</td>
</tr>
<tr>
<td>4.15</td>
<td>Maximum absorbance of the GNP Plasmon peak as a function of time for the room temperature reduced GNPs</td>
</tr>
<tr>
<td>4.16</td>
<td>Graph of the wavelength of maximum absorbance vs. time for the room temperature reduced GNPs in H$_2$O and with CO$_2$</td>
</tr>
<tr>
<td>4.17</td>
<td>Graph of the thermally reduced 0.01 wt % GNPs core diameter (TEM) and hydrodynamic radius (DLS) vs. boiling time (min)</td>
</tr>
<tr>
<td>4.18</td>
<td>UV-vis spectra of the thermally reduced 0.01 wt %PEI GNPs at boiling times of 1 min, 5 min and 15 min under neutral conditions</td>
</tr>
<tr>
<td>A1</td>
<td>Image showing ligand exchange process from an aqueous phase to a hexane phase containing alkane thiols for citrate capped GNPs</td>
</tr>
<tr>
<td>A2</td>
<td>Time resolved UV vis absorption spectra of the aqueous layer from a citrate capped GNPs ligand exchange reaction with dodecanethiol</td>
</tr>
</tbody>
</table>
List of Figures (Continued)

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>A3</td>
<td>$^1$HNMR of pure dodecanethiol and dodecanethiol capped gold nanoparticles from CDCl$_3$</td>
</tr>
<tr>
<td>A4</td>
<td>Calibration curve of dodecanethiol using peak areas obtained via GC</td>
</tr>
<tr>
<td>A5</td>
<td>Figure showing the measured concentration of DDT from ligand exchanged GNPs using GC vs. wash number (top). UV-vis absorption spectra of DDT capped GNPs after 3 washes (bottom). The solvent: anti-solvent ratio ( \sim 1:20 )</td>
</tr>
<tr>
<td>A6</td>
<td>Bar graph depicting the change in concentration of DDT in the organic fraction of the ligand exchange process</td>
</tr>
<tr>
<td>A7</td>
<td>Graph showing the calculated surface coverages for gold and silver NPs capped by dodecanethiol synthesized via a ligand exchange process</td>
</tr>
<tr>
<td>A8</td>
<td>TEM image and histogram of dodecanethiol capped silver nanoparticles washed at a solvent: anti-solvent volume ratio of 1:25 (top) and 1:100 (bottom). All nanoparticles were sized using ImageJ software</td>
</tr>
<tr>
<td>A9</td>
<td>Graph of the average total percentage of weight lost during TGA for each anti-solvent ratio. Error bars represent the Std. Deviation of 3 runs</td>
</tr>
<tr>
<td>A10</td>
<td>Graph displaying the calculated surface coverages for the SNP’s purified at ethanol volume ratios of 1:25, 1:50 and 1:100. Size of particles were approximated to be 8nm for all three processes</td>
</tr>
<tr>
<td>A11</td>
<td>UV-vis absorption spectra of SNP after 0-4 washes with a solvent: anti-solvent volume ratio of 1:10</td>
</tr>
<tr>
<td>A12</td>
<td>TGA curves for SNPs with 0-4 washes with a solvent: anti-solvent volume ratio of 1:10</td>
</tr>
<tr>
<td>A13</td>
<td>First derivative of the TGA curves for SNPs with 0-4 washes with a solvent: anti-solvent volume ratio of 1:10</td>
</tr>
</tbody>
</table>
List of Figures (Continued)

Figure                                                                                                                       Page

A14  Plot showing the measured DDT weight loss percentages and the corresponding calculated surface coverage determined for 6nm 7nm and 8 nm particles .......................................................... 117

A15  Plot showing the calculated surface coverage for 6nm 7nm and 8 nm particles based on the weight fractions of DDT determined via TGA ......................................................................................... 118

B1   Schematic illustration of the Plasmon resonance caused by the oscillating field ................................................................. 120

B2   UV-vis absorption spectra of GNPs of varying sizes .................................................. 121

B3   Electrodynamic modeling calculations of extinction spectra for GNP aggregates (d = 40 +/- 0.5 nm) .................................. 122

C1   Diagram showing the instrumentation of the ellipsometer ........................................................................................................ 123

D1   Image showing the variability in contact angles and how they relate to hydrophobicity and hydrophilicity .......................... 126

D2   Diagram showing the instrumentation setup for making contact angle measurements ............................................................ 127

D3   Images obtained by the Instruments camera for a cleaned silicon wafer (top) and a silicon surface coated with a PEI-sil SAM (bottom) ...................................................................................................... 128
CHAPTER ONE
INTRODUCTION AND BACKGROUND

Significance of Carbon Dioxide

In 1772, Joseph Priestly, an English chemist, reported the invention of soda water as CO\textsubscript{2} was released upon the addition of sulfuric acid to chalk and forced into solution.\[^{[1]}\]

Half a century later, the first reported case of liquid carbon dioxide was published by Davy and Faraday,\[^{[2]}\] while Charles Thilorier yielded its solid state in 1834 after rapidly opening a pressurized liquid carbon dioxide container.\[^{[3]}\] It is now known that these physical states of carbon dioxide are heavily dependent on temperature and pressure as low temperatures promote solid CO\textsubscript{2}, capable of subliming directly into the vapor state upon warming (at less than 5.1 bar). Beginning in the 1930’s \[^{[4, 5]}\], the thermophysical properties of CO\textsubscript{2} have been compiled into an extensive library of data sets and thermodynamic models to correlate density, viscosity, dielectric constant and as functions of temperature and pressure.\[^{[6]}\]

Today carbon dioxide is one of the most well studied molecules and has found its way into to a wide variety of industrial and experimental fields due to its unique physical and chemical properties. For example, CO\textsubscript{2} has emerged as one of the most capable and preferred refrigerants in the food and refrigeration industry and cleaning fluids in the microelectronics industry.\[^{[7]}\] This is attributed to the low surface tension and liquid-like viscosity that makes carbon dioxide a highly compressible fluid compared to other common refrigerants at a given temperature and pressure. Adding to the improved
physical properties are the advantages gained by replacing the environmentally
detrimental chlorofluorocarbons (CFC’s), while its gas-like diffusion properties make
CO₂ advantageous in polymer processing, pesticide fumigation, orange juice
pasteurization, and extraction of nutraceuticals, caffeine, hops, and essential oils.[8] Other
applications for carbon dioxide include fire extinguishers, protective gas in food
preservation along with the steel industries and chemical industries.

**Carbon dioxide as a Solvent**

As seen in Figure 1.1, the density of carbon dioxide is dramatically increased with
increasing pressure at room temperature, producing a liquid CO₂ solvent. Above the
critical temperature of 31.1°C and critical pressure of 73.9 bar, CO₂ is in a supercritical
state having gas like diffusion properties yet adequate solvent power with a density
rivaling that of liquid water.[9] It was asserted, that because of these physical properties,
carbon dioxide could be a useful solvent with strength equal or greater than alkanes and
ketones.[10, 11] However, its potential use as a replacement for these conventional solvents
was initially exaggerated by the miss calculations of earlier models which over predicted
its solubility parameter. Today, after years of advancement, carbon dioxide is seen as a
highly compressible “green” solvent with tunable fluid properties, and possesses many
environmental and chemical advantages with its use within the chemical and materials
research communities.
A major advantage that CO$_2$ has over traditional solvents is its non flammability, which makes it inherently safer for large scale extractions and other industrial processes. Based on the typical working conditions of large scale operations, the 5000 ppm threshold limit value (TLV), of CO$_2$ renders it less toxic than many other organic solvents. Acetone by comparison has a TLV of 750 ppm, while pentane and chloroform are 600 ppm and 10ppm respectively. The surface tension of carbon dioxide is also much lower than traditional solvents, enabling solutes to diffuse at a higher rate due to the lower viscosity. Liquid CO$_2$ also has higher solubility of hydrogen and oxygen than typical organic solvents or water, which is beneficial for hydrogenation or oxygenation reactions.\[12\]

Figure 1.1: Graph showing the density of Carbon dioxide vs. pressure isotherms
Also, the low critical temperature enables supercritical CO₂ to be easily managed and implemented in an environmentally friendly manner as the room temperature operation requires less energy demands. Combined with the increased safety properties and its natural abundance, carbon dioxide is the most commonly used supercritical fluid (SCF) solvent in food applications.\textsuperscript{[13, 14]} \newline

Chemically, the CO₂ molecule is relatively benign, and cannot readily be oxidized as it is already the product of complete oxidation of an organic compound. Hence, it can be very a useful solvent during oxidation reactions and biphasic reactions due to the ease of removal and reduced risk of cross contamination. Eckert et al.\textsuperscript{[15, 16]} investigated CO₂/water mixtures incorporating a phase transfer catalysts as well as employing CO₂ as a phase separation ‘trigger’. In this work CO₂ addition to a mixture of organic and fluorous liquids created a homogeneous single phase, while depressurization afforded the initial two-component, two-phase system.\textsuperscript{[16]} Furthermore, the coffee decaffeination process employs a liquid–liquid extraction between CO₂ and water to recover the extracted caffeine.\textsuperscript{[17]} Other situations where CO₂ can potentially be employed as a solvent include systems where free protons could interfere with the reaction, exploiting its aprotic solvent properties.

However, the use of CO₂ as a solvent does have its disadvantages as higher capital cost exists for a CO₂-based process relative to one using a conventional solvent. The symmetric molecular structure of CO₂ contains a permanent electrical quadrupole moment that contributes to a critical pressure and vapor pressure that is larger than analogous values for other organic solvents; such as alkanes, fluoroalkanes and
hydrofluoroalkanes. Because of this high critical and vapor pressure at room temperature (>60 bar), use of CO₂ in a process clearly requires high-pressure equipment creating a potential danger and larger energy demand.

**Chemical Usage of Carbon Dioxide**

As a chemical reactant, CO₂ has a linear molecular geometry resulting in an apolar property despite having two polar C=O components. The electrophilic carbon atom of the CO₂ has a strong affinity toward nucleophiles; therefore CO₂ can be classified as an “anhydrous carbonic acid” that reacts with basic compounds and nucleophiles in the synthesis of ureas, inorganic carbonates, organic carbonates etc. In fact, the production of ureas and polyurethanes is the largest industrial consumer of carbon dioxide [18, 19] with production estimated to be 157 million tons in 2010 by the International Fertilization Industry. [20] Many other processes exist at both the industrial and lab scale that utilizes carbon dioxide as a reagent or starting material, however, the use of CO₂ as chemical feedstock is limited due to the thermodynamic stability of the molecule, resulting in high energy substances and processes to transform CO₂ into other useful chemicals. [21, 22] However, in this study, we are primarily focused on one type of carbon dioxide reaction, the carbamate formation as a result of CO₂ coupling with primary and secondary amines.
Carbamate Background

Carbamates are a stable group of compounds derived from an unstable intermediate carbamic acid (Figure 1.2). In the case of a proton-containing substance of formula XH, the extent of the displacement depends on the nature of the nucleophile, the reaction medium, and the temperature. Carbamate chemistry has been extensively studied in literature with the resultant carbamates and their intermediate acids or carbonates well characterized.

\[
\begin{align*}
\text{CO}_2^+ + \text{XH} & \rightleftharpoons \text{X}^-\text{COOH} \\
\text{X}^-\text{COOH} & \rightleftharpoons [\text{XH}_2]^+ [\text{XCOO}]^- \\
(\text{XH} = \text{NH}_3, \text{NH}_2\text{R}, \text{NHR}_2, \text{H}_2\text{O})
\end{align*}
\]

Figure 1.2: Reaction scheme showing the formation carbamic/carbonic acid intermediates from coupling of carbon dioxide with amines/water

Figure 1.3: Reaction scheme of reversible alkylammonium carbamate formation from coupling of carbon dioxide and a secondary amine.
The pioneering studies in the first decades of last century first showed that amines react with CO$_2$ to produce alkylammonium alkylcarbamates as seen in Figure 1.3.\cite{23-27}. Later literature proposed that 1 mole of CO$_2$ reacts with 2 moles of primary or secondary amine to form these carbamate structures. The mechanism involves the reaction of CO$_2$ with one amine to form a carbamic acid which then reacts with another basic amine to form the carbamate salt.\cite{28} Kurz et al.\cite{29} also determined these conclusions under anhydrous conditions and atmospheric pressure where a colorless solid was formed upon the uptake of CO$_2$ by neat amines. The amount of carbon dioxide taken up by the carbamate formation corresponded to a final CO$_2$/amine molar ratio close to 0.5. Recent work by Hiyoshi et al. has further shown that there is no bias between the reaction of CO$_2$ with primary and secondary amines, only the availability of the two amine groups is necessary for the reaction to take place.\cite{30} It was also previously reported that the presence of zwitterionic carbamates (\(\pm\)NH$_3$(CH$_2$)$_n$NHCOO\(^{-}\)) due to carbon dioxide-amine reactivity in a [NH$_2$(CH$_2$)$_n$NH$_2$]/CO$_2$ system was a major product.\cite{31} However, further studies into the carbamate intermediates have determined that a mixture of both the zwitterions and the diammonium dicarbamate, [NH$_3$(CH$_2$)$_n$NH$_3$][O$_2$CNH(CH$_2$)$_n$-NHCO$_2$] are present in a diethylether solvent system.\cite{32}

Kinetics of carbamate formation and their intermediates have also determined complicated reaction orders with respect to amine concentration.\cite{33-35} Furthermore \(n\)-substituted carbamates undergoing acid-catalyzed decompositions attributed the decarboxylation of the intermediate zwitterionic carbamic acid as the main mode of carbamate decomposition.\cite{36,37} Although it was later proved that solid state
dialkylcarbamic acids dominated the zwitterionic form, and so decomposition can be attributed to the carbamic acid as well.\textsuperscript{[38]} Other examples of alkylammonium carbamates have been derived by the carbonation of hexyl, octyl, decyl, dodecyl, and cyclohexyl amines with carbon dioxide which shows the robustness and efficiency of this reaction.

The importance of this chemistry can be seen through its vital role in many biological applications. For example, the binding and release of oxygen from hemoglobin proteins found in our blood.\textsuperscript{[39]} Also \(N\)-Substituted carbamic acids are believed to be key intermediates in metabolic reactions via \(CO_2\) transfer through \(N\)-carboxybiotin,\textsuperscript{[40]} along with Rubisco (ribulose 1,5-biphosphate carboxylase) promoted photosynthetic activation of \(CO_2\).\textsuperscript{[41]} However, the most attractive property of this carbamate chemistry is the reversible nature at which the reaction proceeds, a property that has been exploited extensively in recent green chemistry applications.

**Application of Carbamate Chemistry**

Reversible organogel formation through the use of amines as latent low-molecular mass gelators is an application of the carbamate-\(CO_2\) reaction which has been demonstrated by Weiss et al.\textsuperscript{[42-44]} In this work, \(CO_2\) was bubbled through varying solutions of aliphatic amines and the subsequent carbamates produced organogels that are stable for more than 3 months and thermally reversible at moderate temperatures. The variance in thermal stability among the organogels was dependent on the solvent properties as well as amine functionality and concentration, however regeneration of amine functionality occurred at temperatures below 100\(^\circ\)C.\textsuperscript{[42]} Other significant works
utilizing this reversible switch from non-ionic to ionic states includes the design of reversible surfactants,[45] the formation of supramolecular complexes,[46,47] structured organic-inorganic complexes along with clickable supramolecular polymers.[48] Parallel to these advancements, this chemistry is also widely incorporated in various zeolitic membranes and mesoporous silica supports modified with amines, which chemically trap the CO$_2$ by way of ammonium carbamate formation.[49] These supports, modified with various amino containing coatings possess large surface areas for CO$_2$ adsorption and also exhibit regenerative ability.

