PREPARATION, CHARACTERIZATION AND PROPERTY STUDIES OF CARBON NANOSTRUCTURES DERIVED FROM CARBON RICH MATERIALS

SAJINI VADUKUMPULLY

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Abstract

Carbon nanomaterials have always been an area of interest for their applications in all the fields of science starting from materials science to biology. The current research is focused on low cost and simple methodologies to prepare functional carbon nanostructures from carbon rich precursors. Towards this goal, carbon nanofibers were isolated from soot and employed as an adsorbent for the removal of amines from waste water. Besides, various solution phase methods for the production of processable graphene nanosheets directly from graphite were explored. This has been achieved by both non-covalent stabilization and covalent functionalization of exfoliated graphene sheets. Covalent functionalizations enable the incorporation of various functional moieties onto graphene. The applicability of these functionalized graphene sheets in polymer composites and metal hybrids were systematically investigated. Incorporation of graphene improves the mechanical and thermal stability of the composites, along with an increase in the electrical conductance.

Keywords: carbon nanofibers, graphene, covalent and non-covalent functionalization, graphene/polymer composite, graphene/metal nanocomposites.
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# Table of Contents

Acknowledgments i  
Table of Contents ii  
Summary viii  
Abbreviations and Symbols x  
List of Tables xv  
List of Figures xvi  
List of Schemes xxiii  

## Chapter 1  
*Introduction – A Brief Review on Carbon Nanomaterials*

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Introduction</td>
<td>2</td>
</tr>
<tr>
<td>1.1</td>
<td>Carbon Nanomaterials</td>
<td>3</td>
</tr>
<tr>
<td>1.2</td>
<td>Graphene</td>
<td>5</td>
</tr>
<tr>
<td>1.2.1</td>
<td>Preparation of Graphene</td>
<td>6</td>
</tr>
<tr>
<td>1.2.1.1</td>
<td>Mechanical Exfoliation</td>
<td>7</td>
</tr>
<tr>
<td>1.2.1.2</td>
<td>Supported Growth</td>
<td>9</td>
</tr>
<tr>
<td>1.2.1.3</td>
<td>Wet Chemical Methods</td>
<td>13</td>
</tr>
<tr>
<td>1.2.1.3a</td>
<td>Graphenes from GO</td>
<td>14</td>
</tr>
<tr>
<td>1.2.1.3b</td>
<td>Unoxidized Graphene Sheets Directly from Graphite</td>
<td>15</td>
</tr>
<tr>
<td>1.2.1.3c</td>
<td>Molecular Approach for the Production of Graphene</td>
<td>17</td>
</tr>
<tr>
<td>1.2.1.4</td>
<td>Unzipping of CNTs</td>
<td>18</td>
</tr>
</tbody>
</table>
Chapter 2

Carbon Nanofibers Extracted from Soot as a Sorbent for the Determination of Aromatic Amines from Wastewater Effluent Samples

2.1 Introduction 70

2.2 Experimental Section 71

2.2.1 Reagents and Materials 71

2.2.2 Sample Preparation 72

2.2.3 Isolation of CNFs 72

2.2.4 Preparation of Electrospun CNF/PVA Composite Nanofiber Mats 72
| 2.2.5 | Materials Characterization | 73 |
| 2.2.6 | µ-SPE using Electrospun CNF/PVA Composite Nanofiber Mats | 74 |
| 2.2.7 | HPLC Analysis | 74 |
| 2.3 | Results and Discussion | 74 |
| 2.3.1 | Characterization of the CNFs | 74 |
| 2.3.2 | Analytical Evaluation of Electrospun CNF/PVA Composite Nanofiber Mats as Adsorbent for µ-SPE | 77 |
| 2.3.3 | Control Study | 78 |
| 2.3.4 | Extraction Time | 79 |
| 2.3.5 | Desorption Solvent | 80 |
| 2.3.6 | Sample Volume | 81 |
| 2.3.7 | Desorption Time | 82 |
| 2.3.8 | Effect of Ionic Strength | 83 |
| 2.3.9 | Effect of pH | 83 |
| 2.3.10 | Method Validation | 84 |
| 2.3.11 | Application of Method for Real Sample Analysis | 86 |
| 2.4 | Conclusions | 87 |
| 2.5 | References | 87 |

---

**Chapter 3**

*Cationic Surfactant Mediated Exfoliation of Graphite into Graphene Nanosheets and its Field Emission Properties*

| 3.1 | Introduction | 94 |
| 3.2 | Experimental Section | 96 |
Chapter 4

Flexible Conductive Graphene/Poly(vinyl chloride) Composite Thin Films with High Mechanical Strength and Thermal Stability

4.1 Introduction 113

4.2 Experimental Section 115

4.2.1 Materials 115

4.2.2 Preparation of Processable Graphene Nanosheets 115

4.2.3 Fabrication of Graphene/PVC Composite Thin Films 115

4.2.4 Instrumentation 116

4.2.5 Mechanical Characterization 116

4.2.6 Electrical Characterization 117

4.3 Results and Discussion 117
4.3.1 Characterization of Graphene and Graphene/PVC Thin Films 117
4.3.2 Mechanical Characterization of the Graphene/PVC Thin Films 120
4.3.3 Dynamic Mechanical Thermal Analysis 122
4.3.4 Electrical Properties 127
4.4 Conclusions 128
4.5 References 129

Chapter 5

Functionalization of Surfactant Wrapped Graphene Nanosheets with Alkylazides for Enhanced Dispersibility

5.1 Introduction 134
5.2 Experimental Section 136
5.2.1 Materials 136
5.2.2 Analysis and Instruments 136
5.2.3 Preparation of CTAB Stabilized Graphene Sheets 137
5.2.4 General Synthetic Procedure for Alkylazides 137
5.2.5 Synthesis of 11-azidoundecanol (AOU) 138
5.2.6 Synthesis of 11-azidoundecanoic acid (AUA) 138
5.2.7 Functionalization of CTAB Stabilized Graphene Nanosheets with 11-azidoundecanoic acid (AUA) 139
5.2.8 Preparation of Gold/Graphene Nanocomposites 139
5.3 Results and Discussion 140
5.3.1 Characterization of the Functionalized Graphene Nanosheets 140
Chapter 6

Bromination of Graphite - A Novel Route for the Exfoliation and Functionalization of Graphene Sheets

6.1 Introduction 158

6.2 Experimental Section 159

6.2.1 Materials 159

6.2.2 Bromination of Graphite 160

6.2.3 Spreading of Brominated Graphite 160

6.2.4 Alkylation of Brominated Graphene 160

6.2.5 Suzuki Coupling Reaction with Brominated Graphene 161

6.2.6 Characterization 161

6.3 Results and Discussion 162

6.3.1 Brominated Graphite and its Stretching 162

6.3.2 Alkylation of the Brominated Graphite 165

6.3.3 Arylation of the Brominated Graphite by Suzuki Coupling Reaction 170

6.4 Conclusions 173

6.5 References 173

Chapter 7

Conclusions and Future Prospectives 177
Appendix

List of publications and presentations
Summary

Nanostructures made of carbon have always been an area of interest for researchers for their direct applications in all the fields of science starting from material science to biology. Most of the reported procedures for the preparation of functional carbon nanomaterials rely on expensive equipments and resources, high temperature and pressure etc. Besides, most of the methods generate desired nanomaterials along with significant amount of carbonaceous impurities such as amorphous carbon and catalyst particles. Hence a post treatment is required before the material can be employed for certain applications. The main interest of our current work was to pay attention to low cost, simple, environmentally friendly methodology to generate functional carbon nanostructures.

A brief summary of all types of carbon nanostructures, mainly graphene, its methods of preparation, characterization techniques, properties, functionalization techniques and applications have been explained in Chapter 1.

Chapter 2 deals with the isolation and characterization of carbon nanofibers (CNFs) obtained from soot collected from burning of plant seed oil. The isolation is accomplished by solvent extraction. The structure of CNFs is thoroughly investigated using various spectroscopic and microscopic techniques. Moreover, the application of CNFs in water purification is also investigated. CNFs are incorporated into a polymer matrix via electrospinning and the resultant composite material is used as a µ-solid phase extraction device for the extraction and preconcentration of aromatic amines from water samples.

In Chapter 3 we investigated the possibility of solution based exfoliation of graphite into graphene nanosheets without any oxidative or thermal treatments. The combined effect of ultrasonication and non-covalent functionalization using
surfactants are employed for the exfoliation and dispersion of graphene nanosheets in common organic solvents.

**Chapter 4** describes the use of surfactant stabilized graphene nanosheets as reinforcing filler in poly(vinyl chloride) (PVC) matrix at very low loading levels. The composite thin films are prepared by solution phase blending in which PVC is blended with different amounts of graphene nanosheets. Mechanical, thermal and electrical properties of the composite films are investigated in detail.

In **Chapter 5**, the applicability of covalent functionalization on surfactant stabilized graphene nanosheets are explored, where the dispersibility of the graphene nanosheets are considerably enhanced. A series of nitrenes are employed for the covalent functionalization and the role of functional groups on the nitrenes in stabilizing the graphene dispersion is also investigated. Besides, the reactive sites on graphene nanosheets are marked with metal nanoparticles. This approach provides a useful platform for the fabrication of graphene/metal nanocomposites.

**Chapter 6** demonstrates a simple and scalable surface treatment for the exfoliation and subsequent functionalization of graphene sheets. Bromine atoms are covalently attached to graphite, which can be easily substituted with alkylamines or boronic acids, which help in enhancing the dispersibility and processability. This method provides an easy and direct route towards the preparation of highly functionalized graphene sheets.
### Abbreviations and Symbols

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1D</td>
<td>One dimensional</td>
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<tr>
<td>2D</td>
<td>Two dimensional</td>
</tr>
<tr>
<td>3D</td>
<td>Three dimensional</td>
</tr>
<tr>
<td>2L</td>
<td>Bilayer</td>
</tr>
<tr>
<td>Å</td>
<td>Angstrom</td>
</tr>
<tr>
<td>ABA</td>
<td>4-aminobenzoic acid</td>
</tr>
<tr>
<td>AES</td>
<td>Auger electron spectroscopy</td>
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<tr>
<td>AFM</td>
<td>Atomic force microscopy</td>
</tr>
<tr>
<td>ARPES</td>
<td>Angle resolved photoemission spectroscopy</td>
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<td>AUA</td>
<td>11-azidoundecanoic acid</td>
</tr>
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<td>AUO</td>
<td>11-azidoundecanol</td>
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<td>CDCl₃</td>
<td>Chloroform-d</td>
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<td>C₆F₆</td>
<td>Hexafluorobenzene</td>
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<tr>
<td>C₆F₅CF₃</td>
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<td>C₆F₅CN</td>
<td>Pentafluorobenzenitrile</td>
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<td>C₅F₅N</td>
<td>Pentafluoropyridine</td>
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<td>CHCl₃</td>
<td>Chloroform</td>
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<td>CNF</td>
<td>Carbon nanofibers</td>
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<td>CNT</td>
<td>Carbon nanotubes</td>
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<td>CTAB</td>
<td>Cetyltrimethylammonium bromide</td>
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<tr>
<td>CVD</td>
<td>Chemical vapour deposition</td>
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<tr>
<td>DCB</td>
<td>Dichlorobenzene</td>
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<tr>
<td>DCC</td>
<td>$N, N$-dicyclohexylcarbodiimide</td>
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<tr>
<td>Abbreviation</td>
<td>Full Form</td>
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<tr>
<td>DCM</td>
<td>Dichloromethane</td>
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<td>DMA</td>
<td>Dimethylamine</td>
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<td>Dynamic mechanical analyzer</td>
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<td>DMF</td>
<td>N,N-dimethyl formamide</td>
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<td>Dimethyl sulfoxide</td>
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<td>DNA</td>
<td>Deoxyribonucleic acid</td>
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<td>DSC</td>
<td>Differential scanning calorimetry</td>
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<td>Energy dispersive X-ray analysis</td>
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<td>Expanded graphite</td>
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<td>Electron impact</td>
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<td>F4-TCNQ</td>
<td>Tetrafluorotetracyanoquinodimethane</td>
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<td>FESEM</td>
<td>Field emission scanning electron microscopy</td>
</tr>
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<td>FET</td>
<td>Field effect transistor</td>
</tr>
<tr>
<td>FGS</td>
<td>Functionalized graphene sheets</td>
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<td>FTIR</td>
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</tr>
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<td>gm</td>
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<td>GNR</td>
<td>Graphene nanoribbons</td>
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<td>GO</td>
<td>Graphene oxide</td>
</tr>
<tr>
<td>h</td>
<td>Hours</td>
</tr>
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<td>Hexabenzocoronene</td>
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<td>HCl</td>
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<td>HF</td>
<td>Hydrogen fluoride</td>
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<tr>
<td>H$_2$SO$_4$</td>
<td>Sulfuric acid</td>
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<td>HOPG</td>
<td>Highly ordered pyrolytic graphite</td>
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<td>HPLC</td>
<td>High pressure liquid chromatography</td>
</tr>
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<td>HSQ</td>
<td>Hydrogensilsesquioxane</td>
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<td>Hz</td>
<td>Hertz</td>
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<td>HTC</td>
<td>Hydrothermal carbonization</td>
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<td>ITO</td>
<td>Indium tin oxide</td>
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<tr>
<td>KMnO$_4$</td>
<td>Potassium permanganate</td>
</tr>
<tr>
<td>KOH</td>
<td>Potassium hydroxide</td>
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<tr>
<td>LCD</td>
<td>Liquid crystal display</td>
</tr>
<tr>
<td>LEED</td>
<td>Low energy electron diffraction</td>
</tr>
<tr>
<td>LiAlH$_4$</td>
<td>Lithium aluminium hydride</td>
</tr>
<tr>
<td>LLE</td>
<td>Liquid-liquid-extraction</td>
</tr>
<tr>
<td>LLLLME</td>
<td>Liquid-liquid-liquid micro-extraction</td>
</tr>
<tr>
<td>LOD</td>
<td>Limit of detection</td>
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<td>LOQ</td>
<td>Limit of quantitation</td>
</tr>
<tr>
<td>m</td>
<td>Multiplet</td>
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<tr>
<td>µg</td>
<td>Microgram(s)</td>
</tr>
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<td>µ-SPE</td>
<td>Micro-solid phase extraction</td>
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<tr>
<td>Me$_4$Si</td>
<td>Tetramethylsilane</td>
</tr>
<tr>
<td>mg</td>
<td>Milligram(s)</td>
</tr>
<tr>
<td>ml</td>
<td>Milliliter(s)</td>
</tr>
<tr>
<td>mmol</td>
<td>Millimole(s)</td>
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<tr>
<td>mV</td>
<td>Millivolt(s)</td>
</tr>
<tr>
<td>MWNT</td>
<td>Multi-walled nanotubes</td>
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<tr>
<td>Term</td>
<td>Definition</td>
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<td>--------------</td>
<td>-------------------------------------------</td>
</tr>
<tr>
<td>m/z</td>
<td>Mass/charge ratio</td>
</tr>
<tr>
<td>NH₃</td>
<td>Ammonia</td>
</tr>
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<td>NLO</td>
<td>Non-linear optics</td>
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<td>NMP</td>
<td>N-methylpyrrolidone</td>
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<td>NMR</td>
<td>Nuclear magnetic resonance</td>
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<td>ODA</td>
<td>Octadecylamine</td>
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<td>ODCB</td>
<td>1,2-dichlorobenzene</td>
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<td>PANI</td>
<td>Polyaniline</td>
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<td>PDDA</td>
<td>poly(diallyldimethyl ammonium chloride)</td>
</tr>
<tr>
<td>PDI</td>
<td>Perylenediimide</td>
</tr>
<tr>
<td>PEG</td>
<td>Polyethylene glycol</td>
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<td>PES</td>
<td>Photoelectron spectroscopy</td>
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<td>PFPA</td>
<td>Perfluorophenylazide</td>
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<td>Phe(N₃)</td>
<td>Azido-phenylalanine</td>
</tr>
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<td>PMMA</td>
<td>Poly(methyl methacrylate)</td>
</tr>
<tr>
<td>PP</td>
<td>Polypropylene</td>
</tr>
<tr>
<td>PPA</td>
<td>Poly(phosphoric acid)</td>
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<td>PPy</td>
<td>Polypyrrole</td>
</tr>
<tr>
<td>PS</td>
<td>Polystyrene</td>
</tr>
<tr>
<td>PSS</td>
<td>Poly(sodium 4-styrenesulfonate)</td>
</tr>
<tr>
<td>PVA</td>
<td>Poly(vinyl alcohol)</td>
</tr>
<tr>
<td>PVC</td>
<td>Poly(vinyl chloride)</td>
</tr>
<tr>
<td>PyS</td>
<td>Pyrene-1-sulfonic acid sodium salt</td>
</tr>
<tr>
<td>s</td>
<td>Singlet</td>
</tr>
<tr>
<td>RSD</td>
<td>Relative standard deviation</td>
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<td>Abbreviation</td>
<td>Description</td>
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</tr>
<tr>
<td>SAED</td>
<td>Selected area electron diffraction</td>
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<tr>
<td>SDBS</td>
<td>Sodium dodecylbenzene sulphonate</td>
</tr>
<tr>
<td>SDS</td>
<td>Sodium dodecyl sulfate</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>SiC</td>
<td>Silicon carbide</td>
</tr>
<tr>
<td>Si₃N₄</td>
<td>Silicon nitride</td>
</tr>
<tr>
<td>SMA</td>
<td>Styrene-maleic anhydride</td>
</tr>
<tr>
<td>SPANI</td>
<td>Sulfonated polyaniline</td>
</tr>
<tr>
<td>SPE</td>
<td>Solid-phase extraction</td>
</tr>
<tr>
<td>SPME</td>
<td>Solid-phase microextraction</td>
</tr>
<tr>
<td>SPR</td>
<td>Surface plasmon resonance</td>
</tr>
<tr>
<td>STM</td>
<td>Scanning tunnelling microscopy</td>
</tr>
<tr>
<td>SWNT</td>
<td>Single-walled nanotubes</td>
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<tr>
<td>t</td>
<td>Triplet</td>
</tr>
<tr>
<td>TCB</td>
<td>Trichlorobenzene</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermo gravimetric analysis</td>
</tr>
<tr>
<td>THF</td>
<td>Tetrahydrofuran</td>
</tr>
<tr>
<td>TSG</td>
<td>Turbostratic graphite</td>
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<tr>
<td>UV-vis</td>
<td>Ultraviolet-visible spectroscopy</td>
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<tr>
<td>WPU</td>
<td>Polyurethane</td>
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<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>δ</td>
<td>Chemical shift (in NMR spectroscopy)</td>
</tr>
<tr>
<td>Table No.</td>
<td>List of Tables</td>
</tr>
<tr>
<td>----------</td>
<td>----------------</td>
</tr>
<tr>
<td><strong>Chapter 1</strong></td>
<td></td>
</tr>
<tr>
<td>Table 1.1</td>
<td>Summary of supported graphene growth on both metals and carbide substrates.</td>
</tr>
<tr>
<td>Table 1.2</td>
<td>Comparison of different wet chemical approaches to produce graphene suspensions.</td>
</tr>
<tr>
<td>Table 1.3</td>
<td>Comparison of different functionalization methods of graphene.</td>
</tr>
<tr>
<td>Table 1.4</td>
<td>Major applications of graphene and graphene based composite materials.</td>
</tr>
<tr>
<td><strong>Chapter 2</strong></td>
<td></td>
</tr>
<tr>
<td>Table 2.1</td>
<td>Quantitative data: linearity, precision (RSD), limit of detection (S/N = 3), enhancement factors and linear regression data obtained for anilines by the electrospun CNF/PVA composite membrane microextraction coupled with HPLC-UV.</td>
</tr>
<tr>
<td>Table 2.2</td>
<td>Concentrations of target aniline compounds (µg/l) in waste water samples and the average recoveries determined at 5 µg/l (*n.d-not detected. Relative recovery values of spiked wastewater sample at 5 µg/l compared to that of spiked pure water).</td>
</tr>
<tr>
<td>Figure No.</td>
<td>List of Figures</td>
</tr>
<tr>
<td>-----------</td>
<td>----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>Chapter 1</td>
<td></td>
</tr>
<tr>
<td>Figure 1.1</td>
<td>The structures of (A) diamond (B) graphite (C) fullerene ( \text{C}_{60} ) (D) CNTs and (E) graphene.</td>
</tr>
<tr>
<td>Figure 1.2</td>
<td>Schematic illustrations of the structures of (A) armchair (B) zigzag (C) chiral SWNT and (D) TEM image of a MWNT containing a concentrically nested array of nine SWNTs.</td>
</tr>
<tr>
<td>Figure 1.3</td>
<td>Atomic structure of graphene.</td>
</tr>
<tr>
<td>Figure 1.4</td>
<td>Present techniques for making graphene.</td>
</tr>
<tr>
<td>Figure 1.5</td>
<td>Schematic of “Scotch tape” peeling off method to produce graphene.</td>
</tr>
<tr>
<td>Figure 1.6</td>
<td>(A) Structure of HBC and (B) structure of the largest graphene like molecule reported with 222 carbon atoms.</td>
</tr>
<tr>
<td>Figure 1.7</td>
<td>Chemical structure of a small edge-carboxylated graphene nanoflake.</td>
</tr>
<tr>
<td>Figure 1.8</td>
<td>Schematic representation of the reaction between graphite and ABA as a molecular wedge via Friedel Crafts acylation in PPA/P( \text{2O}_3 ) medium.</td>
</tr>
<tr>
<td>Figure 1.9</td>
<td>Schematic representation of alkylation of fluorinated graphene sheets (blue: fluorine; yellow: -R group).</td>
</tr>
<tr>
<td>Figure 1.10</td>
<td>Nitrene addition to exfoliated graphite in refluxing ODCB.</td>
</tr>
<tr>
<td>Figure 1.11</td>
<td>Fabrication of covalently immobilized graphene on silicon wafer via the PFPA-silane coupling agent.</td>
</tr>
</tbody>
</table>
Figure 1.12  Schematic of self-assembly of Au NPs and PDDA-functionalized graphene sheets.

Chapter 2

Figure 2.1  SEM images of the raw soot (A), extracted CNFs (B) and TEM of CNFs (C) obtained from the soot by THF extraction. Inset in C shows the SAED pattern obtained from a single nanofiber.

Figure 2.2  XRD pattern obtained for the isolated CNFs.

Figure 2.3  FTIR (A) and the Raman spectra (B) of the CNFs.

Figure 2.4  HPLC chromatogram obtained for standard 1 mg/l. Peak (1) 3-nitroaniline; (2) 4-chloroaniline; (3) 4-bromoaniline and (4) 3,4-dichloroaniline.

Figure 2.5  Schematic of the extraction and desorption steps involved in electrospun CNF/PVA composite membrane μ-solid phase extraction.

Figure 2.6  Comparison of PVA and composite fiber mats (Extraction conditions are as follows: 10 ml spiked 25 µg/l water solution, no salt added and pH adjusted, extraction time of 30 min, desorption time of 15 min in 100 µl of acetonitrile).

Figure 2.7  Plot of HPLC peak area vs the extraction time (Extraction conditions are as follows: 10 ml spiked 25 µg/l water solution, no salt added and no pH adjustment, desorption time of 15 min in 100 µl of acetonitrile).

Figure 2.8  Comparison of different desorption solvents (Extraction conditions are as follows: 10 ml spiked 25 µg/l water solution, no adjustment of salt and pH, extraction time of 40 min, desorption time of 15 min in 100 µl of acetonitrile).
Figure 2.9  Influence of sample volume on the extraction efficiency (Extraction conditions are as follows: 10 ml spiked 25 µg/l water solution no adjustment of salt content and pH, extraction time of 40 min, desorption time of 15 min in 75 µl of acetonitrile).

Figure 2.10  Plot of HPLC peak area vs desorption time (Extraction conditions are as follows: 30 ml spiked 25 µg/l water solution no adjustment of salt content and pH, extraction time of 40 min, desorption in 75 µl of acetonitrile).

Figure 2.11  Effect of salt addition on the extraction efficiency (Extraction conditions are as follows: 30 ml spiked 25 µg/l water solution, no pH adjustment, extraction time of 40 min, desorption in 75 µl of acetonitrile).

Figure 2.12  Effect of sample pH on the extraction efficiency (Extraction conditions as follows: 30 ml spiked water solution (25 µg/l), no salt addition, extraction time of 40 min, desorption time of 15 min in 75 µl of acetonitrile).

Chapter 3

Figure 3.1  SEM image of the exfoliated product in acetic acid.

Figure 3.2  FESEM (A) and TEM (B) images of SDS stabilized graphene sheets. Inset of figure 3.2B shows the HRTEM image of one the edges of the multilayered graphite flake.

Figure 3.3  (A) UV-vis spectrum of the CTAB stabilized graphene sheets dispersed in DMF. Inset shows a photograph of the DMF solution. SEM of (B) HOPG and (C) the CTAB stabilized exfoliated graphene.

Figure 3.4  (A) TEM image of surfactant stabilized graphene sheets. (B) HRTEM image of a bilayer graphene sheet. (C) STM image of a part of the monolayer graphene (inset highlights the hexagonal lattice of the monolayer). (D) Section analysis along the blue line which showing a width of 1.148 nm for 4 hexagons and (E) along the green
line which showing a width of 0.424 nm for 3 C-C bonds.

**Figure 3.5**  (A) Topographic view (10 × 10 µm) of the graphene layers spin coated on mica. (B) AFM image of a single graphene sheet (1 × 1 µm). (C) Height profile of the image 3B. Statistical analysis of the AFM images of 60 nanosheets: (D) thickness, (E) length and (F) width of the flakes.

**Figure 3.6**  (A) Raman spectra of HOPG and the CTAB stabilized graphene nanosheets deposited on Si and (B) EDX spectrum.

**Figure 3.7**  (A) Schematic representation of the experimental set up for field emission measurement. (B) Graph showing the field emission current density vs applied electric field. (C) Fowler - Nordheim plot indicating the field emission characteristics of exfoliated graphene nanosheets.

**Chapter 4**

**Figure 4.1**  (A) AFM image of the exfoliated graphene nanosheets, (B) height profile of one of the sheets, (C) FESEM image of graphene/PVC composite thin film with 2 wt% concentration of graphene and (D) FESEM image of the fractured end of the composite film after mechanical testing.

**Figure 4.2**  XRD of graphene deposited on glass (trace a), 2 wt% graphene/PVC composite film (trace b) and pure PVC powder (trace c).

**Figure 4.3**  Raman spectra of pure graphene (trace a), 2 wt% graphene/PVC composite film (trace b) and pure PVC powder (trace c).

**Figure 4.4**  (A) Representative stress strain curves for various weight fractions of the graphene/PVC composite films and (B) the calculated Young’s modulus based on the slope of the elastic region.
Figure 4.5 Mechanical properties of PVC thin films with different graphene loadings when stretched at the rate of 0.01 N/min at 20 °C.

