Development of Mild Methods for Selective Covalent Functionalization of Graphene

ANNA LUNDSTEDT
Abstract

This thesis discusses methods for the comparatively mild covalent functionalization of graphene. Several graphene models were investigated: polycyclic aromatic hydrocarbons (PAHs), chemical vapor deposition (CVD)-graphene on SiO$_2$/Si substrate, graphite foil, graphite flakes, kish graphite and highly oriented pyrolytic graphite. The PAHs were viewed as graphene edge analogs with the following molecules representing different edge motifs: pyrene, perylene, benzo[a]pyrene, benzo[e]pyrene, triphenylene, acenaphthylene, and anthracene.

Ozone was used in combination with different solvents to functionalize PAHs, graphite, and CVD-graphene on SiO$_2$/Si. Ozonation in water or methanol resulted in trapping of the carbonyl oxide intermediate that was formed in the reaction, producing a variety of functional groups. Ozonation in hydrogen peroxide solution with sonication promoted radical formation, possibly resulting in edge-oxidation of graphite. The regioselectivity for addition reactions (ozonolysis) and electrophilic aromatic substitution reactions with graphene edges is discussed.

To achieve functionalization of the basal plane of graphite or graphene, white light irradiation was used in combination with several transfer hydrogenation reagents. Formic acid treatment under irradiation resulted in the expected hydrogenation, whereas iso-propanol treatment resulted in iso-propanol attachment to the graphene.

The developed methods provide opportunities for graphene functionalization without the need for metal based reagents or harsh conditions.

Keywords: Polycyclic aromatic hydrocarbons, graphene models, graphite, local ionization energy surfaces, graphene functionalization

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List of Papers

This thesis is based on the following papers, which are referred to in the text by their Roman numerals.


II  Lundstedt, A., Grennberg, H., Ozonolysis of triphenylene in acetone. *Manuscript*

III  Lundstedt, A., Nordlund, M., Ahlberg, P., Grennberg, H. Edge oxidation of graphite using a combined hydrogen peroxide - ozone treatment under sonication conditions. *Manuscript*


*These authors contributed equally to this work

Appendix: Treating polycyclic aromatic hydrocarbons with deuterium chloride

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Contribution Report

The author's contributions to Papers I-V.

I  Contributed to the research idea and formulation. Planned, performed, and evaluated all experiments, analysis, and calculations. Wrote the paper.

II  Contributed with the original research idea. Planned, performed, and evaluated all experiments, analysis, and calculations. Wrote the paper.

III  Contributed with the original research idea. Contributed significantly to the planning, performing, and evaluation of all experiments, analysis, and writing of the paper.

IV  Contributed to the research idea and formulation. Designed some of the experiments with graphene and some with PAHs, conducted some of the experiments with PAHs, analysis with GC-MS, and NMR spectroscopy.

V  Contributed to the research idea and formulation. Contributed significantly to the planning, performing, and evaluation of all experiments and writing of the paper.

Appendix: Planned, performed, and evaluated all experiments.

Parts of section 2.2 and an earlier version of Paper I in this thesis are included in:

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<th>Description</th>
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<tbody>
<tr>
<td>AFM</td>
<td>Atomic force microscopy</td>
</tr>
<tr>
<td>AOP</td>
<td>Advanced oxidation process</td>
</tr>
<tr>
<td>CVD</td>
<td>Chemical vapor deposition</td>
</tr>
<tr>
<td>DCI</td>
<td>Deuterium chloride</td>
</tr>
<tr>
<td>DCM</td>
<td>Dichloromethane</td>
</tr>
<tr>
<td>EAS</td>
<td>Electrophilic aromatic substitution</td>
</tr>
<tr>
<td>FT</td>
<td>Fourier-transform</td>
</tr>
<tr>
<td>GC-MS</td>
<td>Gas chromatography-mass spectrometry</td>
</tr>
<tr>
<td>GNR</td>
<td>Graphene nanoribbon</td>
</tr>
<tr>
<td>GO</td>
<td>Graphene oxide</td>
</tr>
<tr>
<td>HCl</td>
<td>Hydrochloric acid</td>
</tr>
<tr>
<td>HOPG</td>
<td>Highly oriented pyrolytic graphite</td>
</tr>
<tr>
<td>HR</td>
<td>High resolution</td>
</tr>
<tr>
<td>IE</td>
<td>Ionization energy</td>
</tr>
<tr>
<td>IR</td>
<td>Infrared</td>
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<tr>
<td>LC-MS</td>
<td>Liquid chromatography-mass spectrometry</td>
</tr>
<tr>
<td>LOM</td>
<td>Light optical microscopy</td>
</tr>
<tr>
<td>MeCN</td>
<td>Acetonitrile</td>
</tr>
<tr>
<td>MeOH</td>
<td>Methanol</td>
</tr>
<tr>
<td>MS</td>
<td>Mass spectroscopy</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear magnetic resonance</td>
</tr>
<tr>
<td>PAH</td>
<td>Polycyclic aromatic hydrocarbon</td>
</tr>
<tr>
<td>rGO</td>
<td>Reduced GO</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>TFA</td>
<td>Trifluoroacetic acid</td>
</tr>
<tr>
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<td>Thermogravimetric analysis</td>
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<tr>
<td>UV</td>
<td>Ultraviolet</td>
</tr>
<tr>
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<tr>
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1 Introduction