More importantly, this reversible reaction has been utilized in industry for the removal of CO$_2$ from natural gas and coal power plant flue gas through its reaction with aqueous amine solutions such as monoethanolamine (MEA), diethanolamine (DEA) and other tertiary amines. However, due to the high regenerative costs, these aqueous solution methods have limited wide spread application and fall short when compared to proposed ionic liquids (IL’s). IL’s have gained much attention for potential CO$_2$ sequestration based on their high CO$_2$ solubility coupled with their thermal stability, negligible vapor pressure and low flammability.[50-52] Jessop et al. has implemented the formation of the carbamate species in the development of reversible IL solvents that undergo a change in ionic structure upon CO$_2$ exposure. This change significantly alters the polarity of a mixture of hexanol and 1,8-diazabicyclo-[5.4.0]-undec-7-ene (DBU), allowing a miscible mixture with decane to become immiscible and separate once reacted with CO$_2$.[53] Hence creating a smart solvent that can be tailored for specific separation applications.[54,55]
Climate Change attributed to CO$_2$

As stated previously, the application of carbamate chemistry to the sequestration of CO$_2$ is one of the greener applications of this molecule. In this day and age, lasting variations in our planet's weather patterns have become a significant environmental threat, bringing the issue to the forefront of scientific and sociological discussion.$^{[56]}$ These climate changes can be attributed to a number of factors such as solar radiation variability and tectonic plate movements, however, one of the more widely accepted and studied causes of climate change has been the enhanced greenhouse effect due to rising levels of greenhouse gas concentrations in the earth's atmosphere.

As solar radiation is emitted thermally from the surface of the earth, a special class of gases (greenhouse gases) absorbs this energy and radiates a portion back to the lower atmosphere and surface. This blocking of the infrared radiation within the atmosphere that would otherwise escape directly into space is responsible for maintaining the temperature of the Earth's surface. However as the levels of greenhouse gases in the atmosphere increase an elevation of the average temperature of the surface is observed; phenomena which would not occur in the absence of these greenhouse gases. In light of this, the term climate change has become synonymous with global warming, as the physical characteristics and abundance of the greenhouse gases in the atmosphere has contributed to this increased greenhouse effect.

Under clear skies, water vapor is the largest contributor (60% of the total) to the greenhouse effect. But human activity does not greatly contribute to water vapor concentrations globally, and so, it is generally not targeted as one of the root causes of
global warming. Other potential greenhouse gases include nitrous oxide (N\textsubscript{2}O), methane (CH\textsubscript{4}), ozone, fluorocarbons (CFs) and chlorofluorocarbons (CFCs). Yet, despite their longer atmospheric lifetimes and stronger global warming potentials (GWP), the most important greenhouse gas is carbon dioxide (CO\textsubscript{2}), a trace gas having concentrations as less than 1% in our atmosphere.

![Figure 1.4: Depiction of the greenhouse effect](image)

Carbon dioxide is recognized as one of the major components in the carbon cycle, which governs the transport of carbon emissions from plants and animals between the atmosphere and oceans. Within this cycle, atmospheric CO\textsubscript{2} content is delicately balanced by the photosynthesis process of plants and organisms against the respiration
process of living animals and the decomposition of leaves, roots, and organic compounds. There is a seasonal cycle in this atmospheric \( \text{CO}_2 \) as photosynthesis peaks during the growing season, removing large amounts of \( \text{CO}_2 \). Furthermore, natural sinks, such as aquifers, oceans, rivers and lakes, can store the \( \text{CO}_2 \) in a multitude of forms combating the greenhouse effect.

Figure 1.5: Schematic depiction of the Carbon Cycle highlighting the major pathways for movement between the atmosphere, ocean and land.

Trends in Atmospheric Carbon dioxide

Atmospheric data collected at the Mauna Loa Observatory in Hawaii as well as studies conducted on ice cores show that the level of \( \text{CO}_2 \) in preindustrial times were 270 ppmv compared to 315 ppmv in 1958 after modern methods of measurement we
implemented. In 2004, this value had increased to 383 and has reached 390 ppmv as of 2011. This steady increase has resulted in an annual excess of 3.9% CO$_2$ within the natural carbon cycle.$^{[19]}$ According to the International Panel on Climate Change (IPCC), atmospheric carbon dioxide levels may rise as high as 570 ppm by 2100. This is predicted to trigger a rise in the mean global temperature by 1.9°C.$^{[58]}$

There are many sources for this excess CO$_2$, but the combustion of fossil fuels for power generation is by far the largest contributor, along with oil and gas refineries, coal power plants, urea production and ethanol production. When coupled with a reduced capacity for carbon fixation due to deforestation, the increasing amount of carbon dioxide released into the atmosphere has been linked to large scale changes in climate such as oceanic acidification and global warming.

Hence there is a need to develop new ways to mitigate the emissions carbon dioxide through three commonly applied strategies: a reduction in the amount of CO$_2$ produced, capture and storage of CO$_2$ and the sustainable use of CO$_2$.$^{[59, 60]}$ If CO$_2$ could be chemically transformed to fuels, it would re-circulate carbon through the carbon cycle and alleviate the greenhouse effect.$^{[61]}$

**Scope of Dissertation**

This dissertation will focus on the application of CO$_2$ and carbamate chemistry to three research areas. In chapter 2, well ordered amino terminal self-assembled monolayers of aminoethyl-aminopropyl-methyldimethoxysilane (AEAPMDS),
aminohexyl-aminopropyl-trimethoxysilane (AHAPTS) and trimethoxysilyl-
(polyethylenimine) (PEI-silane) were prepared on silicon substrates from toluene
solutions, which were then exposed to CO₂. The subsequent changes in the surface
structure and wettability were characterized by variable angle ellipsometry, atomic force
microscopy (AFM) and static contact angle goniometry. The SAMs showed a reversible
change in layer thickness coupled with an increase in hydrophilicity upon CO₂ exposure.

Chapter 3 explores the use of the reversible CO₂ chemistry as a unique method of
protection for amines during n-propyl benzophenone imine and n-phenyl, n-propyl urea
synthesis. This was a direct implementation of the carbon dioxide in a green chemistry
application as carbon dioxide protection resulted in a 67% decrease in urea yield and a
55% decrease in imine yield, while moderate temperatures reversed the protection and
increased the product yields.

And finally in chapter 4, carbon dioxide was determined to be an inexpensive and
safe additive for the direct synthesis of gold nanoparticles (GNPs) stabilized by
polycationic ligand shells. In this study, low molecular weight Mw ~600
polyethylenimine (PEI) served as the protecting shell during the synthesis of GNPs via
three separate HAuCl₄ reduction pathways; sodium borohydride (NaBH₄), thermal and
room temperature. The particle size increased as the rate of reduction of gold salt
decreased, while concentration and pH had more impact of the stability of the particles.
At a set concentration it was found that lower pH solutions increased the stabilization of
the NPs in solution based on the increase in hydrodynamic radius as pH increased.
Carbon dioxide served as a green method of altering the pH as well as introducing carbamate/carbonate chemistry for added electrosteric stabilization.
CHAPTER TWO
INVESTIGATION OF AMINOSILANE CARBAMATES AND THE DEVELOPMENT OF STIMULI RESPONSIVE SELF-ASSEMBLED MONOLAYERS

Introduction

A variety of advanced materials have been developed utilizing external stimuli to control their physical properties. Known as “smart materials”, these materials employ external triggers such as temperature, pH, electric potential, and light to induce physical changes. The key component in this system is the interaction of the material with an external trigger in its immediate environment. Yet, in spite of the many advantages that these novel systems possess, their reliance on the same stimuli for both the forward and reverse mechanisms is a limitation; protonation of surfaces at low pH and deprotonation at high pH, or the isomerization of azobenzene from its trans to cis conformation under exposure to light while the absence of light returns the molecule to the more stable trans state. Therefore the use of separate forward and reverse stimuli pathways is the next step in smart material development. This can be achieved through the reversible reaction of carbon dioxide (CO$_2$) with free amines, forming robust alkylammonium carbamate structures. This reaction is thermally reversible when saturated with nitrogen or exposed to a reduced pressure, yielding the original amine.

Self-assembled monolayers (SAMs) have been widely used as an efficient method of introducing organic functionality to a surface. Organic SAMs are highly ordered two-dimensional structures that form spontaneously on the substrate of choice. Their simplicity has promoted their used as surface modifiers for practical applications and
basic research since they create the ability to alter and control the chemical nature of surfaces. Yet, despite a well understood and simple mechanism for the formation of amino-terminated SAMs, implementation is limited by the difficulty to produce large area defect free films. This difficulty is due to the lack of direct control over the monolayer formation, varying modes of deposition attributed to hydrogen bonding, and a heavy dependence on experimental and curing parameters. All of which have a significant effect on the resulting monolayer’s thickness, density, coverage and free amine concentration.[73-76]

In this chapter, silicon substrates were functionalized with amino-terminated SAMs and then exposed to CO$_2$, exploiting the chemistry between the gas and free amines to produce surface bound carbamate structures. Here, we propose that the change from non-ionic amines to the ionic carbamate character will result in the transformation of the surface polarity and electrostatic properties. This transformation can be controlled based on the extent of CO$_2$ reaction, extent of surface modifications and the specific regenerative procedures applied. This new mechanism for the dynamic control of surface properties uses CO$_2$ gas as a simple, abundant and non toxic stimulus. This study of the reaction mechanism of these surface modifications could provide opportunities for materials geared towards CO$_2$ capture as well as creating smart surfaces with tailored surface wettability.
Materials and Methods

Materials

Test grade silicon (Si) wafer substrates were purchased predicted from Silicon Quest International. They were N-type, phosphorous doped, with <1-0-0> orientation and 475 – 575 micrometer thicknesses. The following silane coupling agents shown in Figure 2.1 were purchased from Gelest Inc.: trimethoxysilylpropyl (polyethyleneimine) (50%) (PEI-sil), 6-aminohexyl-3-aminopropyl trimethoxysilane (> 95%)(AHAPTS), 2-aminoethyl-3-aminopropyl-methylidmethoxysilane (> 95%)(AEAPMDS). The following reagents were purchased from VWR and used as received: acetonitrile (99.5%), n-hexane (95%), methanol (> 99%), ethanol (90%), toluene (> 99%), sulphuric acid (> 95%), hydrogen peroxide (30%), and acetone (99%). Anhydrous toluene (Acros, > 99%), pentane (EMD, 985), ethylenediamine (Alfa Aesar, 99%), dicyclohexylamine (Alfa Aesar, 98%), decylamine (Aldrich, 95%) and carbon dioxide (National Specialty Gases) were also purchased and used as received.

Carbamate Salt Isolation

12 mM and 0.1M solutions of AEAPMDS, AHAPTS, ethlyenediamine and decylamine were prepared in acetonitrile, n-hexane, acetone and water. Amine solutions had CO$_2$ bubbled through them for 1 minute. The resulting carbamates were filtered, dried with a stream of CO$_2$ and used immediately. The isolated salts were heated in an oven for 15 minutes at 110°C to induce the reverse reaction and obtain their original amines. TGA and ATR FT-IR were used to characterize the reversible reaction of the
carbamate species. Ethylenediamine, decylamine and di-cyclohexylamine were also characterized by thermogravametric analysis (TGA) and attenuated total reflectance Fourier transform infrared (ATR FT-IR) spectroscopy to determine the effects of atmospheric CO$_2$ on the amines.

Figure 2.1: Molecular structures of AEAPMDS (left), AHAPTS (middle) and PEI-sil (right) amino silanes.

Substrate Preparation

Silicon substrates were diced to measure 1 cm x 1.5 cm, washed with acetone and rinsed with DI water. Using a Digital Pro Ultrasonic Cleaner, they were then sonicated in DI water for 30 minutes, followed by sonication in freshly prepared “piranha” solution (7:3 (v:v) concentrated sulfuric acid: 30% hydrogen peroxide) for an additional 60 minutes at 60$^\circ$C. Caution: Piranha solution is corrosive and can react violently with organic compounds. Wafers were subsequently rinsed with excess DI water, blown dry
with nitrogen and used immediately. They are now considered cleaned substrates comprising of hydroxyl rich surfaces ready for further functionalization.

**SAM fictionalization**

Clean silicon substrates were rinsed with methanol, a 1:1 (v:v) mixture of methanol: toluene, and pure toluene respectively. They were then submerged into 2mM solutions of AEAPMDS, AHAPTS and PEI-Silane in anhydrous toluene, with 1% water content, for approximately 1 hr at room temperature. Functionalized substrates were submerged in pure toluene for 30 minutes, sonicated for an additional 10 minutes and finally rinsed with the 1:1 mixture of methanol: toluene and pure methanol respectively. After blowing dry with nitrogen, substrates were oven cured for 60 minutes at 110° C to produce the SAM and used immediately. It should be noted that there are several methodologies for SAM formation in the literature. Many of these methods were explored and the described method was the most reproducible and created the most uniform SAM.

The reaction with CO\textsubscript{2} was done at room temperature and pressure (RTP) using a CO\textsubscript{2} gas cylinder with a low pressure regulator. A pure stream of CO\textsubscript{2} at 30 psi was blown onto wafer for approximately 5 minutes. To induce the reverse reaction and obtain the original SAMs, SAM + CO\textsubscript{2} substrates were heated in oven at 100 °C under a vacuum pressure of 25 inHg.
Characterization

Variable Angle Ellipsometry

The SAM thicknesses were measured using a Beaglehole Instruments Picometer™ variable-angle spectroscopic ellipsometer equipped with a He-Ne laser at a fixed wavelength (λ = 632.8 nm). The incident angle of the laser was varied between 80° to 50°. The monolayer thicknesses were determined by fitting a multilayer Cauchy model to the variable angle data using appropriate refractive index parameters. The refractive indexes of AEAPMDS, AHAPTS obtained from Gelest are 1.4447 and 1.45 respectively. Hence, for simplicity, 1.45 was used for the refractive indexes of these SAMs while 1.51 was used for the PEI-silane SAM.[77] SAM thicknesses were determined by averaging a minimum of 3 measurements at multiple locations on each sample taken in ambient conditions.

Static Contact angle Measurements

Static contact angles were recorded for all three SAMs using a Krüss DSA10-Mk2 goniometer equipped with digital photo analysis software. Using the sessile drop method, a 1 microliter droplet of HPLC-grade water was deposited to the SAM functionalized substrates and the corresponding contact angle was determined by the Young-Laplace fitting method. A minimum of 3 droplets at varying locations on each sample were recorded in ambient air.
**Atomic Force Microscopy (AFM)**

The topography and morphology of the SAMs were acquired using a Veeco Bioscope Instrument with a Nanoscope III SPM controller and a Dimension head (G scanner). A non-contact silicon tip with resonant frequency = 325 kHz, spring constant = 40N/m and cantilever length = 125 micrometers (Micromash Ultrasharp silicon cantilever) was utilized in tapping mode. Tapping mode was also used to evaluate the root-mean-square (RMS) roughness of the monolayers from the AFM images.

**Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR FT-IR)**

A VeeMAX™ II variable angle specular reflectance accessory equipped with a single reflection, 60°, hemispherical Ge crystal plate, ATR pressure clamp and a ZnSe polarizer set for parallel (p) polarization was placed in a sample compartment of a Nexus 870 spectrometer. Silicon substrates were placed onto the Ge crystal while even pressure was applied using a special 7.8mm tip and the ATR clamp. FT-IR data was collected at a 4 cm⁻¹ resolution using 256 scans. The output signal was collected using a deuterated triglycine sulfate (DTGS) room temperature detector.
Results and Discussion

Carbamate Salt Isolation

The carbamate salts of AEAPMDS, AHAPTS, ethylenediamine and decylamine were easily produced and isolated by bubbling low pressure CO\textsubscript{2} through the organic solutions. Initially, the solutions of the amino coupling agents in the organic solvents were either colorless or had a slight yellow hint. Immediately upon exposure to CO\textsubscript{2}, a white precipitate began to form and fall out of the solutions or stick to the walls of the vessel. The amount of precipitate formed depended on both the concentration of the amine and the CO\textsubscript{2} exposure. It was found that the overall carbamate yield was greater and occurred more quickly while in solution versus neat samples. The solvation of the amine groups reduces the intermolecular hydrogen bonding which allows complete interaction with the CO\textsubscript{2}. The solvation of the amines also aids in dissipating the heat evolved from the exothermic carbamate reaction. Under neat conditions however, the reaction is diffusion limited as carbamate formation at the interface hinders the CO\textsubscript{2} from reaching all of the free amines which are trapped within the newly formed polar carbamate layer.