Figure 4.6 (A) Storage modulus and (B) Tan δ curves for the graphene/PVC films when deformed at constant amplitude of 0.1% at a frequency of 1 Hz at various temperatures.

Figure 4.7 Graphs showing the temperature dependence of the relative storage modulus at (A) low temperature regime and (B) glass transition temperature regime.

Figure 4.8 Graph showing the glass transition temperature ($T_g$) and the loss factor (Tan δ) values at various weight fractions of graphene in PVC matrix.

Figure 4.9 (A) TGA curves for graphene/PVC composite films and (B) DSC curves to determine the glass transition temperature.

Figure 4.10 Graph showing the influence of exfoliated graphene on the electrical conductivity of PVC.

Chapter 5

Figure 5.1 (A) AFM image of the CTAB stabilized graphene sheets and (B) corresponding section analysis.

Figure 5.2 SEM images of (A) dodecylazide functionalized graphene sheets and (B) hexylazide functionalized graphene sheets.

Figure 5.3 TEM images of (A) AUO functionalized graphene sheets and (B) corresponding gold/graphene nanocomposite.

Figure 5.4 TEM images of AUA functionalized graphene sheets, with 1:1 weight ratio of graphene vs AUA used. Inset clearly shows the settled particles in the respective dispersed solutions in toluene. All the sheets were found to settle down within 1 h.
Figure 5.5  TEM images of (A) CTAB stabilized and (B) AUA functionalized graphene sheets. (C) FTIR of AUA and AUA functionalized graphene sheets (trace A and B, respectively) and (D) Raman spectra of CTAB stabilized (trace 1), AUA functionalized graphene sheets with 1:1 and 1:10 w/w of graphene to AUA.

Figure 5.6  AFM images of (A) the AUA functionalized graphene sheets and (B) the section analysis.

Figure 5.7  Statistical analysis on the thickness of the AUA functionalized graphene sheets.

Figure 5.8  STM images of (A) CTAB stabilized and (B) AUA functionalized graphene sheets.

Figure 5.9  (A) UV-vis spectra of the AUA functionalized graphene sheets (trace A) and that of the gold/graphene nanocomposites (trace B) solutions. Inset of figure 5.9A shows the photograph of (A) functionalized graphene solution and that of (B) the gold/AUA graphene composite in DMF. (B) TEM image and (C) the AFM image with (D) the cross-section analysis of the gold/graphene nanocomposite sheets.

Figure 5.10  I-V plots of films of (A) AUA functionalized graphene sheets and (B) gold/graphene nanocomposites.

Chapter 6

Figure 6.1  FESEM (A) and AFM (B) image of the brominated graphite drop-casted from toluene suspension.

Figure 6.2  FESEM (A) and TEM (B) image of the brominated graphite sample deposited from water-toluene interface; FESEM (C) and (D) TEM image of the 1:0.02 v/v graphene/MWNT composite.
Figure 6.3  (A) AFM image of the brominated graphite sample deposited from water-toluene interface and (B) AFM image of the 1:0.02 v/v graphene/MWNT composite.

Figure 6.4  (A) Raman spectra of (a) pure graphite (b) brominated graphite (c) alkylated graphene and (d) debrominated graphene sheets after alkylation and (B) FTIR spectra of (a) brominated graphite (b) alkylated and (c) debrominated sheets after alkylation.

Figure 6.5  Weight loss of (a) brominated graphite and (b) dodecylated graphite determined by TGA analyses in nitrogen.

Figure 6.6  (A) FESEM and (B) AFM images of the dodecylated graphene sample (without sonication).

Figure 6.7  (A) AFM image of the dodecylated graphene sheets after dispersion, (B) corresponding section analysis; and (C) TEM image.

Figure 6.8  I-V plots of drop casted films of (a) brominated graphite (b) dodecylated graphene and (c) debrominated product after dodecylation.

Figure 6.9  Absorption (A) and emission (B) spectra for (a) Ph-BTP (b) G-BTP excited at 410 nm; Absorption (C) and emission (D) spectra for (a) Ph-Py (b) G-Py excited at 340 nm.

Figure 6.10  Raman spectra of (A) G-BTP (a - brominated graphite; b - G-BTP; c - debrominated G-BTP) and (B) G-Py (a - brominated graphite; b - G-Py; c - debrominated G-Py).

Figure 6.11  (A) TEM and (B) AFM image of bithiophene coupled graphene; (C) TEM and (D) AFM image of pyrene coupled graphene.
### Scheme No | List of Schemes | Page No.
--- | --- | ---

#### Chapter 1

**Scheme 1.1** Proposed mechanism for the MWNT unzipping. First step (2) is the formation of manganate ester, followed by formation of dione (3), and subsequent induced strain causes the ring opening (4 and 5).

19

**Scheme 1.2** Schematic showing various covalent functional reactions of GO.

24

#### Chapter 3

**Scheme 3.1** Schematic of cetyltrimethylammonium bromide (CTAB) assisted exfoliation.

95

#### Chapter 5

**Scheme 5.1** Schematic representation of the covalent functionalization of graphene sheets with various alkylazides.

135

#### Chapter 6

**Scheme 6.1** Schematic representation of the bromination and subsequent alkylation/arylation using dodecylamine and aryloboronic acids. Reaction conditions: (a) dodecylamine, \((\text{C}_2\text{H}_5)_3\text{N}\), toluene, reflux, 24 h. (b) pyrene 1-boronic acid/5-hexyl-2,2'-bithiopheneboronic acid pinacol ester, \(\text{Pd} (0), \text{K}_2\text{CO}_3\), DMF, 85 °C, 48 h.

159
Chapter 1

Introduction – A Brief Review on Carbon

Nanomaterials
1 Introduction

‘Carbon’ is a unique chemical element in the periodic table, which is known to man since antiquity. Carbon and its compounds form the basis of all known forms of life on earth. The abundance along with diverse properties makes this element a unique one. Different allotropes of carbon exist in nature such as graphite, diamond, fullerenes and amorphous carbon. Physical and chemical properties of carbon vary in each of the allotropes. For example, diamond is one of the hardest materials existing in nature and graphite is as the soft materials known. Moreover, diamond has $sp^3$ hybridized carbon atoms forming an extended three dimensional network, whereas carbon atoms are $sp^2$ hybridized in graphite forming planar sheets. Figure 1.1 shows the structures of some of the carbonaceous materials existing in nature.

![Figure 1.1](image)

Figure 1.1 The structures of (A) diamond (B) graphite (C) fullerene ($C_{60}$) (D) CNTs and (E) graphene.

The importance and uniqueness of carbon have now been extended to nanomaterials. Carbon based nanomaterials have attracted worldwide attention in the past 20 years because of their typical chemical, physical, electrical, thermal and mechanical properties.\textsuperscript{1-10} Some of the extensively studied structures are fullerenes, nanotubes,
nanofibers, nanodiamond and most recently, graphene. This chapter gives a brief review on the structure, preparation, characterization, properties, reactions and applications of carbon nanomaterials, in particular, graphite and graphene.

1.1 Carbon Nanomaterials

Fullerenes, carbon nanotubes (CNTs), carbon nanofibers (CNFs) and nanodiamond are some of the well studied carbon nanostructures. Fullerenes are the newest carbon allotrope discovered in 1985 by Kroto and co-workers. Structure of fullerenes is like that of a soccer ball and each fullerene \( (C_n) \) consists of 12 pentagonal rings and any number of hexagonal rings \( m \), such that \( m = (C_n - 20)/2 \) by Euler’s theory.  

On the other hand, CNTs are unique tubular structures made of sp\(^2\) hybridized carbon atoms with high length/diameter ratio. These structures were first observed by Iijima in 1991. There are mainly two types of CNT, the first type called multi-walled nanotubes (MWNT) are closer to hollow graphite fibers and are made of concentric cylinders placed around a common central hollow with spacing between the layers close to that of interlayer spacing in graphite (≈ 0.34 nm).

Figure 1.2 Schematic illustrations of the structures of (A) armchair (B) zigzag (C) chiral SWNT and (D) TEM image of a MWNT containing a concentrically nested array of nine SWNTs. (adapted from ref. 15)
The second type known as single-walled nanotubes (SWNT) is identical to a fullerene fiber. It consists of a single graphite sheet seamlessly wrapped into a cylindrical tube.

CNFs are cylindrical nanostructures with graphene layers arranged as stacked cones, cups or plates. They have lengths in the order of micrometers and the diameter varies between tens of nanometers up to 200 nm. Their mechanical strength and electric properties are similar to CNTs while their size and graphitic ordering can be well controlled.\textsuperscript{16,17}

Diamond structures at the nanoscale (length $\sim$ 1 to 100 nm) include pure-phase diamond films, diamond particles, one dimensional (1D) diamond nanorods and two dimensional (2D) diamond nanoplatelets. There is a special class of nanodiamond material called as ‘\textit{ultra-nanocrystalline}’ diamond with basic diamond constituents having the size of just a few nanometers, which distinguishes it from other diamond based nanostructures with characteristic sizes above $\sim$ 10 nm.\textsuperscript{4,18}

Generally, all of these carbon nanostructures are prepared by laser ablation of graphite or coal,\textsuperscript{19-21} metal-catalyzed arc evaporation,\textsuperscript{22-25} catalytic chemical vapour deposition (CVD),\textsuperscript{25-28} pyrolysis,\textsuperscript{29} solvothermal reduction,\textsuperscript{30} hydrothermal carbonization (HTC)\textsuperscript{31} and detonation of a mixture of explosives and hexogen composed of C, N, O and H with a negative oxygen balance so that ‘\textit{excess}’ carbon is present in the system.\textsuperscript{32} The structures obtained vary upon the resources, decomposition temperature and deposition kinetics. These materials are generally characterized using Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), X-ray crystallography and microscopic techniques such as scanning electron microscopy (SEM), transmission electron microscopy (TEM), scanning tunnelling microscopy (STM) and atomic force microscopy (AFM).

Carbon nanomaterials are widely used in various fields such as storage devices,
photovoltaics, sensors, field emission displays, field effect transistors, catalysts, for bio imaging, drug delivery, water filtration, as AFM probes, high strength composites and in CO$_2$ sequestration.$^{33-43}$ Even though these nanomaterials have many interesting features, some of the problems involving aggregation, bundling and difficulty in controlling the processability forced researchers to look out for alternatives with superior properties. These investigations led to the discovery of planar single atom thick sheet of carbon known as graphene. Discovery of graphene revolutionized the material science community and eventually won the Nobel Prize in Physics in 2010. Subsequent section gives an updated review on the synthesis, properties, functionalizations and important applications of graphene.

1.2 Graphene

Graphene is an infinite single atom thick sheet of sp$^2$ bonded carbon atoms derived from graphite. The ideal interplanar distance of graphite is 0.345 nm, and hence the ideal thickness of single layer graphene should be 0.345 nm.$^{44}$ It can be considered as the mother form of all other carbon nanomaterials, which can be wrapped into 0D fullerenes, rolled into 1D CNTs or stacked to form 3D graphite.

![Figure 1.3 Atomic structure of graphene. (redrawn from ref. 44)](image)
As can be seen in figure 1.3, the lattice of graphene is made up of two interpenetrating triangular sub-lattices shown in two different colours. The atoms of one sub-lattice (A-blue) are at the centre of the triangle defined by the other lattice (B-red) with C–C inter atomic length of 1.42 Å. One s orbital and two in-plane p orbitals in each carbon atom contributes to the mechanical stability of graphene sheet. The remaining p orbital, perpendicularly oriented to the molecular plane hybridizes to form the conduction (\(\pi\)) and valence (\(\pi^*\)) bands, which is responsible for the planar conduction.

While the term “graphene” has been known only as a theoretical concept, the experimental investigations of graphene properties were inexistent till the recent years because of the difficulty in identifying and isolating a single atom thick sheet. This challenge was solved in 2004, when Geim and co-workers showed that monolayers of graphene could be produced from graphite by simple “Scotch tape” peeling method. The remarkable properties of graphene reported so far include high values of its surface area (\(\sim 2500 \text{ m}^2/\text{g}\)), thermal conductivity (\(\sim 5000 \text{ W/m K}\)), intrinsic charge mobility (\(\sim 200,000 \text{ cm}^2/\text{V s}\)), Young’s modulus (\(\sim 1 \text{ T Pa}\)) and optical transparency (\(\sim 97\%\)).

### 1.2.1 Preparation of Graphene

For many years, graphene was a concept used by solid state theoreticians and later on by some experimentalists to investigate the structure of graphitic monolayers on certain metal substrates. Efforts to slim down graphite into graphene has started in 1960’s, when Fernandez-Moran extracted millimeter sized graphite sheets as thin as 5 nm by mechanical exfoliation. Later in 1962, colloidal suspensions of single and bi layer graphite oxide were observed with electron microscopy by Boehm et al. The interest in graphene was renewed after the discovery of fullerenes and CNTs in
1990’s, when several groups showed that graphite can be thinned down by various techniques such as AFM manipulation and rubbing of pre-fabricated graphite pillars on certain substrates. But these approaches failed to produce isolated single layer graphene sheets. Later in 2004, Geim et al, presented a simple method to produce single layer graphene in which graphite crystal was repeatedly cleaved with an adhesive tape followed by transfer of the thinned down graphite onto oxidized silicon surface. This discovery became a landmark in graphene research. Eventually, chemists and physicists came up with different methods for the production of graphene such as epitaxial growth, CVD and wet chemical routes. Figure 1.4 shows a summary of different techniques used for the production of graphene, which are discussed in detail in the following sections.

**Figure 1.4** Present techniques for making graphene.

### 1.2.1.1 Mechanical Exfoliation

Graphite is stacked layers of many graphene sheets bonded together by weak van der Waals forces. The interlayer van der Waals interaction energy in graphite is about 2 eV/nm² and the force required to overcome this energy is of the order of 300 nN/µm². This force can be easily achieved using mechanical or chemical energy.
The first attempt in this direction was by Viculis et al., who used potassium metal to intercalate graphite and then exfoliate it with ethanol to form the dispersion of carbon sheets.\textsuperscript{52b} TEM analysis of the suspension showed presence of $40 \pm 15$ layers in each sheet. Mechanical exfoliation of graphite using a Scotch tape allowed preparation of a few layers of graphene.\textsuperscript{45}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{fig15}
\caption{Schematic of “Scotch tape” peeling off method to produce graphene.}
\end{figure}

This method consists of repeated stick and peel process using a common adhesive tape, which brings down the thick graphite flake to a monolayer thin sample (Figure 1.5). Smooth and thin fragments on the tape are then transferred to cleaned substrates by a gentle press of the tape. The most crucial aspect of this process is the suitable choice of substrate to visualize graphene.\textsuperscript{53} Visibility of graphene under optical microscope arises from an interference phenomenon in the substrate and it can be easily changed by modifying the dielectric layer thickness (SiO$_2$ thickness).\textsuperscript{53b} Optical images of graphene layers deposited on a 300 nm thick SiO$_2$ layer indicated that thicker graphitic samples (more than 50 layers) appear as yellow in colour whereas the thinner samples appear in bluish or in slightly lighter colour shades. One disadvantage of this method is that it leaves glue residues on the samples, which
adversely affect the electronic properties.\textsuperscript{46c,54} Hence, a post deposition treatment is required, and at present the substrate is either baked under \( \text{H}_2/\text{Ar} \) atmosphere or joule heated under vacuum up to 500 °C to remove the glue residue.\textsuperscript{55} Later on, slight variations of the original “Scotch tape method” were also reported. It was shown by Hue and co-workers that large graphene sheets can be produced by manipulating the substrate bonding of HOPG on Si substrate and controlled exfoliation.\textsuperscript{56a} In a similar approach, millimeter sized, single to a few layered graphene sheets were produced by bonding bulk graphite to borosilicate glass followed by exfoliation.\textsuperscript{56b} Both these methods point to the need for suitable modification of bonding between the substrate and graphite to generate large area graphene sheets. Even though micromechanical exfoliation produces the best quality graphene sheets reported so far, large scale production is expected to be difficult. Moreover, it produces uneven films which can be easily removed from the substrates by solvent washing.\textsuperscript{57} Hence other strategies have to be looked at for the scalable production of high quality graphene.

1.2.1.2 Supported Growth

Graphene could be grown on solid substrates \textit{via} two different mechanisms, (i) decomposition of hydrocarbons onto various metal substrates (CVD) and (ii) thermal decomposition of metal carbides (epitaxial growth). Table 1.1 summarizes the type of substrates and growth parameters reported so far for the supported growth of graphene. The decomposition of hydrocarbons in presence of metal catalysts has been extensively used for the mass production of CNTs. In an early method to produce graphene, ethylene was decomposed on Pt(111) substrates at 800 K and it resulted in the formation of nanometer-sized uniformly distributed graphene islands.\textsuperscript{50a} Recently, graphene monolayers were grown on Ru(0001) by thermal annealing, and it was
confirmed that the monolayer was formed by carbon atoms present in bulk Ru, which then segregated and accumulated on the surface during the annealing process.\textsuperscript{50d} Most interestingly, graphene monolayers were formed continuously over areas larger than several millimeter square. In another approach, 1-2 nm thick graphene sheets were shown to be grown on Ni substrate by thermal CVD, in which a mixture of H\(_2\) and CH\(_4\) were used as the precursor. The sheets were found to have smooth micrometer size regions separated by ridges. The ridge formation was attributed to the difference in thermal expansion coefficients of Ni and graphite.\textsuperscript{50c} Similarly, growth of graphene over polycrystalline Ni surface by thermal CVD has also been reported.\textsuperscript{50h} In this method, 500 nm thick Ni film was sputtered on Si/SiO\(_2\) substrate and was annealed in H\(_2\)/Ar atmosphere at 1000 °C for 20 min. Ni can be easily removed using dilute HCl, which facilitates the transfer of graphene from metal substrate to any other substrates.\textsuperscript{50h} In the latest developments, different substrates such as polycrystalline Cu, Fe-Co/MgO supported graphite, W and Mo have also been employed to grow graphene by CVD.\textsuperscript{50b,i,j}

The thermal decomposition of silicon carbide (SiC) at high temperature under vacuum also results in the growth of graphene islands. Thermal treatment of carbides under high vacuum result in the sublimation of Si atoms and the carbon-enriched surface undergoes re-organization and graphitization at high temperatures.\textsuperscript{49b} Controlled sublimation result in the formation of very thin graphene coatings over the entire surface. But the graphitization of carbon on SiC cause surface roughening and form deep pits that induce wide graphene thickness distribution and limited lateral extension of crystallites. Later on, it was found that the quality of epitaxial graphene can be improved by using 900 mbar Ar atmosphere and higher annealing temperature (1650 °C).\textsuperscript{49f}
Table 1.1 Summary of supported graphene growth on both metals and carbide substrates.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Growth conditions</th>
<th>Lateral size / thickness</th>
<th>Characterization</th>
<th>Ref</th>
</tr>
</thead>
</table>
| Pt(111)            | Source: ethylene  
Temp: 800 K  
Pressure: 10⁻⁵ Pa  | 2-3 nm sized graphite islands  | LEED, STM, AES             | 50a |
| Ru(0001)           | Source: carbon present in bulk Ru  
Temp: 1350 K  
Pressure: 10⁻⁸ Pa  | a few mm / monolayer        | LEED, STM, XPS, AES        | 50d |
| Ir(111)            | Source: ethylene  
Temp: 1320 K  
Pressure: 10⁻⁸ Pa  | a few μm / monolayer        | STM                         | 50e |
| Ni                 | Source: H₂/methane  
Temp: 1223 K  
Pressure: 10⁻⁴ Pa  | ~ 1 μm / 1.5 ± 0.5 nm       | SEM, Raman, STM             | 50c |
| Stainless steel    | Source: H₂/methane  
Pressure: 4000 Pa  
power: 1200 W  
Temp: 1073 K  | 2 - 40 μm / 0.5-3 nm       | SEM, AFM, Raman             | 50f |
| Si, W, Mo, Zr, Ti, Hf, Nb, Ta, Cr, 304 stainless steel, SiO₂, and Al₂O₃ | Source: methane  
Pressure: ~ 12 Pa  
power: 900 W  
Temp: 953 K  | ~ 1 μm / ~ 1 nm            | SEM, TEM, Raman             | 50b |
| Substrate free     | Source: ethanol atmospheric pressure microwave (2.45 GHz) Ar plasma reactor | a few 100 nm / 1-2 layers  | EELS, TEM, Raman             | 58  |
| Cu foil            | Source: H₂/methane  
Temp: 1273 K  | ~ 1 cm / 95% monolayer      | SEM, Raman                  | 50g |
| Polycrystalline Cu | Source: hexane  
Pressure: 1200 Pa  
(Ar/H₂)  
Temp: 1223 K  | ~ 1.5 - 3.5 cm / 1-4 layers | AFM, STM                    | 50i |
| Polycrystalline Ni | Source: H₂/methane  
Temp: 1173-1273 K  
low pressure UHV  | ~ 20 μm / 1-2 layers        | AFM, Raman, TEM, electron diffraction | 50h |
<table>
<thead>
<tr>
<th>Surface</th>
<th>Source</th>
<th>Temp</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polycrystalline Ni</td>
<td>C₂H₂/H₂</td>
<td>973-1273 K</td>
<td>rapid thermal CVD</td>
</tr>
<tr>
<td>Fe-Co/MgO catalyst supported on graphite</td>
<td>acetylene</td>
<td>973-1273 K</td>
<td>Argon as carrier gas</td>
</tr>
<tr>
<td>SiC</td>
<td>Thermal splitting of SiC</td>
<td>2273 K</td>
<td>50-300 nm / 0.3 ± 0.04 nm</td>
</tr>
<tr>
<td>6H-SiC-(0001)</td>
<td>UHV, sublimation of Si</td>
<td>1300 °C</td>
<td>1-3 layers</td>
</tr>
<tr>
<td>Amorphous SiC deposited on SiO₂</td>
<td>1373 K</td>
<td>rapid thermal annealing at ambient pressure</td>
<td>~ 2-15 μm / 6.5-10 nm</td>
</tr>
<tr>
<td>TiC(111)</td>
<td>CVD, Temp: 1770 K</td>
<td>~ 200 nm / 1-2 layers</td>
<td>XPS, LEED</td>
</tr>
<tr>
<td>TaC(111)</td>
<td>Ethylene</td>
<td>1570 K</td>
<td>1-2 layers</td>
</tr>
</tbody>
</table>

Metal carbides have also been used to produce supported graphene. For example, decomposition of ethylene gas over Ta(111) and Ti(111) carbides produce graphene monolayers.⁵⁹a,b The morphology of metal carbide determines the structure of graphene formed. In the case of terrace free TiC(111), monolayer graphene was formed, whereas on 0.886 nm wide terrace of TiC(410), graphene nanoribbons (GNRs) were obtained.

The islands of graphene films grown via both epitaxy and CVD produce even films with high structural quality. Besides, these methods have opened the prospect of growing large graphene films, which later can be transferred to any substrates. However, the major drawback of this method is the strong metal-graphene interaction, which will alter the transport properties of pristine graphene.⁶⁰ Further, it requires high temperature and high vacuum. Hence, it can be concluded that these methods
will be relevant only for high performance applications. For low end applications, wet chemical approaches provide wide range of alternatives, which is discussed in the subsequent section.

### 1.2.1.3 Wet Chemical Methods

Wet chemical approaches for the production of graphene proceeds by weakening the interlayer van der Waals interaction forces in graphite by intercalation of reactants. Decomposition of the intercalate releases high gas pressure, which results in loosening and disruption of the $\pi$-stacking. Consequently, some of the $sp^2$ hybridized carbon atoms change their hybridization to $sp^3$, which prevent the $\pi-\pi$ stacking.$^{51g}$ Wet chemical approach is scalable, allows the possibility of bulk production and more versatile in terms of being well suited to chemical functionalizations. These advantages could be utilized for a wide range of applications. Wet chemical methods for the preparation of graphene can be generally classified into two processes based on the precursors, one from graphene oxide (GO) and the second from graphite or its derivatives. Table 1.2 summarizes the different wet chemical approaches to produce graphene suspensions, which are discussed in detail in the following sections.