The rapid technological advances in society put new and ever increasing demands on further development of materials. Graphene, a newly isolated and characterized material, has the potential to cause a paradigm shift in how technological devices are built. Graphene is lightweight, strong, almost transparent, and conductive, all desirable properties for materials in fields like electronics, medicine, biomaterials, construction, and energy storage. One challenge in order to realize the potential of graphene lies in the production and modification of cost-efficient, processable graphene.

The main aim of the work presented in this thesis was to expand the toolbox for making graphene-derived materials by developing methods for covalent functionalization of graphene. The selectivity and reactivity of different types of chemical reactions have been investigated using spectroscopy and microscopy. The analytical methods used depended on the system under investigation. These graphene systems included: polycyclic aromatic hydrocarbons (PAHs), different types of graphite, and chemical vapor deposition (CVD)-grown graphene on silicon oxide on silicon (SiO$_2$/Si).

A brief introduction to the graphene family and its fabrication and modification, the chemistry explored and the aims of this work are given in the first chapter.

1.1 The graphene family

*Graphite, graphene and graphene nanoribbons*

Graphite consist of stacked sheets of graphene that interacts through non-covalent π-π interactions with a distance of 0.335 nm. Although graphite contains mostly carbons atoms, there are many different types of graphitic materials, *e.g.* natural graphite flakes, highly oriented pyrolytic graphite (HOPG), kish graphite and graphite foil. (Figure 1)
Graphite has a high melting point, is nearly inert and conducts both heat and electricity well. The various types of graphite differ according to the amounts and types of impurities, the alignment and spacing of the sheets, and the grain size (size of the sheets). For example, synthetic graphite (e.g. pyrolytic graphite and kish graphite) usually contains almost perfect graphite. Graphite flakes, a natural form of graphite, are found and mined in various locations in the world. The grain size, and amount and type of impurities vary according to the mine site. Graphite flakes can be used to make the commonly used graphite foil (also named flexible graphite). The graphite market is large; graphite-derived materials have a broad range of uses, e.g. as insulators, lubricants, heat sinks, flame retardants, gas adsorbers, seals, gaskets and in batteries.\(^2\)\(^-\)\(^4\)

The structure of graphene, a honeycomb lattice, arises from the sp\(^2\) hybridized carbons in graphene which are arranged in a flat hexagonal pattern where each carbon atom is bonded to three other carbons. This 'infinite' sp\(^2\) carbon network results in the unique mechanical, optical and electronic properties of graphene. These properties are suppressed when graphene is stacked together to form graphite.\(^5\) Since its isolation and characterization by Geim and Novoselov in 2004,\(^6\)\(^,\)\(^7\) graphene-like materials have been tested in applications such as sensors,\(^8\) programmable self-folding paper,\(^9\) corrosion-free paint,\(^10\) flexible touch screens,\(^11\)\(^,\)\(^12\) with a multitude of further applications on the horizon.\(^13\)\(^-\)\(^15\)

Graphene nanoribbons (GNRs) are more well-defined than graphene but still not soluble like nanographenes (discussed in section 1.1.2). Control of the shape, edge type and also edge termination of GNRs has been demonstrated, and GNRs can be prepared by lithography or bottom-up fabrication.\(^16\)\(^,\)\(^17\)
One of the challenges with realizing the potential of graphene is its lack of solubility, which makes modifying, cleaning, processing and handling difficult.\textsuperscript{18}