This physical change observed in Figure 2.2 is attributed to the change in ionic structure of the coupling agents as charged carbamate species precipitate out of the organic solvents.
As expected precipitation or the carbamates is not observed in aqueous environments as the ions dissociate into the aqueous solution, however spectroscopic analysis confirms the carbamate formation. The formation of the precipitate was reversed by heating the carbamate solutions to ~70°C, providing enough energy to evolve the CO\(_2\) and return the solution to the original colorless or yellow hint. Shown in Figure 2.3, the AEAPMDS carbamate structures exhibited TGA weight losses of 17.4% from a temperature of 45°C. Samples were heated in aluminum trays at a rate of 5°C per minute and a nitrogen purge gas flow rate of 5mL/min. Based on the percentage of weight lost, it was calculated that 1 mole of CO\(_2\) reacted per mole of diamine, a trend which is also observed for AHAPTS (Figure 2.4), decylamine and dicyclohexylamine carbamate structures. AHAPTS began its 20% decrease in weight from a temperature of around 55°C while both decylamine and dicyclohexylamine started near 40°C, losing 17% and 7% respectively.
Figure 2.3: TGA spectra of pure AEAPMDS (solid) and isolated AEAPMDS carbamate salt (dashed)

Figure 2.4: TGA spectra of pure AHAPTS (solid) and isolated AHAPTS carbamate salt (dashed)
It is very important to note that upon exposure to air, the silanes will react with moisture and hydrolyze the alkoxy groups to silanols, which can then hydrogen bond to the free amines as well as themselves. Also, the amines themselves are affected by exposure to air as they react with ambient CO$_2$ to form their carbamate structures. Hence a complete cycle of CO$_2$ exposure and heat treatment is performed before obtaining TGA data allowing the formation of siloxane bonds between molecules and reducing the number OH groups available for interaction with the reactive amine groups.

The ATR-FTIR spectra of the carbamates showed a distinct loss of the 3375 cm$^{-1}$ peak, changing the region from a triplet, due to free primary and secondary amine stretching frequencies, to a singlet at 3275 cm$^{-1}$ as seen in Figures 2.5b. There is a slight shoulder at 3375 cm$^{-1}$ attributed to a small fraction of unreacted amines among the carbamates. In all of the carbamate spectra, a broad ammonium absorption band between 2100 cm$^{-1}$ to 3000 cm$^{-1}$ overlapping the C-H region was observed. According to Dreyfuss et. al., this change is consistent with the formation of the carbamate structure. Similarly, the observed IR absorption bands near 1630 cm$^{-1}$, 1570 cm$^{-1}$ and 1480 cm$^{-1}$ seen in Figure 2.5a are assigned to the NH$_3^+$ deformation, C=O stretch and RNHCOO$^-$ carbonyl of the carbamate salt, which is the primary evidence for the carbamate structure formation.$^{[30]}$ These absorption peaks are absent in the pure AEAPMDS spectra and the carbamate spectra that has undergone the reverse reaction. A transition from the singlet back to triplet and a re-emergence of the 3375 cm$^{-1}$ peak within the N-H stretching frequencies are observed after the heating induced reverse reaction. Similar FT-IR absorbance measurements were obtained with AHAPTS, PEI and ethylenediamine.
Figure 2.5: ATR FT-IR spectrum of AEAPMDS reaction cycle within a) Carbonyl Region (top) b) N-H stretching region (bottom)
Figure 2.6 displays a shoulder at 1635 cm\(^{-1}\) and peak at 1575 cm\(^{-1}\) identical to those obtained in Figure 2.5a for AEAPMDS once the pure AHAPTS has undergone the reaction. An important observation is the presence of these carbamate characteristic in the FT-IR spectra of ethylenediamine which was simply exposed to the atmosphere. Comparing Figures 2.5a, 2.6 and 2.7, we see that exposure to ambient air is enough to produce a change in FT-IR spectra similar to that of the CO\(_2\) reaction.

![Figure 2.6: ATR FT-IR spectrum of pure AHAPTS and isolated AHAPTS carbamate salt](image)

The investigation of carbamate formation and characterization serves as the proof of concept for reversible reactivity between CO\(_2\) and the silane coupling agents.
Results of SAM deposition

There are many techniques for depositing a SAM onto a Si substrate which are all sensitive to the experimental parameters used; water content, concentration, time of deposition and curing temperature. The method employed in this paper follows Figure 2.8, whereby the alkoxy silanes are hydrolyzed to silanols, which then condense onto a hydroxyl rich substrate and are cured to form the covalent siloxane bonds on the substrate surface.
There are various modes of attachment for which a diamine can adhere to the Si substrates.\cite{78, 79} As shown in Figure 2.9, they may hydrogen bond with a hydroxyl group on the surface as well as form an ionic bond through proton transfer. Due to the ability to hydrogen bond or ionic bond with a methoxysilane group, a silanol and other amino groups of neighboring coupling agent, AHAPTS and AEAPMDS easily form aggregates on the substrate surface and tend to form polysiloxane layers, rather than monolayers. These polysiloxane layers can reduce the amount of free amines, affect surface roughness, hinder surface reactions as well as create large defects. To reduce this effect, sonication in excess toluene followed by oven curing greatly increases the percentage of free amines and reduces the excess layers resulting in a more uniform SAMs.
The relative thicknesses of the surfaces were determined by variable angle ellipsometry using the refractive index of Si (3.875 – 0.023i), the respective refractive indices of the amines and by subtracting an oxide thickness of 1.8 nm from the measured value. The occurrence of polysiloxane layers explains the measured 2.8 nm AHAPTS SAM thickness when the length of a fully extended coupling agent, calculated using Material Studio is 1.42 nm (from the terminal nitrogen atom to the opposite Si atom). The AEAPMDS SAM had a thickness of 0.75 nm, which is comparable to the length of the molecule if it were within a homogeneous monolayer (Figure 2.1), but this thickness is also highly dependent on the time of deposition if all other parameters are kept constant.

Seen in Figure 2.10, the AEAPMDS thickness exhibits a maximum of 0.86nm at a deposition time of 1 hr, after which it steadily decreases with increasing time. This finding correlates very well with literature which reported that SAMs of aminopropyl trimethoxysilane underwent similar maxima as deposition time increased.\[76\]
Figure 2.10: Graph of AEAPMDS SAM thickness vs. time of deposition

The variance between AEAPMDS and AHAPTS thicknesses is likely due to the formation of multilayer’s as a result of the degree of silane functionalization. AHAPTS is a tri-functional silane with a greater number of attachment modes, not including the amines, and therefore assembles as a multilayer, while AEAPMDS is di-functional and deposits as dense homogeneous monolayers. Since AEAPMDS deposits as a dense monolayer, the coupling agent behaves differently in this ordered packed conformation as they interact with each other. This explains why the SAM thickness is less than the length of the actual coupling agent. Ellipsometric measurements along the Si substrate, coupled with static contact angle measurements indicated that the monolayers were relatively uniform and contained no large defects. The variability in SAM thickness was 15% of the average for AEAPMDS and 8% for AHAPTS, while the variability in the measured
contact angles was 4% and 3% respectively. AFM images of the monolayers also showed a root mean square (RMS) roughness of 0.19 nm providing further evidence of uniform SAM deposition (Figure 2.12a).

**Effect of Carbon Dioxide on SAMs**

![Diagram](image)

Figure 2.11: Scheme showing the deposition of the coupling agents onto Si substrate followed by the reversible reaction with CO₂ leading to the formation of the carbamate structures.

The SAM-CO₂ reaction is proposed to take place on the surface in the same fashion as the silane coupling agents in solution (Figure 2.11). Upon the reaction with CO₂, there is a 5% and 12% increase in the thickness of the AEAPMDS and AHAPTS monolayer respectively. This increase is attributed to the formation of charged ions within the structure which can have both attractive and repulsive effects on the system. Along with these electrostatic forces, the absorption of CO₂ onto the free primary amine
which terminates the SAM will add a COO⁻ carbonyl group onto the molecule increasing its overall length which explains the increasing thickness.

As a direct result of the formation of carbamate species, the static contact angle measurements exhibit an increase in hydrophilicity, an expected result since we are forming a charged surface that should have a greater affinity to water. The static contact angles for fresh AHAPTS and AEAPMDS SAM’s are both $64 \pm 2^\circ$ before the reaction (Table 1), corresponding well to literature values for similar amino-terminated surfaces.$^{[73, 74, 81]}$ The similarity in contact angle indicates comparable structure and chemical reactivity of these two silanes (Figure 2.1) and the values decreased by an average of $10^\circ$ after the reaction with CO$_2$

Table 2.1: Table of the AEAPMDS, AHAPTS and PEI-Sil monolayer thicknesses, static water contact angles and calculated solid surface tensions before and after CO$_2$ exposure

<table>
<thead>
<tr>
<th>Silane</th>
<th>SAM thickness (nm)</th>
<th>SAM contact angle (deg)</th>
<th>Surface Tension (mN/m)</th>
<th>COS (θ)</th>
<th>SAM + CO$_2$ thickness (nm)</th>
<th>SAM + CO$_2$ contact angle (deg)</th>
<th>Surface Tension + CO$_2$(mN/m)</th>
<th>COS (θ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AEAPMDS</td>
<td>0.76</td>
<td>64.7</td>
<td>41.5</td>
<td>0.43</td>
<td>0.8</td>
<td>55.3</td>
<td>47.7</td>
<td>0.57</td>
</tr>
<tr>
<td>AHAPTS</td>
<td>2.36</td>
<td>64.3</td>
<td>41.5</td>
<td>0.43</td>
<td>2.66</td>
<td>53.8</td>
<td>48.7</td>
<td>0.59</td>
</tr>
<tr>
<td>PEI-Sil</td>
<td>2.16</td>
<td>49.3</td>
<td>51.6</td>
<td>0.65</td>
<td>3.56</td>
<td>45.2</td>
<td>54.4</td>
<td>0.70</td>
</tr>
</tbody>
</table>

The static water contact angles for PEI-SAM were less hydrophobic than AHAPTS and AEAPMDS with a maximum of $50^\circ$ and exhibiting a small decrease of $4^\circ$ once reacted. This was not an expected result as the increased number of amine groups within the SAM should lead to larger physical changes in surface properties. However, an
explanation for this small change could be due to the reaction of the amines with ambient CO$_2$ before and during characterization, a phenomenon observed with the carbamate salt isolation. This small change could also be due to the lack of organization within the film.

The PEI-silane is a bulky precursor that can form films with a reduced number of amines perpendicular to the surface. These amines are thought to be inactive and do not react once exposed to CO$_2$.

\[
\cos \theta = -1 + 2 \frac{\sigma_s}{\sigma_l} e^{-B(\sigma_l - \sigma_s)^2}
\]  

(2.1)

The Young equation coupled with a thermodynamic equation of state yields equation 1, a simple relationship which allows the calculation of the surface tension of the solid ($\sigma_s$) from a single contact angle measurement. The model utilizes the average contact angles for each SAM, the surface tension of the liquid ($\sigma_l$) (water = 71.97 mN/m) along with a constant $\beta = 0.0001247$. According to equation 1, the SAM surface tensions were found to be 41.48 mN/m, 41.54 mN/m and 51.58 mN/m for AEAMPDS, AHAPTS and PEI respectively. After CO$_2$ exposure, the surface tension of the substrate increased by an average of 16% for AEAMPDS and AHAPTS along with a 5% increase for PEI (Table 2.1). This energy model does not take the type of interactions (polar or dispersive) which determine surface tensions into consideration and so, its simplicity affects the numerical values of the surface tension, but has little effect on the changes in surface tension upon carbamate formation. A more complex model, taking these polar, dispersive
and hydrogen bonding forces into consideration would yield more accurate surface tension values. Likewise the cosine of measured contact angles for other liquids of known surface tensions can yield a critical surface tension of the SAM based on the Young-Dupree equation. (Appendix D)

Once the carbamate structure has formed, the initial amine functionality and surface properties were regenerated by the same reverse reaction utilized with the isolated carbamate salts. Hence, the decrease in the contact angles and increase in SAM thickness for all coupling agents is reversed as the Si substrates are heated under reduced pressure and cooled with a stream of nitrogen.

![Graph showing average ellipsometry measurements of AEAPMDS SAM](image)

**Figure 2.12: Average ellipsometry measurements of AEAPMDS SAM demonstrating the reversible switch in surface property**

Figure 2.12 shows the complete ellipsometric cycle of the initial AEAPMDS SAM after CO₂ exposure and after heating under reduced pressure. The reported values represent the overall average thickness from the study while the error bars represent the
variability in thicknesses from all the substrates functionalized rather than an error in individual measurements. From this graph, we can see that the average SAM thickness has increased once reacted with CO$_2$ and decreases to a comparable value once reversed. One limitation of the self assembling technique is its difficulty to reproduce uniform SAM which leads to the large overlapping error bars due to the variability in initial SAM thicknesses before reaction with CO$_2$. The relative change in SAM thickness upon CO$_2$ exposure is consistent throughout the experiment.

![Graph showing average static water contact angle measurements](image)

Figure 2.13: Average static water contact angle measurements of the AEAPMDS and AHAPTS SAMs demonstrating the reversible switch surface property

Figure 2.13 also displays the average contact angle measurement for all the substrates developed within the study. It shows a reversible change in wettability, although initial SAM contact angles are not attained after the reverse reaction. This can be attributed to structural changes in the SAM orientation due to interactions between the adjacent amines once the CO$_2$ has evolved, altering the surface conformation and its
wettability. Alauzun et. al.\textsuperscript{7} found that the release of CO\textsubscript{2} from their ordered aminosilane structures resulted in very similar interlamellar distances between the amines. They attributed these phenomena to the promotion of hydrogen bonds after CO\textsubscript{2} removal since the amines are directly facing each other once decarboxylation occurs. We can apply similar conclusions to our results as the SAMs possess similar characteristics. Hence, surface properties after regeneration consists of a reduced number of free amines and therefore results in lower contact angles.

A major parameter in the dynamic control over the surface properties of the amino-terminated SAMs are the regeneration parameters utilized. That is the temperature, pressure and time of heat treatment for amine recovery. Heat treating at 100\textdegree\textsuperscript{\textordferv{0}} C for one hour may not be enough time and energy to reverse the surface reaction and obtain the initial surface properties. Despite Hyoshi et. al.\textsuperscript{[30]} regenerating amino functionalized SBA–15 at 100\textdegree\textsuperscript{\textordferv{0}} C for 1 hr, Bacsik et. al.\textsuperscript{[82]} utilized 6 – 12 hrs at 150\textdegree\textsuperscript{\textordferv{0}} C and vacuum pressure for the regeneration of modified mesocaged silica used for CO\textsubscript{2} uptake. Similar studies also employed higher temperatures and longer times than those utilized in this paper while still exhibiting slight loss in original product property.\textsuperscript{[62]} It can be concluded that the reverse reactions experimental parameters are subject to the system at hand and vary from one study to another.

Further analysis using AFM demonstrates a change in the physical structure of the SAM as the carbamates are formed. Fresh AEAPMDS-SAMs possess a root mean square (RMS) roughness of 0.19nm in the scan area shown in Figure 12a. There are no micro structural defects in the fresh AEAPMDS SAM which confirms the formation of
uniform, defect free monolayers. Although still very uniform, Figure 2.14b shows the AFM image of AEAPMDS SAM once reacted with CO$_2$. Its RMS roughness has increased to 0.27 nm, attributed to the formation of carbamate structures with charged interactions as well as the addition of carbamate NHCOO$^-$ functional groups. Both AFM images are on a 1µm scale with a vertical axis of 4nm.

![AFM images of AEAPMDS SAM](A) (B)

Figure 2.14: AFM images of AEAPMDS SAM a) before and b) after CO$_2$ exposure.