**Table 1.2** Comparison of different wet chemical approaches to produce graphene suspensions

<table>
<thead>
<tr>
<th>Starting material</th>
<th>Reducing agent &amp; dispersible solvents</th>
<th>Lateral size</th>
<th>Thickness</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>GO</td>
<td>Isocyanate Water, DMF</td>
<td>560 ± 60 nm</td>
<td>~ 1 nm</td>
<td>51b,61a</td>
</tr>
<tr>
<td>GO</td>
<td>Hydrazine vapour / NH$_3$ Water</td>
<td>500-700 nm</td>
<td>~ 1-1.4 nm</td>
<td>51c</td>
</tr>
<tr>
<td>GO</td>
<td>Hydrazine hydrate Water</td>
<td>200-500 nm</td>
<td>~ 1-2 nm</td>
<td>61b</td>
</tr>
<tr>
<td>GO</td>
<td>Hydroquinone Water</td>
<td>500-1000 nm</td>
<td>~ 1-1.4 nm</td>
<td>61c</td>
</tr>
</tbody>
</table>
1.2.1.3a Graphenes from GO

One method to disrupt the π-stacking of layers is through oxidation of graphite. This has been mainly achieved by Brodie,66 Staudenmaier67 and Hummers68 methods. All the three methods involve oxidation of graphite in presence of strong acids or oxidants. The level of oxidation can be controlled on the basis of the method chosen, reaction conditions and the graphite source used. The resultant greyish brown material can be easily separated into individual GO sheets using mild sonication. Oxidation of graphite introduces hydroxyl, carbonyl and epoxide moieties in the basal plane and this accounts for the colloidal stability of GO suspension in polar solvents.51f Besides, the measurement of surface charge of GO sheets by zeta potential measurements showed a negative charge when dispersed in water.51e In addition, XRD analysis of GO showed absence of typical graphite interlayer spacing (0.34 nm) peak and the
appearance of a new peak around 0.6-1.2 nm, indicating a larger interlayer spacing.\textsuperscript{51c}

Even though GO forms stable colloidal suspensions, they are electrically insulating due to the disrupted π - conjugation. Hence, a post chemical treatment is essential to restore the properties. GO sheets in solution are reduced using hydrazine or hydrogen plasma.\textsuperscript{46e,69} But it results in aggregation of the reduced sheets, unless a stabilizing agent is present. Various stabilizers such as polymers, amines, surfactants, aromatic compounds and biomolecules have been used to stabilize the reduced GO sheets.\textsuperscript{51,70}

Even though, the electronic properties can be partially restored upon reduction, it still leaves significant amounts of defects in the lattice. Elemental analysis (atomic C/O ratio, ~ 10) of the reduced GO measured by combustion revealed the existence of significant amount of oxygen, indicating that reduced GO is not the same as pristine graphene.\textsuperscript{61b} But the reasonable conductivity and excellent transparency of reduced GO thin films make it a promising component in transparent conductors as well as reinforcement and anti-aging agent in polymer composites.\textsuperscript{51g}

A few methods for producing colloidal suspensions of graphene sheets without the help of surfactants or stabilizers have also been reported. Aqueous suspensions of reduced GO under basic conditions do not aggregate.\textsuperscript{51c} This could be attributed to the conversion of neutral carboxylic acid groups to negatively charged carboxylate groups under basic conditions. Thermal treatment is another method that has been used to reduce GO. For example, rapid heating upto 1050 °C resulted in exfoliation and reduction of GO.\textsuperscript{71}

1.2.1.3b Unoxidized Graphene Sheets Directly from Graphite

An alternative strategy to produce defect free, unoxidized graphene sheets is based on solvation, in which dispersed graphene sheets are stabilized by solvent adsorption.
Hernandez et al., demonstrated that simple sonication of pristine graphite in solvents such as NMP, DMF or DMA result in well dispersed stable suspensions of unoxidized graphene sheets.\textsuperscript{63d} XPS investigations on the dispersed sheets support the conclusion that the sheets are not oxidized. 1,2-dichlorobenzene (ODCB) also proved to be a good solvent for the dissolution of graphite into graphene.\textsuperscript{72} The dispersions in these solvents can be further improved by intercalating alkaline metals, surfactants or polymers.\textsuperscript{64a,73} Even, aromatic compounds such as pyrene and perylene derivatives with solubilizing functional groups have been employed for the exfoliation of graphite.\textsuperscript{74} These aromatic compounds prevent graphene sheets from aggregation and also act as healing agents to cover the defects in graphene sheets during annealing.\textsuperscript{74c} Dispersion of unoxidized graphene in water was obtained with the sonication of graphite in water in presence of sodium cholate.\textsuperscript{73c,d} It was found that the dispersed concentration increased with sonication time and the average flake consisted of 4 stacked graphene sheets with length and width of 1 µm and 400 nm, respectively. In addition to normal organic solvents, perflourinated solvents such as hexafluorobenzene (C\textsubscript{6}F\textsubscript{6}), octafluorotoluene (C\textsubscript{6}F\textsubscript{5}CF\textsubscript{3}), pentafluorobenzonitrile (C\textsubscript{6}F\textsubscript{5}CN) and pentafluoropyridine (C\textsubscript{5}F\textsubscript{5}N) have been employed for the liquid phase exfoliation of graphite.\textsuperscript{75a} The mechanism of exfoliation and solubilization involves charge transfer through π - π stacking from the electron-rich carbon layers to the electron-deficient solvent molecules containing electron withdrawing fluorine atoms. Similarly, chlorosulphonic acid also proved to be a useful solvent for the exfoliation of graphite and the solubility of graphene was found to be as high as \( \sim 2 \) mg/ml.\textsuperscript{75b} In another approach, Billups et al., showed that reduction of graphite by lithium in liquid ammonia yields graphite salts that can be reacted with alkyl iodides to form soluble graphite platelets.\textsuperscript{63b} The average thickness of the soluble platelets was found to be
3.5 nm corresponding to 10 layers of graphene. Another approach employing the thermal exfoliation of graphite at 1000 °C, followed by re-intercalation with oleum and expansion with tetrabutylammonium hydroxide was developed earlier. In addition to organic solvents, ionic liquids and supercritical fluids have also been reported to exfoliate graphite into individual graphene sheets either in solution or via electrochemical methods. These solution processable graphene sheets are open to different types of chemical functionalizations, which offer new pathways to generate multifunctional graphene based devices or composites.

In oxidation and solvation assisted exfoliation, the separation depends on the mechanical disruption of the graphitic network. When the samples are extensively sonicated, it result in the fragmentation of graphene into small ribbons called as GNRs. These ribbons are highly promising since electronic properties of graphene are known to be governed by the edge states and were shown to be semiconducting.

1.2.1.3c Molecular Approach for the Production of Graphene

An additional option to produce defect free, solution processable graphene sheets is by bottom-up approach, which starts with carbon precursors and to convert them to large graphene like structures. One bottom-up approach involved the use of common laboratory reagents ethanol and sodium, which upon solvolysis followed by low temperature flash pyrolysis yielded single layer graphene sheets in gram quantities. Another strategy was thermal conversion of nano-diamond clusters into nanosized graphene islands. Enoki and co-workers have shown that nano-diamond clusters can be converted to nano-graphene islands by thermal graphitization process at 1600 °C. In contrast to the GNRs produced from graphite or CNTs, these nano-graphene islands showed sharp arm chair or zigzag edges when imaged with STM. Another
method is the molecular level synthesis of large polycyclic aromatic molecules. The synthetic routes towards graphene like molecules have been largely explored by Müllen and co-workers.\textsuperscript{82} Hexabenzocoronene (HBC), and its derivatives upon oxidative cyclohydrogenation reactions lead to planar graphene like discs (Figure 1.6).

![Figure 1.6](image)

**Figure 1.6** (A) Structure of HBC and (B) structure of the largest graphene like molecule reported with 222 carbon atoms. (redrawn from ref.\textsuperscript{82a})

Till now, the largest graphene like molecule reported is the one with 222 carbon atoms in their core.\textsuperscript{82b} Although such large molecules can be synthesized; one disadvantage associated with it is the limited solubility. Solubility can be enhanced with the incorporation of peripheral side chains, which will allow these materials to show liquid crystalline properties and to form thin films.\textsuperscript{82a}

### 1.2.1.4 Unzipping of CNTs

CNTs are made up of rolled cylinders of graphene sheets. Hence, longitudinal unzipping of CNTs will result in the formation of nanoribbons of graphene. Recently, this strategy has been successfully demonstrated by various research groups. Tour \textit{et al}, showed that oxidized GNRs can be produced by treatment of MWNTs with conc.
H\textsubscript{2}SO\textsubscript{4} and KMnO\textsubscript{4} mixture at room temperature.\textsuperscript{83} Mechanism of the tube opening is given in scheme 1.1. In a similar approach, Dai \textit{et al}, unzipped MWNT by mild gas phase oxidation.\textsuperscript{83b} In the first method, GNRs were found to have many functional groups at the edges, whereas in the latter, the side walls remained intact.

![Scheme 1.1 Proposed mechanism for the MWNT unzipping. First step (2) is the formation of manganate ester, followed by formation of dione (3), and subsequent induced strain causes the ring opening (4 and 5). (redrawn from ref. 83a)](image)

A few other groups also have successfully unzipped MMNT; for example, intercalation of ammonia and lithium metal into MWNT followed by HCl and thermal treatment led to the formation of GNRs.\textsuperscript{84} Another route is by embedding MWNT in PMMA matrix followed by etching of the exposed surface by Ar plasma.\textsuperscript{85} Unzipping of CNTs provide an easy way to control the structure of GNRs. Arm chair nanotubes upon unzipping can result in zigzag GNRs.\textsuperscript{83,85} Therefore, it is possible to produce large scale, well aligned semiconducting GNRs for practical applications such as room temperature transistors.

### 1.2.2 Characterization Techniques

Even though, structure of graphene is known for years, experimental proof for the
existence of graphene has been difficult, because of the limitations in identifying the single atom thick sheet. But now, there are appropriate tools to visualize and characterize graphene, which include optical and electron microscopy, scanning probe techniques (AFM and STM), Raman scattering and complex spectroscopic techniques (XPS, PES etc).

Optical microscopy is one of the simplest tools to identify the presence of monolayer graphene sheets. Normally, Si wafers with 300 nm thick SiO$_2$ layer on the top is widely used as the substrate, where the maximal contrast occurs at a wavelength of 550 nm. As alternatives to silica, graphene is visible on Si$_3$N$_4$ using blue light, Al$_2$O$_3$ on Si wafer and on 90 nm PMMA using white light.

AFM is used to establish the thickness of graphene layers. Although AFM is limited to lateral scans, it is the best tool to monitor the topological quality of substrate supported graphene samples. TEM has also been widely used as a characterization tool for colloidal graphene suspensions. Moreover, single atom thick graphene is an excellent support film for high resolution and spherical aberration corrected TEM studies. Electron diffraction studies can also be used to distinguish a single layer from a bilayer, since the ratio of the intensities for [2110] and [1100] spots is inverted for the two samples as predicted by Horuichi et al.

Raman scattering provide direct insight on the crystalline and electronic structure of graphene. Raman spectra of graphene shows three major peaks, one at $\sim 1570$ cm$^{-1}$ (G band) corresponding to the E$_{2g}$ phonon at the centre of the Brillouin zone, and the second one at $\sim 1350$ cm$^{-1}$ (D band) corresponding to the out of plane breathing mode of sp$^2$ carbon atoms. Intensity of D band is an effective probe to assess the disorders and impurities in graphene. The most important peak, which can be considered as the finger print of graphene is the D’ (2D) band at $\sim 2700$ cm$^{-1}$. The
shape, position and intensity of this band is highly dependent on the number of layers. Advanced spectroscopic techniques such as XPS and ARPES also provide direct evidence for the electronic structure of graphene.

1.2.3 Reactions of Graphene

From the point of view of its electronic properties, graphene is a zero band gap semiconductor. Before it can be employed in various applications, the problem of absence of band gap has to be resolved. For epitaxially grown graphene sheets, the band gap can be engineered by electronic coupling between the sheets and the substrate. An alternative option for tuning the band gap of solution processable graphene sheets will be the chemical functionalization or molecular doping on graphene sheets. The main approaches for chemical modification of graphene can be grouped into following categories.

- Covalent functionalization of the π-conjugated skeleton with different reactions such as hydrogenation, cycloaddition reactions, nitrene and carbene insertions.
- Non-covalent functionalization by wrapping or adsorption of different functional molecules such as polymers and small molecules.
- Molecular doping.

1.2.3.1 Covalent Modifications

One of the convenient ways to introduce solution processability is by covalently grafting polymers and small molecules onto graphene by hydrogenation, fluorination, simple coupling, cycloaddition, amidation and nitrene insertion. Covalent functionalizations on graphene can be generally classified into two. The first category belongs to covalent attachment of different molecules on GO and the second involves
the use of unoxidized graphene sheets.

1.2.3.1a Hydrogenation

Hydrogenation of carbon nanomaterials are of considerable interest because the physical properties of hydrogenated materials are entirely different from that of the starting materials. Hydrogenated graphene has also drawn great interest because of its predicted magnetism. Hydrogenation of graphene is not a simple task. The first step requires breaking apart of the diatomic molecules of hydrogen, which has very high binding energy (∼ 2.4 eV/atom). First experimental evidence for successful hydrogenation of graphene was demonstrated by Geim et al, by exposing mechanically exfoliated graphene to atomic hydrogen generated by low pressure (0.1 mbar) H$_2$/Ar plasma. The authors also showed that the hydrogenation is reversible and most of the properties can be restored by annealing the samples at higher temperatures. In completely hydrogenated graphene, alternating carbon atoms are pulled out of the plane in opposite directions with the attached hydrogen atoms.

Several alternative approaches were made to hydrogenate graphene. In one approach, reversible hydrogenation was achieved by the dissociation of hydrogen silsesquioxane (HSQ) coated on graphene. Hydrogen atoms were generated by breaking the Si-H bonds of HSQ by e-beam lithography. It was found that monolayer graphene can be easily hydrogenated than two layered (2L) graphene sheets. This enhancement in reactivity is attributed to the lack of π-stacking in single layer graphene sheets, which is required to stabilize the transition state of the hydrogenation reaction. Another method to hydrogenate graphene was proposed by Ao et al, who suggested the possibility of hydrogenation by exposing graphene to molecular hydrogen in presence of a strong perpendicular electric field. It was found that a
negative electric field can act as a catalyst to suppress the reaction energy barrier while a positive electric field has the opposite effect.

As an example of chemical species which can provide, similar to hydrogen, a complete coverage of graphene is fluorine. Fluorine is one of the promising candidates for functionalization since it produces a very homogeneous structure and can be substituted with other functional groups. Fully fluorinated analogue of graphene known as perfluorographene with the formula \((\text{CF})_n\) has been synthesized.\textsuperscript{95a} Besides fluorine, addition of HF, HCl and methyl radicals onto graphene have also been theoretically investigated.\textsuperscript{95b-e}

1.2.3.1b Covalent Modifications on GO

Acid oxidation of graphite results in the generation of highly oxygenated species known as GO. Epoxy, hydroxyl and carboxylic groups on the material make it negatively charged and assist in dispersion and solvation as individual sheets. GO can be reduced back to graphene sheets in presence of stabilizers. Reduction of GO partially restores the \(\pi\) - conjugation. Different varieties of chemical and physical methods have been developed for this purpose. Scheme 1.2 shows the different routes followed for the covalent functionalization of GO.

Acylation reactions are one of the common approaches used for coupling functional moieties onto GO.\textsuperscript{96a,b} The acylation reaction between the carboxyl groups in the edges of GO sheets (after activation of the COOH group by SOCl\(_2\)) and amine groups were used to modify GO with long alkyl chains, porphyrins, fullerenes and oligothiophenes (route I in scheme 1.2). Attachment of these functional moieties improves the solubility and dispersion stability of graphene based materials in common organic solvents.
GO covalently functionalized with porphyrin and fullerenes via acylation showed superior non-linear optical (NLO) performance in the nanosecond regime.\textsuperscript{96a,b,h} Superior NLO properties are induced by photo induced electron or energy transfer between the attached moieties and graphene.\textsuperscript{96a,b,h}

Extending this functionalization chemistry, GO can be functionalized with PEG and poly-l-lysine to obtain biocompatible conjugates, which can be used to load hydrophobic aromatic drugs.\textsuperscript{97,98} High density loading can be achieved, because of the efficient π stacking. It is well known that some of the anticanerous drugs are water insoluble. Covalent linking of these drugs to GO via PEG linkage make it highly water soluble with excellent cancer killing potency similar to the free drugs in organic solvents.\textsuperscript{97}

Similarly, hydrazine reduced GO are functionalized by treatment with aryl diazoinum salts (route II in scheme 1.2).\textsuperscript{96c} Like acylation reactions, diazonium chemistry also gives the capability of tailoring the functional materials by changing the addents. Another strategy relies on epoxide nucleophilic ring opening reactions.\textsuperscript{51e} Epoxide rings in GO undergo ring opening when treated with amine terminated organic molecules (route III in scheme 1.2). GO has been shown to functionalize with octadecylamine (ODA) with high dispersibility in common organic solvents.\textsuperscript{51e} Another extension of this concept is the use of amine terminated ionic liquids.\textsuperscript{99} These hybrids also showed enhanced dispersibility in organic solvents because of better electrostatic inter-sheet repulsion provided by the ionic liquid units.

Besides small molecules, GO sheets can be functionalized with polymers such as PVA via carbodiimide activated esterification reactions.\textsuperscript{100} Carboxylic acid groups on the GO sheets were reacted with hydroxyl groups on PVA in presence of DCC, 4-(dimethylamino)-pyridine and N-hydroxybenzotriazole in DMSO (route IV in scheme
Recently, another method to functionalize GO sheets have been reported in which GO is treated with sodium azide, followed by reduction with LiAlH₄ (route V in scheme 1.2). It introduced free amino groups on both the sides of reduced GO sheets. These free functional groups can form covalent bonds with isothiocyanates, which is promising for immobilizing graphene monolayers on any isothiocyanate treated substrates. Another approach involves the synthesis of polypropylene/graphene oxide (PP/GO) nanocomposites via in situ Ziegler-Natta polymerization.

1.2.3.1c Covalent Modifications on Unoxidized Graphene Sheets

Majority of the covalent functionalizations use GO as the starting material. GO is hydrophilic and hence requires more processing time. One major drawback associated with GO is that it requires a second reduction step to remove the excess oxides present. Hence attempts were made using unoxidized graphene sheets. Unoxidized graphene sheets can be modified either through selective edge functionalization and surface functionalization.

![Chemical structure of a small edge-carboxylated graphene nanoflake.](redrawn from ref. 103a)

**Figure 1.7** Chemical structure of a small edge-carboxylated graphene nanoflake. (redrawn from ref. 103a)
Even though, theoretical predictions of selective edge functionalization of graphene exist,\textsuperscript{102} very few experimental evidences are reported.\textsuperscript{103} This could be due to the difficulties in controlling the reactivity only over the edges. Salzmann and co-workers demonstrated the synthesis of edge carboxylated graphene nanoflakes by a single step oxidation of CNTs using nitric acid (Figure 1.7).\textsuperscript{103a} The presence and location of functional groups were determined by various spectroscopic techniques. Tour and co-workers demonstrated that thermally expanded graphite when functionalized with 4-bromophenyl addends using diazonium chemistry result in the formation of exfoliated graphene sheets which are selectively functionalized over the edges.\textsuperscript{103c} Elemental mapping and energy filtered TEM measurements revealed that majority of the Br signals came from the edges of the functionalized sheets, indicating that the basal planes were not highly functionalized.

\textbf{Figure 1.8} Schematic representation of the reaction between graphite and ABA as a molecular wedge via Friedel Crafts acylation in PPA/P$_2$O$_5$ medium. (redrawn from ref.\textsuperscript{103d} - dotted lines indicate the extended graphene network)

In a slightly different approach, organic molecules were covalently grafted to the edges of graphite via an electrophilic substitution reaction (Figure 1.8).\textsuperscript{103d} 4-aminobenzoic acid (ABA) was treated with graphite in poly(phosphoric acid) (PPA)/phosphorus pentoxide (P$_2$O$_5$) medium. This resulted in grafting of ABA onto
the defect sites (mostly sp² C–H) located mainly on the edges of graphite followed by exfoliation following Friedel Crafts acylation. ¹⁰³d

Surface/basal plane functionalization is comparatively easier for graphene, since all the atoms are exposed to the same chemical environment. Besides, unoxidized sheets have extended conjugated double bonds, which can be subjected to all the addition reactions of unsaturated aromatic compounds. In one approach, graphene sheets were directly fluorinated with plasma enhanced CVD followed by alkylation (Figure 1.9). ¹⁰⁴a

![Figure 1.9 Schematic representation of alkylation of fluorinated graphene sheets (blue: fluorine; yellow: -R group).](image)

Alkylation of fluorinated graphite has been done in a similar manner by Billups et al. ⁹⁵c ODCB suspension of graphene was functionalized with perfluorinated alkenes via free radical additions. ¹⁰⁴b The reaction was initiated by the thermal decomposition of benzoyl peroxide in the reaction mixture. Advantage of this kind of one-pot functionalization procedure is that pristine graphite is used as the starting material, which avoids the oxidation/reduction steps. ¹⁰⁴b

It has already been reported that CNTs and fullerenes can be functionalized by nitrene additions, which are produced in situ by thermal decomposition of azido starting materials. ¹⁰⁵ It involves [2+1] cycloaddition of nitrenes to C–C bonds, resulting in the formation of aziridino-ring linkage. Azido starting materials can be
synthesized in gram scale and offer a wide range of functional group tolerance.

Figure 1.10 Nitrene addition to exfoliated graphite in refluxing ODCB. (redrawn from ref.106a)

Barron et al, reported a high yielding method for the functionalization of graphene sheets through addition of azido-phenylalanine [Phe(N$_3$)] to exfoliated microcrystalline graphite (Figure 1.10). In this work, graphite was exfoliated in ODCB with ultrasonication followed by reaction with Boc-Phe(4-N$_3$)-OH at refluxing temperatures. In a similar approach, epitaxial graphene was covalently modified with azidotrimethylsilane and found that the band gap can be tuned by controlling the amount of incorporated nitrene. A similar cycloaddition reaction involve aryne cycloaddition, in which graphene was covalently functionalized with 2-triflatophenylsilane benzyne precursors. The functionalized sheets were found to be well dispersible in solvents such as ODCB, ethanol, chloroform and water, depending on the functional groups present.

In a similar approach, a few-layer graphene suspension in NMP was functionalized using the 1,3-dipolar cycloaddition of azomethine ylides. The same approach was used for immobilizing graphene on silicon wafers using perfluorophenylazide (PFPA) as the coupling agent (Figure 1.11). Graphene sheets were covalently attached to PFPA-functionalized wafer surface by a simple heat treatment under ambient
conditions. Solution phase PFPA coupling to solvent exfoliated graphene is also reported, where PFPA with different functionalities were reacted with graphene by photochemical or thermal activation.\textsuperscript{109}

\textbf{Figure 1.11} Fabrication of covalently immobilized graphene on silicon wafer \textit{via} the PFPA-silane coupling agent. (redrawn from ref.\textsuperscript{57})

All the reported covalent approaches towards functionalization of graphene offer many opportunities such as tailoring the optical and electronic properties, investigating the interfacial chemistry of graphene and incorporation of various functional groups on the surface. Besides, this gives an opportunity for the integration of electrically conductive graphene with biological systems which can have potential applications in medical diagnostics, bioelectronics and bio-sensors.

\textbf{1.2.3.2 Non-covalent Modifications}

One of the main challenges in the production of graphene is to overcome the strong interlayer van der Waals forces. Even though micromechanical exfoliation gives the best quality graphene samples, mass production is very tedious and time consuming. Besides, the sheets obtained in this manner contain different number of layers and is easily removed by solvent treatment or sonication.\textsuperscript{57} An alternative way for the production of graphene is by thermal expansion or metal intercalation. But
dispersibility of the exfoliated sheets will be a challenge in such cases. In solution phase methods, exfoliated graphene can be dispersed in solution by non-covalent wrapping of individual sheets by various species of polynuclear aromatic compounds, surfactants, biomolecules and polymers.\textsuperscript{51,110-112}

The non-covalent interactions are very promising because it offers the possibility to homogeneously disperse the graphene sheets without disturbing its electronic network, unlike the covalent functionalization. It is based on van der Waal’s forces and $\pi - \pi$ stacking between graphene and the added moieties.\textsuperscript{110,111} Both graphene and GO can undergo $\pi$ stacking. Aromatic compounds such as coronene, pyrene, porphyrin and perylene derivatives have been used to stabilize graphene in various organic solvents.\textsuperscript{110} All these aromatic compounds are large structures, which can anchor onto the hydrophobic surface of graphene sheets via $\pi - \pi$ stacking without disrupting the electronic conjugation. Theoretically, both donor and acceptor type aromatic molecules can be stacked onto the graphene surface, which tunes the $\pi$-electron density on graphene. For example, pyrene-1-sulfonic acid sodium salt (PyS) as an electronic donor and the disodium salt of 3,4,9,10-perylenetetracarboxylic diimide bisbenzenesulfonic acid (PDI) as an electronic acceptor were used for non-covalently functionalizing graphene.\textsuperscript{110a} Besides, the negative charges in both the molecules act as stabilizing species that maintain a strong static repulsion force between the negatively charged reduced graphene sheets in solution. The composites of PDI with graphene sheets resulted in an increase in conductivity for graphene-PDI (13.9 S cm$^{-1}$) compared to pristine reduced graphene (3 S cm$^{-1}$), whereas a 30% increase in conductivity was observed for graphene-PyS composite (1.9 S cm$^{-1}$). Charge transfer interactions between graphite and aromatic compounds have also
been employed for non-covalent modifications. These approaches yield novel class of dispersible materials with tunable optoelectronic properties.

Besides aromatic compounds, polymers were also used for the non-covalent stabilization of graphene sheets in solution. Use of graphene as a viable and inexpensive filler substitute for CNTs in nanocomposites has triggered the search for suitable agents to disperse graphene in the polymer matrix of choice. The first work related to this was reported by Ruoff et al, who showed that the in situ reduction of GO in the presence of an anionic polymer, poly(sodium 4-styrenesulfonate) (PSS) form a stable aqueous dispersion of graphene sheets. Following a similar approach, Shi et al, reported that in situ reduction of GO sheets in presence of sulfonated polyaniline (SPANI) lead to the formation of water soluble and electrochemically active composite. The functionalized sheets could be dispersed in water at a concentration higher than 1 mg/ml. Polyurethane (WPU) was also used for the non-covalent functionalization of thermally reduced graphene sheets. Graphene/WPU composite films showed an increase in the storage modulus compared with that of the films obtained by physical blending. This reinforcing effect of graphene can be attributed to the presence of residual oxygen and epoxides present on the sheets’ surface which might interact with the monomers. Other polymers, which have been used for the non-covalent stabilization of graphene and GO include amine terminated PS, poly(vinyl alcohol), polyacrylonitrile, PMMA and nafion. Like polymers, some polyelectrolytes and ionic liquids have also been proved as successful candidates for the non-covalent functionalization of graphene sheets. Niu et al, reported the supramolecular functionalization of graphene sheets with an anionic conjugated polyelectrolyte named poly(2,5-bis(3-sulfonatopropoxy)-1,4-ethynylphenylenealt-1,4-ethynylphenylene) sodium salt (PPE-SO\textsubscript{3}). This
polyelectrolyte has a poly(phenylene ethylenene) based back bone, which undergoes π - π stacking with the graphene sheets and the anionic counterpart imparts excellent water dispersibility and the possibility for self-assembly through electrostatic interactions. Cationic polyelectrolytes are also being employed in the non-covalent functionalization.\textsuperscript{113c} Graphene was modified with poly(diallyldimethyl ammonium chloride) (PDDA) and used as a building block for the self assembly of Au NPs on the surface.\textsuperscript{113c}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.12.png}
\caption{Schematic of self-assembly of Au NPs and PDDA-functionalized graphene sheets. (redrawn from ref.\textsuperscript{113c})}
\end{figure}

In contrast to the reported \textit{in situ} synthesis of hybrid materials based on graphene, self-assembly method provides an alternative to obtaining the graphene NP hybrids with high-loading and uniform dispersion due to the wide adaptability of electrostatic interactions (Figure 1.12).\textsuperscript{113x} Surfactants and biomolecules were also employed for the non-covalent functionalization. Sodium dodecylbenzene sulphonate (SDBS) was used for the stabilization of reduced GO sheets.\textsuperscript{96c} Stabilization by surfactants is attributed to the presence of surface charge, which attracts a diffuse layer of counter ions from the liquid to form an electric double layer. Coulombic repulsion between the nearby charged graphene sheets prevents them from aggregation.\textsuperscript{114} Likewise, adsorption of biomolecules such as DNA onto the surface of the graphene is
facilitated by non-covalent π - π stacking interactions involving both purine and pyrimidine bases of the DNA molecules.\textsuperscript{115a} On the other hand, the sugar-phosphate backbone stays away from the surface to produce a hydrophilic outer layer, which facilitates the dispersion in aqueous medium.\textsuperscript{115a} Other biomolecules such as vitamin C, lignin and cellulose derivatives were also reported to be used as stabilizers for graphene.\textsuperscript{115b,c}

\subsection*{1.2.3.3 Molecular Doping}

Graphene being a zero band gap material, it is highly desirable to have a tunable band gap because it would allow great flexibility in design and optimization of electronic devices. One possible way to achieve this is by doping, where the concentration and type of the charge carriers in the graphene sheets can be controlled.\textsuperscript{116} Chemical doping has larger implications in graphene research in terms of room temperature superconductivity and ferromagnetism.\textsuperscript{117} If graphene is covalently functionalized with electron withdrawing functionalities, p-doping can be induced.\textsuperscript{116} Similarly, graphene functionalized with electron donating groups can be n-doped.\textsuperscript{118} If the interface between p-doped and n-doped graphene regions is precisely controlled, it is possible to engineer p-n junctions.\textsuperscript{118a}

In addition, graphene can also be p-doped by absorbing metals with high electron affinity such as gold, bismuth and antimony.\textsuperscript{116} In contrast, doping with alkaline metals results in n-doping. This is attributed to the release of their valence electrons into the conduction band of graphene.\textsuperscript{118} In addition to such metals, other elements such as Ca, Al, K, Mn, Cu, Pt, Ag, Si, P and S can also be used as dopants to graphene.\textsuperscript{118} It has been theoretically shown that Ca doping induces superconductivity in graphene, whereas transition metal doping result in ferromagnetism due to the
hybridization between the transition metal and the carbon orbital.\textsuperscript{117a,c,d}

Alternatively, molecular doping of graphene can be accomplished \textit{via} charge transfer between electron-donor and electron-acceptor molecules such as tetrafluorotetracyanoquinodimethane (F4-TCNQ)\textsuperscript{119a} and viologen.\textsuperscript{119b} This gives rise to significant changes in the electronic structure of graphene. This is confirmed with the changes in Raman and photoelectron spectra.\textsuperscript{49c,119c} Theoretical calculations have demonstrated that small molecules like H\textsubscript{2}O, NH\textsubscript{3}, CO, NO\textsubscript{2} and NO can also be adsorbed onto graphene and influences the electronic and magnetic properties.\textsuperscript{119d} Recently, Ajayan and co-workers provided experimental evidence for change in the band gap of graphene by adsorption of H\textsubscript{2}O molecules.\textsuperscript{119e} Table 1.3 summarizes the different functionalization methods reported for graphene.