\textit{Nanographenes - polycyclic aromatic hydrocarbons (PAHs) and the edge structures and defects of graphene}

Nanographenes or PAHs consist, like graphene, of flat aromatic hexagons comprised of carbon and have therefore the same structural features as graphene. (Figure 2)

![Figure 2. Photo of CVD-graphene on SiO$_2$/Si substrate and illustration of the basal plane of graphene and the structural similarity to nanographenes.](image)

Regardless of the graphene quality, each sheet has specific structural features such as edges and defects. Dangling bonds, holes and grain boundaries are some commonly discussed defects. The amount and type of defects and the grain size of the graphene vary according to how it was produced.\textsuperscript{17, 19}
Several types of defects have been observed by high resolution electron microscopy in a single layer of graphene. Some examples are Stone Wales defect, single vacancies and double vacancies (Figure 3). Other types of defects include point defects, grain boundary defects, carbon adatoms, foreign adatoms, and holes.\(^{20,21,17}\)

![Figure 3. Examples of observed defects in the basal plane of graphene, with the number of atoms in each ring indicated. A) Stone Wales, B) single vacancy and C-E) double vacancies. \(^{21}\)](image)

The edges of the graphene may be folded or terminated by various entities, depending on the source of the material.\(^{22}\) The termination of the edges of a single layer of graphene can be controlled during CVD preparation of graphene; for example, the edges can be terminated by hydrogen atoms (Figure 4).\(^{23}\)

![Figure 4. Graphene edge terminated by hydrogen atoms.](image)

Dangling bonds are often mentioned in the context of graphene defects. Dangling bonds, which can be described as unpaired electrons or radicals on immobilized atoms, can form during CVD growth of graphene. They are highly reactive and unstable, and are thus unlikely to survive under ambient conditions.\(^{24,25}\)
The two shapes of graphene edges (zigzag and armchair) are also found in PAHS. The armchair or zigzag configurations can be combined into different regions: coves, bays, fjords, or K-regions. (Figure 5). These different structural features result in different properties, e.g. armchair edges are more thermodynamically stable than zigzag edges. Cove and fjord regions distort the structure because of steric repulsion between attached hydrogens, e.g. helicenes (PAHS) are chiral because of this distortion. The combination of both solubility and structural similarities found in PAHS make them ideal models for studying graphene edge reactivity. Furthermore, due to their limited molecular size they are more easily handled than graphene. The selection criteria for the PAHS investigated in this thesis involved solubility and edge type. Seven PAHS were investigated: pyrene (1), perylene (2), benzo[a]pyrene (3), benzo[e]pyrene (4), triphenylene (5), acenaphylene (6) and anthracene (7) (Figure 5).

Figure 5. The seven PAHS investigated in the thesis and the edge types they represent. Pyrene (1), perylene (2), benzo[a]pyrene (3), benzo[e]pyrene (4), triphenylene (5), acenaphylene (6) and anthracene (7). The PAHS are color coded for the respective edge types.

Another benefit obtained by studying PAHS as graphene edge models is that they are not as computationally challenging as graphene itself, and thus higher level calculations can be utilized.
Calculations of local ionization energy (IE) surfaces have been shown by Brown and Cockcroft to be a useful tool for predicting the regioselectivity for reactions with PAHs. Local IE surfaces reveal the most nucleophilic sites in PAHs; lower IE values (brighter regions) indicate higher reactivity. The type of electrophilic reaction that is kinetically favored, addition or substitution, is also shown by this method. If the location of the minimum is on top of an atom, substitution at this position is likely and, if it is located on top of a bond, addition is preferred. Figure 6 shows the local IE surface of pyrene.

It should be emphasized that non-functionalized PAHs, can be used as model compounds only for hydrogen-terminated graphene.

Beyond the use as model compounds, the reactivity of PAHs are of more general interest. They are for example, found in many materials and applications. Furthermore, their carcinogenic and mutagenic properties make them an important class of compounds to study.