Despite the apparent advantages to this technique, SAMs are mechanically brittle due to their thin structure, only introducing organic functionality to the very surface of the substrate. Also, the relatively low initial contact angles of the fresh amino-terminated SAMs coupled with the difficulty in reproducing uniform defect free SAMs and their ability to react with ambient air led to a small change in surface wettability. However, this change can be controlled by the amount of CO$_2$ exposure and is a novel method for developing smart materials due to its reversible properties.
Conclusions

This study demonstrates the ability to react CO$_2$ with free primary and secondary amines, forming a carbamate structure that is thermally reversible at moderate temperatures. This switch from non ionic to ionic nature uses a simple, well studied switching mechanism applicable to neat, solution and surface bound amines. The formation of charged carbamate structures onto the surfaces of the Si substrates increased its wettability as well as altered the physical thickness and roughness of the SAM. These changes were reversible at moderate temperatures and reduced pressure, however the original SAM contact angle and thickness values were not observed due to incomplete reversal of the forward mechanism and structure retention. The limitation of this technique is its applicability to open systems as the ambient CO$_2$ will react with fresh substrates. This is also a major finding which could explain phenomena in other studies utilizing amino-terminated surfaces in open systems that do not account for carbamate formation. In conclusion, the reaction can be controlled by varying the amount of CO$_2$ exposure and has the potential of developing into a fully dynamic system for control over surface properties and wettability.
CHAPTER THREE
EMPLOYING CARBON DIOXIDE AS A PROTECTION/DE-PROTECTION MECHANISM FOR AMINES

Introduction

Protecting groups provide a vital role within the field of organic synthesis, enabling the coupling of various organo-functional groups in the presence of competing reactive functional groups. This protection also needs to be stable under a broad range of reaction conditions and both moderately and selectively cleavable. Thus, choosing the right type of protective group is of primary significance, especially in the presence of amino containing compounds that tend to be very reactive, basic in nature and form strong hydrogen bonds. In addition to sulfonamides and amides, carbamates are the most popular and widely used protective mechanism utilized for amino groups. Such protecting groups includes the carboxybenzoyl group (CBZ), di-tertiary butoxy carbonyl group (Di-t-BOC) and the 2-(trimethylsilyl)ethylsulfonyl) group (SES), each having their own set of advantages and disadvantages. The CBZ group protects primary and secondary amines via. the formation of benzyl carbamates, while deprotection is achieved by cleaving the CBZ group by acidolysis, catalytic hydrogenation, or reduction with dissolved metals. The t-BOC and Di-t-BOC protecting groups are utilized quite frequently in literature due to the stability during catalyzed nucleophilic substitutions, as well as, catalytic hydrogenation reactions. However deprotection requires strong acids and long reaction times. Despite the popularity of many amine protection mechanisms,
the use of milder reagents and reaction conditions is an area for significant improvement and many alternative methods have been studied.\[87, 88\]

Despite the recent advancements in protection/deprotection mechanisms for amines, traditional methods are typically energy intensive, costly and/or use corrosive chemicals. In the case of the t-butyl carbamates, deprotection by acidolysis has shown to generate t-butyl cations leading to the need for scavengers to prevent undesirable side reactions\[89\]. Hence, this work focuses on the development of a simpler, greener approach at amine protection/deprotection. Our approach incorporates a single reversible reaction that utilizes a relatively safe and cheap protecting group, carbon dioxide. The reaction of carbon dioxide (CO\(_2\)) with primary or secondary amines forms robust alkylammonium carbamate species; shown in Figure 2.1. The reaction is also reversible where the original amine can be obtained by applying heat, exposing to a reduced pressure and/or by saturating the system with nitrogen. These carbamate structures serve as a potential switch in both the physical and chemical properties of the amine as discussed in the prior chapters.

This reaction has been extensively studied in literature with a variety of applications in different fields.\[43, 44, 46, 47, 53, 90\] More specifically, the protective capabilities of carbon dioxide is demonstrated in the development of ordered laminar materials comprised of amino-terminated silanes.\[48\] In this study CO\(_2\) induced carbamates act as bridging groups during the poly-condensation of the silanols, and the formation of interparticle bonds inhibits the amines interaction with the silanols through hydrogen bonding. After a thermal treatment of the product, the original amine
functionality was regenerated. The formation of these laminar siloxane backbones of the hybrid material could not be possible if the amine functionality were present and not the carbamates. A similar technique was applied by Eckert et. al.\textsuperscript{[28]} where carbon dioxide expanded liquids at 30 bar were used to increase the yield of primary amine synthesis from the hydrogenation reactions of benzonitrile and phenylacetonitrile with NiCl$_2$/NaBH$_4$ in ethanol. In this study, the CO$_2$ was introduced as a means of preventing side reactions by carbamate formation, which precipitated out of solution, simplifying the purification. In this system, the amine is the product and does not require the protected carbamate to react in any further coupling reactions.

![Figure 3.1: Reaction scheme displaying imine and urea products along with alkylammonium carbamate for amine protection](image)

This chapter further explores the use of the reversible CO$_2$ chemistry as a unique method of protecting amines during simple coupling reactions (Figure 3.1). All reactions were carried out with the non-protected amine, the carbamate analogs that were formed
via reaction with CO₂, and then with the de-protected amine regenerated through a thermal treatment of the carbamates. The reaction products were characterized via gas chromatography (GC), ¹H NMR, ATR-FTIR and TGA/DSC.

**General Procedures**

*General amine protection*

Required quantity of amine was added to the reaction vessel before the addition of any other component. CO₂ was then introduced into the closed vessel via a carbon dioxide gas cylinder equipped with a low pressure regulator for approximately 5 minutes resulting in the exothermic formation of solid white powders. The reaction solvent was then added with additional CO₂ being bubbled through the solution for a further 3 minutes. The original volume of the solution was made up with pure solvent after the CO₂ bubbling in order to preserve concentrations. The reactions with protected amines were carried out under a CO₂ atmosphere.

*General amine deprotection*

Carbamate solutions of the alkylamines were de-protected using a heat gun set at a temperature of 110°C. An ice cooled condenser was equipped to the top of the reaction vessel while a steady stream of nitrogen was introduced to aid in the reversal. This was carried out for 10 minutes after which fresh solvent was added to maintain the reaction concentration after nitrogen saturation. The procedure ensured that all carbamates were
converted back to the original amines. The de-protected amines were then employed in the urea/imine synthesis to ensure complete deprotection and no loss of reactivity.

*General Characterization*

An aliquot of the reaction mixture (1.5 ml) was taken from each reaction vessel and injected into an Agilent 7695A GC using the Agilent 7683B automatic liquid sampler. The inlet temperature was set at 300°C with a pressure of 16 psi, the oven at 80°C with a heating rate of 20°C/min to 250°C. The FID was set at 300°C. A calibration curve for benzophenone (BP) was created by plotting the integral of the BP peak versus known concentrations of BP ($R_t = 14.5$ min).

Melting points were determined from DSC spectra obtained using a Thermal Analysis SDT Q600 equipped with alumina pans. A steady heating rate of 5°C/min was maintained to 350°C with a nitrogen purge of 100 ml/min.

IR spectra were collected on a Nexus 870 spectrometer with a 4 cm$^{-1}$ resolution using 64 scans. A fixed angle single reflection 60° hemispherical Ge crystal plate, equipped with an ATR pressure clamp, was placed in a sample compartment. The output signal was collected using a deuterated triglycine sulfate (DTGS) room temperature detector. $^1$H NMR spectra were obtained on a Bruker 300MHz in CDCl$_3$. 
Synthesis of n-alkyl, n-phenyl urea

Figure 3.2: Reaction scheme for n-phenyl, n-alkylurea synthesis using: A) non-protected amines, B) carbamates induced from CO$_2$ and C) deprotected amines obtained from the thermal treatment of carbamates

50 ul (0.0545 g, 0.46 mmol) of phenyl isocyanate was added dropwise to a solution of alkyamine (0.92 mmol) in 2 ml of dry CHCl$_3$ at 0°C. The resulting solution was stirred for 60 min at room temperature and then precipitated into 25 mL of pentane. The product was isolated as a white powder via filtration and washed with several portions of pentane before being dried under vacuum at 50°C. The products isolated from the alkylcarbamates were alternatively re-dispersed in dry CHCl$_3$ and underwent thermal treatment to remove any residual carbamates. The ureas were then re-crystallized in pentane again and isolated via filtration.
Results and Discussion for the synthesis of n-alkyl, n-phenyl urea

$^1$H NMR and FTIR results

The coupling of amines with isocyanates to form ureas is well studied and characterized.$^{[91, 92]}$ Isolated ureas, characterized via FTIR, demonstrated high purity through the absence of carbamate or other reaction byproducts for all three synthetic starting materials (non-protected, protected and de-protected). Figure 3.3 displays the FTIR spectra of the n-propyl urea and n-decyl ureas obtained from the non-protected, protected and de-protected propyl and decylamine (DA) respectively. In each spectra, the characteristic carbonyl (C=O) and secondary amine (N-H) absorbance associated with urea formation are consistent within all isolated products. The results obtained also correlates very well to the molecular structure of the individual amines as C-H (2800 – 3000cm$^{-1}$) absorption levels for the decylurea are significantly higher compared to the propylurea due to the elevated CH$_2$ functionality in the longer alkyl chain backbone. The three states of amine (non-protected, protected and de-protected) all produced an isolated urea product displaying similar absorbance bands. This indicates that these products obtained were spectrally identical and not side products due to residual carbamate presence.
Figure 3.3. ATR-FTIR of n-phenyl, n-alkylureas showing the similar absorption spectra and characteristic carbonyl and secondary amine peak.
The purity of the isolated ureas was further determined by $^1$H NMR, displaying chemical shifts characteristic to our desired products. Also, the products isolated using non-protected, protected and de-protected amines all displayed similar chemical shifts as shown in Figure 3.4,

Figure 3.4: $^1$H NMR of n-phenyl, n-propylurea. $\delta = 1.0$ (t, 3H), 1.6 (m, 2H), 3.3 (t, 2H), 4.9 (s, 1H), 6.4 (s, 1H), 7.1 -7.5 (5H).
The $^1$H NMR spectra of the isolated decylurea show similar chemical shifts to the spectra obtained for the propylurea. The main difference is the chemical shift at 1.3 ppm attributed to the alkyl backbone of the decylamine while integration of the peaks further proves its structure and purity. The $^1$H NMR of the hexyl and octadecyl ureas obtained from non-protected, protected and de-protected amines also showed similar chemical shifts, affirming the purity of all of our isolated products.

Figure 3.5: $^1$H NMR of n-phenyl, n-decylurea.
**DSC results**

The urea product melting temperatures ($T_m$) were determined by DSC (Table 3.1). All the measured values correlated well with literature values and had a small melting temperature range which is indicative of high purity.\[93\] The n-propyl urea has the highest melting point and crystallization temperature despite possessing the shortest carbon chain, and highest volatility. TGA analysis done on the propyl and hexyl carbamates showed an increase in onset temperature of degradation due to the stronger charged carbamate interactions present. Similarly, the ureas not only contain hydrogen bonding donors ($\text{NH}_2$), but the C=O hydrogen bonding acceptor as well. The smaller alkyl chains contribute less steric hindrance and thus, a higher degree of hydrogen bonding can occur. As we increase the chain length, the alkyl backbone should disrupt the urea-urea hydrogen bonds and thus reduce the melting point as seen with n-hexyl urea (68 – 69°C). However, as we increase the alkyl chain, the $T_m$ increases from 82°C for decylamine to 95°C for stearyl amine due to increase in energy demand for the onset of melting as the molecular weight of the urea increases.

Table 3.1: n-phenyl, n-alkylurea melting points and crystallization temperatures determine from DSC

<table>
<thead>
<tr>
<th>Entry</th>
<th>MP (deg. C)</th>
<th>Recrystallization Temp (deg. C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-phenyl, n-propyl urea</td>
<td>112 - 114</td>
<td>89</td>
</tr>
<tr>
<td>n-phenyl, n-hexyl urea</td>
<td>68 - 70</td>
<td>47</td>
</tr>
<tr>
<td>n-phenyl, n-decyl urea</td>
<td>81 - 83</td>
<td>61</td>
</tr>
<tr>
<td>n-phenyl, n-stearyl urea</td>
<td>95 - 97</td>
<td>84</td>
</tr>
</tbody>
</table>
Figure 3.6 displays a typical DSC curve used to determine $T_m$ for each urea isolated. From the image, we can further conclude urea purity consistency throughout each amine state. As seen in the FTIR data above, the protected and deprotected samples all provide isolated products which are chemically identical. Furthermore, all the ureas, exhibit a similar melting/crystallization DSC curve as seen in Figure 3.7 which can be used to calculate the percent of crystalline regions in our sample.

Figure 3.6: DSC spectra of n-propyl urea isolated from all three amine starting materials. Ramp rate = 5°C per minute to 140°C followed by equilibration to 60°C and repeated heating.
Figure 3.7: DSC spectra of n-propyl urea at ramp rate 5°C per minute to 140°C followed by equilibration to 60°C and repeated heating.

Effect of carbon dioxide protection on Synthesis

The urea synthesis in chloroform showed 95% yield for propylamine, while the other amines achieved comparable yields of 85% for hexylamine, 91% for decylamine, and 90% for octadecylamine (Table 3.2). Once protected in the carbamate form, the reactivity was significantly reduced for the shorter chained amines with an average decrease calculated to be 62%. After the heat treatment, it is evident that deprotection of the propyl, hexyl and decyl amine was successful by the increase in urea yield to values comparable to the unprotected amine. Incomplete deprotection could be a major factor in the lower product yields, but a loss of amine could also be the root cause due to the
volatility of the propyl and hexylamine. Decylamine, with its low volatility and ease of carbamate reversal saw a de-protected urea yield comparable to that of the pure amine. The octadecyl carbamate showed minimal reduction in yield, especially compared to the de-protected reactivity. This was not an expected result as a protection /deprotection cycle had been achieved separately for the octadecyl amine, whereby octadecyl-carbamate formation resulted in a dense white precipitate while deprotection regenerated the soluble amine analog. The CO$_2$ reacts with one primary amine to form carbamic acid, which then further reacts with free amine to form the carbamate structure.

Due to the long alkyl chains, it is possible that the formation of the carbamate was inhibited and resulted in insufficient protection. The mole ratio of isocyanate to amine also attributes to this observation as an excess amount of octadecyl amine will contain non-protected amines among the carbamates.

\textit{Table 3.2. Percentage yields of the N-phenyl-N-alkyl ureas of for pure, protected and de-protected amine}

<table>
<thead>
<tr>
<th>Amine</th>
<th>n</th>
<th>Non-protected</th>
<th>Protected</th>
<th>De-protected</th>
</tr>
</thead>
<tbody>
<tr>
<td>propylamine</td>
<td>1</td>
<td>95</td>
<td>28</td>
<td>85</td>
</tr>
<tr>
<td>hexylamine</td>
<td>4</td>
<td>85</td>
<td>20</td>
<td>80</td>
</tr>
<tr>
<td>decylamine</td>
<td>8</td>
<td>91</td>
<td>38</td>
<td>93</td>
</tr>
<tr>
<td>octadecylamine</td>
<td>16</td>
<td>90</td>
<td>69</td>
<td>72</td>
</tr>
</tbody>
</table>
Synthesis of n-propyl, benzophenone(BP) imine

![Reaction scheme for benzophenone-imine synthesis in Methanol using A) non-protected amines, B) carbamates induced from CO\textsubscript{2} and C) deprotected amines obtained from the thermal treatment of carbamates](image)

Propylamine (5 mmol) was added to 5 ml of dry methanol, followed by benzophenone (BP) (2.5 mmol) and titanium(IV)-isopropoxide (3.3 mmol). The solution was stirred under nitrogen at room temperature while aliquots were taken at 3, 6 and 24 hrs for GC analysis and ATR-FTIR monitoring. Alternatively, the reaction was separated into 4 GC vials and sampled in-situ without stirring. Each GC vial represented a reaction vessel that was used to monitor the reaction kinetics.
Results and discussion for the synthesis of n-propyl, benzophenone (BP) imine

Effect of carbon dioxide on Imine Yield from GC

Ti(IV) isopropoxide is a low cost mediator in the synthesis of the BP imines.\textsuperscript{[94-98]}

According to the Figure below, we can see that the initial BP concentration of 0.45 M is slowly reduced to 0.26 M after 3h and finally 0.11M after 24h as the regular reaction proceeds forward. Gas chromatography determined an overall yield of 75% for the pure amine while only a 25% yield is obtained for the protected and 50% for de-protected propylamine. Once again we see a similar trend of de-protected amines not obtaining the original product yield attributed to the incomplete reversal of carbamates and loss of propylamine from the deprotection process.