\textbf{Table 1.3} Comparison of different functionalization methods of graphene.

<table>
<thead>
<tr>
<th>Precursors</th>
<th>Methods</th>
<th>Advantages / Disadvantages</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Covalent Modifications</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Graphite</td>
<td>hydrogenation</td>
<td>control of electronic properties / causes defects</td>
<td>93,94</td>
</tr>
<tr>
<td>Graphite</td>
<td>fluorination</td>
<td>subsequent functionalization is easier / causes defects</td>
<td>95a</td>
</tr>
<tr>
<td>GO</td>
<td>acylation</td>
<td>enhanced dispersibility</td>
<td>96a,b,h</td>
</tr>
<tr>
<td>GO</td>
<td>epoxide ring opening</td>
<td>enhanced dispersibility</td>
<td>51e</td>
</tr>
<tr>
<td>GO</td>
<td>esterification</td>
<td></td>
<td>100</td>
</tr>
<tr>
<td>GO</td>
<td>diazonium addition</td>
<td>enhanced dispersibility; properties can be tailored by changing the addents</td>
<td>96c</td>
</tr>
<tr>
<td>Expanded graphite</td>
<td>diazonium addition</td>
<td>selective on edges</td>
<td>103a</td>
</tr>
<tr>
<td>Graphite</td>
<td>Friedel Crafts acylation</td>
<td>selective on edges</td>
<td>103b</td>
</tr>
<tr>
<td>Graphene</td>
<td>fluorination followed by</td>
<td>single step functionalization; avoids oxidation and</td>
<td>104</td>
</tr>
<tr>
<td>alkylation reduction steps</td>
<td>Graphene</td>
<td>nitrene insertion</td>
<td>single step reaction; band gap can be easily tuned</td>
</tr>
<tr>
<td>---------------------------</td>
<td>----------</td>
<td>-------------------</td>
<td>---------------------------------------------------</td>
</tr>
<tr>
<td>Graphene aryne</td>
<td>reduction</td>
<td>cycloaddition</td>
<td>enhanced dispersibility</td>
</tr>
<tr>
<td>Graphene ylide</td>
<td>reduction</td>
<td>cycloaddition</td>
<td>-</td>
</tr>
</tbody>
</table>

### Non-covalent Modifications

<table>
<thead>
<tr>
<th>GO/graphene</th>
<th>large polycyclic aromatic compounds</th>
<th>electronic network is not disturbed; enhanced dispersibility</th>
<th>110</th>
</tr>
</thead>
<tbody>
<tr>
<td>GO/graphene</td>
<td>polymers</td>
<td>dispersibility in a variety of solvents; reinforcing composites</td>
<td>51a, 111,112</td>
</tr>
<tr>
<td>GO/Graphene</td>
<td>polyelectrolytes</td>
<td>-</td>
<td>113</td>
</tr>
<tr>
<td>GO/graphene</td>
<td>surfactants</td>
<td>dispersibility in a variety of solvents depending on the tail groups</td>
<td>96c</td>
</tr>
<tr>
<td>GO</td>
<td>biomolecules</td>
<td>dispersibility in polar solvents</td>
<td>114,115</td>
</tr>
</tbody>
</table>

### 1.2.4 Properties of Graphene

Monolayer, bilayer, a few-layer graphene and GO exhibits diverse set of unusual properties, which overcome the limitations of other materials such as CNT, graphite or ITO in many applications. The most remarkable property of graphene is the high charge mobility at room temperature.\(^{46c}\) This has led to the conclusion that graphene shows anomalous quantum Hall effect.\(^{120}\) Improved sample preparation, post fabrication techniques and annealing of single layer graphene sheets allowed the mobility to reach values up to \(~ 200,000 \text{ cm}^2/\text{V s}\), which is the highest mobility reported for any semiconductor or semimetal.\(^{46c}\) In addition, the mobility remains unaffected even at the highest electron-field-carrier concentrations and also by chemical doping.\(^{121}\) This suggests the possibility of achieving ballistic transport regime on a sub-micrometer scale at 300 K.\(^{122}\) It shows, room temperature ambipolar
characteristics, i.e. the charge carriers can be altered between holes and electrons depending on the nature of gate voltage.\textsuperscript{45}

The larger size, high mobility and sensitivity to field effect make graphene a contender for CNTs in field effect transistors.\textsuperscript{45} But the main problem associated with graphene is the zero band gap which has to be increased for FET device fabrication. This can be achieved either by the inclusion of sp$^3$ defects in the sp$^2$ lattice or by the distortion of graphene lattice under uniaxial strain.\textsuperscript{60} The most simple approach may be the introduction of basal interaction of graphene with various molecules or substrates.\textsuperscript{60}

In addition to these interesting electronic properties, thin films of graphene and its derivatives possess nearly 90\% optical transparency. Optical transparency along with high conductance enables graphene to be a tough competitor to the industrial standard, ITO.\textsuperscript{46e,123} Interestingly, the optical transmittance follows a linear relation with the thickness of graphene films, which is related to the 2D gapless electronic structure of graphene. The white light absorbance observed for suspended single and double layer graphene sheets was found to be 2.3 and 4.6\%, respectively, with a minimal reflectance (< 0.1\%). This linearity has been demonstrated upto five monolayers.\textsuperscript{124}

Another important property of graphene is its mechanical robustness.\textsuperscript{60} Suspended defect free graphene sheets are reported to have the highest Young’s modulus of $\sim$ 0.5 - 1 TPa, which is very close to that of bulk graphite.\textsuperscript{46c} Surprisingly, suspended GO sheets retained almost the same mechanical stabilities with a Young’s modulus of $\sim$ 0.25 TPa to that of graphene.\textsuperscript{125} High mechanical strength, thermal stability and conductance combined with low cost and ease of blending into matrices make this material an ideal candidate for mechanical reinforcement.\textsuperscript{126} Besides, graphene bears
enhanced potential as the ultimately thin material such as pressure sensors and resonators.\textsuperscript{60}

### 1.2.5 Graphene Based Hybrid Materials

High conductivity, large surface area, high mechanical stability and the unique graphitized planar structure make graphene a viable substitute for other conventional carbon nanomaterials in hybrids. Graphene based hybrid materials can be prepared either by physical blending or by chemical methods.

One class of hybrid materials, in which graphene is being used is polymer nanocomposites, where graphene act as reinforcing filler. Pure GO is not suitable for conventional nanocomposites, because it can be easily dispersed in water that are incompatible with any other organic solvents. In addition, GO is electrically insulating, which limits its application in conventional nanocomposites. GO has to be chemically modified before it can be employed in nanocomposites. A great deal of work has been done on graphene/polymer composites. Generally, graphene/polymer composites have been developed using three strategies; (1) solvent processing, (2) melt processing and (3) \textit{in situ} polymerization.\textsuperscript{127} The first strategy consists of three steps such as dispersion of graphene and the polymer in a suitable solvent, physical blending and finally the removal of solvent. Several composites have been prepared in using this strategy both in aqueous and organic media.\textsuperscript{126a,128} Even though, solvent processing is a simple technique, it is associated certain disadvantages such as solvent adsorption on graphene sheets. Melt processing involves the direct addition of graphene into a melted polymer using a twin screw extruder. Thermally exfoliated graphene and polymers such as polycarbonate, polyamide and polyurethane have been mixed in melt processing.\textsuperscript{128d,129} Even though, this method is environmentally
friendly, one of the major disadvantages is the low degree of dispersion resulting in poor mechanical and transport properties. In *in situ* polymerization, chemically modified graphene sheets are mixed with monomers or polymer precursors, followed by polymerization. Polymers are grafted to modified graphene sheets either by covalent functionalization or *via* atom transfer free radical polymerization.\(^{130a,b}\) The main advantage of this strategy is the strong chemical interaction between graphene and the polymer matrix and also the homogeneous dispersion.\(^{130}\) However, this method is associated with viscosity changes that hinders higher loading.\(^{127}\) The studies focussing on the mechanical and thermal properties of graphene based polymer composites revealed an increase in the storage modulus and thermal stability as a function of loading.\(^{126,128}\) Besides, the small wrinkles present on the graphene surface is expected to enhance the mechanical interlocking and adhesion.\(^{128a}\) Similarly, incorporation of conducting graphene sheets in the polymer matrix enhances the electrical conductivity with very low percolation thresholds.\(^{128,129}\) The percolation thresholds vary over a wide range of loading fractions, from the lowest at 0.07 vol.% for high molecular weight polyethylene\(^{126a}\) and 0.1 vol.% for PS\(^{129a}\) to 3.8 vol.% for polyamide.\(^{129c}\) Compared to mechanical reinforcement and electrical conductivity, thermal conductivity of graphene filled polymer composites has received minimal attention. The reason is that thermal energy is transmitted by the interaction of adjacent particles through vibrations and free electrons, which requires strong filler/polymer interface.\(^{127}\) In the case of graphene based polymer composites, it can be only achieved with *in situ* polymerization. Fang *et al* reported an increase in the thermal conductivity of PS films filled with 2 wt.% polystyrene-grafted graphene from 0.158 W m\(^{-1}\) K\(^{-1}\) to 0.413 W m\(^{-1}\) K\(^{-1}\).\(^{130a}\) Similarly, graphene/silicone foams produced by *in situ* polymerization showed a 6% increase in the thermal conductivity
with a loading fraction of 0.25 wt.%.  

Another class of graphene based hybrid materials is graphene/metal or metal oxide nanosystems. In these systems, metals, semiconductors or metal oxides are distributed onto the surface of graphene or between the layers. Generally, these are fabricated via solution phase methods, in which the metal ions or the precursors are reduced in presence of chemically modified graphene sheets. Compared to conventional carbon nanomaterials, graphene provide higher surface area for better interactions.

The integration of graphene and functional nanoparticles such as metal nanoparticles (Au, Ag, Pt, Pd), quantum dots (CdS, CdSe, ZnS) and metal oxides (ZnO, TiO\(_2\), CuO, SnO\(_2\), Co\(_3\)O\(_4\), Fe\(_3\)O\(_4\), MnO\(_2\)) present special features in the new hybrids, especially in catalysis, optics, electronics, sensors and energy storage devices. For example, Pd/graphene composite is used as a highly active catalyst in Suzuki-Miyaura Coupling Reaction. Compared with the conventional Pd/C catalyst, graphene based catalyst showed much higher activities with very low Pd leaching (< ppm). Similarly, Ag/graphene hybrid systems have been used as an active SERS substrate. CdSe/graphene composite films have shown improved photosensitivity compared with pure CdSe films. Moreover, the photoconductivity and flexibility of the films were also found to be enhanced compared with pure QD arrays. Hybrids of graphene with TiO\(_2\), ZnO and other metal oxides have been used for photocatalytic water splitting and for energy storage applications.

Other than metal or metal oxide/graphene hybrids, graphene forms stable composites with CNTs and fullerenes. CNT/graphene composites were reported to show comparable optical transparency and conductivity to that of ITO. Besides, the fabrication of these composites is very facile, inexpensive and is compatible with any flexible substrates.
1.2.6 Applications of Graphene

Graphene can be used as a sensor material because all the atoms in a graphene sheet are exposed to the environment, chemically stable and functionalization towards a specific interaction is possible. Moreover, mechanical robustness and transport properties remain unchanged even after the local destruction of the $sp^2$ lattice. The operation principle of graphene based sensors relies on the changes in electrical conductivity due to the adsorption of molecules on graphene. Suspended graphene sheets being under tension and impermeable provides an optimized atomically thin supporting membrane for gas sensing. In the case of gas sensing, adsorption of a gas molecule onto the graphene surface cause changes in the carrier concentration, which can be monitored electrically in a transistor like configuration. In contrast to other materials, the high mobility, large area ohmic contact and metallic conductivity observed in graphene limit the background noise in transport measurements and this confers high sensitivity to detect parts per billion levels or even a single molecule at a rapid rate. Further, it can be chemically functionalized for specific interactions and the variations in electronic and mechanical properties can be exploited to form the transduction of the sensing signal. Several research groups have demonstrated the good sensing ability of graphene towards NO$_2$, NH$_3$, H$_2$O, CO and DNT. The sensing mechanism of NO$_2$ and DNT is based on the hole induced conduction as these species withdraw an electron from graphene and in the case of NH$_3$, it is electron induced conduction as it donates an electron to graphene. Similarly, electrochemical sensing ability of graphene based composite materials has also been evaluated. Pt nanoparticle embedded graphene hybrid nanosheets were used as a new electrode material and it showed enhanced electrocatalytic and sensing abilities compared to pure glassy carbon electrodes. Graphene and its composites have been
used as sensors for heavy metal ions based on the fluorescence quenching ability.\textsuperscript{137} In addition to these, biosensing properties have also been demonstrated.\textsuperscript{138} For example, Shan \textit{et al} constructed a graphene based biosensor using glucose oxidase as the enzyme model.\textsuperscript{138a} A linear response up to 14 mM of glucose was observed in the constructed device. Similarly, graphene has been used for the detection of neurotransmitters such as dopamine and serotonin and it was found that graphene electrodes were more sensitive than CNTs.\textsuperscript{138b} Likewise, graphene hybrids were used as high performance biosensors for DNA and organophosphates.\textsuperscript{138c-e}

Another important application of graphene is in the fabrication of FET. Since graphene being a zero band gap semiconductor, it cannot be directly employed in FETs.\textsuperscript{45} A band gap suitable for room temperature FET applications should be imposed on graphene. One way to achieve this is by manipulating the graphene structure by cutting into small stripes known as GNRs.\textsuperscript{80,139} Besides being used in FETs, graphene can be employed in LCD displays and as transparent electrodes for solar cells.\textsuperscript{123a} As described previously, extraordinary thermal, mechanical and chemical stability of graphene along with high optical transparency make it an ideal candidate for transparent electrodes.\textsuperscript{123}

Another area in which graphene can be employed is in Li-ion batteries, where graphite is usually employed as the anode material.\textsuperscript{140} Graphene can replace graphitic carbon, owing to superior electrical conductivity, high surface area and chemical tolerance. Different metal oxide/graphene composites have been synthesized for battery applications which include SnO\textsubscript{2}/graphene,\textsuperscript{140a} TiO\textsubscript{2}/graphene,\textsuperscript{140b} CuO/graphene\textsuperscript{140c} and Co\textsubscript{3}O\textsubscript{4}/graphene\textsuperscript{140d} hybrid systems. Though a few reports on graphene based composite materials as electrodes in Li-ion batteries are available, further research is needed to understand the mechanism of the electrochemical
processes involved. Some other notable applications of graphene are as supercapacitors,\textsuperscript{46a,141} polymer composites,\textsuperscript{126-130,142} energy and hydrogen storage devices.\textsuperscript{138a,143} Table 1.4 summarizes the major applications of graphene and the graphene based composite materials.

**Table 1.4** Major applications of graphene and graphene based composite materials

<table>
<thead>
<tr>
<th>Source</th>
<th>Applications</th>
<th>Properties</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>micromechanically cleaved graphene; RGO; Pt embedded graphene; graphene/metal oxide composites</td>
<td>sensors</td>
<td>highly sensitive/single molecule detection/electrochemical response/fluorescence quenching ability</td>
<td>121,125,134-136</td>
</tr>
<tr>
<td>GNRs; graphene</td>
<td>transistors</td>
<td>tuned band gap/ballistic electron transport</td>
<td>139</td>
</tr>
<tr>
<td>graphene films; RGO films; graphene composite films</td>
<td>LCD displays and transparent electrodes</td>
<td>optical transparency/conductivity/ultra thin films/mechanical stability and flexibility</td>
<td>123,133</td>
</tr>
<tr>
<td>P3HT/graphene composite; graphene films</td>
<td>photovoltaic/solar cells</td>
<td>a novel electron acceptor/high electrocatalytic activity and stability</td>
<td>13d,144</td>
</tr>
<tr>
<td>RGO films; graphene/PANI composites;</td>
<td>capacitors</td>
<td>good cycling stability/high specific capacitance/high conductivity over a wide range of voltage scans</td>
<td>46a,141,145</td>
</tr>
<tr>
<td>graphene films; TiO\textsubscript{2}/graphene; SnO\textsubscript{2}/graphene; CuO/graphene; Co\textsubscript{3}O\textsubscript{4}/graphene</td>
<td>lithium ion batteries</td>
<td>high specific capacitance/enhanced Li ion insertion or extraction good cyclic performance</td>
<td>140</td>
</tr>
<tr>
<td>chemically modified graphene films; RGO films</td>
<td>graphene bio devices</td>
<td>large surface area/biocompatible/sensitive to electrochemical changes</td>
<td>138d,146</td>
</tr>
</tbody>
</table>
1.3 Aim and Scope of the Thesis

Nanostructures from carbon have always been an area of interest to researchers for their direct applications in the fields of science starting from material science to biology. Most of the reported procedures for the preparation of functional carbon nanomaterials rely on expensive equipments, resources, high temperature and pressure. Besides, most of the methods generate desired nanomaterials along with significant amount of carbonaceous impurities such as amorphous carbon and catalyst particles. Simple and cost-effective production of carbon nanomaterials is very crucial for the development of functional materials. The overall focus of the thesis is twofold:

- Develop simple, environmentally friendly methods to generate functional carbon nanomaterials. Towards this goal, a novel solvent based extraction method was employed to selectively separate carbon nanofibers from soot. The extracted fibers were employed in μ-solid phase extraction for the separation and pre-concentration of aromatic amines from aqueous samples. The proposed method offers advantages such as easy operation, minimal use of organic solvent and elimination of tedious solvent evaporation and reconstitution steps.

- Build up simple solution phase approaches for the production of processable graphene sheets. Even though micromechanical cleavage is the basic platform for the production of high quality graphene sheets, the yield is very poor that it cannot be used for bulk production and chemical reactions. Other reported methods also have certain disadvantages such as lack of control over size, shape, dispersibility and the number of layers. In order to scale up the production of graphene for technological applications, new production methods and surface functionalization methods have to be developed. Based on this, two different approaches have been
employed for the solution phase exfoliation of graphene.

(a) Surfactant assisted exfoliation of graphite into graphene without any oxidation/thermal treatment. The effect of ultrasonication and non-covalent stabilization were combined for the exfoliation and dispersion of graphene nanosheets. The stabilized sheets were incorporated in poly(vinyl chloride) matrices to generate flexible conductive composite thin films with high mechanical strength and thermal stability. This approach might prove useful for the use of graphene as a substitute for other carbon based fillers because of its superior properties.

(b) Majority of the covalent functionalizations uses GO as the starting material. GO is extremely hydrophilic and hence it requires more processing time. In addition, one major drawback associated with GO is that it requires a second reduction step to remove the excess oxides present. Hence, covalent functionalizations were carried out using unoxidized graphene samples. Azide insertion and bromination followed by alkylation/arylation were successfully carried out on graphene samples. Chemical functionalization of the carbon network in graphene by grafting atoms or molecules is very important because this provides a method for the introduction of interesting photoactive molecules for the development of optoelectronic materials.

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Chapter 2

Carbon Nanofibers Extracted from Soot as a Sorbent for the Determination of Aromatic Amines from Wastewater Effluent Samples

Papers published from this chapter:

2.1 Introduction

Since the discovery of fullerenes$^1$ and CNT$^2$, various kinds of nano-size carbon materials are studied for different applications. A few of the best known structures are CNTs and CNFs.$^3$ CNTs and CNFs have been attracting a great deal of academic and industrial interest due to their novel structural features and interesting properties. CNFs are solid carbon fibers with lengths in the order of a few microns and diameters below 100 nm. Owing to their unique physical and chemical properties, these have been used in areas as diverse as electrochemical devices,$^4$ field emission devices,$^5$ sensors,$^6$ gene delivery agents,$^7$ high strength composites,$^8$ hydrogen and charge storage devices.$^9$

Carbon soot collected from burning of renewable sources such as plant seed oil or natural materials has been extensively studied during the last decade.$^{10-12}$ The nanostructures obtained vary upon the renewable resources, combustion temperature and deposition kinetics. A variety of natural materials were explored to get good yield of desired carbon nanostructures and the flames was called ‘sooting’ flames as they spontaneously generated condensed carbon in the form of soot agglomerates suspended in flame gases. Instead of using hydrocarbon as fuel, recently Sarkar et al reported the synthesis of CNTs by pyrolysing mustard oil.$^{13}$

All synthetic methods generate desired carbon nanostructures along with significant amounts of carbonaceous impurities such as amorphous carbon, fullerene, turbostratic graphite (TSG), polyhedral carbon nanoparticles and catalyst particles.$^{14-17}$ In order to obtain the optimum performance for carbon nanomaterials, it is important to purify the soot and remove all unwanted materials. Several techniques for isolation of pure materials have been applied such as chemical oxidation,$^{17}$ use of
polymers, surfactant assisted extraction, centrifugation, sonication and filtration.

Carbon nanomaterials such as CNTs have been successfully used as a new sorbent material in solid phase extraction for preconcentration of analytes. Aromatic amines, widely used in the manufacturing process of pesticides, polymers, pharmaceuticals and dyes are suspected carcinogens and are highly toxic to aquatic life. Hence, it is necessary to determine these compounds in waste water by rapid and sensitive analytical techniques. Miniaturized extraction techniques such as solid-phase micro-extraction (SPME) and liquid-liquid-liquid micro-extraction (LLLME) have been employed in the extraction of aromatic amines from aqueous samples. However, the application of CNFs in this area has not been well explored. CNFs offer large surface area and high chemical stability which are ideal for a potential sorbent material for solid-phase extraction. In this chapter we discuss the successful extraction, purification, characterization of new CNFs and its performance as a sorbent material for the extraction and preconcentration of aromatic amines.

2.2 Experimental Section

2.2.1 Reagents and Materials

Good quality edible oil was purchased from local market. Poly(vinyl alcohol) (PVA) (average molecular weight = 124,000-186,000; 87-89% hydrolyzed) and phosphoric acid were purchased from Sigma-Aldrich. Glutaraldehyde for cross-linking of fibers was obtained from Alfa Aesar. HPLC-grade methanol, acetonitrile, THF, sodium acetate and glacial acetic acid were bought from Merck. Ultrapure water was obtained from Mili-Q (Milford, MA, USA) water purification system. Aromatic amine standards 3-nitroaniline, 4-chloroaniline, 4-bromoaniline and 3,4-chloroaniline were
obtained from Fluka chemicals and were used without any further purification.

2.2.2 Sample Preparation

The standard stock solution of 1 mg/ml of each analyte was prepared by weighing appropriate quantities of individual compounds and dissolving in methanol. A standard solution containing all the four aromatic amines (at 5 µg/ml) was prepared by mixing an appropriate volume of 1 mg/ml stock solutions in ultrapure water. All solutions were filtered and stored at 4 °C. All aqueous samples with total amine concentrations of 25 µg/l were freshly prepared before each extraction by spiking the standard mixture into ultrapure water. The aqueous samples for calibration were obtained by spiking ultrapure water with the standard mixture at desired concentrations.

2.2.3 Isolation of CNFs

The oil was placed in an open container and burned using a small cotton thread at a controlled rate in ambient conditions. The emitted carbon smoke was then condensed onto a cold surface placed on top, but at a short distance from the flame. This process was continued for several days to collect the carbon soot, which was used for subsequent experiments. Briefly, about 25 mg of soot was mixed with 50 ml THF with the aid of ultrasonication for 20 min. Only CNFs were extracted using exposure of THF to the soot. After 6 h, the supernatant solution was collected and the solvent was evaporated. The solid product was dried thoroughly in oven at 85 °C for overnight and was re-suspended in THF for subsequent characterization and analysis.

2.2.4 Preparation of Electrospun CNF/PVA Composite Nanofiber Mats

An aqueous solution of PVA (10 wt%) was prepared by dissolving it in ultrapure
water at 50 °C with constant stirring for about 12 h. A fixed amount of CNFs were then added to the PVA solution (3 ml). The solution was stirred for 12 h and was further ultrasonicated for 30 min to obtain homogenous dispersions of CNFs in PVA solution with a variation in the weight of the CNFs from 0.3-7.0 wt%. The CNF/PVA solution was electrospun into fiber mats. In order to reduce the swelling of fibers in water, the CNF/PVA composite fiber mats were placed in 1 vol.% glutaraldehyde-acetone solution for 15 h to achieve cross-linking. The resultant composite fiber mat was rinsed with ultrapure water followed by acetone and dried at ambient conditions.