Graphene oxide (GO) and reduced graphene oxide (rGO)

Graphite oxide, the precursor of GO, was first obtained by oxidation of graphite by Brodie in 1859. GO is obtained by exfoliation of graphite oxide. The properties of GO differ from those of graphene; GO, for example, is soluble and non-conductive.

The oxidation methods are harsh; for example, in the Brodie method, potassium chlorate is added to a suspension of graphite powder in fuming nitric acid. In 1898, Staudenmaier also added concentrated sulfuric acid to the recipe and in 1958, Hummers and Offeman reported a method using concentrated sulfuric acid, potassium permanganate and sodium nitrate (Figure 7). Today, the most commonly used methods for oxidizing graphite are versions of the Hummers method.

Figure 7. Various methods for oxidizing graphite to graphite oxide using oxidative acids and reagents. Graphite oxide is exfoliated to graphene oxide (GO) which can be reduced to reduced graphene oxide (rGO).
Other, more recently developed, methods for preparing GO use treatment with: chromium trioxide, concentrated sulfuric acid and potassium permanganate,\textsuperscript{34} or titanium dioxide, and hydrogen peroxide under ultraviolet (UV) irradiation,\textsuperscript{35} or potassium ferrate and concentrated sulfuric acid.\textsuperscript{36,37} The identity of the oxygen-containing functional groups and the characterization of the GO with regard to impurities, grain size, and holes depends on the method of preparation and the quality of the graphite.\textsuperscript{36-41}

Since the isolation of graphene in 2004, GO has been investigated as a precursor of graphene. GO far surpasses graphene both in scalability and processability. Graphene-like materials, such as rGO, can be obtained from GO by thermal, chemical or photochemical reduction. The properties of rGO depend on the quality of the graphite starting material, the oxidation method for obtaining the GO and the method of reduction to rGO.\textsuperscript{42-44}

1.2 Analysis methods

The analysis of graphene and graphite usually only gives averaged indications of the structure. In contrast, using PAHs as graphene edge models provide reactivity information on the atomic level.

\textit{Analysis of graphite and graphene}

When analyzing graphene and graphite, analytical techniques commonly used for small organic molecules such as chromatography, nuclear magnetic resonance (NMR) spectroscopy, liquid chromatography-mass spectrometry (LC-MS) or gas chromatography-mass spectrometry (GC-MS) cannot be used. Therefore, information is difficult to obtain at an atomic level for graphene and graphite, which are non-homogeneous materials. Usually it is only a cumulative effect of the measured range of the analyzed material than can be observed.

Information about the surface of graphite and graphene can be obtained by a variety of microscopic techniques, \textit{i.e.} light optical microscopy (LOM), atomic force microscopy (AFM), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). Sometimes, if high resolution instruments are available, information down to atomic levels can be achieved.\textsuperscript{45}

Raman spectroscopy can show how much the material deviated from graphene or graphite and can, for example, be used to detect the amounts of defects introduced, such as holes, edges, sp\textsuperscript{3}-carbons, aggregation and folding. Upon analysis of graphene and graphite with Raman spectroscopy, the D and G peaks are integrated and the ratio between them calculated (I\textsubscript{D}/I\textsubscript{G} ratios), this value indicate the defect content.\textsuperscript{38,46}
X-ray photoelectron spectroscopy (XPS) or electron spectroscopy for chemical analysis (ESCA), show what elements and bonds there are and are powerful techniques for the analysis of surfaces.47

Thermogravimetric analysis (TGA) is a bulk method that can provide information about the presence of functional groups. More information is achieved through coupling with an IR spectrometer or also a GC-MS instrument.48

Another method for bulk characterization of materials regarding the presence of functional groups is FT-IR spectroscopy. This method provides the identity of functional groups, and is useful for characterizing GO and other materials where graphene has been extensively functionalized.49

It is also possible to follow successful functionalization by observing changes in macroscopic properties. One method is to measure the change in the wettability of graphite by measuring the water contact angle (WCA). This method allows changes in the polarity of the material introduced by certain functional groups to be observed.50, 51

Analysis of PAHs
The methods used for analyzing graphene and graphite are also possible for PAHs, but due to their solubility additional analytic techniques are available. Since analysis of PAHs provides structural information on the atomic level they provide better understanding of the details of the functionalizations.