![Figure 3.9: Plot of BP concentration determined via GC for the non-protected, protected and de-protected propylamine reactions at 3, 6 and 24hrs.](image-url)
Although FTIR is not commonly used as a powerful quantitative tool, it was used to confirm the presence of our imine species, as well as, calculate the BP conversion. Figure 3.10 shows the strongly absorbing C=N shift to 1620 cm\(^{-1}\) from the C=O at 1660 cm\(^{-1}\) of the original BP\[^{[99]}\]. This shift in the absorbance proves that the desired imine species was obtained during the BP–propylamine reactions which was further evidenced via H\(^1\)NMR and GC-MS.
Figure 3.11: ATR-FTIR spectra of non-protected BP reactions at 3hrs (A) and at 12 hrs (B). ATR-FTIR of protected BP reaction at 3hrs(C) and at 12hrs (D)
The qualitative analysis was conducted over a period of 12 hrs, during which time ATR-FTIR spectra of aliquots of the reaction vessels were collected and analyzed to confirm the appearance of the imine product. As the reaction proceeds forward, the concentration of imine in the reaction solution will increase until equilibrium has been reached. From Figure 3.11 we can clearly see that the ratio of C=O to C=N absorbance decreases as reaction time increases, thus indicating more imine product as evidenced by the growth of the 1620 cm$^{-1}$ peak. The maximum of absorbance of a particular peak is directly proportional to the amount of product in the sample, where higher concentrations lead to more absorption at that specific wavelength. Hence, using the ratio of C=O to C=N absorbances, the percentage of imine in the reaction was determined (Table 3.3). These values correlate very well to the percentage conversion obtained via GC and support our initial hypothesis that CO2 is a viable tool for the protection and inhibition of free primary amines to undergo coupling reactions.

Table 3.3: Determined BP conversion from GC analysis compared to BP conversion calculated from IR spectral C=N:C=O absorbance ratio.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Calculated IR Conversion %</th>
<th>Conversion % from GC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non-protected 3hrs</td>
<td>35</td>
<td>33</td>
</tr>
<tr>
<td>Non-protected 12 hrs</td>
<td>55</td>
<td>65</td>
</tr>
<tr>
<td>Protected 3 hrs</td>
<td>16</td>
<td>18</td>
</tr>
<tr>
<td>Protected 12 hrs</td>
<td>26</td>
<td>20*</td>
</tr>
</tbody>
</table>
**BP imine synthesis in the absence of Mechanical stirring**

This imine formation can also take place without the presence of mechanical stirring (Figure 3.12). These reaction mixtures were separated into 4 GC vial and monitored in-situ at varying times. Here, we see that the percentage conversion correlates very well despite running the reaction in separate vials; each color denotes a separate reaction vial sampled at varying times after initiation. The maximum conversions obtained are identical to those obtained above in Figure .12. The non-protected reaction reaches 75% conversion after 15 hrs, and remains at that conversion, while protected propylamine only yields 25% conversion even after 36 hrs. The de-protected sample obtains a conversion of 50% after 5 hrs yet never attains higher conversions even at 24 hrs, a phenomena that has been consistent throughout this work. This loss in amine conversion post deprotection can be the result of many factors. Despite careful attention during the thermal de-protection procedure, loss of starting propylamine is the major contributor for this reduced yield. Confirmed by FTIR a distinct reduction in CH₂ and CH₃ absorption provides evidence to support the loss of starting amine concentration. An alternative explanation for the reduction in imine and urea yield using the de-protected amines is the formation of isocyanate side products during the thermal treatment.¹⁰⁰
Figure 3.12. BP conversion % of Non-protected (left), Protected (middle) and De-protected (right) reactions monitored in-situ from 4 reaction vials.
In the presence of methanol, CO$_2$ will preferentially react with the alcohol to form an alkylcarbonic acid that then reacts with the amine to form methyl carbamates, as opposed to the alkylammonium carbamates obtained under aprotic conditions.$^{[101]}$ The resulting carbonic structure has a larger energy requirement to cleave the methyl group and release the carbon dioxide. It is hypothesized that the reduced BP conversion for the de-protected reactions is due to the increased difficulty to reverse the protection as the protic methanol solvent interacts with the carbamate. However, a clear reduction in reactivity is achieved through the use of carbon dioxide induced carbamate formation despite side reactions which hindered the reversibility.

Lastly, the reaction of CO$_2$ with propylamine takes place instantaneously and is thermodynamically favorable. Therefore the 25 % conversion of starting material measured by GC does not represent a complete protection of the propyl amine as BP is converted to imine. According to Salmi et. al.$^{[97]}$, the reductive amination of BP proceeds through an imine species while the presence of a titanium complex intermediate was not observed via NMR. Hence the complexation of BP with the Ti is not a cause for the reduction in starting material concentration. It was also determined from solutions of the Ti catalyst and BP in the absence of amine that the loss in BP concentration was not due to this complexing of BP to Ti. Therefore we conclude that the conversion of starting material under protected conditions is primarily due to incomplete protection of the propylamine which is already in a stochiometric excess.
Conclusions

In conclusion, we have shown that the reaction of CO\textsubscript{2} with alkyl amines forming reversible carbamate species was enough to reduce the amine reactivity, resulting in a significant decrease in product yield. This was applied to the synthesis of n-phenyl ureas and n-propyl benzophenone imine with reversal of the protection using moderate heating. Despite the novelty, the temperature dependence of the reverse reaction does introduce limitations. The ability to efficiently protect and de-protect the amine and the solubility of the carbamates in the reaction solvent are also potential limitations. This technique will be applied to high pressure systems in an attempt to create a more environmentally safe protection method. The energy input to maintain higher pressures may increase, but it can be offset by the reduction in solvents for conducting the three separate steps in traditional protection methods. However, despite these draw backs, reversible carbamate formation via carbon dioxide alone shows great potential as a simple, green protecting mechanism alternative for amine protection in simple low temperature coupling reactions.
CHAPTER FOUR
DIRECT SYNTHESIS OF CATIONIC GOLD NANOPARTICLES USING
POLYETHYLENEIMINE (PEI) AND CARBON DIOXIDE

Introduction

As a noble metal, gold has superior electron conduction and stability compared to many nanomaterials. Gold can bind to sulfur atoms allowing for organic-metallic complexes, making the application of gold nanoparticles (GNPs) more attractive within both fundamental and applied sciences. [102, 103] During GNP synthesis, the use of various surfactants, sugars or polymers can directly control particle size, shape and surface functionality, which has led to a specialized area of research focused solely on tailoring and understanding the surface chemistry of gold and other nanomaterials. [104-107] Recently, a class of polymers known as polyelectrolytes which provide both steric and electrostatic stabilization, have been used to synthesize nanoparticles in solution. [108]

Among these polyelectrolytes are cationic polymers such as polyethyleneimine (PEI), a highly branched polymer with a high pH-buffering capacity and the ability to stabilize GNPs. One of the more common applications of PEI capped nanoparticles is within the field of biomedical materials and applications. [109-112] More specifically, it has been used in the development of new DNA/gene transfection and delivery agents which exploits the polymers cationic attraction to the negatively charged phosphate backbone of the DNA. [113] However; since exposure to high levels of PEI can severely affect the viability of the cells, there is an advantage for the use of lower molecular weight PEI for
In vivo studies. In literature, there are a limited number of studies which use low $M_w$ PEI since the most stable PEI-coated metal nanoparticles are synthesized at higher $M_w$.

Lee et. al. synthesized cationic silver nanoparticles from $M_w \sim 25,000$ PEI in the presence of sodium borohydride. In this work, it was determined that the stability of the particles was dependent on the concentration of the polymer in solution where particle size and clustering increased as PEI concentration decreased. Schiffman et. al. synthesized $M_w \sim 2000$ PEI capped SNPs using a NaBH$_4$ reduction method as a biocidal coating for modified poly-sulfone mats. Sun et. al. demonstrated the reduction of the metal precursor in the absence of external reducing agents, where the branched PEI acts as both reducing and capping agent. In Sun’s work, stabilized GNPs were synthesized in a single step while the initial molar ratio of polyelectrolyte to HAuCl$_4$ was varied. They determined that the nucleation kinetics and growth of the resulting particles can be influenced by this molar ratio and in turn, determines particle size and stability. Also, the rate at which the PEI reduces the HAuCl$_4$ precursor is influenced by temperature, leading to a thermally reduced GNP whose properties are subject to heating rates as well as molar ratios. 

To alleviate this need for high molecular weight polymers for the stabilization of the GNPs and enable the use of low $M_w$ PEI, the reversible carbamate chemistry between carbon dioxide and amines was exploited to promote the particle stability. This involves a single reversible reaction that uses a safe and inexpensive additive, carbon dioxide (CO$_2$)
which, upon exposure with an amine, results in carbamate structures that provides a reversible switch in both the physical and chemical properties of the PEI.

This chapter explores the use of low molecular weight PEI in the synthesis of cationic GNPs and examines the role of pH and carbon dioxide on the resulting particle core size and stability from three different methods of Au ion reduction.

**Experimental Procedures**

**Materials**

Hydrogen tetrachloroaurate (III) trihydrate (HAuCl$_4$·3H$_2$O, 99.99%), branched polyelectrolyte polyethyleneimine (PEI) of molecular weight ~600 and reducing agent sodium borohydride (NaBH$_4$, 98%) were purchased from VWR and used as is.

**Synthesis**

The Au nanoparticles were first synthesized by the reduction of Au$^{3+}$ ions in an aqueous solution of PEI using sodium borohydride (NaBH$_4$) as a reducing agent. Briefly, 100 µL aliquot of a 0.05 M aqueous HAuCl$_4$·3H$_2$O solution along with 50 - 200µL of a 2wt% PEI (0.005 - 0.02wt% solution) was added to 20 mL of deionized water (DI-H$_2$O) in a clean scintillation vial. Subsequently, 100uL of a freshly prepared 0.05M NaBH$_4$ solution was added to the vial and stirred for15 minutes to allow for complete reduction and formation of GNPs. This quickly changes the color of the solution, visually indicating the initial formation of Au nanoparticles.
**Thermal Reduction**

For GNP synthesis by thermal reduction, 100uL of 0.05M HAuCl₄ was dissolved in 20ml of a 0.005-0.020wt% PEI aqueous solution. The solution was then brought to boil on a hot plate and the reduction process was observed by the solution color evolution from yellow to orange to red. The nanoparticle solution continued to boil for a period not exceeding 15 minutes.

**Room temperature reduction**

The same solution (0.25mM HAuCl₄, 0.005 - 0.02wt% PEI) previously mentioned was added to a clean scintillation vial and allowed to sit at room temperature and pressure without the addition of NaBH₄ or other external reducing agents. The formation of nanoparticles was evidenced by the gradual evolution of color from the solutions over time and the particles were further characterization as formed.

The effect of pH and CO₂-PEI on the synthesis of GNPs was examined by replacing the DI-H₂O with 1mM HCl solutions and by bubbling carbon dioxide through aqueous PEI solutions for 2 minutes to promote a carbamate formation.

**Characterization**

UV-vis absorption spectra of the particle dispersions were measured using a Varian Cary 50 UV-Vis-NIR spectrophotometer. Transmission electron microscopy (TEM) imaging was performed on a Hitachi 7600 with a 120 kV accelerating voltage. A glass nebulizer was used to aerosolize liquid suspensions of the nanoparticle dispersion.
onto 300 mesh Formvar carbon coated copper TEM grids (Ted Pella). The nanoparticle size distributions were obtained by image analysis with the ImageJ software counting at least 200 particles. Zeta-potential measurements were performed on a Malvern Zetasizer Nano-ZS (ZEN3600) at 25 ºC with an incident wavelength of 633 nm and a 173º backscattering angle. 1cm path length disposable zeta potential cells were rinsed with deionized water and loaded into machine. The viscosity, refractive index, and absorption values were provided in the Malvern software for water (\(\mu = 0.8872\) cP, RI = 1.333) and crystalline silver (RI = 0.135, absorption = 3.987). Dynamic Light Scattering (DLS) was performed on the Malvern Zetasizer Nano-ZS (ZEN3600) at 25 ºC with an incident wavelength of 633 nm and a 173º backscattering angle with 1cm path length disposable cuvette.

**Results and Discussion**

The formation of gold nanoparticles was confirmed by the physical change in the reaction mixture from a clear solution to a colored colloidal suspension. The color of the subsequent PEI-GNPs was dependent on the concentration and reduction method utilized. Figure 4.1 displays 11.7 nm diameter PEI-GNPs with the size determined by TEM, which possess a characteristic surface plasmon resonance bands observed using UV-vis spectroscopy. This characteristic absorbance observed at 524 nm suggests that the PEI is an effective ligand for the synthesis and stabilization of colloidal gold. An absorption band at 360nm is also observed in the UV-vis spectrum which attributed to the PEI itself. TEM images of the PEI-GNPs displayed a spherical shape and a monomodal distribution.
with relatively small standard deviations. On average, the zeta potential of the GNPs all displayed positive ranges which are consistent with a positively charged cationic ligand shell using a low molecular weight PEI. These PEI-GNPs synthesized had a positive zeta potential of approximately +28 mV. Hence, under aqueous conditions, the positively charged PEI molecules are stable due to the inherent electrostatic repulsion of the branched amino polymer.

Figure 4.1: TEM image of PEI-GNPs along with the corresponding particle size distribution histogram and UV-vis absorption spectrum. Particles were synthesized via thermal reduction with a boiling time of 1 minute. The sizes of the particles were determined using Image J software.

Effect of Reduction Method

The reduction of the gold ions to metallic gold is the driving force behind nanoparticle nucleation and growth. It has been suggested that the formation of the PEI-GNPs in the absence of NaBH$_4$ is a product of the direct redox reaction between the PEI branches and the HAuCl$_4$.$^{[121]}$ Coordination between the amino groups with the metal
ions results in the PEI acting as both a reductant and stabilizer, thus allowing the formation of the PEI-GNPs at room temperature in the absence of NaBH₄.

Figure 4.2: GNP mean core size for each reduction method using 0.01wt %PEI with varying solvent conditions. The error bars represent the standard deviation of the particle size distribution for each sample population. Thermal boiling time = 1 min

Figure 4.2 summarizes the nanoparticle core diameters obtained from TEM analysis of all three reduction methods and three solvent conditions. There are significant differences in the average particle core size among the three reduction methods, with values ranging from 4.9 ± 1.3 nm, 11.7 ± 3.6 nm and 17.7 ± 6.7 nm for the NaBH₄, thermal and room temperature methods for DI water respectively. A similar trend is observed in the UV-vis absorption maxima for the three methods, with average Plasmon resonance bands at 510 nm, 520 nm and 527 nm respectively. This UV-vis absorption is
directly related to the size of the nanoparticles as well as the degree of clustering; which results in the red shifting of the wavelength of maximum absorbance ($\lambda_{\text{max}}$) with increasing particle size and broadening with increasing polydispersity.\[^{122}\] (Appendix B)

Figure 4.3: TEM images of PEI capped GNPs synthesized using NaBH$_4$, thermal and room temperature reductions. Average core size and zeta potential determined.