For the electrospinning system, assembled parts were bought from OptroBio Technologies Pte Ltd, Singapore. The electrospinning set up consists of a plastic syringe with a metal syringe needle, a syringe pump, a high voltage power supply and a grounded flat collector. The inner diameter of the syringe needle used was 0.2 mm and the distance between the syringe tip and the grounded flat collector was maintained at 10 cm. In the electrospinning, the CNF/PVA solution was placed into the plastic syringe and charged with voltage (15 kV) via connecting the syringe needle to the power supply. The flow rate of the CNF/PVA solution was optimized at 5-10 µl/min.

2.2.5 Materials Characterization

FTIR spectra were recorded at 1 cm⁻¹ resolution with 32 scans in the wave number range of 4000-400 cm⁻¹ using a Bio-Rad FTS 165 FTIR spectrophotometer using samples dispersed in KBr pellets. SEM and EDX spectra of the CNFs and electrospun fibers were obtained using a JEOL JSM-6710F scanning electron microscope. TEM and SAED images were taken using JEOL JEM-2010 transmission electron microscope operating at 200 KeV. Raman spectroscopy was performed on Renishaw
system-2000, with an excitation wavelength of 532 nm.

### 2.2.6 μ-SPE using Electrospun CNF/PVA Composite Nanofiber Mats

10 mg of each of the nanofibers mat was placed in the samples and stirred at 900 rpm for 40 min. After extraction, the mat was removed, rinsed in ultrapure water, dried with lint free tissue and placed in a 250 µl auto-sampler vial. The analytes were desorbed by ultrasonication for 15 min in 75 µl acetonitrile, out of which 20 µl was used for HPLC analysis. The composite membrane can be re-used after ultrasonication in acetonitrile for 20 min to remove traces of impurities.

### 2.2.7 HPLC Analysis

All analyses were performed on a Shimadzu Prominence system (Shimadzu, Kyoto, Japan) consisting of a CBM-20A system controller, a LC-20AD pump, a SIL-20A auto sampler, a CTO-20A column oven, a DGU-20A5 degasser and a SPD-20A UV-vis detector. Separation of the four aromatic amines at room temperature was accomplished using a 50 mm × 3.0 mm I.D. MetaSil 5 µm ODS column (Varian, Palo Alto, CA, USA). The detection wavelength was set at 254 nm. A mobile phase ratio of acetate buffer (pH 3.5)-acetonitrile (85:15, v/v) at a flow rate of 0.3 ml/min was used.

### 2.3 Results and Discussion

#### 2.3.1 Characterization of the CNFs

The carbon soot is obtained via burning common edible oil in air and collecting soot on a cold surface. The raw soot contained aggregated structures of carbon nanoparticles (Figure 2.1A) and THF extract from the soot showed high aspect ratio nanofibers (Figure 2.1B). From figure 2.1B, it can be seen that the THF extract
contained nanofibers in high yield, along with small amounts of carbon particles.

Figure 2.1 SEM images of the raw soot (A), extracted CNFs (B) and TEM of CNFs (C) obtained from the soot by THF extraction. Inset in C shows the SAED pattern obtained from a single nanofiber.

The CNFs were of several micrometers in length and expected to have very high surface area. The CNFs isolated were of 20-50 nm in diameter. Elemental analysis and EDX confirmed the presence of carbon (86 atom%) and oxygen (12 atom%) in the THF extracted sample. The TEM image and SAED pattern indicated amorphous character for the nanofibers (Figure 2.1C). There is no interlayer correlation and therefore no significant long range of order to produce lattice diffraction (inset in figure 2.1C).

Figure 2.2 XRD pattern obtained for the isolated CNFs.

XRD analysis also indicated low range of graphitization in the CNFs (Figure. 2.2). The two predominant peaks at ~ 27 and 43.5° could be assigned for (002) and (100) diffraction planes of hexagonal graphite, respectively. The fact that (002) diffraction
peak was relatively low in intensity and broad in shape, suggesting that the CNFs have low graphitization and crystallization which in turn supports the SAED observations. The broadening of peak also indicated the presence of disordered structures in the products.\textsuperscript{28}

FTIR spectrum of the CNFs (Figure 2.3A) showed the peaks at 2915 cm\textsuperscript{-1} and 2865 cm\textsuperscript{-1} which correspond to the aromatic –CH stretching. Bands centered at 1623, 1455 and 1386 cm\textsuperscript{-1} could be due to C=C stretching vibrations.\textsuperscript{29} Besides, it is seen that the sample have a peak around ∼ 3400 cm\textsuperscript{-1}, indicating the presence of –OH groups. We believe that the π-π electrostatic and hydrophobic interactions between the analytes and the large surface area CNFs facilitated the adsorption of amines, rather than the presence of surface functional groups. Presence of surface functional groups certainly enhances the adsorption efficiency. In the Raman spectrum (Figure 2.3B) of the isolated CNFs, there were two predominant peaks at 1347 and 1589 cm\textsuperscript{-1} respectively, corresponding to the disorder induced (D band) and E\textsubscript{2g} (G-band) mode of graphite. It is known that the G band corresponds to stretching vibrations of sp\textsuperscript{2} hybridized carbon atoms and D band is associated with disorder-induced symmetry lowering effects.\textsuperscript{30} Band at 1347 cm\textsuperscript{-1} arises from the amorphous graphite particles and defect sites on the carbon nanofibers.

![Figure 2.3 FTIR (A) and the Raman spectra (B) of the CNFs.](image-url)
2.3.2 Analytical Evaluation of Electrospun CNF/PVA Composite Nanofiber Mats as Adsorbent for μ-SPE

The extraction efficiency of the CNF/PVA composite nanofibers mats was evaluated based on the peak areas obtained from HPLC analysis (Figure 2.4). Extractions were repeated three times to obtain the statistical mean.

Figure 2.4 HPLC chromatogram obtained for standard 1 mg/l. Peak (1) 3-nitroaniline; (2) 4-chloroaniline; (3) 4-bromoaniline and (4) 3,4-dichloroaniline.

Figure 2.5 gives a pictorial representation of the extraction and desorption steps involved in the electrospun CNF/PVA composite nanofibers mat based μ-SPE.

Figure 2.5 Schematic of the extraction and desorption steps involved in electrospun CNF/PVA composite membrane μ-solid phase extraction.
Cross linked CNF/PVA composite fiber mat was used for the extraction of aniline compounds from water and the performance of CNF/PVA composite nanofiber mats as a µ-SPE device for the determination of anilines was optimized by investigating several factors which affect the extraction and desorption steps. The factors include extraction time, desorption solvent, sample volume, desorption time, salting-out effect and pH effect.

2.3.3 Control Study

The CNF/PVA nanofiber mat µ-SPE was compared with pure PVA fiber mat µ-SPE device to prove that the extraction of anilines from water is mainly due to interaction of anilines with the novel CNFs surface instead of the PVA support. As shown in figure 2.6, the extraction efficiency of the four aniline compounds is greatly enhanced with the incorporation of CNFs into PVA fibers.

![Figure 2.6](image)

**Figure 2.6** Comparison of PVA and composite fiber mats (Extraction conditions are as follows: 10 ml spiked 25 µg/l water solution, no salt added and pH adjusted, extraction time of 30 min, desorption time of 15 min in 100 µl of acetonitrile).

A comparison of the extraction efficiency between the soot obtained after burning oil and the CNFs extracted using THF was also carried out. The results show a better
extraction performance of CNFs compared to the soot particles. The extraction efficiency depends on the interaction between anilines and the electrospun CNF/PVA composite fibers. The adsorption of analytes on the electrospun CNF/PVA composite fibers is facilitated by the presence of electrostatic and hydrophobic interactions between anilines and graphitic sp\textsuperscript{2} hybridized carbon atoms in the CNFs. In addition, extraction efficiency is also attributed to the large surface area of electrospun nanofibers.

2.3.4 Extraction Time

Membrane based µ-SPE is an equilibrium-dependent extraction procedure operating with the principle of partitioning analyte on the sorbent material. The amount of analyte extracted depends on the mass transfer from the sample solution to the sorbent. Since mass transfer is a time-dependent process, the effect of time on the extraction efficiency was investigated. The sample was continuously stirred at room temperature with a magnetic stirrer to facilitate the mass transfer process and to decrease the time required for equilibrium to be established.

![Figure 2.7](image)

**Figure 2.7** Plot of HPLC peak area vs the extraction time (Extraction conditions are as follows: 10 ml spiked 25 μg/l water solution, no salt added and no pH adjustment, desorption time of 15 min in 100 μl of acetonitrile).
The stirring speed was fixed at 900 rpm. The extraction profile of aniline compounds on the CNF/PVA composite fiber mat at a range of 10 to 60 min is shown in figure 2.7. The extraction efficiency increase gradually with time and a maximum was achieved in 40 min. Therefore, 40 min was adopted as optimum extraction time for the subsequent experiments.

### 2.3.5 Desorption Solvent

![Desorption Solvent Graph](image)

**Figure 2.8** Comparison of different desorption solvents (Extraction conditions are as follows: 10 ml spiked 25 µg/l water solution, no adjustment of salt and pH, extraction time of 40 min, desorption time of 15 min in 100 µl of acetonitrile).

In order to effectively desorb the hydrophobic analytes from CNF/PVA composite fibers, selection of suitable organic solvent is critical. Factors such as solubility of analytes, solvent polarity, compatibility with HPLC, solubility and swelling of composite fibers were taken into consideration during the extraction. Since the cross-linked electrospun CNF/PVA composite fibers were insoluble in common organic solvents, solvents such as methanol, acetonitrile and acetate buffer were investigated.
Figure 2.8 shows the influence of desorption solvent on µ-SPE performance. The polarity order of the solvents investigated and the analytes are as follows: methanol > acetonitrile > anilines. The more polar solvent (methanol) gave poor desorption than acetonitrile. Thus, subsequent analyses were carried using acetonitrile as desorption solvent.

2.3.6 Sample Volume

The effect of sample volume (5-30 ml) on the extraction efficiency was investigated. Figure 2.9 shows the influence of sample volume on µ-SPE.

As shown in figure 2.9, the analyte enrichment and extraction efficiency increases with increase in sample volume. Lower sample volumes gave poor analyte enrichment. The latter was at its maximum for all the analytes when 30 ml of sample was used. As explained earlier, the amount of analyte that can be extracted depends
on the partition coefficient of the analyte between the sample and the CNF. This type of behavior is common in microextractions. With the high surface area for adsorption of analytes, the electrospun membrane can take up significant amount of analytes as the sample volume goes up. However, considering the increase in extraction efficiency with the sample volume is only gradual after 10 ml and it is less feasible to have large sample volume for the extraction set-up, 30 ml was chosen as the optimum sample volume.

### 2.3.7 Desorption Time

Desorption of analyte was carried out via sonication of the fiber mat with adsorbed analytes in acetonitrile. Figure 2.10 shows the plot of peak area vs desorption time.

**Figure 2.10** Plot of HPLC peak area vs desorption time (Extraction conditions are as follows: 30 ml spiked 25 µg/l water solution no adjustment of salt content and pH, extraction time of 40 min, desorption in 75 µl of acetonitrile).

There was a small increase in desorption peak area within 15 min for 3-nitroaniline and 3,4-dichloroaniline, other compounds did not show any significant change in peak area with changes in desorption time. Hence desorption time was kept as short as possible without compromising the extraction efficiency and 15 min was chosen as
optimum desorption time.

### 2.3.8 Effect of Ionic Strength

The salting out effect has been used in SPME\textsuperscript{32} and LLE.\textsuperscript{33} Generally, addition of NaCl enhances the extraction efficiency of some organic compounds, since the solubility of analytes in aqueous solutions decreases with increasing ionic strength. However, no significant variation in the extraction efficiency with increase in salt content in the sample was observed (Figure 2.11). Another effect of salt addition is the increase in viscosity of sample solution, which in turn, impedes the mass transfer rate and reduces extraction efficiency. Therefore, no salt addition was used in further experiments.

### 2.3.9 Effect of pH

The influence of pH in the extraction was evaluated since pH plays a significant role in ionizable compounds such as anilines. The pH values of water sample were
adjusted using 1M NaOH for alkaline sample and 1M HCl for acidic sample before spiking the analytes.

![Graph showing peak area vs pH for different compounds](image)

**Figure 2.12** Effect of sample pH on the extraction efficiency (Extraction conditions as follows: 30 ml spiked water solution (25 µg/l), no salt addition, extraction time of 40 min, desorption time of 15 min in 75 µl of acetonitrile).

As shown in figure 2.12, the extraction efficiency for the four compounds increases with the increase in pH initially and level off after pH 7. pKa values for the deprotonation of protonated salts of 3-nitroaniline, 4-chloroaniline, 4-bromoaniline and 3,4-dichloroaniline are 2.47, 4.15, 3.86 and 2.97, respectively. At acidic conditions, all the four aniline compounds are expected to be protonated and the resulting cations have poorer affinity over their neutral form for the surface of CNF/PVA composite fibers. Thus pH 7 (ultra-pure water without salt adjustment) was selected as optimum condition.

### 2.3.10 Method Validation

To assess the feasibility of CNF/PVA electrospun nanofiber mat as extraction device, the validation was established for the determination of several performance parameters such as linearity, precision, limit of detection (LOD) and enrichment factors under the optimized extraction conditions. Table 2.1 summarizes the analytical
data obtained using the CNF/PVA membrane extraction.

**Table 2.1** Quantitative data: linearity, precision (RSD), limit of detection (S/N = 3), enhancement factors and linear regression data obtained for anilines by the electrospun CNF/PVA composite membrane microextraction coupled with HPLC-UV.

<table>
<thead>
<tr>
<th>Analytes</th>
<th>Enrichment factor</th>
<th>R.S.D (%) (n=3)</th>
<th>Correlation coefficient (r)</th>
<th>Linearity range (µg/l)</th>
<th>LOD (µg/l)</th>
<th>LOQ (µg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-nitroaniline</td>
<td>66</td>
<td>4.8</td>
<td>0.998</td>
<td>0.5-50</td>
<td>0.009</td>
<td>0.030</td>
</tr>
<tr>
<td>4-chloroaniline</td>
<td>57</td>
<td>5.8</td>
<td>0.989</td>
<td>0.5-50</td>
<td>0.024</td>
<td>0.080</td>
</tr>
<tr>
<td>4-bromoaniline</td>
<td>82</td>
<td>4.5</td>
<td>0.996</td>
<td>0.5-50</td>
<td>0.081</td>
<td>0.269</td>
</tr>
<tr>
<td>3,4-dichloroaniline</td>
<td>109</td>
<td>5.5</td>
<td>0.998</td>
<td>0.5-50</td>
<td>0.019</td>
<td>0.062</td>
</tr>
</tbody>
</table>

Calibration curves were obtained by plotting the peak area vs the corresponding spiked concentrations in ultrapure water. The linearity of the calibration plot was evaluated over a range of 0.5-50 µg/l by least square linear regression analysis. All the four amine compounds exhibited good linearity with correlation coefficient (r) above 0.9897. This shows a directly proportional relationship between the extracted amount of analytes and the initial spiked concentration. The precision, which is expressed as relative standard deviation (RSD), were determined on triplicate analyses at different concentrations. The RSD obtained were in the range of 4.5-5.8%. The good repeatability is mainly due to simple extraction methodology and use of auto-sampler in HPLC-UV for the analysis. The LOD determined for the aniline compounds are in range of 0.009-0.081 µg/l and the limit of quantitation (LOQ) is within a range of 0.030-0.269 µg/l. Our data is consistent with the LOD reported for extraction of anilines in aqueous samples using LLLME.
2.3.11 Application of Method for Real Sample Analysis

Table 2.2 Concentrations of target aniline compounds (µg/l) in waste water samples and the average recoveries determined at 5 µg/l (* n.d-not detected. Relative recovery values of spiked wastewater sample at 5 µg/l compared to that of spiked pure water).

<table>
<thead>
<tr>
<th>Analytes</th>
<th>Environmental water sample</th>
<th>Relative recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
<td>B</td>
</tr>
<tr>
<td>3-nitroaniline</td>
<td>2.3</td>
<td>n.d</td>
</tr>
<tr>
<td>4-chloroaniline</td>
<td>n.d</td>
<td>n.d</td>
</tr>
<tr>
<td>4-bromoaniline</td>
<td>6.9</td>
<td>0.46</td>
</tr>
<tr>
<td>3,4-dichloroaniline</td>
<td>n.d</td>
<td>n.d</td>
</tr>
</tbody>
</table>

The current method was developed as pre-treatment for analysis of aniline compounds in environmental water samples. Water samples were analyzed to assess the contamination of the four aniline compounds. 3 out of 5 samples were found to contain some of the aniline compounds and results are shown in table 2.2. However, the complex matrix of environmental sample affects the performance of the composite fiber mat in the extraction process. A standard addition method was used to study the matrix effect and relative recovery of the aniline compounds. From the results shown in table 2.2, it could be seen that relative recoveries for 4-chloroaniline and 3,4-dichloroanilines are comparatively lower, which is about 70%. The low recovery could be due to the clogging of nanofibers surface by the particulate matters present in the sample. It could be concluded that the applicability and performance of electrospun composite fiber mat as µ-extraction device depend upon the types of water sample. CNF/PVA composite nanofibers are suitable for relatively clean water samples such as filtered water samples or treated water sample to assess the
performance of treatment plant in removing amine compounds. The proposed extraction method using the CNF/PVA composite nanofibers is more cost-effective since it is robust, durable and reusable. Furthermore, it is fast and simple involving only a few steps.

2.4 Conclusions

CNFs were isolated from carbon soot by a simple and effective methodology in good yield. The isolated CNFs were characterized in detail by spectroscopic and microscopic techniques. The CNFs were of several micrometers in length and 20-50 nm in diameters. The high surface area electrospun CNF/PVA composite fiber mat has been successfully developed as a novel sorbent material for micro-extraction of aniline compounds. The presence of CNFs in the composite membrane ensures and enhances the extraction efficiency of method under optimum conditions. The composite membrane sorbent yielded satisfactory parameters for micro-extraction. Finally, the applicability of the method was further validated to determine aniline compounds in environmental samples. The proposed micro-extraction method offers advantages such as easy operation, high recovery, fast extraction, minimal use of organic solvent and elimination of tedious solvent evaporation and reconstitution steps.

2.5 References

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29. Nakamoto, K. Infrared and Raman spectra of Inorganic and Co-ordination


Chapter 3

Cationic Surfactant Mediated Exfoliation of Graphite into Graphene Nanosheets and its Field Emission Properties

Publications from this chapter:

3.1 Introduction

The recent discovery of free standing graphene\textsuperscript{1} has attracted worldwide attention because of its interesting electronic, mechanical and thermal properties.\textsuperscript{2-10} Graphene is considered as the mother form of all the 3D carbon nanostructures, and is made up of a monolayer of carbon atoms closely packed in a honeycomb lattice.\textsuperscript{4}

One of the main challenges associated with the production of graphene sheets is to prevent the re-stacking. Lack of suitable methods to produce quality graphene sheets in significant quantities limits some of its applications. The interlayer attractive forces in graphite should be prevailed over to exfoliate it into graphene. Micromechanical cleavage of graphite using “Scotch tape” is the standard procedure used for the preparation of graphene.\textsuperscript{5} Even though, this method gives the best quality samples with the highest charge mobility reported so far,\textsuperscript{11,12} mass production is very tedious and time consuming. Moreover, the sheets obtained in this manner can be easily removed from the substrates by simple solvent treatment. Alternatively, methods such as exfoliation of graphite by metal intercalation followed by microwave heating,\textsuperscript{13} growing graphene by CVD of hydrocarbons on metal substrates\textsuperscript{14} and thermal reduction of SiC have also reported.\textsuperscript{15,16} All these methods require very high temperatures and obtaining a uniform graphene layer still remains a challenge.

Recently, many solution based approaches for the exfoliation of graphite into graphene has been reported, which mainly involves the chemical oxidation of graphite into GO followed by reduction in presence of various stabilizers such as polymers,\textsuperscript{17} hydrazine,\textsuperscript{18} surfactants,\textsuperscript{19} pyrene and perylene derivatives,\textsuperscript{20,21} ODA\textsuperscript{22} and various biomolecules.\textsuperscript{23} But chemical oxidation disrupts the electronic structure of graphene and introduces many carbonyl (−C=O), hydroxyl (−OH) and epoxide groups in the
basal plane of the sheets. Even though, reduction can remove most of the functionalizations, it still leaves significant number of defects which alters the electronic properties. Very recently, sonication assisted dispersion of graphene in NMP and DMF\textsuperscript{24,25} and ionic-liquid assisted electrochemical methods\textsuperscript{26} for the production of graphene from graphite has reported. Graphene sheets produced \textit{via} these methods show agglomeration over a period of time which hinders the potential applications. Hence a simple, solution phase approach for the production of unoxidized but stabilized graphene sheets is needed to explore its potential applications.

In this chapter, we outline a simple solution based method for preparing a few layered graphene nanosheets directly from graphite without any oxidative or thermal treatment. The effect of ultrasonication and non-covalent stabilization are combined for the exfoliation and dispersion of graphene.

\textbf{Scheme 3.1} Schematic of cetyltrimethylammonium bromide (CTAB) assisted exfoliation.

Mild sonication of HOPG nanosheets in presence of various surfactants (both cationic and anionic) and acetic acid led to the exfoliation of graphite into graphene nanosheets. The cationic surfactant CTAB stabilized graphene samples were found to
be more stable in solution than the anionic surfactant sodium dodecyl sulfate (SDS) stabilized samples. The mechanism of stabilization involves the adsorption of amphiphilic CTAB molecules onto the electron rich graphene surface through electrostatic interactions. The hydrophobic interaction of the alkyl chains of CTAB molecules on the graphene surface could prevent the re-stacking and agglomeration of the exfoliated sheets. The nanosheets thus obtained were characterized using AFM, HRTEM, FESEM, EDX, STM, Raman spectroscopy and field emission measurements.

3.2 Experimental Section

3.2.1 Materials and Methods

HOPG was purchased from Good Fellow Ltd, USA. CTAB, SDS, glacial acetic acid and DMF were purchased from Sigma-Aldrich and were used without further purification. Milli-Q water was used for washings.

3.2.2 Preparation of Processable Graphene Nanosheets

In brief, 100 mg of HOPG nanosheets were sonicated (Elma E-30H ultrasonicator, operating at 37 kHz ultrasonic frequency and 115 W) with 0.5 M CTAB solution in glacial acetic acid for 4 h. The resultant solution was then refluxed for 48 h under N₂ atmosphere. Reaction mixture was left to stand overnight to allow aggregated sheets to settle down. The supernatant was decanted and then centrifuged at 20,000 rpm for 45 min. The resultant black residue obtained could be re-suspended in DMF.

3.2.3 Instrumentation

UV-vis spectrum was recorded using Shimadzu 1601 PC spectrophotometer. SEM images and EDX spectra were obtained from JEOL JSM-6710F scanning electron
microscope. For SEM imaging, a dilute solution of the exfoliated sample was drop-casted on ITO coated glass substrate and dried in the oven. EDX spectrum was recorded from drop casted sample on conductive Si substrate. HRTEM analyses were carried out using JEOL JEM-2010 F electron microscope, operating at 200 keV. STM measurements were performed on Au(111) substrate (Goodfellow, UK) using a NanoScope IIIa MultiMode SPM (Digital Instrument, Veeco Metrology Group) with electrochemically etched Pt(8) Ir(2) tips (0.25 mm diameter). A drop of graphene solution deposited on Au(111) substrate was used for STM measurements and the images were obtained at a tunneling current of 2 pA and a bias voltage of 50 mV. AFM images were recorded using Agilent AFM with Pico plus molecular imaging system in the non-contact mode. Samples for AFM were prepared by spin-coating a dilute suspension of graphene on freshly cleaved mica at a speed of 5000 rpm and then dried at room temperature. Raman spectra were recorded with a Renishaw system-2000 operating at an excitation wavelength of 532 nm. Sample for field emission studies was prepared on conducting Si substrate. The Si wafers were washed with piranha solution and Milli-Q water, respectively and air dried before drop casting the sample. The graphene deposited on the Si wafers served as the cathode while an ITO coated glass kept at a distance of 100 µm acted as the anode. A vacuum of ~ 10^{-7} torr was applied in the chamber. Voltage was supplied using a programmable high voltage source and the resulting emitting current was measured (see figure 3.7A for the schematic representation of experimental set-up).

## 3.3 Results and Discussion

Ultrasonication is a powerful tool for extracting nanomaterials from bulk.\textsuperscript{25,26} Sonication of HOPG in CTAB-acetic acid mixture facilitated the exfoliation of
graphite without any oxidation. It can be explained by the effect of acoustic cavitation of high frequency ultrasound in the formation, growth and collapse of microbubbles in solution,\textsuperscript{27} which induces shock waves on the surface of the bulk material, causing exfoliation. Even though, surface energy of acetic acid is not very close to that of graphite,\textsuperscript{28} dispersion quality of acetic acid is comparable with that of the best solvents reported for a good dispersion of graphene.\textsuperscript{22} Hence acetic acid was chosen as a solvent for the exfoliation of graphite. Both cationic and anionic surfactants (CTAB and SDS, respectively) were used for the exfoliation and stabilization. But, only CTAB stabilized sheets were found to be stable in solution. It could be attributed to the strong electrostatic interactions between the quaternary cationic head groups in CTAB and the electron rich graphene surface. Besides, the hydrophobic interactions of long alkyl chains of CTAB molecules prevent the re-stacking and agglomeration of the exfoliated sheets. The yield of a few layered graphene nanosheets from this approach was found to be $\sim 10\%$.

3.3.1 Control Studies

![SEM image of the exfoliated product in acetic acid.](image)

**Figure 3.1** SEM image of the exfoliated product in acetic acid.

Exfoliation of graphite was attempted in acetic acid without the use of any surfactants. The resultant product was found to settle down in solution over a period of time ($> 1$
Figure 3.1 shows the FESEM image of the settled product obtained. From the image, it can be concluded that sonication in presence of acetic acid exfoliates the sheets to certain extent, but the centrifuged product seem to appear as agglomerated. It implies that acetic acid alone is not sufficient to stabilize or prevent the re-stacking of the exfoliated sheets.

3.3.2 Exfoliation of Graphite in Presence of SDS

When SDS-acetic acid mixture was used, the exfoliated sheets were agglomerated and precipitated when the excess SDS was removed by centrifugation and washing (SEM and TEM image in figure 3.2A and B). This could be due to the repulsion between negatively charged SDS molecules and electron rich graphite sheets. However, when graphite was sonicated in presence of acetic acid and CTAB, graphite nanosheets exfoliated to form planar a few layered graphene nanosheets and it was found to form stable suspensions in DMF, NMP and DMSO.

3.3.3 Exfoliation of Graphite in Presence of CTAB

The exfoliated nanosheets stabilized by CTAB were characterized by various
spectroscopic and microscopic techniques. Figure 3.3A shows the UV-vis spectrum and the inset shows a photograph of the surfactant stabilized graphene suspension in DMF.