The observed trends are directly related to the reductive power each technique has to quickly create nucleation of the Au atoms. The fastest method of reduction incorporates an external reducing agent, NaBH$_4$, which results in the smallest particles with the smallest size distribution, followed by the thermal reduction, and finally the room temperature reduction; hence the comparative core sizes and UV-vis absorption correlate very well to each other as decreasing power of reduction leads to increase in overall particle size.
**Effect of Concentration and pH**

The electrostatic charge of the amino groups serves as one of the primary driving forces for particle stability during synthesis and reduction of the gold salt. As the wt % of PEI increases, the greater number of PEI molecules can lead to a decrease the particle size as they are more readily available to cap the metallic core and stop particle growth. At the same time PEI can act as a reductant as well, which accelerates the nucleation and growth of the GNPs, producing larger particle cores and higher polydispersity when the wt% of PEI is increased under neutral conditions \[116\]

According to Table 4.1, the wt % PEI in solution increased the resulting GNP core size during the NaBH$_4$ reduction under neutral conditions from 4.6 ± 1.6 nm to 6.9 ± 2.9 nm. This agrees with the findings of Lee et. al. \[116\] who attributed the dominant role of PEI as a reductant as the cause for the increased polydispersity and particle size. The $R_h$ values are also more than doubled when PEI increases from 0.005 wt% to 0.02 wt %, leading us to conclude the formation of clusters. However, under acidic conditions (1mM HCl) there is a decrease in size distribution from 5.5 ± 2.5 nm to 4.9 ± 1.5 nm as PEI concentration in increases. (Figure 4.4)
### Table 4.1: Table showing GNP core size obtained from TEM, Zeta Potential and Hydrodynamic radius ($R_h$) from DLS.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Reductive Method</th>
<th>Thermal</th>
<th>RT</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Core size (nm)</td>
<td>$R_h$ (nm)</td>
<td>Zeta Potential (+mV)</td>
<td>Core size (nm)</td>
<td>$R_h$ (nm)</td>
<td>Zeta Potential (+mV)</td>
<td>Core size (nm)</td>
<td>$R_h$ (nm)</td>
<td>Zeta Potential (+mV)</td>
</tr>
<tr>
<td>Water</td>
<td>0.005</td>
<td>4.6±1.6</td>
<td>7.4</td>
<td>-</td>
<td>0.005</td>
<td>15min</td>
<td>111±3.9</td>
<td>8.0</td>
<td>20.9</td>
<td>0.010</td>
</tr>
<tr>
<td></td>
<td>0.010</td>
<td>4.9±1.3</td>
<td>11.0</td>
<td>-</td>
<td>0.010</td>
<td>15min</td>
<td>148±3.8</td>
<td>28.0</td>
<td>28.3±11.5</td>
<td>0.010</td>
</tr>
<tr>
<td></td>
<td>0.020</td>
<td>6.9±2.9</td>
<td>16.0</td>
<td>-</td>
<td>0.020</td>
<td>15min</td>
<td>113±4.0</td>
<td>55.0</td>
<td>25.0</td>
<td>0.005</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.010</td>
<td>5min</td>
<td>135±3.8</td>
<td>-</td>
<td>-</td>
<td>0.020</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.010</td>
<td>1min</td>
<td>117±3.4</td>
<td>16.7±107</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1mM HCl</td>
<td>0.005</td>
<td>5.5±2.5</td>
<td>-</td>
<td>-</td>
<td>0.005</td>
<td>15min</td>
<td>157±5.5</td>
<td>-</td>
<td>34.7</td>
<td>0.010</td>
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<tr>
<td></td>
<td>0.010</td>
<td>5.5±1.9</td>
<td>-</td>
<td>29.1</td>
<td>0.010</td>
<td>15min</td>
<td>124±4.6</td>
<td>-</td>
<td>23.6</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>0.020</td>
<td>4.9±1.5</td>
<td>-</td>
<td>-</td>
<td>0.020</td>
<td>15min</td>
<td>123±4.2</td>
<td>-</td>
<td>21.2</td>
<td>-</td>
</tr>
<tr>
<td>CO2/H2O</td>
<td>0.010</td>
<td>3.7±1.0</td>
<td>-</td>
<td>23.6</td>
<td>0.010</td>
<td>15min</td>
<td>160±5.0</td>
<td>-</td>
<td>33.4±4.7</td>
<td>0.010</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.010</td>
<td>5min</td>
<td>124±5.5</td>
<td>-</td>
<td>-</td>
<td>0.020</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.010</td>
<td>1min</td>
<td>124±5.0</td>
<td>-</td>
<td>19.5±108</td>
<td>-</td>
</tr>
</tbody>
</table>
It can be hypothesized that as the concentration of the PEI increases, the NaBH$_4$ does not fully disperse within the solution as quickly as it would at lower PEI concentrations due to the highly branched structure of the polymer, thus resulting in the larger particle cores. Furthermore, the Au precursor becomes more associated and intertwined within the chains of the branched PEI and may not be accessible when the NaBH$_4$ is introduced. Sun et. al$^{[118]}$ also mentions the formation of a polysalt between the nitrogen of a protonated amino dendrimer and the AuCl$_4$. Hence, this can result in reduced nucleation of the Au ions and produce larger particles as the reduction time is increased.
However, at the lower pH, the protonation of the PEI leads to an increase in electrostatic repulsion among branched PEI monomers, which allows the AuCl$_4$ to be dispersed more freely through the PEI solutions, resulting in the smaller core size at 0.02 wt%. Another theory is that the lower pH of the HCl solutions produces an environment with increased ion mobility, thus allowing the AuCl$_4^-$ ions to reduce more quickly when the NaBH$_4$ is introduced, countering the effect of the increased steric hindrance at 0.02 wt%.

According to Figure 4.5, the effect that pH has on the resulting UV-vis absorption bands of the GNPs synthesized during a NaBH$_4$ reduction is apparent. The 0.005wt% PEI and 0.01wt% PEI particles synthesized at a low pH (1mM HCl) only exhibit slight shoulders, while the 0.02wt% PEI in H$_2$O exhibits a broad peak at 534nm. The 0.02wt% PEI in 1mM HCl and the 0.01wt% PEI in H$_2$O exhibit almost identical spectra with maximum absorption at wavelength 512 nm. This supports our theory that a reduced pH environment, promotes faster reduction of the Au precursor and smaller particle cores despite a higher PEI concentration. This is attributed to their similarity in pH, which are 7.7 and 7.1 respectively, indicating that the concentration is responsible for adjusting the pH but is not a major driving force during the synthesis.
Figure 4.5: UV – Vis absorption spectra of NaBH4 reduced GNPs using 0.005 – 0.02 wt % PEI solutions in pure DI- H2O and in 1mM HCl.
The thermal reduction is also affected by the pH of the PEI solution as seen in Figure 4.6. The GNPs synthesized in low pH environments exhibit sharp Plasmon resonance bands indicating well dispersed particles and minimal clustering, while a pH of 9.1 and 7.7 show a significant red shift and broadening of the UV–vis spectra. This is once again characteristic of polydispersity due to clustering or increased core sizes. (Appendix B). Coupled with Figure 4.7 a better understanding of the effect of pH on the interparticle stability is gained. As the pH increases from 3.2 to 9.1, so does the hydrodynamic diameter of all the GNPs, while the core sizes remain relatively low. This
trend further promotes the claim of increased clustering at the higher PEI concentrations which can be mitigated through the acidification of the solvent.

Figure 4.7: Graph of the core diameter (TEM) and hydrodynamic diameter (DLS) of thermally reduced GNPs using 0.005 - 0.02 wt % PEI in 1mM HCl and DI-H₂O

According to Figure 4.8, the formation and growth of the PEI-GNPs synthesized by room temperature reduction are also enhanced at a lower pH with the addition of 1mM HCl. After only 2 hrs, the Plasmon resonance bands of the GNPs can be detected under acidic conditions. However there is a concentration limitation evident when comparing the two 0.005 wt% reactions. The particles synthesized at the lower pH (3.4) grow slower than those at pH 4.2, while the increase in PEI concentration to 0.01 wt% leads to faster reduction of the Au and hence a quicker growth in the UV-Vis absorption when compared to 0.005 wt%.
After 2 weeks, it is clear that under basic conditions the GNPs are highly clustered and polydispersed. It is important to note that the PEI-GNPs synthesized at pH 9.3 and pH 7.7 have the same wt% of PEI, which further supports our claim that electrosteric stabilization due to protonation of the amines is the driving force behind this particle stability. Hence, pH has a major effect on the particle UV-vis absorption of the GNPs which is independent of reduction source.
Effect of Carbon dioxide

Carbon dioxide reacts with amines to form a carbamic acid, which leads to a reduction in the pH of the resulting reaction solutions (Figure 4.9). Carbon dioxide is also well known to form carbonic acid in the presence of water which also lowers the pH of the reaction solution. This reaction between the CO$_2$ and the polymer solution occurs very readily, and the time of carbon dioxide exposure does have an effect on the resulting pH of the PEI solution. However, an equilibrium pH of ~5 is obtained within 30 seconds of bubbling CO$_2$ at 10psi and is therefore not a major variable in this study as all PEI solutions were exposed for a minimum of 2 minutes (Figure 4.10). By varying the CO$_2$-PEI reaction sequence, we found that the reduction in the UV-vis absorption shown in Figure 4.12 is independent of the order in which the CO$_2$ is introduced, (Figure 4.11). All combinations of the starting materials (Au, PEI and CO$_2$) were tested, each producing particles with similar UV-vis absorption, leading us to conclude that the Au precursor is not affected during the electrosteric stabilization of the Au cores.
Figure 4.9: Reaction scheme of PEI with Carbon dioxide forming carbamic acid. This acid forms a carbonate in the presence of water (a) or a carbamate salt in the presence of another amine (b). In the presence of an acid the amine is protonated (c).

Figure 4.10: Image showing the pH of a 0.01 wt% PEI solution vs. the carbon dioxide bubbling time (left) and the respective GNPs synthesized using the NaBH₄ reduction method at the specific pH’s.
Figure 4.11: UV-vis absorption spectra of NaBH$_4$ reduced GNPs obtained while varying the sequence of CO$_2$ exposure with reagent addition.

This increased stabilization due to carbon dioxide addition results in a decrease in the core size of the NaBH$_4$ reduction method from 4.9 ± 1.9 nm to 3.7 ± 1.0 nm. This decrease in core size is also exhibited in the UV-vis spectrum as the absorption peak at 503nm attributed to the 0.01wt% PEI GNPs in DI-H$_2$O is reduced to a shoulder as the carbon dioxide exposure increases (Figure 4.12). Furthermore, Figure 4.13 displays the effect of concentration and carbon dioxide as we can visually see the clustering and aggregation of the GNPs at 0.02wt% PEI by its dark black color, while 0.02 wt% PEI+CO$_2$ still exhibits a lighter brown color due to less clustering.
Figure 4.12: UV – vis absorption spectra of NaBH$_4$ reduced Gold nanoparticles with increasing CO$_2$ exposure at a PEI concentration of 0.01 wt%.

Figure 4.13: Image of GNPs synthesized from a NaBH$_4$ reduction utilizing PEI and the PEI+CO$_2$ solutions.
Contrary to the NaBH$_4$ reduction method, the introduction of CO$_2$ has little or no effect on the UV-vis spectra of the thermally reduced particles (Figure 4.14). This is due to the thermally reversible carbamate chemistry which converts the C=OO$^-$ backbone of the carbonate that is formed back to an amine during the boiling process. Thus CO$_2$ is not a suitable additive for stabilization during the synthesis, but can always be introduced post synthesis for increased electrostatic repulsion. It was found that the optimal boiling time was 1 minute with a PEI concentration of 0.01 wt %.

Figure 4.14: UV-Vis absorption spectra of thermally reduced GNPs using 0.01wt% PEI and 0.01wt% PEI-CO$_2$ at 1, 5 and 15 minutes boiling times along with an image of the thermally reduced 0.01wt% PEI GNPs at various boiling times.
Time resolved UV-vis absorption studies of PEI-GNPs reduced at room
temperature showed very good stability over a two week period; inferred from the stable
Plasmon resonance bands measured each day. The 0.005 wt% PEI solutions had an
absorption increase over the entire two weeks, while the 0.01 wt% PEI-CO$_2$ increased an
then decreased after one week indicating slower growth for the 0.005 wt%. This
correlates very well as the 0.005 wt% PEI solution has less reductive power due to fewer
PEI chains. One might expect that the 0.02 wt% PEI solutions to have a faster reduction
with increased PEI molecules; however, due to the clustering of the GNPs at that
concentration, there is significant red shifting of the spectra. The lack of red shifting for
the 0.02 wt% PEI which was reacted with CO$_2$ (PEI+) further supports the addition of
carbon dioxide. Overall, the GNPs wavelength of maximum absorbance remained
constant (except for the 0.02 wt % in H2O) (Figures 4.15-16). Furthermore, as seen in
Figure 4.2, the addition of carbon dioxide to the room temperature reduction method
resulted in smaller particles at a 0.01 wt% PEI concentration, proving to be a suitable
additive for the synthesis of stable GNPs and can replace the mineral acid (HCl) as the
pH adjuster.

Finally the hydrodynamic radius of the PEI+CO$_2$ GNPs seen in Table4.1 further
supports the UV-vis data as carbon dioxide addition reduces the radii as well as the
deviation. This is more apparent at the higher concentrations of PEI where we believe the
electrosteric repulsions are more greatly felt.
Figure 4.15: Maximum absorbance of the GNP Plasmon peak as a function of time for the room temperature reduced GNPs.

Figure 4.16: Graph of the wavelength of maximum absorbance vs. time for the room temperature reduced GNPs in $H_2O$ and with $CO_2$. 

86
Effect of boiling time

The thermal reduction method utilizes the heat from the boiling solution to reduce the Au ions at a faster rate than at room temperature. The technique of injecting the Au precursor into the solution while stirring promotes a fast, uniform reduction of the HAuCl$_4$ and the formation of more monodisperse particles. During the thermal reduction, the ability of the PEI to both reduce and stabilize the Au core efficiently is exploited, while the characteristics of the resulting particles are highly dependent on the boiling time of the PEI solutions. At an optimal concentration of 0.1 wt % PEI, TEM analysis of the thermally reduced PEI-GNPs determined that an increasing boiling time led to a 27% increase in particle core size from 11.7 ± 3.4 nm at 1 minute to 14.8 ± 3.8 at 15 minutes (Figure 4.17). However, this increase is negligible compared to the increase in hydrodynamic radius (Rh) from 10.2 ± 3.5 nm to 34.1 ± 16.9 nm for the identical time intervals.

This increase in core size is further evidenced by the broadening and red shifting of the UV-vis spectra seen in Figure 4.16. However, we concluded that the increase in TEM core size is not large enough to produce that degree of broadening and red shifting in the UV-vis absorption, and have attributed it to significant clustering (Figure 4.18 supports this conclusion as the GNPs boiled for 15mins are black in color). It is thought that the low molecular weight PEI is degraded as the boiling time increases, leading to a diminished electrosteric stabilization potential of the polymer shell. This diminished polymer shell results in the increasing degree of clustering and thus larger Rh.
Figure 4.17: Graph of the thermally reduced 0.01 wt % GNPs core diameter (TEM) and hydrodynamic radius (DLS) vs. boiling time (min).

Figure 4.18: UV-vis spectra of the thermally reduced 0.01 wt %PEI GNPs at boiling times of 1 min, 5 min, and 15 min under neutral conditions.
Conclusions

In conclusion, cationic gold nanoparticles were consistently synthesized using a low molecular weight (M_w ~ 600) polyethylenimine as the stabilizing ligand with three varying reduction methods. The pH of a synthesis is a driving force for the reduction and stabilization of the PEI capped GNPs which can be manipulated using traditional mineral acids or via carbonate production from a safe, cheap additive carbon dioxide. The PEI-GNPs had an average positive zeta potential of approximately +28 mV and formed stable colloidal suspensions through the increased electrostatic repulsion caused by the carbon dioxide additive. At low PEI concentrations, the reduction in pH led to a slight increase in particle core size. However, there was a significant reduction in particle clustering as pH decreased. Overall, the addition of carbon dioxide improved the stability of PEI capped gold nanoparticles by providing improved electrostatic repulsion due to reversible carbamate chemistry. This was determined from the hydrodynamic radii of the GNPs synthesized along with the positive zeta potentials obtained. Finally, the carbon dioxide produced slightly smaller particle cores at room temperature for both the NaBH_4 assisted and the direct PEI reduction methods.
CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

As carbon dioxide emissions continue to rise due to our growing energy demand, new avenues for the usage and application must be developed in order to offset the greenhouse effect caused by its rising atmospheric concentration. In this dissertation, three different areas of research have been demonstrated that implement the reversible carbamate chemistry that exists between amines and carbon dioxide. Although the scale at which these studies were carried out had little impact on the amount of CO$_2$ emissions, the results show great potential for future applications for materials and green chemistry.

The switch from non-ionic to ionic nature as the reaction proceeds forward has significant effects on the physical properties of a solvent system. Using this simple, well studied and instantaneous switching mechanism, neat amine solutions were used to explore the carbamate chemistry and extended it to surface bound amino-terminated films. It was determined that the reaction can be controlled by the amount of CO$_2$ exposure and has the potential of developing into a fully dynamic system for control over polarity, thickness and wettability. This application of CO$_2$ is a novel technique that can be employed in future smart materials and next generation stimuli responsive polymers. We believe that this concept can be utilized for carbon capture and sequestration purposes as is demonstrates the ability to reversibly trap the carbon dioxide through surface bound amines.
We have also shown that the reaction of CO$_2$ with low molecular weight alkyl amines was effective at reducing amine reactivity, resulting in decreased conversion during nucleophilic substitution reactions. This reversible carbamate formation via gaseous carbon dioxide alone shows great potential as a simple, “green” protection mechanism alternative compared to traditional methods that require harsh chemicals and more energy intensive reaction conditions. We anticipate that the results from this work will encourage chemists to not only design greener routes for amine protection/deprotection mechanisms, but also to learn about the many advantages that carbamate chemistry has to contribute to safer lab practices.