**Figure 3.3** (A) UV-vis spectrum of the CTAB stabilized graphene nanosheets dispersed in DMF. Inset shows a photograph of the DMF solution. SEM of (B) HOPG and (C) the CTAB stabilized exfoliated graphene.
The graphene suspension in DMF was stable without any visible aggregation for several weeks. It is known from the literature that hydrazine reduction of the GO solution cause a red shift in the absorption maximum from 231 to 275 nm, indicating a partial restoration of the electronic structure. In the case of CTAB stabilized graphene suspension, it showed a strong absorption band at around 280 nm, showing the formation of stable graphene nanosheets without any disruption in the electronic structure.

Figures 3.3B and C show a comparison of the SEM image of HOPG with that of the exfoliated product. Several graphene layers stack each other in a highly ordered fashion in HOPG because of the strong van der Waal’s forces of attraction (Figure 3.2B). Upon exfoliation in presence of CTAB, large number of different types of sheets was formed. From figure 3.3C, it could be seen that most of the exfoliated sheets were very thin and transparent to the SEM beam. Most of the thin nanosheets were of the order of 1-2 µm in size with folds over the edges. In addition to this, some multilayered graphitic nanosheets were also observed.

Low resolution and high resolution TEM images of the nanosheets are depicted in figure 3.4A and B. Several nanosheets were observed on the TEM grid and were found to be stable under the electron beam. The sheets were crumpled and it could be due the extra thermodynamic stability of the 2D membranes arising from microscopic crumpling involving either bending or buckling. Figure 3.4B shows the HRTEM image of one end of a scrolled graphene nanosheet. The ordered graphite lattices were clearly seen on the edges. The distance between the lattice planes (Figure 3.4B) were found to be 0.34 nm, which corresponds to the bilayer distance between the graphitic planes. STM image of a monolayer graphene is shown in figure 3.4C, where the hexagonal packing of carbon atoms is clearly visible. Inset of figure 3.4C clearly
show the hexagonal symmetry obtained for graphene nanosheets. Presence of small non-uniformities in the pattern could be attributed to the presence of residual surfactants on the surface.

Figure 3.4 (A) TEM image of surfactant stabilized graphene nanosheets. (B) HRTEM image of a bilayer graphene sheet. (C) STM image of a part of the monolayer graphene (inset highlights the hexagonal lattice of the monolayer). (D) Section analysis along the blue line which showing a width of 1.148 nm for 4 hexagons and (E) along the green line which showing a width of 0.424 nm for 3 C-C bonds.

Figure 3.4D is the section analysis along the blue line (Figure 3.4C) which shows a width of 1.148 nm for 4 hexagons (hexagon width of 0.287 nm). Similarly, figure 3.4E is the section analysis along the green line which shows a width of 0.424 nm for 3 C–C bonds (C–C bond length of 0.14 nm).

Thickness and morphology of the sheets was further probed using AFM. A large area image of the graphene nanosheets spin coated on the mica sheet from DMF
suspension is shown in figure 3.5A. Figure 3.5B and C represent the AFM image of an individual graphene nanosheet and its height profile, respectively.

**Figure 3.5** (A) Topographic view (10 × 10 µm) of the graphene layers spin coated on mica. (B) AFM image of a single graphene sheet (1 × 1 µm). (C) Height profile of the image 3B. Statistical analysis of the AFM images of 60 nanosheets: (D) thickness, (E) length and (F) width of the nanosheets.

Contrast difference between the edge and the centre of nanosheet clearly shows the sharp and rolled edge (Figure 3.5B). The height of the sheet was found to be ~ 1.3
nm, corresponding to ~ 1-3 graphene layers. AFM images clearly indicated that nanosheets are very small with dimensions of the order of < 1 µm. Dimensions (height, length and width) of a large number of nanosheets (60) were measured and the statistical analyses are plotted in figure 3.5D, E and F. Average thickness of the nanosheets was found to be 1.18 nm. Most interestingly, more than 85% of the nanosheets were less than 4 layers thick (Figure 3.5D). The average length and width were found to be 0.7 and 0.5 µm, respectively (Figure 3.5E and F). Decrease in the sheet dimensions could be attributed to the breakage due to sonication.

![Graphene Raman spectra and EDX spectrum](image)

**Figure 3.6** (A) Raman spectra of HOPG and the CTAB stabilized graphene nanosheets deposited on Si and (B) EDX spectrum.

Significant structural changes occurred during the exfoliation of HOPG to graphene were clearly reflected in the Raman spectra (Figure 3.6A). Raman spectrum of HOPG displayed mainly a prominent G band at 1582 cm\(^{-1}\), corresponding to the first-order
scattering of the $E_{2g}$ mode and a 2D band at $\sim 2715$ cm$^{-1}$.\textsuperscript{30} However, the spectrum of the exfoliated graphene showed the presence of D band at 1352 cm$^{-1}$ which indicates the presence of defects. The D band is due to the breathing modes of sp$^2$ carbon atoms and requires a defect for its activation and the intensity of D band is directly related to the amount of disorder present in the graphene sheets.\textsuperscript{30}

Defects in the exfoliated samples might be due to the disorders induced by sonication and decrease in the average size of the sp$^2$ domains.\textsuperscript{31} Raman spectrum of CTAB stabilized graphene sheets also showed the presence of G band at $\sim 1582$ cm$^{-1}$ and the 2D band at $\sim 2715$ cm$^{-1}$. Since no defects are required for the activation of two phonons with the same momentum, the 2D band is always seen, even when no D band is present.\textsuperscript{22} EDX spectrum of the exfoliated product showed absence of any oxidized structure (Figure 3.6B). Spectrum showed peaks due to ‘C’ and ‘Si’, but not corresponding to ‘O’. Absence of the peak corresponding to ‘O’ indicate that the exfoliated products are not oxidized. The peak corresponding to ‘Si’ is from the substrate.

### 3.3.4 Field Emission Properties of Graphene Nanosheets

The field emission characteristics of the graphene nanosheets were studied using parallel plate diode geometry with an anode to cathode spacing of 100 µm (Figure 3.7A). A plot of current density vs the applied electric field is shown in figure 3.7B. The turn on voltage for the onset of electron emission (10 µA/cm$^2$) was approximately 7.5 V/µm. Emission current densities as high as 0.15 mA/cm$^2$ was obtained at an applied potential of 10 V/µm. The sheets were stable under high applied electric fields.\textsuperscript{32} Plot of corresponding ln ($J/E^2$) vs 1/E follows a linear relationship over the field emission range as predicted by the Fowler-Nordheim relationship (Figure 3.7C).
Figure 3.7 (A) Schematic representation of the experimental set up for field emission measurement. (B) Graph showing the field emission current density vs applied electric field. (C) Fowler-Nordheim plot indicating the field emission characteristics of exfoliated graphene nanosheets.
The field amplification factor $\beta$, which describes the geometrical shape and surroundings of the emitter is calculated using the Fowler-Nordheim law.\textsuperscript{33}

$$I \propto \frac{F^2}{\phi} \exp \left( \frac{B\phi^{3/2}}{F} \right)$$

where $I$ is the emitted current, $F$ is the local field at the emitter surface, which is calculated as $F = \frac{\beta V}{d}$, where $V$ is the applied potential and $d$ is the distance between cathode and anode, $\phi$ is the work function (5 eV for graphite) and $B = 6.83 \times 10^9$ V eV$^{-3/2}$ m$^{-1}$. The field amplification factor $\beta$ was calculated to be $\sim 1250$. The field amplification factor $\beta$ of a free standing graphene sheet can also be theoretically calculated using the empirical formula proposed by Watcharotone \textit{et al.}\textsuperscript{34}

Accordingly, field amplification factor across the surface of the corner $\beta_{\text{corner}}$ can be calculated as

$$\beta_{\text{corner}} = 2.07 \left( \frac{l}{t} \right)^{0.75} \left( 1 + 0.09 \left( \frac{l}{w} \right) \right) (0.5 + 0.5 \cos \theta)$$

where $l$, $w$ and $t$ respectively represents the length, width and thickness of the graphene nanosheets. $\theta$ is the subtended angle at the centre of curvature between the point of consideration at the corner and the midpoint of the corner. The field amplification factor along the edges of the sheet $\beta_{\text{edge}}$ can be calculated as

$$\beta_{\text{edge}} = 1.77 \left( \frac{l}{t} \right)^{0.75} \left( 1 + 0.09 \left( \frac{l}{w} \right) \right) (0.75 + 0.25 \cos \phi) \left( \frac{d}{t} \right)^{-0.19}$$

where, $d$ is the distance from the junction of the edge and corner. $\phi$ is the subtended angle at the centre of curvature between the point of consideration and the nearest point at the middle of the rounded edge.\textsuperscript{34} The average length, width and thickness of the graphene nanosheets were taken as 0.7 µm, 0.5 µm and 1.18 nm, respectively for
the calculations. The maximum field amplification factor \( (\theta = 0) \) at the corner can be calculated as 313 and at edges as 85. This is low compared to the experimentally obtained effective value of 1250. This could be because the sheets are practically having very sharp edges and multiple corners, a situation highly different from the assumed rectangular geometry. Moreover, the sheets appeared to be curved at the edges which enhance the field emission effects and are not considered while deducing the value from the empirical formula. Field emission studies of carbon nanosheets grown by radio-frequency plasma-enhanced chemical vapor deposition technique\(^\text{35}\) showed emission current levels of 1.3 mA. Graphene nanosheets obtained by our method have lesser emission current, which could be attributed to the low graphene sheet density on the substrate and also to the curved morphology.

### 3.4 Conclusions

A simple, solution phase method for producing graphene nanosheets directly from graphite using sonication and CTAB as a stabilizer has been demonstrated. The sheets could be dispersed in organic solvents such as DMF. Characterization of the sheets by UV-vis, SEM, TEM, AFM and Raman spectroscopy showed the successful exfoliation into graphene nanosheets of \( \sim 1.18 \) nm average thicknesses. Field emission measurements showed a turn on voltage of 7.5 V/\( \mu \)m and emission current densities of 0.15 mA/cm\(^2\). This approach for the production of graphene is expected to be a step forward in the challenging global efforts to solubilize graphene and in the formation of conducting composite materials. Next chapter describes the use of these CTAB stabilized graphene nanosheets for the preparation of flexible, conducting graphene/PVC composite films.

### 3.5 References


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Chapter 4

Flexible Conductive Graphene/Poly(vinyl chloride)

Composite Thin Films with High Mechanical Strength and Thermal Stability

Publications from this chapter:

4.1 Introduction

In recent years, interest in polymeric nanocomposites has been increased tremendously, since they represent an alternative to the conventional filled polymers or polymer blends.\textsuperscript{1-3} In contrast to the conventional systems, nanocomposites use at least one filler in the nanoscale range at very low loading levels.\textsuperscript{4} This characteristic feature allow these nanocomposites to match with or to exceed the material performance of conventional composites. Different types of fillers such as inorganic and carbon based materials have been employed which provide superior mechanical, thermal and conducting properties.\textsuperscript{2-6} At present, carbon-based filler materials used in polymer nanocomposites are dominated by CNTs, but high cost of production, presence of metal catalyst impurities and intrinsic aggregation impede its applications.\textsuperscript{7} The present day challenge is to find an alternative for CNTs and graphene can be a suitable candidate because of its outstanding mechanical properties and ultra large interfacial surface area.\textsuperscript{8,9} Incorporation of graphene nanosheets into elastomeric polymer matrix generates high performance composites with improved mechanical and functional properties.\textsuperscript{4,10-12} Other interesting properties such as high dielectric permittivity and low percolation threshold have also been observed in graphene incorporated composites of poly(vinylidene fluoride) and PS, respectively.\textsuperscript{13,14} Recently, GO has also been used as a filler in various polymer matrices, due to their hydrophilicity and ease of formation of stable colloidal suspensions.\textsuperscript{11,12} Besides, functionalized graphene sheets (FGS) are also employed as they provide better interactions with the host polymers compared to unmodified CNTs or traditional expanded graphite (EG).\textsuperscript{10} Functional groups on the surface of graphene sheets can be modified to incorporate strong graphene-polymer interactions.
In our current investigation, poly(vinyl chloride) (PVC) is chosen as the host polymer matrix because of its wide range of applications, low cost, chemical stability, biocompatibility and sterilizability. However, PVC has low thermal stability, which hinders some of its applications. The present day challenge is to introduce thermal stability along with high mechanical strength and electrical conductivity for PVC with the use of minimum amount of fillers. Substantial amount of work has been carried out in the past few decades towards this goal. Fillers such as clay, wood flour, wood fibers, agricultural residues, cellulose whiskers and calcium carbonate were used to improve the thermal and mechanical stability of PVC. In order to improve the electrical conductivity, carbon black and other conjugated polymers such as PANI and polypyrrole (PPy) were incorporated in the PVC matrix. Recently, CNTs have also been identified as a suitable filler material for PVC. Kevlar coated CNTs used as additives to PVC resulted in composites with improved mechanical properties demonstrating upto 50 and 70% increase in tensile strength and Young’s modulus, respectively at very low CNT loading. Similarly, CNTs grafted with styrene-maleic anhydride copolymers (SMA) was found to enhance the interaction with PVC matrix and both thermal and mechanical stabilities improved considerably. But dispersion of CNT in organic solvents is a challenge, which is very critical for the preparation of polymer composites. Moreover, no studies are available on the use of graphene as a filler material in PVC films.

This chapter elaborates on the use of CTAB stabilized dispersible graphene nanosheets as reinforcing filler for PVC at very low loading levels. In order to have efficient reinforcement in polymer nanocomposites, it is important to have homogeneous dispersion in the polymer matrix. In our case, both PVC and graphene nanosheets are readily dispersible in DMF for solution blending, which enable
homogeneous dispersion. The films are prepared by a solution blending route in which PVC is blended with different amounts of CTAB stabilized graphene sheets and the mechanical, thermal and electrical properties of the composite thin films are investigated.

4.2 Experimental Section

4.2.1 Materials

Graphite powder, CTAB and PVC in powder form (M<sub>w</sub>: 120,000) were purchased from Sigma-Aldrich. Glacial acetic acid and DMF purchased from local suppliers were used as received. Milli-Q water was used for the washings.

4.2.2 Preparation of Processable Graphene Nanosheets

A few grams of graphite flakes were sonicated with 0.5 M CTAB solution in glacial acetic acid for several hours and the resultant solution was then heated at 100 °C for 48 h in nitrogen atmosphere. Black powder obtained after centrifugation was washed with distilled water to remove the excess acid and CTAB. The resultant product formed stable dispersions in DMF.<sup>33</sup>

4.2.3 Fabrication of Graphene/PVC Composite Thin Films

Liquid phase blending method was used to make all the composite thin films. PVC was dissolved in DMF. The graphene sheets dispersed in DMF were mixed with appropriate weight fractions of PVC solutions and sonicated for 2 h. The mixtures were then drop casted in glass cells and kept in an oven at 120 °C to evaporate the solvent to get the ultrathin graphene/PVC composite films. The films were peeled off from the cells and further annealed at 100 °C for 3 h to remove remaining traces of solvent.
4.2.4 Instrumentation

AFM images were recorded using Agilent AFM with Pico plus molecular imaging system in the non-contact mode. FESEM images were recorded with JEOL JSM-6710 F field emission electron microscope. Thermal properties of the composites were studied by TGA and DSC. TGA was done using TA instrument 2960 with heating rate of 10 °C/min under N₂ and DSC with TA instrument 2920 at a heating rate of 10 °C/min under N₂ at a flow rate of 90 ml/min. Powder XRD was obtained with D5005 Siemens X-ray diffractometer with Cu Kα(1.5 Å) radiation (40 kV, 40 mA). Raman spectra were recorded with Renishaw system-2000 with an excitation wavelength of 532 nm.

4.2.5 Mechanical Characterization

A dynamic mechanical analyzer (DMA Q800, TA Instrument) was used for mechanical characterization of the composite thin films. Rectangular thin film strips of width 3 mm were used for the tensile testing. The film strips were clamped on the tension clamp such that the specimen length was 10 mm. DMA controlled force mode was used with a preload force of 0.001 N. The temperature of the chamber was raised to 20 °C and was kept constant during force ramping. The force was ramped at a rate of 0.01 N/min till the fracture occurred and the obtained mechanical properties were evaluated. For DMA, multifrequency-strain mode was utilized. A static load of 0.1 N was used and the amplitude of dynamic strain was kept constant at 0.1%. To find the influence of frequency, the specimen was held isothermally at 20 °C and deformed at the constant amplitude (strain 0.1%) over a range of frequencies and the mechanical properties were measured. To evaluate the thermal properties, the specimens were exposed to a series of increasing isothermal temperatures. At each temperature, the
material was deformed at constant amplitude (strain 0.1%) over a frequency of 1 Hz and the subsequent mechanical properties were evaluated.

4.2.6 Electrical Characterization

Film strips were accurately cut from the samples for conductivity measurements. Silver electrodes were fabricated at the end of these strips using a conductive silver pen (RS components). Tungsten probes with tip diameter 2.4 µm were used for two probe conductivity studies. A source meter (Keithley 6430) was used for I-V measurements, at room temperature. The volume fraction of graphene \( V_f \) was calculated according to the equation,

\[
V_f = \frac{W_g \rho_g}{W_g \rho_g + W_p \rho_p}
\]

where, \( W_g \) is the weight fraction of graphene and \( W_p \) the weight fraction of PVC.\(^{11}\) Density of PVC (\( \rho_p \)) was taken as 1.37 g/cc and the density of graphene (\( \rho_g \)) was taken as 2.2 g/cc for calculations.\(^{11,13}\)

4.3 Results and Discussion

4.3.1 Characterization of Graphene and Graphene/PVC Thin Films

Graphene nanosheets used in this method were prepared by CTAB assisted exfoliation of graphite described in the previous chapter. Figure 4.1A displays the tapping mode AFM image of graphene nanosheets, deposited onto the mica sheets from DMF suspension. AFM image indicated that the sheets were very small with dimensions of the order of < 1 µm. From the height profile (Figure 4.1B), the thickness was found to be of the order of 1.2 nm. Average thickness of the sheets was found to be 1.18 nm, corresponding to ~ 1-3 graphene layers. The thickness of the
films prepared was in the range of 5-7 µm. The dispersion state of graphene in PVC matrix was investigated using FESEM. Since the graphene sheets were small, it was hard to locate them.

**Figure 4.1** (A) AFM image of the exfoliated graphene nanosheets, (B) height profile of one of the sheets, (C) FESEM image of graphene/PVC composite thin film with 2 wt% concentration of graphene and (D) FESEM image of the fractured end of the composite film after mechanical testing.

Figure 4.1C shows the SEM image of graphene/PVC film with 2 wt% loading of graphene. The image shows that most of the graphene nanosheets are well dispersed in the PVC matrix, with a few restacks. It also demonstrates the random dispersion of graphene in the 3D polymer network. It should be noted that graphene sheets tend to organize inside the polymer matrix and are well dispersed in PVC. Figure 4.1D shows one of the fractured ends of the film after mechanical testing, which reveals the stacked graphene sheets. The thicknesses of the graphene sheets are increased due to complete covering of the sheets by the polymer medium.
XRD and Raman spectroscopy have also been employed to evaluate the structure of the composites. But analyses of our composite samples were difficult because of the low X-ray diffraction intensity of PVC\textsuperscript{34} and low amounts of added graphene. XRD of pure graphene showed a broad peak in the region of 20-30 degrees (Figure 4.2). However, after dispersing graphene nanosheets into the PVC (trace b in figure 4.2) matrix, no significant changes were observed.

**Figure 4.2** XRD of graphene flakes deposited on glass (trace a), 2 wt% graphene/PVC composite film (trace b) and pure PVC powder (trace c).

![XRD Graph](image)

**Figure 4.3** Raman spectra of pure graphene (trace a), 2 wt% graphene/PVC composite film (trace b) and pure PVC powder (trace c).

![Raman Spectra](image)
The Raman spectra of the 2 wt% graphene/PVC composite films were generally similar to that of the surfactant stabilized graphene sheets, indicating the distribution of graphene in the polymer matrix. Signature features of graphene (D, G and 2D bands) were clearly seen in the 2 wt% graphene/PVC composite films (Figure 4.3). The Raman spectrum of PVC and the graphene/PVC composite showed a few extra peaks around 1100, 1300, 1430 and 2250 cm\(^{-1}\). The peaks around 1100 and 1300 cm\(^{-1}\) arise from the C=C stretching of the PVC backbone and -CH bending of the –CHCl group, respectively. The peak at 1430 cm\(^{-1}\) is assigned to the CH\(_2\) scissors vibration. The origin of peak around 2250 cm\(^{-1}\) is not understood.

### 4.3.2 Mechanical Characterization of the Graphene/PVC Thin Films

It was expected that incorporation of graphene nanosheets in PVC matrix would enhance the mechanical properties of PVC, because of the strong adhesion at the interface.

![Figure 4.4](image)

**Figure 4.4** (A) Representative stress strain curves for various weight fractions of the graphene/PVC composite films and (B) the calculated Young’s modulus based on the slope of the elastic region.

The mechanical performance of graphene/PVC composite films was significantly increased compared with pure PVC film. Representative stress-strain curves for various weight fractions of graphene/PVC composite films are plotted in figure 4.4A.
The slope of the curves increases with increasing the concentration of graphene content. The presence of graphene in the PVC matrix offers resistance to the segmental movement of polymer chains upon application of the tensile stress, which led to enhancement in modulus. The toughness of the composite is estimated from the stress-strain curve. It is seen that toughness is reduced significantly for lower weight fractions. However, for higher weight fractions (wt% >5), the toughness is not reduced significantly. The corresponding Young’s modulus values are shown in figure 4.4B. The addition of graphene significantly increased the Young’s modulus. For the composite film with 2 wt% of graphene loading, Young’s modulus increased to 2 GPa, corresponding to an increase of 58% (relative to the pure PVC film).

![Graphene (wt%) vs elongation break (%)](image)

**Figure 4.5** Mechanical properties of PVC thin films with different graphene loadings when stretched at the rate of 0.01 N/min at 20 °C.

The percentage elongation at breakage and the tensile strength of the graphene/PVC films are summarized in figure 4.5. It is obvious that the addition of graphene has a significant effect on the mechanical behavior of pure PVC. The average value of percentage elongation decreased to 85% for 0.5 wt% graphene loading from 124% for the pure PVC film. A further increase in graphene loading significantly reduced the percentage elongation before fracture (Figure 4.5). This can be attributed to the
interaction between graphene and the polymer matrix which restricts the movement of polymer chains.

On the other hand, tensile strength increases with increase in the graphene content. The average tensile strength for pure PVC thin film is 24 MPa. The strength gradually increased to 30 MPa for 1 wt% and further to 55 MPa for 2 wt% of graphene loading, which corresponds to an improvement of 130%. Further increase in the graphene content did not produce significant changes. When the graphene content was increased beyond 2 wt%, the tensile strength increased slightly from 55 to 56 MPa (for 5 wt% loading). Besides, the change in value of elongation at break is also not very prominent (40% for 2 and 38% for 5 wt% graphene loading). This kind of behavior could be due to the restacking of graphene flakes after certain level of loading. This offers no significant improvement in mechanical properties. Beyond this critical loading limit, tensile strength will not be significantly affected.\textsuperscript{11}

4.3.3 Dynamic Mechanical Thermal Analysis

Dynamic analysis was done at various temperatures to evaluate the thermal stability. Significant increase in storage modulus was observed (Figure 4.6A).

![Figure 4.6](image)

**Figure 4.6** (A) Storage modulus and (B) Tan δ curves for the graphene/PVC films when deformed at constant amplitude of 0.1% at a frequency of 1 Hz at various temperatures.
In both glassy and rubbery regions, the storage moduli of the graphene/PVC composite thin films are higher than that of pure PVC film. For instance at 20 °C, the storage modulus is only 0.5 GPa for pure PVC film whereas it was increased to almost 3 GPa (approximately fivefold increase) for 2 wt% graphene/PVC films. At lower temperatures, the material is in the glassy state and undergoes a transition from glassy to rubbery state with increase in temperature. The storage moduli fall by a few orders of magnitude. Energy dissipation is maximum during this transition as the loss factor (Tan δ) peaks to maximum (Figure 4.6B). The thermal stability of the graphene/PVC composite films have also been greatly improved as seen from the glass transition peaks in the Tan δ curves. The glass transition occurs at 85-88 °C for pure PVC films, whereas it shifts to temperatures as high as 105 °C for 2 wt% graphene loaded PVC films. The maxima of the Tan δ occurs at a temperature where the energy loss due to additional degrees of freedom takes place, which is a measure of the $T_g$ associated with α-relaxation of the polymeric material. The peaks also have been significantly broadened. Both the graphs in figure 4.6 point to a rise in $T_g$ accompanied by a broadening of this relaxation indicative of restriction in segmental relaxation. It could be inferred that molecular dynamics in the composites is highly influenced by the fillers, thereby increasing the glass transition temperature and the thermal stability of the composites as compared to pure PVC films. The well dispersed graphene nanosheets restrict the segmental motion of polymer chains inside the matrix.

To further analyze the influence of the graphene reinforcement, the storage modulus of the composites relative to that of pure PVC ($E'_{\text{composite}}/E'_{\text{PVC}}$) was measured at 1 Hz and plotted as a function of temperature. Moderate increase in
storage modulus (upto 5 times) can be seen in the glassy regime (Figure 4.7A) and improved further in the glass transition regime (Figure 4.7B). For 1 and 2 wt% of graphene loading, the relative modulus $E'_{\text{composite}}/E'_{\text{PVC}}$ drastically increased upto a maximum value at about 100 °C. With further rise in temperature after glass transition, the rubber-like regime persisted and the relative moduli decreased slightly.

![Graphs showing the temperature dependence of the relative storage modulus at (A) low temperature regime and (B) glass transition temperature regime.](image)

**Figure 4.7** Graphs showing the temperature dependence of the relative storage modulus at (A) low temperature regime and (B) glass transition temperature regime.

The relative moduli above $T_g$ are greater than the respective values below $T_g$. The storage modulus values are highly influenced by the interfacial interactions between the graphene sheets and PVC matrix. The observed results suggest a strong interfacial bonding between graphene and the PVC segments. The polymer chain mobility was confined near $T_g$ by graphene so that the relative storage modulus was increased.

The $T_g$ values at various weight fractions of graphene filling and the values of loss factor (Tan $\delta$) are summarized in figure 4.8. It could be seen that the loss factor reduces significantly with increase in graphene content. Tan $\delta$ reflects the mobility and movement capacity of molecule chain segments during glass transition. It is clear that the movements of PVC chain segments during glass transition were significantly limited and obstructed by the presence of graphene layers, resulting in much smaller
Tan $\delta$ peaks in composite samples. The graphene layers act as “physical crosslink” which limits the movements of macromolecular chains of PVC during glass transition. The low value of loss factor also depicts an elastic polymeric behavior, whereas the high value shows a viscous behavior. The presence of graphene in the PVC matrix makes the material more elastic in nature, especially in the glass transition regime, which indicates enhanced thermal stability of the material.

![Graph showing the glass transition temperature ($T_g$) and the loss factor (Tan $\delta$) values at various weight fractions of graphene in PVC matrix.](image)

**Figure 4.8** Graph showing the glass transition temperature ($T_g$) and the loss factor (Tan $\delta$) values at various weight fractions of graphene in PVC matrix.

Thermal properties of the composite films were further evaluated with TGA and DSC. The TGA curves of the pure PVC and graphene/PVC composite films are shown in figure 4.9A. Both pure PVC and the nanocomposites follow two stage degradation processes. The first thermal decomposition onset temperature is shown as $T_1$ and the second thermal decomposition onset temperature as $T_2$. Two major weight losses were observed in all cases (Figure 4.9A). The first weight loss was observed in the range 250-360 °C for pure PVC, which corresponds to the loss of HCl.$^{37}$ At this temperature, the Cl radicals formed from the cleavage of –C–Cl bonds abstract a
hydrogen from the neighbouring C–H bond resulting in the evolution of HCl molecules from the polymer chain. Once the reaction is initiated, the “allyl” activation continues and all the Cl atoms get dislocated along the macromolecule chain leaving behind the polyene backbone.\textsuperscript{37}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4_9.png}
\caption{(A) TGA curves for graphene/PVC composite films and (B) DSC curves to determine the glass transition temperature.}
\end{figure}

From the TGA traces, it was observed that $T_1$ reduced to 230 °C by increasing the graphene content from 0.5 to 2 wt%. This is because the graphene nanosheets act as reinforcing particulate filler which attracts Cl, thus the C–Cl bonds in PVC are destabilized at this temperature. From 360 to 420 °C, no weight loss was observed, indicating the stability of the composite films at this temperature. The second major weight loss ($T_2$) was observed in between 420 and 500 °C, and it was much shorter than $T_1$. Thermal degradation of the polyene backbone takes place at this stage, resulting in the formation of volatile aromatic compounds and a stable carbonaceous residue.\textsuperscript{36} The amount of carbonaceous residue increases with increase in the amount of graphene loading (Figure 4.9A). $T_g$ of the composite films obtained from DSC (Figure 4.9B) were 80.8 (0 wt% graphene) and 84.3 (2 wt%). Reinforcing effect of the
graphene content reduces the chain segmental mobility and hence the enhancement in $T_g$ was observed with increase in the graphene content. Difference in $T_g$ values obtained from DMA analysis and DSC measurements can be accounted with the fact that $T_g$ from DMA is highly dependent on the test frequency and variations in the $T_g$ values are possible. The surface area of individual graphene flakes is large, so the interaction between PVC chains and graphene layers might limit the conformations of polymer molecules in the composites. Moreover, if the radius of gyration of polymer chain (a few nm) is larger than the interlayer distance of graphene in the PVC matrix, the polymer chains intercalates between the layers and confined environment will restrict the mobility of PVC segmental chains.

### 4.3.4 Electrical Properties

![Graph showing the influence of exfoliated graphene on the electrical conductivity of PVC.](image)

**Figure 4.10** Graph showing the influence of exfoliated graphene on the electrical conductivity of PVC.

The electrical conductivity, $\sigma$ of graphene/PVC composite thin films plotted as a function of volume percentage of graphene is shown in figure 4.10. The conductivity of pristine PVC thin film is less than $10^{-16}$ S/cm. At a graphene content of about
0.025, 0.05 and 0.075 vol%, the composite films did not show any measurable values of conductivity. However at about 0.1 vol%, a sharp increase in the conductivity was observed. A further increase in the volume fraction of graphene gave rise to a sharp increase in the conductivity (Figure 4.10). At 0.12 vol%, the conductivity was $3.19 \times 10^{-9}$ S/cm, whereas at 0.3 vol% the conductivity increased to $2.14 \times 10^{-7}$ S/cm. Subsequent increase in concentration to 0.6 and 1.3 vol% led to an increase of conductivity to $4.92 \times 10^{-7}$ S/cm and $7.81 \times 10^{-6}$ S/cm, respectively. A further increase in concentration levels upto 6 vol% give only moderate rise in conductivity. From the graph, it can be clearly seen that there is a rapid increase in the conductivity at 0.6 vol% of the filler content, which is the percolation threshold for the composite films. Thus, it is concluded that the conductivity increases drastically upto 0.6 vol% of graphene, above which the rate of increase was minimum. The maximum conductivity observed was 0.058 S/cm, at 6.47 vol% of the filler content which is 10 times higher than that of the SWNT/PVC composites.

4.4 Conclusions

Ultrathin composite films of CTAB stabilized graphene nanosheets and PVC was fabricated and its mechanical, thermal and electrical properties were investigated. The composite thin films were prepared by a solution blending route in which the PVC was appropriately blended with graphene nanosheets prepared by CTAB assisted exfoliation. A significant enhancement in the mechanical properties of pure PVC films was obtained with a 2 wt% loading of graphene, such as a 58% increase in Young's modulus and an almost 130% improvement of tensile strength. Thermal stability was found to be improved to a greater extent with an increase in the glass transition temperature. The films were found to possess high electrical conductivity
with a low percolation threshold of 0.6 vol%. Composites using graphene is promising, but the availability of processable graphene sheets in large quantities is crucial and challenging. Next chapter deals with the covalent functionalization on CTAB stabilized graphene sheets, which enhance the processability in common organic solvents. This is very essential for its applications in polymer and inorganic composites.

4.5 References


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Chapter 5

Functionalization of Surfactant Wrapped Graphene Nanosheets with Alkylazides for Enhanced Dispersibility

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5.1 Introduction

Graphene is an infinite 2D sheet of $sp^2$ bonded carbon atoms with extended electronic conjugation. Since its discovery in 2004, the material has triggered enormous interest in both fundamental and applied science communities because of the unique electrical, thermal and mechanical properties.\textsuperscript{1-12} However, use of this new material in sensors, electronic and photovoltaic devices has been hindered by the unavailability of stable and processable graphene structures.\textsuperscript{12c,13-16} Pure graphene sheets are highly hydrophobic and easily agglomerates because of the strong $\pi - \pi$ interactions. Recently, considerable efforts have been made to improve the dispersibility of graphene sheets \textit{via} covalent and non-covalent interactions. One of the strategy relies on the use of GO. Covalent and non-covalent modifications of GO using various stabilizers such as polymers,\textsuperscript{17} hydrazine,\textsuperscript{18} amine derivatives,\textsuperscript{19} diazonium salts,\textsuperscript{20} phenyl isocyanates,\textsuperscript{21} aromatic compounds\textsuperscript{22} and biomolecules have been reported.\textsuperscript{23} GO is easy to stabilize in aqueous and polar conditions because it contains chemically reactive oxygen functionalities such as hydroxyl and epoxide groups.\textsuperscript{20b} Even though, reduction can remove most of the oxygen functionalizations, significant amount of oxygen groups still remains in the basal plane, which disrupts the $\pi$ - conjugation. Sonication assisted dispersion of graphene in DMF\textsuperscript{24} or NMP\textsuperscript{25} and electrochemical methods\textsuperscript{26} have also been reported, however only small graphene fragments can be obtained through this method.

Given the interest in graphene chemistry, it is desired to have convenient dispersion routes to increase the availability and processability of graphene. To improve the solution processability of graphene, a few methods that have been
employed for the functionalization and stabilization of CNTs can be adopted.\textsuperscript{27,28} Moreover, chemical functionalization of the carbon network in graphene by grafting atoms or molecules is very important because this provides a method for the introduction of interesting photoactive molecules for the development of optoelectronic materials. An interesting functionalization to try on graphene is the azide addition because many organic azides have been used for the covalent modification of single-walled and multi-walled CNT.\textsuperscript{29} Azides are considered as one of the useful reactive intermediates during nucleophilic aromatic substitution in organic reactions and are frequently used in a variety of reactions.\textsuperscript{30}

\begin{equation}
\begin{array}{cccccc}
\text{R} & \text{N}_3 & \rightarrow & \text{R} & \text{H} & \text{OH} \text{COOH}
\end{array}
\end{equation}

**Scheme 5.1** Schematic representation of the covalent functionalization of graphene sheets with various alkylazides.

Based on this concept, a mild covalent functionalization of CTAB wrapped graphene sheets using a series of azides, which include alkylazides (hexyl and dodecyl), 11-azidoundecanol (AUO) and 11-azidoundecanoic acid (AUA) is described in this chapter. Besides azido group, other functional groups such as hydroxyl and carboxylic groups are incorporated to enhance the dispersibility in common organic solvents. The functionalized sheets are characterized by FTIR, Raman spectroscopy and various imaging techniques. Besides, the reactive sites on the graphene sheets were marked
using gold nanoparticles. Free carboxylic acid groups present in the AUA functionalized sheets bind with gold nanoparticles, indicating that the reaction has taken place not just at the edges but also at the internal C–C bonds of graphene. In short, our results show that the covalent functionalization using azides provides a useful platform for the synthesis of functional graphene nanocomposites using metal nanoparticles.

5.2 Experimental Section

5.2.1 Materials

Sodium azide (NaN₃), 11-bromoundecanoic acid, 11-bromo-1-undecanol, dodecyl bromide, hexyl bromide, anhydrous Na₂SO₄, CTAB, graphite powder (> 45 µm), chloroauric acid (HAuCl₄·3H₂O) and NaBH₄ were from Sigma-Aldrich and used as received. The solvents were of analytical grade and were obtained from local suppliers.

5.2.2 Analysis and Instruments

NMR of the synthesized organic compounds was recorded using Bruker ACF spectrometer operating at 300 MHz. Chloroform-d (CDCl₃) was used as the solvent and tetramethylsilane (Me₄Si) as internal standard. Electron impact (EI) mass spectrum was recorded using Finnigan MAT95XL-T mass spectrometer. UV-visible spectrum was recorded using Shimadzu 1601 PC spectrophotometer. FTIR spectra were recorded at 1 cm⁻¹ resolution in the wave number range of 4000-400 cm⁻¹ using a Bio-Rad FTS 165 FTIR spectrophotometer. HRTEM images were taken using JEOL JEM-2010 F electron microscope, operating at 200 keV. STM measurements were performed on Au (111) substrate (Goodfellow, UK) using a NanoScope IIIa
MultiMode SPM (Digital Instrument, Veeco Metrology Group) with electrochemically etched Pt(0.8) Ir(0.2) tips (0.25 mm diameter). A drop of graphene solution deposited on Au(111) substrate was used for STM measurement. STM images were obtained at a tunneling current of 2 pA and a bias voltage of 50 mV. AFM images were recorded using Agilent AFM with Pico plus molecular imaging system in the non-contact mode. Samples for AFM were prepared by drop casting a dilute suspension of graphene on freshly cleaved mica and then dried at room temperature. Raman spectra were recorded with a Renishaw system-2000 operating at an excitation wavelength of 532 nm. A source meter (Keithley 6430) was used for the I-V measurements at room temperature. The samples for electrical characterization were prepared by drop casting the DMF suspensions of the samples on Si substrate with 300 nm SiO\textsubscript{2} coating. The sheets were found to be intercalated and formed a continuous network over the SiO\textsubscript{2} surface. Tungsten probes with a tip diameter of 2.4 µm were precisely positioned over the thin films at a distance of 10 µm.

5.2.3 Preparation of CTAB Stabilized Graphene Sheets\textsuperscript{31}

In brief, 100 mg of graphite powder were sonicated with CTAB solution in glacial acetic acid for 4 h. The resultant solution was then refluxed for 48 h under N\textsubscript{2} atmosphere. The reaction mixture was left to stand overnight to allow the aggregated sheets to settle down. The supernatant was decanted and centrifuged at 20,000 rpm for 45 min. The resultant black residue obtained could be resuspended in DMF.

5.2.4 General Synthetic Procedure for Alkylazides

To a solution of alkyl bromide in DMSO, solid NaN\textsubscript{3} was added at a time. The solution was stirred at room temperature for 20 h before it was quenched with excess amount of water. It was extracted with DCM. The combined organic layer was dried
over anhydrous Na$_2$SO$_4$ and evaporated under reduced pressure to get the colourless liquid.

(1) **Dodecylazide**: Dodecyl bromide (1 g, 4.02 mmol), NaN$_3$ (0.314 g, 4.82 mmol), DMSO (20 ml), Yield = 0.7 g, 83%. $^1$H-NMR (CDCl$_3$, 300 MHz): δ 3.22 (t, CH$_2$N$_3$, 2H) 1.64 - 1.26 (m, 10 CH$_2$, 20H).

(2) **Hexylazide**: Hexyl bromide (1 g, 6.06 mmol), NaN$_3$ (0.475 g, 7.31 mmol), DMSO (20 ml), Yield = 0.63 g, 82%. $^1$H-NMR (CDCl$_3$, 300 MHz): δ 0.88 (t, CH$_3$, 3H), 1.41 - 1.28 (m, 5 CH$_2$, 10H).

5.2.5 Synthesis of 11-azidoundecanol (AUO)$^{32}$

A mixture of the 11-bromo-1-undecanol (1 g, 3.98 mmol), NaN$_3$ (0.777 g, 11.95 mmol) in dry DMF (20 ml) was stirred at 80 °C overnight under N$_2$ atmosphere. After removing the DMF by evaporation, the residue was dissolved in DCM, washed with water, dried over anhydrous Na$_2$SO$_4$ and evaporated to get a yellowish liquid (0.78 g, 92%). $^1$H-NMR (CDCl$_3$, 300 MHz): δ 3.54 (t, CH$_2$OH, 2H), 3.19 (t, CH$_2$N$_3$, 2H), 1.56 - 1.22 (m, 9 CH$_2$, 18H).

5.2.6 Synthesis of 11-azidoundecanoic acid (AUA)$^{33}$

NaN$_3$ (294 mg, 4.52 mmol) was dissolved in a solution of 11-bromoundecanoic acid (1 g, 3.77 mmol) in DMSO (20 ml). It was stirred at room temperature for overnight. The reaction mixture was diluted with water and 1M HCl was added. The aqueous phase was extracted (3 × 15 ml) with ethyl acetate and the combined organic layers were washed with water, dried over anhydrous Na$_2$SO$_4$ and evaporated to get the 11-azidoundecanoic acid (0.67 g, 78%) as a pale brown oil (Elemental analysis, found: C, 58.2; H, 9.2; N, 18.5; O, 14.1. C$_{11}$H$_{21}$N$_3$O$_2$ requires C, 58.12; H, 9.32; N, 18.49; O, 14.08%); $^1$H-NMR (CDCl$_3$, 300 MHz): δ 10.25 (s, COOH, 1H), 3.22 (t, CH$_2$N$_3$, 2H),
2.31 (t, CH$_2$COOH, 2H), 1.59 - 1.54 (m, CH$_2$CH$_2$N$_3$ and CH$_2$CH$_2$COOH, 4H) and 1.27 (m, 6 × CH$_2$, 12H); m/z (EI) 140.1 (M$^+$, C$_4$H$_7$O$_2$ C$_7$H$_{14}$N$_3$ requires 140.12), 126 (5%), 112 (8), 98 (9), 84 (26), and 70 (100).

5.2.7 Functionalization of CTAB Stabilized Graphene Nanosheets with 11-azidoundecanoic acid (AUA)

For AUA functionalized graphene sheets, two different weight ratios of graphene to AUA (1:1 and 1:10) were used to check the changes in dispersibility with the extent of functionalization. Weight of graphene was kept constant for convenience. Briefly, 20 mg of the CTAB assisted exfoliated graphene$^{31}$ was dispersed in 50 ml of ODCB. The solution was purged with nitrogen and preheated to 160 °C. Different amounts of AUA (20 and 200 mg, respectively) in 5 ml of ODCB were then added drop wise to the reaction mixture over a period of 20-30 min. The temperature was maintained at 160 °C for 45 min, after which the product was cooled to room temperature. The suspension was diluted with acetone to flocculate the functionalized graphene sheets. Subsequent washing and centrifugation resulted in the removal of all by-products. The nanosheets were decanted and dried.

5.2.8 Preparation of Gold/Graphene Nanocomposites

Gold nanoparticles were synthesized in presence of AUA functionalized graphene sheets. To 10 ml of the functionalized graphene suspension (∼ 0.05 mg/ml) in DMF, HAuCl$_4$ solution was added so that the final concentration of Au$^{3+}$ was 10 mM. It was then reduced with the addition of 500 µl freshly prepared NaBH$_4$ (2 × 10$^{-4}$ M) solution with continuous stirring. The color of the solution gradually changed from grayish black to dark pink. Formation of nanoparticles was confirmed using spectroscopic and microscopic techniques.
5.3 Results and Discussion

5.3.1 Characterization of the Functionalized Graphene Nanosheets

Scheme 5.1 illustrates the process of covalent functionalization of CTAB stabilized graphene nanosheets\textsuperscript{31} with various alkylazides. A large area AFM image of the CTAB stabilized graphene nanosheets are shown in figure 5.1A.

![Figure 5.1](image)

**Figure.** 5.1 (A) AFM image of the CTAB stabilized graphene sheets and (B) corresponding section analysis.

When the CTAB stabilized sheets are treated with azides, nitrenes are inserted into the double bonds on graphene and the alkyl chains with different functional groups at the terminals. It is conceivable that the presence of long alkyl chains and polar functional groups improves the dispersibility. The functionalization with dodecylazide, AUO and AUA improved the dispersibility of graphene sheets in common organic solvents such as toluene and acetone and the dispersions were stable for a few days (Figure 5.2A). In the case of hexylazide, the dispersions were not stable and the sheets were agglomerated (Figure 5.2B). It can be attributed to the shorter alkyl chain of hexylazide. In the case of AUO and AUA, the functionalization led to an enhanced dispersibility in common solvents. Presence of polar functional groups on the
graphene surface is desirable because it assist in enhancing the dispersibility.

![Figure 5.2](image1.png)

**Figure 5.2** SEM images of (A) dodecylazine functionalized graphene sheets and (B) hexylazine functionalized graphene sheets.

![Figure 5.3](image2.png)

**Figure 5.3** TEM images of (A) AUO functionalized graphene sheets and (B) corresponding gold/graphene nanocomposite.

Besides, functional groups such as \(-\text{COOH}\) and \(-\text{OH}\) can anchor metal nanoparticles onto the surface, which may help in visualizing the reactive sites. Hence, gold nanoparticle synthesis was attempted in presence of both AUO and AUA functionalized graphene sheets. In presence of AUO functionalized sheets, the gold nanoparticles were aggregated on their surface. TEM images of the AUO functionalized sheets and the gold nanocomposites are given in figure 5.3A and B, respectively. A possible reason for this may be the poor stabilizing/co-ordinating
effect of hydroxyl groups. However, gold nanocomposites with AUA functionalized graphene sheets were found to be stable without any visible aggregation. Hence we focused our studies with AUA functionalized graphene owing to the fact that the presence of –COOH groups on the surface might enhance the metal nanoparticle/graphene composite stabilities and dispersibility. Dispersibility of the resultant product was poor when 1:1 weight ratio of graphene to AUA was used for functionalization. It could be due to minimal functionalization on the graphene sheets. TEM image of the dispersed sample is given in figure 5.4.

![TEM image of dispersed AUA functionalized graphene sheets](image)

**Figure 5.4** TEM images of AUA functionalized graphene sheets, with 1:1 weight ratio of graphene vs AUA used. Inset clearly shows the settled particles in the respective dispersed solutions in toluene. All the sheets were found to settle down within 1 h.

Treatment of graphene with AUA at 1:10 ratio led to the formation of considerably dispersible solid. These sheets were found to be easily dispersible in polar solvents with a mild sonication. These samples were used for subsequent experiments. The dispersibility was found to be high in DMF. In the case of CTAB stabilized graphene sheets, the maximum dispersibility achieved was ~ 0.005-0.01 mg/ml, but for AUA functionalized sheets, it could reach up to a maximum of ~ 0.05-0.1 mg/ml.
Figures 5.5A and B show the TEM micrographs of the CTAB stabilized and AUA functionalized graphene sheets, respectively. Due to the distortions caused by the covalent functionalization, sheets attain a crumpled topology (Figure 5.5B). As reported previously, crumpling and scrolling are intrinsic properties of thin graphene sheets, which is due to the extra thermodynamic stability of the 2D membranes arising from microscopic crumpling either by bending or buckling.\textsuperscript{34}

![TEM images](image)

**Figure 5.5** TEM images of (A) CTAB stabilized and (B) AUA functionalized graphene sheets. (C) FTIR of AUA and AUA functionalized graphene sheets (trace A and B, respectively) and (D) Raman spectra of CTAB stabilized (trace 1), AUA functionalized graphene sheets with 1:1 and 1:10 w/w of graphene to AUA.

To verify the covalent functionalization of graphene sheets with AUA, FTIR was performed (Figure 5.5C). Traces A and B correspond to the IR spectrum of AUA.
and AUA functionalized graphene sheets (1:10 w/w of graphene to AUA), respectively. The peak at ~ 2100 cm\(^{-1}\) corresponds to the azido stretching\(^{35}\) and that at 1730 cm\(^{-1}\) to the carbonyl stretching from the \(-\text{COOH}\) group. Absence of azido stretching peak in AUA functionalized graphene sheets implies the covalent functionalization.\(^{29b}\) Azides are added onto C=C bonds on graphene with the elimination of N\(_2\). IR spectrum of the AUA functionalized graphene sample showed the presence of C–N (\(~ 1128 \text{ cm}^{-1}\) ) and C=C stretching (\(~ 1630 \text{ cm}^{-1}\) ).

Figure 5.5D shows the Raman spectra of CTAB stabilized graphene sheets (trace 1) and the AUA functionalized sheets with 1:1 and 1:10 w/w of graphene to AUA (traces 2 and 3, respectively). The peak centered at \(~ 1350 \text{ cm}^{-1}\) corresponds to the disorder induced D band and that at \(~ 1580 \text{ cm}^{-1}\) to the E\(_{2g}\) phonon of sp\(^2\) atoms.\(^{36}\) Intensity of the D band is directly proportional to the amount of disorder present in the sheets. The D band intensity increased considerably with azide functionalization, owing to the disorders induced by the addition of nitrenes to the double bonds. Another prominent feature in the Raman spectra of graphene samples is the 2D (or G') peak. No defects are required for the existence of this band and is seen even when no D band is present.\(^{25}\) The number of layers present in the graphene sheets can be evaluated from the shape of 2D peak.\(^{37}\) Graphene sheets with less than five layers have very broad 2D peak, which can be clearly seen in the case of both CTAB stabilized and AUA functionalized graphene samples.

The thickness and morphology of the functionalized graphene sheets was evaluated using AFM (Figure 5.6A). From the cross section analysis of one of the flakes, thickness was found to be 1.12 nm (Figure 5.6B). Analysis of a large number of AFM images revealed graphene sheets with lateral dimensions of 500-
2000 nm and thickness in the range of 1-1.3 nm (Figure 5.7). Thickness of a monolayer of graphene sheets is 0.34 nm as predicted by theory,\(^4\) while our samples showed an average thickness of 1.3 nm, indicating the presence of 2-3 layered graphene sheets.

Figure 5.6 AFM images of (A) the AUA functionalized graphene sheets and (B) the section analysis.

Figure 5.7 Statistical analysis on the thickness of the AUA functionalized graphene sheets.

Slight increase in the thickness of the sheets as compared with the CTAB stabilized sheets\(^{31}\) can be attributed to the presence of long alkyl chains present on both sides of the sheets. Finally, STM analysis was carried out on the samples to detect the disorders caused by functionalization. Highly ordered hexagonal lattice
of graphene was seen in the case of CTAB stabilized graphene flakes (Figure 5.8A). Small non-uniformities arose from the presence of loosely bound residual surfactants.

Figure 5.8 STM images of (A) CTAB stabilized and (B) AUA functionalized graphene sheets.

However, the STM image of AUA functionalized sheets clearly showed many bright regions, lacking the hexagonally ordered arrangement. These disorders could be due to the functionalization on certain areas (Figure 5.8B). The functionalized regions are highlighted with white contours.

5.3.2 Characterization of Gold/Graphene Nanocomposites

It is conceivable that the presence of –COOH groups present in the anchored AUA moieties on graphene helps in binding the nanoparticles on the graphene surface. Hence gold nanoparticles were synthesized in presence of AUA functionalized graphene sheets. Figure 5.9A shows the absorption spectra recorded for the AUA functionalized graphene sheets (trace A) and the gold-graphene nanocomposite solutions (trace B), respectively. Inset of figure 5.9A shows the photograph of corresponding solutions (solutions are diluted 10 times for better contrast). Gold/
AUA functionalized graphene nanocomposites formed were stable for several days, with no visible aggregation. It is well known that surface plasmon resonance (SPR) of the metal nanoparticles depends on their size. In our sample, the SPR band was around 520 nm, which corresponds to a size > 5 nm. The size and shape of gold nanoparticles on graphene sheets were further confirmed using TEM and AFM measurements.

Figure 5.9 (A) UV-vis spectra of the AUA functionalized graphene sheets (trace A) and that of the gold/graphene nanocomposites (trace B) solutions. Inset of figure 5.9A shows the photograph of (A) functionalized graphene solution and that of (B) the gold/AUA graphene composite in DMF. (B) TEM image and (C) the AFM image with (D) the cross-section analysis of the gold/graphene nanocomposite sheets.

Homogeneous grafting of gold nanoparticles on the graphene film is visible in the TEM image (Figure 5.9B). From the TEM images, average size of the
nanoparticles was found to be $9.5 \pm 2.2$ nm. The AFM image also depicts fine
distribution of nanoparticles on the graphene nanosheets (Figure 5.9C). From the
cross sectional analysis (Figure 5.9D), the height from background was found to
be $\sim 1.26$ nm, corresponding to the AUA functionalized graphene sheet thickness.
The smaller peaks seen in the cross section were from the gold nanoparticles
anchored on the graphene surface. Even though the reaction mechanism is not
clear at this stage, it is believed that the nanoparticles are adhered onto the
functionalized graphene sheets via electrostatic interactions and $-\text{COOH}$ groups.
Uniform distribution of the nanoparticles on the AUA functionalized graphene
indicates that the reaction has taken place not just at the edges of the graphene
sheets but also at the central C–C bonds. This is very interesting because this
method of functionalization can open up new reaction routes for the synthesis of
graphene based functional composite materials.