Lastly, the addition of carbon dioxide improved the stability of PEI capped gold nanoparticles by providing enhanced electrostatic repulsion. The driving force behind this result was the reduction in pH of the solvent as a result of the carbamic acids. In addition to the improved interparticle stability; the presence of carbon dioxide produced slightly smaller cores with smaller size distributions at room temperature. This is an important result in the development of nanomaterials and the increased stability found in this study can be applied to many GNP systems presently being used for biomedical applications.

However, there are some overall limitations which were found during this dissertation for the application of this carbamate mechanism to be successful in other systems. Firstly; consideration must be taken to minimize the effect of ambient air and the effect of polar protic solvents (especially water). Amine rich compounds will react with the carbon dioxide in ambient air to produce the alkylcarbamate salts while the presence of water results in dissociation of these salt into carbamic acids and carbonates. If the end
application is pH sensitive then care must be taken to ensure an anhydrous environment. Secondly, the temperature at which you reverse the carbamate chemistry is highly dependent on the intermolecular bonds of the carbamates and should be tailored for the specific task at hand.

Overall, these three examples only scratch the surface as to the number of potential applications of this unique switching mechanism. Based on these findings, I see the need for further experiments to fully harness the power of the reversible carbamate chemistry towards next generation materials.

Firstly, the application of carbamate protection to diamino silanes during the deposition process will help develop more uniform coatings and surface modifications. The problem with multi amino coupling agents is the number of modes of attachment that can exist between itself and the substrate. By implementing similar carbamate protection used in this work, I hypothesize that more uniformed SAMs can be engineered due to the reduction in amine reactivity. The deposition of the SAMs should be done in a polar protic solvent so as to form carbamic esters rather than the dimerization of the coupling agents. Once deposited, the removal of polysiloxane layers and the regeneration of amine can be achieved by using an organic bath heated to reflux. This work will build upon chapters 2 and 3 from this dissertation while coupling previous literature. In addition, there is a need to accurately model the SAM formation to quantify the chain density along with the theoretical amount hydroxyl groups per area obtained during the cleaning process.
The green amine protection reported in Chapter 3 needs to be expanded to a broader range of reactions and solvents. The protection mechanism should be implemented in a competitive reaction where amine functionality is required post protection for a separate coupling reaction. This will truly test the limits and efficiency of the proposed protection/de-protection technique. I will however suggest that non-polar organic solvents be used so as to fully utilize carbamate chemistry and not the carbonates which arise in the presence of water. An investigation into the kinetics of the carbamate reactivity can also provide useful information on the degree of protection. By fully understanding the relationship that exists between carbamates and the amine-CO$_2$ system, we can calculate expected yields of the product based on the equilibrium constant of the carbamate formation.

Another potential application of CO$_2$ protection lies in the use of atom transfer radical polymerization (ATRP); a well-established technique for controlled synthesis of polymers. The copper catalysts used during ATRP can be deactivated and “stripped” from its metal complex in the presence of amines. The result is excess copper catalyst, residual copper within the synthesized polymer, and requires more expensive, strongly binding ligands. I believe that the application of carbon dioxide to the solvent system can render the amine groups of the monomer protected, thus allowing the polymerization to proceed with minimal residual copper. These experiments can be conducted in bulk solution and analyzed via elemental analysis, ICP and TGA.

Lastly, the development of cationic nanoparticles can be achieved through the use of ligand attachment rather than a direct polymer coating. Nanoparticles have previously
been synthesized with citrate or mercaptosuccinic acid using methods reported in this
dissertation. Initial experiments have proved that the phase transfer of these hydrophilic
nanoparticles into an organic phase can be achieved by coupling the carbonyl of the
citrate or mercapto-acid to a hydrophobic alkylamine using 1-ethyl-3-(3-
dimethylaminopropyl)carbodiimide (EDC). This technique will allow ripened/aged
nanoparticles which do not undergo efficient ligand exchanges to simply build upon the
already stable shell and bypass the exchange mechanism completely. This can increase
the shelf-life of the nanoparticle and allow for bulk production coupled with simple
onsite phase transfers. Also, the amine used in this coupling technique can be tailored for
specific applications, which expand the limitations of this technique and opens up new
avenues for nanomaterial applications.
APPENDICES
Appendix A

The Effect of Post-Synthesis and Post-Ligand Exchanged Purifications on Gold and Silver Nanoparticles.

Introduction

Engineered nanomaterials have great potential use in a wide array of fields including biomedical applications\textsuperscript{[123-127]}, catalysis\textsuperscript{[128]} and sensory devices.\textsuperscript{[103, 129]} This is attributed to the unique physical properties that these materials possess at the nano scale\textsuperscript{[130, 131]}. More specifically, the size-dependent properties of gold and silver metallic nanoparticles include surface Plasmon resonances\textsuperscript{[132, 133]}, applications in catalysis\textsuperscript{[128]}, as well as photo-thermal activity.\textsuperscript{[126]}

One of the most important characteristics of these metallic nanoparticles is their surface chemistry, given that the size, shape, charge and chemical functionality can be dictated by tailoring the surface chemistry. It is the ligands surrounding the nanoparticle that are responsible for the interaction with the immediate surrounding environment.\textsuperscript{[104]}

Hence, nanoparticles are functionalized for differing applications through the use of specific ligands containing optimized chemistries. Furthermore the control of the nanoparticle size, shape, and aspect ratio is also possible through variation of temperature, concentration and addition of other structure directing agents.\textsuperscript{[122]}

A widely utilized technique for tailoring NP surface chemistry is through a ligand exchange process, where a labile ligand molecule is replaced with a ligand that has a higher binding affinity to the metal surface. In the case of gold, thiols are readily used to
displace citrate on the particle surface, altering their surface chemistry and physical properties.

Despite the synthetic route or exchange process used, most applications of these materials require very monodispersed populations which are free of the excess surfactants introduced during the synthesis process. This is commonly achieved by post-synthesis processing/purification, a critical step in the removal of any reaction byproducts from solution that may be detrimental to the end application. In a typical post synthesis procedure, an anti-solvent precipitation technique coupled with a centrifugal deposition is used to purify and size fractionate the nanoparticles.\textsuperscript{[134]} The solvent/anti-solvent pairs that enable this nanoparticle size-selective precipitation and isolation include toluene/ethanol or hexane/ethanol for hydrophobic alkanethiol modified gold nanoparticles.\textsuperscript{[135]} Carbon dioxide has also been demonstrated as an effective ant solvent as well.\textsuperscript{[136-139]} Following precipitation and isolation by removal of the supernatant, the nanoparticles can be redispersed in neat solvent, free of the excess surfactants and ligands that remain in the supernatant; a process termed nanoparticle washing. Nanoparticles are usually “washed” multiple times with centrifugation and redispersion in-between each washing, resulting in size-monodisperse nanoparticle dispersions that are free from excess ligands and surfactants.

Despite the broad use of this nanoparticle processing, knowledge of the nanoparticle – ligand interactions and the effect of these purification procedures on the stabilizing ligand shell are not fully understood. This work explores the effect of multiple washes on the shell coverage of gold and silver nanoparticles through thermogravimetric
analysis (TGA), gas chromatography (GC) and UV-vis spectroscopy. Both GC and TGA were determined to be viable methods to quantify the ligand concentration on gold and silver nanoparticles, which are further used to calculate the surface coverage and potential stability.

Experimental

Citrate capped particle synthesis

For GNP synthesis, 250 µl of 0.05M citrate and 0.05M HAuCl₄ aqueous solutions were added to 50 ml of DI-H₂O while gently stirring. 500 µl of chilled 0.05M NaBH₄ in DI water was then added and the resulting solution was stirred at 400 rpm for 15 minutes as the color of the solution changed from colorless to red. For SNP’s, the preceding procedure was repeated using 0.05M Ag₂NO₃ as the metal salt precursor and the formation of SNPs afforded a yellow solution.

Dodecanethiol capped GNP’s and SNP’s via ligand exchange

Figure A1: Image showing ligand exchange process from an aqueous phase to a hexane phase containing alkane thiols for citrate capped GNPs
To achieve ligand exchange, 50 ml of toluene was added to 50 ml of citrate capped GNP’s or SNP’s in a glass jar. To that, 500 ul of dodecanethiol was added to the hexane phase and the solution was shaken vigorously and stirred until all nanoparticles were transferred to the organic phase (Figure A1)

Purification of ligand exchange GNPs and SNPs

The dodecanethiol capped NP solutions obtained via ligand exchanges were concentrated to a 2 ml sample using a rotary evaporator and then transferred to a centrifuge tube for purification. Ethanol was added to each tube making the volume equivalent to the starting volume of the NP synthesis, and then centrifuged at 14,000 rpm for 10 minutes to precipitate the particles. The supernatants were decanted and analyzed via GC while the residual particles are redispersed in minimal toluene. This is process is considered one complete wash which was repeated up to 3 times.

Direct Synthesis of alkanethiol capped SNPs

These nanoparticles were synthesized per the “two-phase arrested precipitation method” developed by Brust et al. [140] A typical synthesis of SNPs requires a solution of 0.19 g of AgNO3 in 36 ml of DI-H2O mixed with 24.5 ml of chloroform solution consisting of 2.7 g of tetraoctylammonium bromide (TOABr), the phase-transfer catalyst. This mixture was stirred for 1 hr upon which the aqueous phase was clear due to transfer into the organic phase. This aqueous phase was then pipetted out and 240 μl of dodecanethiol was added to remaining chloroform mixture. This was allowed to stir for
5–10 min. while a solution of 0.5 g of NaBH4 in 30 ml of D-H$_2$O was freshly prepared, and then added as a reducing agent. The suspension was further stirred for 4–12 h. The dark brown organic dispersion contained thiol stabilized SNPs.

*Purification of the SNPs synthesized by the direct synthesis method.*

Anti-solvent (ethanol) was added to 0.4 mL of particles initially synthesized above in a centrifuge tube. The centrifuge tube was shaken vigorously for one to two seconds and then allowed to sit for 15 minutes so that the mixture could come to equilibrium. The volume ratio of solvent to ethanol was varied between 1:100, 1:50, and 1:25 (i.e. either 40 mL, 20 mL or 10 mL of ethanol was added to the centrifuge tube as anti-solvent, respectively). The solution was then centrifuged at 14500 rpm for 10 minutes precipitating the particles out of solution and allowing the supernatant (containing excess ligands and by products) to be decanted. The tubes were inverted and allowed to air dry, representing a single washing step that was repeated up to 4 times. Each additional wash required 0.4 mL of toluene added to the centrifuge tube followed by 2-3 minutes of water bath sonication to re-suspend the nanoparticles. Once in solution, the anti-solvent is introduced and the centrifugation precipitation is repeated. At the end of the washing procedure 0.15 mL of n-hexane was added to the centrifuge tube after air drying followed by sonication for 2-3 minutes to re-suspend the nanoparticles before further characterization. The hexane allows for quicker TGA sampling as it evaporates more quickly leaving behind little to no residual solvent.
Results and Discussion

Effect of purification/washing on ligand exchanged gold nanoparticles

UV-vis spectroscopy, $^1$H NMR and FT-IR all confirm the exchanging of citrate for DDT on both the GNPs and SNPs, transferring from the aqueous phase to the organic phase due to the change in surface chemistry. By monitoring this exchange with situ UV-vis spectroscopy, the wavelength of maximum absorbance of the aqueous layer shifts from 506nm to 534nm after 10 minutes before slowly decreasing as the number of particles in the aqueous layer decreased. This confirms the ligand exchange reaction and complete phase transfer of the NPs from the aqueous to the organic phase.

Figure A2: Time resolved UV vis absorption spectra of the aqueous layer from a citrate capped GNPs ligand exchange reaction with dodecanethiol
\(^{1}\)H NMR provides further proof of the purity of our ligand shell and ensures that complete ligand exchanges have occurred. Observed in Figure A3 the loss in resolution of the chemical shifts attributed to protons situated closest to the point of thiol attachment along with a broadening of the methylated protons confirms thiol attachment to the gold. Methylenes closer to the Au core are assumed to be more densely packed which affect their spin relaxations and results in the disappearance of the chemical shifts of protons (A) in the NMR Spectra. We can also observe a weak chemical shift attributed to the free DDT ligand in solution. Overall, the proton NMR data correlates very well to the proton NMR results of other GNP systems involving thiolated ligands.\(^{105, 141}\) However, this broadening is not a completely conclusive method for determining surface structure and although other techniques are more suitable for determining structure on GNP’s they each possess their own difficulties.\(^{142}\)

![Figure A3: \(^{1}\)HNMR of pure dodecnaethiol and dodecanethiol capped gold nanoparticles in CDCl\(_3\)](image-url)
In order to use gas chromatography as an effective means for ligand quantification, a calibration curve was first constructed using GC chromatographs of known concentrations of DDT. As seen in Figure A4, a linear calibration curve was obtained and used to determine the DDT concentration in the supernatant post-exchange and after each wash. This is an indirect method of determining the DDT concentration left free in solution after ligand exchanging onto the gold particle surfaces and with each wash.

The GNPs and SNPs in this work are very stable and do not precipitate out of solution completely under centrifugal forces alone. To increase the rate of particle precipitation, the addition of ethanol anti-solvent reduces the stabilizing ability of the DDT shell by altering the polarity of the solvent environment. Combined with concentration of the NPs by rotary evaporation, ethanol addition allows for precipitation during the purification steps and significantly reducing the amount of anti-solvent usage.\textsuperscript{141}
As the number of washes increases during the purification step, we believe that the excess DDT is removed from solution along with some of the bound ligands on the NP. The equilibrium that the ligands maintain while in solution, always shifting between particle bound and solution phase, explains the presence of DDT even after 3 washes have been undertaken; although the concentration measured from the 3rd wash is very small. From the graph below (Figure A5), the concentration of the ligand found in the supernatant has been significantly reduced after the 2nd wash, with three washes yielding almost negligible concentrations, suggesting the removal of all the excess alkanethiol. The 90% reduction of DDT surfactant concentration in the nanoparticle system doesn’t affect the UV-vis absorption spectra of the GNPs and SNPs. The wavelength of maximum UV-vis absorption (GNP ~520nm, SNP ~ 450nm) remains constant over the 3 washes, leading us to conclude the NPs are not clustering or increasing in size during the purification steps (Figure A5).
However, while the NP core remained unchanged, there is a noticeable decrease in the precipitation of the GNPs after wash number 2, leading to increased centrifugation times required to precipitate the particles. We hypothesize that the reduction in concentration of DDT by increasing washes leads to the longer required centrifugation...
times when the particles no longer have a significant excess of DDT present in solution. A similar effect is observed by Zhang et al.\textsuperscript{[143]} during the adsorption of a heterocyclic mercaptobenzimidazole onto 13nm GNP surfaces which also reported an increase in centrifugation time by 25 minutes once the ligand concentration was less than 1.25uM.\textsuperscript{[143]}

By analyzing the amount of thiol in the supernatants, the total number of moles of thiol that are separated with the nanoparticles during precipitation is displayed in Figure A6. This shows that gold and silver NPs synthesized under identical experimental parameters exhibited 34 % and 33% ligand transfer respectively. There was therefore no preference in the type of metal exchanged as both have a well-established affinity for thiolated molecules.\textsuperscript{[104, 143-145]}

![Figure A6: Bar graph depicting the change in concentration of DDT in the organic solvent as a result of the ligand exchange process.](image)
TEM provided an average core diameter of 10 nm for both metals. The NPs were modeled as spheres with radius \( r \) and assuming a size distribution with very low polydispersity. Using the total number of moles of DDT transferred to the particles \( (M_i) \), the surface coverage per nanoparticle \( (SC_{NP}) \), and surface coverage per square nanometer \( (SC_{nm^2}) \) were calculated using equation A-1 and equation A-2 respectively; where the initial mass of metal added \( (m_{metal}) \) determined the total number of particles by utilizing the mass of one 10 nm particle \( (m_{NP}) \).

\[
SC_{NP} = \frac{N_{molecules}}{N_{NP}} = \frac{M_i.N_{AV}.m_{NP}}{m_{metal}} \quad (A-1)
\]

\[
SC_{nm^2} = \frac{M_i.N_{AV}.m_{NP}}{m_{metal}.SA_{NP}} \quad (A-2)
\]

The calculated surface coverages in Figure A7 are three orders of magnitude higher than the theoretical maximum for 100% ligand coverage, indicating that DDT is in gross excess. One theory behind this unexpected result is the effect of solvent removal on the equilibrium position of the ligands between the particle surface and solution. This equilibrium is difficult to predict and is affected by many factors which include ligand-ligand interactions as well as ligand-solvent interactions.\(^{[104]}\) As the concentration of the particles in solution increases, the intermolecular interactions of the free ligands and bound ligands are increased. Thus, centrifugation leads to the co-precipitation of free
ligands along with the particles, resulting in the unreasonable estimated surface coverage. This is a phenomena that is also observed with SNPs synthesized via the direct method and is discussed in more detail below.