![Figure 5.10 I-V plots of films of (A) AUA functionalized graphene sheets and (B) gold/graphene nanocomposites.](image)

Primary investigations on the applicability of gold/graphene composite as a
conducting composite material were carried out using I-V measurements. Figure
5.10 shows the I-V plots of drop casted films of AUA functionalized graphene
sheets and gold/graphene nanocomposite. It is evident from the graph that AUA functionalized graphene sheets show low conductivity due to the lack of extended $\pi$-conjugation. The film showed conductance of 22 nA at an applied voltage of 10 V (trace A). In the case of gold/graphene nanocomposite, the conductivity increased approximately three fold as compared to pure functionalized sheets. Gold/graphene nanocomposite films showed conductance of 76 nA at an applied voltage of 10 V (trace B). The increase in conductance for the gold/graphene composites can be attributed to the presence of attached gold nanoparticles. Both the drop casted samples contained the same concentration of graphene sheets. Hence, it can be concluded that the increased conductivity is due to the embedded gold nanoparticles. Some of the earlier works on GO based composites showed 6 fold$^{39}$ and 270000 fold$^{40}$ increases in conductance on reduction of GO by chemical means. This increase can be attributed to the restoration of $\pi-\pi$ electronic conjugation or presence of metallic impurities on the graphene surface. In our case, there is no restoration of the extended conjugation or use of metallic reducing agents, therefore the increase in conductivity is mainly due to the embedded gold nanoparticles which create the conducting pathways. The conductivity obtained is lower than that of bulk graphite since the measurement was done on drop-casted films with multiple discontinuities.

5.4 Conclusions

In conclusion, we have demonstrated a mild and simple functionalization technique for dispersing graphene sheets. CTAB stabilized graphene sheets were functionalized with various alkylazides. Sheets functionalized with azides having longer alkyl chains and polar functional groups showed enhanced dispersibility in
common organic solvents such as acetone and toluene. AUA functionalized sheets showed better dispersibility and stability in the solution state. The functionalizations were confirmed using various imaging and spectroscopic techniques. Thicknesses of the functionalized sheets were found to be in the range of 1-1.3 nm. This approach can be used for the introduction of various functional moieties into graphene sheets, this may prove to be very useful for applications in electronic devices and graphene based composite materials. Anchoring of gold nanoparticles onto AUA functionalized graphene sheets were also demonstrated. This gold/graphene nanocomposite was stable in solution for several days and showed threefold increase in conductivity as compared to the pure AUA functionalized sheets. Such metal nanocomposites could be promising candidates for catalytic and electronic applications.

5.5 References


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Chapter 6

Bromination of Graphite - A Novel Route for the Exfoliation and Functionalization of Graphene Sheets
6.1 Introduction

In the recent years, there has been an increased interest in producing a few-layered or individual graphene sheets.\textsuperscript{1-3} The unique electronic, thermal and mechanical properties of graphene make it a suitable substituent for other carbon nanostructures.\textsuperscript{2a,4-6} Graphene and its composites are used as building blocks for different devices such as transistors, organic photovoltaic devices and transparent anodes.\textsuperscript{7-9} In addition, graphene also provides a high surface area scaffold for the covalent attachment of organic molecules, which is highly beneficial for the incorporation of graphene into polymer composites with enhanced mechanical and electronic properties.\textsuperscript{3a,10}

Majority of the reports on covalent functionalizations of graphene relies on the use of GO. GO is produced by the chemical oxidation of graphite, which introduces many epoxide, carboxyl and hydroxyl functional groups in the basal plane.\textsuperscript{11} While covalent functionalization using GO produce functionalized material, the processing is limited to polar or aqueous conditions.\textsuperscript{12} Besides, an additional reduction step is required for the removal of excess oxides present, which might leave significant amount of defects leading to reduced electronic properties.\textsuperscript{13} Therefore, it is important to develop direct functionalization methods for graphene to obtain processable graphene layers and to modify the electronic properties according to the applications.

In this regard, bromination of graphene sheets is explored using the facile intercalation of graphite by liquid bromine/bromine vapor.\textsuperscript{10b} Bromination of graphitic materials takes place via electrophilic addition of bromine molecules to the aromatic double bonds. In this chapter, we show that the brominated graphene sheets can be transferred to various substrates either by deposition from organic-water
interface or by spreading of carbon nanotubes on the surface. Besides, bromine atoms covalently linked to graphene sheets are substituted with alkyamines and coupled with arylboronic acids which offer an opportunity to integrate graphene into various devices. Bromination and subsequent reactions might lead to a change in the carrier density of graphene and may be useful to alter the electronic properties.

Scheme 6.1 Schematic representation of the bromination and subsequent alkylation/arylation using dodecylamine and arylboronic acids. Reaction conditions: (a) dodecylamine, \((\text{C}_2\text{H}_5)_3\text{N}\), toluene, reflux, 24 h. (b) pyrene 1-boronic acid/5-hexyl-2,2'-bithiopheneboronic acid pinacol ester, Pd (0), \(\text{K}_2\text{CO}_3\), DMF, 85 °C, 48 h.

6.2 Experimental Section

6.2.1 Materials

Graphite powder (> 45 μm), MWNT, liquid bromine, DMF, dodecylamine, triethylamine, pyrene 1-boronic acid, 5-hexyl-2,2'-bithiopheneboronic acid pinacol ester and Pd(PPH₃)₄ were purchased from Sigma-Aldrich. Solvents were bought from the local suppliers and were used without further purification.
6.2.2 Bromination of Graphite

Graphite powder (500 mg) was dispersed in DMF and liquid bromine (4 ml) was added drop wise under N\textsubscript{2} atmosphere. The reaction mixture was heated under inert atmosphere for several days. The brominated graphite sample was washed with excess water to remove the physisorbed bromine and DMF. The brominated graphite could be dispersed in common organic solvents with a mild sonication.

6.2.3 Spreading of Brominated Graphite

Different methods were attempted to spread the brominated graphene sheets.

(i) Deposition from Air - Water Interface

Brominated graphite was dispersed in toluene with the aid of sonication for less than 5 min. It was then filtered to remove the insoluble larger aggregates. The clear brown suspension was diluted with chloroform until the colour became pale brown. It was then drop-casted onto water surface and transferred to various substrates and characterized using various microscopic techniques.

(ii) Brominated Graphene-MWNTs Composites

MWNTs were used as such without any purification. MWNT (1 mg/ml) dispersion in DMF was prepared and mixed with brominated graphene suspension in DMF at various volume proportions. It was found that high MWNT content in the mixture led to precipitation and the supernatant became colourless. A low MWNT content tend to stabilize and solubilize graphene. It was then diluted with DMF for subsequent characterizations.

6.2.4 Alkylation of Brominated Graphene

Brominated graphite (100 mg) in toluene (10 ml) was added to a three neck flask.
Dodecylamine (2.3 ml, 10 mmol) and triethylamine (1.39 ml, 10 mmol) were added to it. The resulting mixture was refluxed for 24 h, excess solvent was evaporated under reduced pressure and the obtained solid was used for debromination.

For debromination, 50 mg of the alkylated sample was dispersed in acetic acid (5 ml) and refluxed in presence of Zn dust (50 mg) for 24 h. The reaction mixture was cooled to room temperature, filtered, washed repeatedly with water and dried.

### 6.2.5 Suzuki Coupling Reaction with Brominated Graphene

Brominated graphite (20 mg) was dispersed in DMF (10 ml) for 10 min. K$_2$CO$_3$ (0.3455 g, 2.5 mmol) and 0.5 M solution of the respective boronic acids (0.25 mmol) in toluene (0.5 ml) was added to the reaction mixture. The mixture was degassed and filled with N$_2$. Pd (0) was added to the reaction mixture under dark and stirred at 85 °C for 48 h. The reaction mixture was cooled to room temperature, diluted with THF and the unreacted solids were removed by filtration. Excess solvent was removed under reduced pressure and the resultant waxy solid was washed with methanol and water. The final product was dispersible in THF, toluene, chloroform and DMF and used for subsequent characterizations.

For debromination, 50 mg of the alkylated sample was dispersed in acetic acid (5 ml) and refluxed in presence of Zn dust (50 mg) for 24 h. The reaction mixture was cooled to room temperature, filtered, washed repeatedly with water and dried.

### 6.2.6 Characterization

The functionalized samples were characterized by Raman spectroscopy, FTIR, FESEM, AFM, TEM and EDX. FESEM images and EDX spectra were obtained from JEOL JSM-6710F scanning electron microscope. TEM analyses were carried out using JEOL JEM-2010 F electron microscope, operating at 200 keV. A dilute
suspension of the samples in THF was drop-casted on the copper grid for TEM measurements. AFM images were recorded using commercial AFM (Dimension 3100, Digital Instruments) in the non-contact mode. Samples for AFM were prepared by drop casting dilute suspensions of the samples on freshly cleaved mica and then dried at room temperature. Raman spectra were recorded with a Renishaw system-2000 operating at an excitation wavelength of 532 nm. TGA was done using TA instrument 2960 with heating rate of 10 °C/min in N₂ atmosphere.

6.3 Results and Discussion

6.3.1 Brominated Graphite and its Stretching

Bromination is one of the important halogenation reactions reported for various carbon nanostructures such as fullerenes, graphite and carbon nanotubes. Graphite can be readily intercalated with bromine at room temperature when subjected to liquid bromine or bromine vapour. Bromination of graphite is expected to change the hybridization of graphitic carbon atoms from sp² to sp³ which changes the planar morphologies to a rough textured sheet. This was confirmed from the FESEM and AFM analysis (Figure 6.1).

![Figure 6.1](image_url)

**Figure 6.1** FESEM (A) and AFM (B) image of the brominated graphite drop-casted from toluene suspension.
The samples for FESEM were prepared by drop-casting a toluene suspension. The sheets were of 10-15 µm in size with many wrinkles which is clearly visible from the AFM image. Section analyses of several sheets revealed that the thickness ranged between 1.5-3 nm indicating that the sheets were crumpled and contain multiple folds. Elemental analysis of the brominated graphite sample gave 68.1 wt% of carbon and 31.8 wt% of bromine. It indicated that the brominated sample has one bromine atom per 14 graphitic carbon atoms.

Since the brominated graphite samples were crumpled and had a rough surface, attempts were made to spread it into flat sheets. One approach used was to spread the sheets at the air-water interface and collect the sheets on various substrates. Figure 6.2A shows the FESEM image of the brominated graphite collected on nitrocellulose membrane from the interface. As compared to brominated graphite directly drop casted from toluene suspension, the sheets were stretched to almost a flat sheet (Figure 6.2B). The sheets were of 10-15 µm in size. An alternative approach employed to spread the sheets was to make use of the mechanical stretching induced by the addition of CNTs. Figures 6.2C and D shows the FESEM and TEM images of 1:0.02 v/v graphene/MWNT composite, respectively. Inset of figure 6.2D shows one of the MWNT present on the surface of the brominated graphite. The diameter of the MWNTs used was of the order of 10-20 nm. But when the amount of MWNT added reached a critical concentration; a solid precipitated out of the solution and hence 1:0.02 v/v mixing of brominated graphite and MWNT was taken as the optimum condition. The stretched sheets could be a better candidate for fabrication of devices or composites owing to large surface area and better interaction with the host matrices as compared with the curled and folded samples.
Figure 6.2 FESEM (A) and TEM (B) image of the brominated graphite sample deposited from water-toluene interface; FESEM (C) and (D) TEM image of the 1:0.02 v/v graphene/MWNT composite.

Figure 6.3 (A) AFM image of the brominated graphite sample deposited from water-toluene interface and (B) AFM image of the 1:0.02 v/v graphene/MWNT composite.
The thickness of the stretched sheets was further confirmed with AFM (Figure 6.3A and B). The average thickness of the sheets were found to be ∼ 1-1.2 nm in both the cases, which supports the fact that sheets were less folded and crumpled compared with the drop-casted samples. The small discrepancies in the height profile of figure 6.3B correspond to the MWNTs present on the graphene surface.

6.3.2 Alkylation of the Brominated Graphite

Brominated graphite was subjected to alkylation by treatment with dodecylamine. The alkylated sample showed enhanced dispersibility in chloroform, toluene, THF and DMF as compared to the brominated graphite. Evidence of functionalization was determined by obtaining the Raman spectrum as shown in figure 6.4A. Pure graphite powder showed only the G band at ∼ 1580 cm$^{-1}$, but in the case of brominated graphite, the disorder induced D band appear at ∼ 1350 cm$^{-1}$, which becomes more prominent in the case of alkylated sample. The Raman spectra of the dodecylated graphene were almost similar to that of brominated graphite sample, except that the D band intensity is higher. This could be attributed to the increase in disorders caused by the mild sonication used for dispersion. During the alkylation reaction, all bromine atoms were not substituted with alkyl chains. Remaining bromine atoms were removed by Zn dust treatment and confirmed by elemental analysis, which showed only negligible amount of bromine. The ratio of the intensities of D and G ($I_D/I_G$) bands in Raman spectra can be used as an indication of the level of chemical modification in graphene.$^{17}$ The Raman spectrum of pure graphite showed a minimal disorder mode with $I_D/I_G$ ratio of 0.12 (trace a), whereas the brominated graphite (trace b), alkylated graphene (trace c) and the debrominated graphene after alkylation (trace d) showed an increase in the disorder mode with increased $I_D/I_G$ ratio of 0.75,
1.01, and 0.97, respectively (legend of figure 6.4A). This can be attributed to an increase in the number of sp\(^3\) hybridized carbon atoms that were formed during the functionalization.

**Figure 6.4** (A) Raman spectra of (a) pure graphite (b) brominated graphite (c) alkylated graphene and (d) debrominated graphene sheets after alkylation and (B) FTIR spectra of (a) brominated graphite (b) alkylated and (c) debrominated sheets after alkylation.

Furthermore, dodecylation on the brominated graphene has been supported by FTIR investigations (Figure 6.4B). Brominated graphite exhibited IR stretching absorptions between 600-700 cm\(^{-1}\) (trace a in figure 6.4B), all samples showed the C=C aromatic stretching at ~ 1470 cm\(^{-1}\) indicating the existence of unreacted double bonds. In the case of the dodecylated sample, in addition to the absence of C–Br stretching (600-700 cm\(^{-1}\)), the material showed C–H stretching bands associated with the dodecyl groups at 2800-3000 cm\(^{-1}\). This is in accordance with the previous reports on the reductive alkylation of fluorinated graphite.\(^{18}\)

Bromination and alkylation were further investigated using TGA analyses. Traces a and b in figure 6.5 shows the TGA curves obtained for brominated and alkylated samples, respectively. TGA analysis of the brominated graphite showed a weight loss of ~ 10% in between 100-150 °C, which could be attributed to the elimination of
physisorbed bromine and solvent molecules (trace a). The major weight loss up to 48% take place between 200 and 400 °C, with a temperature of maximum decomposition at 260 °C. These could be associated with the loss of chemically bound bromine molecules.

![TGA analysis graph](image)

**Figure 6.5** Weight loss of (a) brominated graphite and (b) dodecylated graphite determined by TGA analyses in nitrogen.

Furthermore, if the high uncertainty of the TGA measurements and the removal of physisorbed bromine and solvent molecules were taken into account, the overall weight loss is about 40% which is in agreement with the values obtained from the elemental analysis results (Br content 31.8 wt%). The TGA weight loss of dodecylated graphene sheets (Figure 6.5) was near to 30%, and all the weight loss was in between 250 and 560 °C, which is predominantly from the decomposition of dodecyl functionalities. A similar TGA profile was observed in the alkylated graphite *via* fluorination route.\(^\text{18}\)

A small portion of the alkylated samples were found to be dispersible in solvents without sonication and the sheets were of several micrometers in size. Figure 6.6
shows the FESEM and AFM images of the dodecylated sample. The sheet dimensions remained the same as that of the brominated graphite suspensions. Average thicknesses of the alkylated samples were of the order of 1-1.4 nm, which is slightly higher than the brominated graphene suspensions. It could be attributed to the long alkyl chains present on both sides of the sheets.

![FESEM and AFM images of the dodecylated graphene sample](image)

**Figure 6.6** (A) FESEM and (B) AFM images of the dodecylated graphene sample (without sonication).

Elemental analysis of the dodecylated graphene sample indicated that the sample still contained some bromine (~ 17.3 wt%). Hence, debromination of the alkylated sample was carried out. After debromination, the content of bromine was significantly reduced and it was found to be only 0.5 wt%. It indicated that the π-conjugation is partially restored with debromination, which was evident from the Raman measurements also (trace d in figure 6.4A). When the debrominated samples were subjected to mild sonication (less than 5 min), it resulted in better exfoliation and dispersion, the average thickness varied between ~ 1 to 1.2 nm. But sonication reduced the sheet dimensions significantly and the sheets dimensions were of the order of 1-3 μm. Additional evidence for the distribution of functionalized graphene samples were supported with TEM and AFM measurements (Figure 6.7).
Figure 6.7 (A) AFM image of the dodecylated graphene sheets after dispersion, (B) the corresponding section analysis; and (C) TEM image.

Electrical properties of the dodecylated and the debrominated samples were measured using a two-probe conductivity measurement system. Figure 6.8 shows the I-V plots of brominated graphite (trace a), dodecylated graphite (trace b) and the debrominated product (trace c). It is evident from the I-V plot that brominated and alkylated samples have low electrical conductivity due to the lack of effective $\pi - \pi$ conjugation. The drop casted films of brominated graphite and dodecylated graphene suspensions showed conductance of 19 and 27 nA, respectively at an applied voltage of 10 V. There were no significant changes in conductance before and after alkylation. After debromination of alkylated graphene, conductance was increased to 75 nA at an applied voltage of 10 V. This increase in conductance must be due to the partially restored extended $\pi - \pi$ conjugation. Such condensation and coupling reactions might be useful for the synthesis of electrically conductive polymer composites for photovoltaic or sensing applications.
Figure 6.8 I-V plots of drop casted films of (a) brominated graphite (b) dodecylated graphene and (c) debrominated product after dodecylation.

6.3.3 Arylation of the Brominated Graphite Using Suzuki Coupling Reactions

Considering that most of the Suzuki coupling reactions requires halogenated substrates, the coupling reactions on brominated graphene using pyrene 1-boronic acid and 5-hexyl-2,2'-bithiopheneboronic acid pinacole ester were conducted. It was found that the coupled products; pyrene coupled sample (G-Py) and 5-hexyl-2,2'-bithiopheneboronic acid pinacole ester coupled sample (G-BTP), exhibited enhanced dispersibility in THF, chloroform and toluene and the solutions remained stable for several days without any visible aggregation. UV-vis and emission characteristics of the products were collected in THF. In order to compare the photophysical properties, model compounds were prepared with coupling of the respective boronic acid esters with bromobenzene. Figure 6.9 shows the UV-vis and emission characteristics of the coupled products. Concentrations of the model compounds and coupled product were kept constant for all measurements. G-BTP shows an absorption maximum at 410 nm and the model compound exhibits an absorption maximum at 350 nm. For the emission spectra, model compound and G-BTP were excited at 410 nm, and it was
found that the bithiophene grafted graphene hybrid exhibits strong fluorescence quenching, which indicates the occurrence of photoinduced charge or energy transfer from polymer to graphene (Figure 6.9B).

**Figure 6.9** Absorption (A) and emission (B) spectra for (a) Ph-BTP (b) G-BTP excited at 410 nm; Absorption (C) and emission (D) spectra for (a) Ph-Py (b) G-Py excited at 340 nm.

Similar trend was observed in the case of G-Py (Figure 6.9 D). Further evidence for the coupling has been provided by elemental analysis, and it was found that G-BTP hybrid contained only the elements C (92.3%), S (5 %) and O (1.7%). Whereas G-Py contained only C (98.7%) and O (1.3%). Presence of oxygen could be from trace amounts of THF present in the material.

Raman spectra were recorded for the coupled products and the respective debrominated products (Figure 6.10). Debromination of G-BTP and G-Py did not
have any significant influence on the $I_D/I_G$ ratio (legends of figure 6.10A and B), indicating that all the bromine atoms present on graphene were reacted with boronic acids.

![Figure 6.10](image1)

**Figure 6.10** Raman spectra of (A) G-BTP (a - brominated graphite; b - G-BTP; c - debrominated G-BTP) and (B) G-Py (a - brominated graphite; b - G-Py; c - debrominated G-Py)

These results support the elemental analysis data which showed the absence of bromine in the coupled products.

![Figure 6.11](image2)

**Figure 6.11** (A) TEM and (B) AFM image of bithiophene coupled graphene; (C) TEM and (D) AFM image of pyrene coupled graphene.
Figure 6.11 shows the TEM and AFM images of G-BTP and G-Py drop-casted from THF. From the AFM measurements, it was found that the thickness of the sheets increased and was of the order of 2.5-3 nm. It could be due to accumulation of organic moieties on the graphene surface. The thickness can be controlled with the initial boronic acid concentration and the reaction time.

### 6.4 Conclusions

As a summary, we demonstrate a simple covalent functionalization method for graphene sheets. Bromine atoms are covalently attached to the graphene sheets through C-Br bonds which lead to stable dispersions in organic solvents. Subsequent alkylation and arylation of these brominated sheets suggest the possibility of a broad range of condensation and coupling reactions on the surface of graphene sheets, leading to the production of new graphene based hybrid systems.

### 6.5 References


11. Mkhoyan, K. A.; Contrryman, A. W.; Silcox, J.; Stewart, D. A.; Eda, G.;

Chapter 7

Conclusions and Future Prospects
Carbon nanomaterials have always been a fascinating area for researchers owing to their unique properties and wide range of applications. Most of the reported procedures for the preparation of functional carbon nanostructures rely on the use of extreme reaction conditions such as high pressure and temperature. Simple and cost-effective methodologies for the production of functional carbon nanomaterials are very crucial for practical applications. In the present work, we developed simple solution phase methods for the production of carbon nanomaterials from carbon rich precursors.

Initial investigations were focussed on solution based extraction methods for the isolation of novel carbon nanofibers from natural soot. The isolated fibers were characterized using various spectroscopic and microscopic techniques. These fibers were utilized for preparing electrospun CNF/PVA composite fiber mats as a sorbent for microextraction of aniline derivatives from waste water. The performance of CNF/PVA composite nanofiber mats as a μ-SPE device for the determination of anilines was optimized by investigating several factors such as extraction time, desorption solvent, sample volume, desorption time, salting-out effect and pH effect. The composite membrane sorbent yielded satisfactory parameters for microextraction. The LOD determined for the aniline compounds were in range of 0.009 - 0.081 µg/l and LOQ was within the range of 0.030 - 0.269 µg/l, which was comparable with that of other existing techniques. This method offer certain advantages such as easy extraction, minimal use of solvents and elimination of tedious solvent evaporation and reconstitution steps.

Later on, simple methods for the preparation of solution processable graphene sheets were explored, which include non-covalent stabilization of exfoliated graphene sheets with surfactants such as CTAB. Graphene nanosheets were exfoliated directly
from graphite making use of the combined effect of sonication and non-covalent stabilization. This method eliminated the use of any oxidation/reduction steps. The sheets could be dispersed in solvents such as DMF and were found to have an average thickness of 1.2 nm. The sheets were characterized in detail using AFM, STM, TEM and Raman spectroscopy. Field emission measurements showed a turn on voltage of 7.5 V/µm and emission current densities of 0.15 mA/cm². This approach is expected to be a step forward in the challenging global efforts to solubilize graphene and in the formation of conducting composite materials.

CTAB stabilized graphene nanosheets were used as reinforcing filler for PVC. In order to have efficient reinforcing effect, it is essential to have homogeneous dispersions. In our investigations, both the polymer and graphene could be dispersed in the same solvent, which enabled homogeneous mixing and dispersion. A significant enhancement in the mechanical properties of pure PVC films was obtained with very low loadings of graphene (2 wt%), such as a 58% increase in Young's modulus and an almost 130% improvement of tensile strength. Thermal stability was also found to be improved to a greater extent with an increase in the glass transition temperature. Moreover, The composite films had very low percolation threshold of 0.6 vol.% and showed a maximum electrical conductivity of 0.058 S/cm at 6.47 vol.% of graphene loading.

Use of graphene in composites is highly beneficial but it is equally challenging due to the unavailability of solution processable graphene in larger quantities. Hence, a different approach to stabilize graphene was adopted, which involved covalent modifications on graphene sheets. Nitrene insertion was employed to functionalize the exfoliated graphene sheets. The approach involved functionalization of dispersible unoxidized CTAB stabilized graphene sheets with various alkylazides and 11-
azidoundecanoic acid proved to be the best azide for enhanced dispersibility. The functionalization was confirmed by FTIR and STM. The functionalized samples showed enhanced dispersibility and solution stability compared with CTAB stabilized sheets. Besides, the reactive sites on azide functionalized graphene sheets were marked with gold nanoparticles. The interaction between gold nanoparticles and the graphene sheets was followed by UV-vis spectroscopy. TEM and AFM investigations revealed uniform distribution of gold nanoparticles all over the surface and this composite material was found to be electrically conducting and the conductivity was found to be three times as compared with azide functionalized graphene films. This finding could be promising for device or sensor applications.

Another covalent functionalization, which was attempted, was the direct bromination of graphite. Bromination of graphite takes place via electrophilic addition of bromine molecules to the aromatic double bonds, which can be replaced with alkyl or aryl substituents. It was seen that bromination followed by alkylation or Suzuki coupling reactions lead to stable dispersions of graphene in common organic solvents such as THF, toluene and chloroform. The average thickness of the alkylated graphene sheets were found to be of the order of 1 - 1.2 nm. Graphene sheets coupled with pyrene or bithiophene moieties showed an increased thickness of 2.5 - 3 nm, which can be attributed to the accumulated organic molecules on the surface. Besides, graphene coupled with pyrene and biothiophene showed fluorescence quenching. This could be due the efficient charge or energy transfer from bithiophene or pyrene moieties to graphene. This novel method offers an opportunity to integrate graphene into various optoelectronic devices in an easy and direct manner.
**Future prospects**

Non-covalent and covalent interactions to stabilize graphene in common organic solvents are a step forward in graphene based composite materials. Incorporation of graphene sheets will enhance the mechanical, electrical and thermal properties of the composite materials. These materials will be ideal candidates for fabricating mechanically reinforced electro conducting plastics. Besides, improved thermal conductivity of the graphene-polymer composite will make it suitable for aerospace applications, where aerospace structures produce considerable amount of heat energy.

Lithium-ion batteries containing graphite anodes are now the most widely used power sources for portable electronic devices. Recently, various anode materials have been proposed to overcome the limited capacity of graphite (372 mAh g\(^{-1}\)). Use of graphene composites as anode material for lithium ion batteries can be thought of, which is expected to show better electrochemical properties.

Attachment of Pt or Ni nanoparticles to graphene via covalent interactions is expected to be highly impactful in catalysis such as oxygen reduction reactions.
## Appendix

<table>
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<tr>
<th>Fillers Used</th>
<th>Modulus</th>
<th>Strength</th>
<th>Ductility</th>
<th>Toughness</th>
<th>Electrical conductivity</th>
<th>Percolation threshold</th>
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<td>0.1 S cm(^{-1})</td>
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