![Figure A7: Graph showing the calculated surface coverages for gold and silver NPs capped by dodecanethiol synthesized via a ligand exchange process](image)

**Effect of post synthesis purification on DDT capped Silver nanoparticles (SNPs) via the direct Method**

The amount of anti-solvent added during the purification process has a significant effects on the NP precipitation efficiency as solvent conditions become less favorable when the solvent:anti-solvent ratio increases. TEM analysis determined that core sizes of these SNPs were not significantly affect by either increases in solvent ratio or by increases in washing number. The measured particles washed at a ratio of 1:25 had an average core size of 8.2nm after 2 washes and 8.6 after 3 washes; and with standard deviations of 2.3nm and 3nm respectively, This was further evidenced by the UV-vis
absorption spectra maxima over the washing process as all volume ratio’s exhibited absorption maxima ~430nm, with relatively small deviation and no clear trends as wash number increases.

Figure A8: TEM image and histogram of dodecanethiol capped silver nanoparticles washed at a solvent: ethanol volume ratio of 1:25 (top) and 1:100 (bottom). All nanoparticles were sized using ImageJ software.

These particles underwent a more direct method of quantifying the number of DDT molecules on the surface by utilizing thermogravametric analysis (TGA). The reduction in percentage weight loss of organic DDT bound or coupled to the SNPs is
plotted in Figure A9. Also, trends in the percentage of weight lost attributed to DDT versus wash number at all the solvent:anti-solvent ratios are displayed. The most significant result was the lower DDT weight fractions obtained at the smallest volume ratio (1:25), along with a decrease in DDT as the number of washes increases. Similar to the ligand exchanged particles mentioned above, these SNPs also became more stable with each successive wash, requiring more time and energy for particle precipitation once 2 washes had been completed; further supporting our claim that 2 washes were enough to remove the majority of the free excess ligand.

Figure A9: Graph of the average total percentage of weight lost during TGA for each anti-solvent ratio. Error bars represent the standard deviation of 3 runs.

As you increase the ethanol fraction from 1:25 to 1:50, we believe that the change in solvent polarity forces the non-polar alkane thiols to associate more strongly with the
capped SNPs, creating an increase in the ligands around the SNPs and enabling them to phase separate out of solution more easily during centrifugation. This leads to excess unbound ligands in the particle residue which explains why the weight percentage of DDT lost via TGA remains above 50% throughout the purification process when compared to a 1:25 solvent:anti-solvent volume ratio. This elevated DDT weight loss percentage supports our claim and explains the need for longer centrifugation as multiple washes are conducted.

At a solvent:anti-solvent volume ratio of 1:100, we attribute the overall increase in volume for the removal of the excess DDT that has been loosely bound to the NP core. Taking the standard deviations of all of washes into consideration, we can conclude that the higher anti solvent ratios results in a less efficient washing process as excess free ligand is precipitated out with the SNPs and that little effect is observed for subsequent washes, particularly for the higher anti-solvent ratios.

Once again, the DDT surface coverage was calculated by modeling the SNPs as spheres with radius \( r = 4 \) nm (Figure A8). By utilizing the weight fraction of DDT \( (w_l) \), the weight fraction of the NP core \( (w_{NP}) \) and the surface area of an individual particle the surface coverage was calculated using equation A-3.(Figure A10)

\[
SC_{nm^2} = \frac{m_{NP}.w_l.N_{AV}}{w_{NP}.MW_l.SA_{NP}}
\]  

(A-3)

The surface coverages reported in Figure A10 not only illustrate the variability in sample sets but the effect of solvent:anti-solvent ratios on the number of molecules per
nm$^2$. It must be noted that the 1:25 samples are the only particles which afforded chain density values close to the theoretical maximum given a thiol head group of ~20Å$^2$ and a densely packed monolayer.

One source of error in this model, which is based on the experimental TGA measurements, is the polydispersity of the SNPs. Although the effect is minimal the core size variability can affect the overall DDT weight fractions and hence, affect the calculated values for SC.

Figure A10: Graph displaying the calculated surface coverages for the SNP’s purified at solvent: ethanol volume ratios of 1:25, 1:50 and 1:100. Sizes of particles were approximated to be 8nm for all three processes.
Optimized solvent:anti-solvent volume ratios for purification of DDT SNPs. Synthesized via the Direct Method.

From the work addressed in the above two sections, it was determined that a lower solvent:antisolvent volume ratio produced SNPs that contained less excess alkanethiol molecules post purification. Building on these findings, the volume ratio of solvent:anti-solvent used to purify the SNPs was reduced even further to 1:10.

As with the citrate-dodecanethiol exchanged particles, and the direct synthesis of SNPs reported in the above section, washes 3 and 4 were centrifuged for 10 – 15 minutes longer to ensure complete precipitation of the particles. The wavelength of maximum UV-vis absorption (~425nm), the hydrodynamic radius obtained from DLS and the diameter of the NP core determined from TEM all remained constant during these washing steps.
Figure A11: UV-vis absorption spectrum of SNP after 0-4 washes with a solvent:anti-solvent ratio of 1:10.
Figure A12: TGA curves for SNPs with 0-4 washes with a solvent:anti-solvent volume ratio of 1:10.

An important feature observed from the TGA spectra of freshly prepared particles is the presence of two weight loss transitions. These separate processes are more clearly defined by analyzing the first derivative of the TGA data showing onsets at 180°C and 215 °C (Figure A13) The first and second weight loss transition is attributed to unbound (free) and bound thiol respectively. After 1 wash, there is only ~57% decrease in weight and only one degradation transition observed from the 1st derivative spectra. As the wash number increases, so does the onset temperature for the degradation transitions.
This trend is attributed to the increase in the amount of energy required to release the thiol-GNP bond as the removal of the excess free ligands and weakly bound chains results in a larger percentage of thiols attached to the surface.

Finally, identical surface calculations were conducted using equation A-3, giving rise to Figures A14-15, which displays the weight loss percentages, calculated chain densities and estimated surface coverages vs. wash number. Three nanoparticle sizes were modeled encompassing the average core size of these SNPs (8nm). Based on these plots, the chain density of the particles drops below a value of 5 molecules/nm$^2$ after 4
washes for all SNP sizes. Furthermore the surface coverages calculated are below the theoretical maximum as seen in Figure A15. Hence, we can conclude that all excess ligand has been removed from the solution after 4 washes based on the TGA data obtained.

Figure A14: Plot showing the measured DDT weight loss percentages and the corresponding calculated surface coverage determined for 6nm 7nm and 8nm diameter particles.
Conclusions

In this work we highlighted the importance of post synthesis purification towards the development of monodisperse gold and silver nanoparticles and the need for removal of excess surfactants. We can conclude that the volume ratio of solvent: anti solvent is a key component in the successful removal of all excess ligands and phase transfer agents. More specifically, using ethanol as the anti solvent to induce solvent polarity changes leads to increased centrifugation times for the precipitation out of solution as the number of washes increases. We have attributed this observation to the reduced concentration of excess alkane thiol molecules, limiting the number of chains that can weakly bind to the

Figure A15: Plot showing the calculated surface coverage for 6nm 7nm and 8nm diameter particles based on the weight fractions of DDT determined via TGA
NPs. As the amount of ethanol is increased these excess molecules, precipitate out along with the metallic particles, thus maintaining a relatively steady concentration of excess thiol (as evidenced by TGA) throughout the washing procedure.

In conclusion, an optimized purification procedure, for the removal of all excess DDT, was developed and explored for the purification of SNPs synthesized via a direct method. The significance of this work will enable researchers to fully understand the effect of anti solvents on the partition of excess ligands in solution. The scope of this study also highlighted the use of TGA as a means of quantifying surface coverage on SNPs.
Appendix B

Surface Plasmon Resonance (SPR) Background

Figure B1: Schematic illustration of the Plasmon resonance caused by the oscillating field

At a specific wavelength (frequency) of light, collective oscillation of electrons on the gold nanoparticle surface cause a phenomenon called surface Plasmon resonance resulting in strong extinction of light (Figure B1). The electric field of an incoming light wave induces a polarization of the electrons which results in the net charge difference felt at the nanoparticle surface. The gold nanoparticle size, shape, surface and agglomeration state strongly affects the particular wavelength, or frequency of light where this absorption occurs.\textsuperscript{[146]}
Figure B2: UV-vis absorption spectra of GNPs of varying sizes

From Figure B2, the peak intensity and wavelength of maxima absorption ($\lambda_{\text{max}}$) of the SPR band is increases (redshifts) as the particles metal core increases in size from 20 nm to 100 nm. Also the peak bandwidth becomes broad with increased particle size as seen in previous work.\textsuperscript{[122]}

Red shifting of the SPR bands can also occur from interparticle interactions. When spherical gold particles come into close proximity to one another, there is an interparticle dipole coupling that becomes effective at distances smaller than 5R (where, $R$ is the radius of the particles). This interaction has shown to complicate the absorption spectra due to the variability in the size and shape of the formed particle aggregate.\textsuperscript{[132]} In spite of this interaction, effective medium theories, developed by Maxwell-Garnett have been successfully applied to account for GNPs present in closely packed assemblies.
which takes not only the single spherical particle absorptions in consideration but clusters as well.\textsuperscript{[147]}

Figure B3 below, shows the calculated absorption spectra for linear assemblies of GNPs with 40 nm diameters. A systematic red shift in $\lambda_{\text{max}}$ is expected with increasing aggregate size.\textsuperscript{[148]}

Figure B3: Electrodynamic modeling calculations of extinction spectra for GNP aggregates ($d = 40 \pm 0.5$ nm).
Appendix C

Variable Angle Ellipsometry Instrumentation

Ellipsometry is a non-destructive optical technique which utilizes the reflection coefficients of a substrate to determine layer thickness and as well as film refractive index.[149-154] This is calculated using the optical properties of polarized light which undergoes a reflection from the sample surface. In ellipsometry the comparison is made by polarizing the incident beam so that it has two coherent parallel and perpendicular waves, whose amplitude and phase are then altered by reflection onto the substrate. The reflected light becomes elliptically polarized, hence the name of the technique. The ellipse of polarization of the reflected waves is then measured by the analyzer.

Figure C1: Diagram showing the instrumentation of the ellipsometer.

In the dissertation, ellipsometric measurements are performed on a three phase optical system consisting of an ambient air-SAM-Si substrate, which made it very
possible to determine the thickness of the film once the refractive indexes for the SAMs are known.

*Experimental*

Ellipsometry data were collected with a Beaglehole picometer ellipsometer (Wellington, New Zealand). A photoelastic birefringence modulator was used with the modulation frequency set at 50 KHz. The light source was a HeNe laser (632.8 nm) and the detector was an end-on photomultiplier. Measurements were performed between 70° and 80° at 1° intervals.

The sample was placed onto the stage holder and the region of study was moved into the path of the laser. Using the stage adjuster knobs, the detector was aligned to ensure accurate and reliable results. Measurements were taken at a minimum of 3 separate locations along the substrate surface to ensure uniformity within the film layer.
Appendix D

Static Contact Angle Measurements

Overview

The static contact angle measurements of water on a substrate are an ideal method of determining the hydrophobicity or hydrophilicity of the surface. The surface interactions compete with the van der waals forces, dipole interactions, proton exchanges as well as hydrogen bonding that occurs within the water droplet. If the contact angle of water on a surface is less than 30 degrees, this is determined to be a hydrophilic surface while angles of 10 degrees and less are considered super hydrophilic. In this case, the water droplet completely wets the surface and an angle cannot be determined as seen in the picture below. On a hydrophobic surface however, water forms distinct droplets as the greater the hydrophobicity the greater the contact angle. Surfaces with contact angles greater than 90° are designated as hydrophobic. However the contact angle of water is not a good indicator of the wettability of other liquids on the same substrate.
There are many different methods to obtain the contact angle of a surface, however in this dissertation, the sessile drop method was utilized. This method is an optical contact angle method used to estimate wetting properties on a solid surface. The angle between the baseline of the drop and the tangent at the drop boundary is measured which makes it an ideal technique for SAM analysis on flat Si substrates.

**Experimentation**

The Kruss DSA10 was powered up and ensured that the solvent reservoirs are filled with HPLC grade water. Started the drop shape analysis (DSA) software and clicked for a live image using the upper utility panel of the. The Si substrate placed onto sample holder and raised so that the substrate can be seen in the live image of the camera.

The camera angle should be no more the 3 degrees above the substrate looking down onto the droplet. It may be easier to determine the baselines if 0 degrees is selected.

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Figure D1: Image showing the variability in contact angles and how they relate to hydrophobicity and hydrophilicity
and have the camera looking exactly horizontally to the drop. The camera angle does not significantly affect the reading however baseline inaccuracy is the primary contributor to contact angle inaccuracy.

![Diagram showing the instrumentation setup for making contact angle measurements.](image)

Auto-align the dispensing needle and then dispense 1 ul of water from the needle using the DSA software. Slowly raise the sample platform until the Si substrate touches the bottom of the droplet so that the adhesion to the surface will pry it from the needle. Ensure that it does not fall from the needle so as to minimize kinetic spreading of the droplet which can result in lower measured angles. Images of water droplets on a Si substrate which has been cleaned by piranha solution (left) and water droplet on a Si substrate after PEI SAM functionalization
Figure D3: Images obtained by the Instruments camera for a cleaned silicon wafer (top) and a silicon surface coated with a PEI-sil SAM (bottom)

Contact Angle Calculation

The Young-Laplace fitting model is the most complicated, but also the theoretically most exact method for calculating the contact angle of the sessile droplet. It takes the complete contour of the droplet into consideration and accounts for the weight of the liquid along with the interfacial effects. After the successful fitting of the YP
equation, the contact angle is determined as the slope of the contour line at the 3-phase contact point.

Once this Contact angle has been obtained the surface energy can be calculated using the equation of state derived from the equation of young. This model utilizes one contact angle from a liquid of known surface tension. The basic principle of this model is outlined below:

The balance between the forces which create a droplet onto the substrate gives rise to the equation of Young (B-1),

$$\gamma_2 = \gamma_{12} + \gamma_1 \cos \theta$$  \hspace{1cm} (B-1)

A second equation is required which describes the surface energy of the solid as a function of the interfacial tension of the solid/liquid and the surface energy of the liquid ($\sigma_1$) The work of adhesion ($W^a$) seen in equation B-2, serves as this link that can then be substituted into the Young Equation to yield the Young-Dupree Equation (B-3)

$$W^a = W_{12} = \gamma_1 + \gamma_2 - \gamma_{12}$$  \hspace{1cm} (B-2)

$$W^a = \gamma_1(1+\cos \theta)$$  \hspace{1cm} (B-3)
According to Good and Girifalco, the $W^a$ can be expressed as:

$$W^a = 2\Phi \left(\gamma_1\gamma_2\right)^{1/2}$$  \hspace{1cm} (B-4)

Which becomes equation B-5 when an equation of state is introduced for the interaction parameter ($\Phi$). The use of large data banks of contact angle data empirically determined an equation of state (B-5), where the constant $\beta$ in the exponent has a value of 0.0001247.

$$\cos \theta = -1 + 2\sqrt{\frac{\sigma_s}{\sigma_l}} e^{-\beta (\sigma_l - \sigma_s)^2}$$  \hspace{1cm} (B-5)

This equation allows for the calculation of the interfacial surface tension of the solid $\sigma_s$ from a single contact angle if the liquid surface tension ($\sigma_l$) is known:
REFERENCES


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