Information about the number of different compounds in a mixture and their molecular mass can be obtained by GC-MS or LC-MS. NMR spectroscopy, the most powerful analytical technique, can be used to reveal the molecular structure of the compound. Some changes to the structure of conjugated systems can also be revealed by UV/vis spectroscopy.

1.3 Graphene fabrication methods
Graphene and graphene-like materials can be obtained by chemical reduction of graphene oxide (GO) to reduced graphene oxide (rGO),19, 43, 52 chemical vapor deposition to CVD-graphene on a substrate,53 heating silicon carbide,54 the scotch tape method on graphite, or liquid exfoliation of graphite.55 The quality (e.g. grain size, number of layers, impurities, and defects), properties, edge-termination, scale, environmental impact and reactivity of the material varies according to how the graphene was obtained and supported (in a liquid or on a solid substrate).
1.4 Functionalization of graphene

As discussed in section 1.1.1, the reactivity differs between the edges, defects, and basal plane. This difference in reactivity can be used for selective chemical functionalization. Graphene can be covalently and non-covalently functionalized, and the functionalization can be edge-selective or non-selective (Figure 8).\textsuperscript{56-61}

Functionalization of graphene is important for two main reasons: to change the properties and to improve the processability (e.g. solubility). It is important to understand the reactivity of graphene's many different sites (e.g. edges, defects and holes) and the origin of the material in order to successfully functionalize graphene with high reproducibility.

When the basal plane is covalently functionalized, the carbon hybridization is changed from sp\textsuperscript{2} to sp\textsuperscript{3}. This gives longer carbon-carbon bonds and a tetrahedral arrangement of bonds around the carbon atom that has reacted. In contrast, the edges of graphene can react without affecting the main sp\textsuperscript{2} carbon network and the overall geometry. This is the main reason for the much higher reactivity observed at the edges and grain boundaries of graphene compared to the basal plane. Most of the properties of graphene will not be affected since the sp\textsuperscript{2} network of the basal plane is left intact.\textsuperscript{62-64}

**Edge-selective functionalization of graphene**

Functionalizing the edges can provide points of attachment,\textsuperscript{64-67} and improve solubility or dispensability.\textsuperscript{68, 69}

Several approaches for achieving covalently functionalized edges have been reported,\textsuperscript{61} including construction of graphene from smaller fragments (bottom-up), cutting with a directed beam of highly focused electrons or ions or etching with reactive plasma (lithography), and solution-based methods. Solution-based methods for edge functionalization, such as Birch reduction,\textsuperscript{70, 71} and diazonium chemistry\textsuperscript{69} have been reported. Several edge selective methods for graphite or graphene oxidation have also been reported. These use successive treatments with potassium permanganate, con-
centrated sulfuric acid, ammonia and hydrogen peroxide\textsuperscript{68} or ozone,\textsuperscript{72} or treatment with ozone under UV irradiation,\textsuperscript{73} or treatment with ozone in water under sonication.\textsuperscript{74}

Regioselectivity between the zigzag and armchair edges can be expected for most edge-selective reactions. Several studies report that the armchair-edge structures are less reactive than the zigzag-edge structures.\textsuperscript{75,25}

*Basal plane functionalization of graphene*

Basal plane functionalization is another type of graphene reaction. However, covalent functionalization is normally not possible without simultaneous reaction of the edges and defects.

Basal plane functionalization changes the properties of the material more drastically than edge functionalization. The sp\textsuperscript{2} network is disturbed and the bandgap and other properties arising from the sp\textsuperscript{2} network will be affected. The extent of the effects on the properties of the sp\textsuperscript{2} network depends on the extent of the functionalization, the properties of the functional groups, and whether holes or other types of defects are also introduced. For example, hydrogenation of graphene either to fully hydrogenated graphane or partially reduced graphene has been suggested to introduce properties such as band gap tuneability and fluorescence and to have potential for hydrogen storage.\textsuperscript{76-78} However, methods for reducing graphene to graphane usually involve harsh reaction conditions.

Other basal plane reactions for graphene include radical reactions,\textsuperscript{79, 80} fluorination by atomic fluorine,\textsuperscript{81} and reductive alkylation.\textsuperscript{48}

### 1.5 Aims of the research and structure of this thesis

The aims of the projects presented here were:

1. To develop reactions for covalent functionalization of graphene resulting in materials that require no subsequent processing and generate little waste.
2. To understand the selectivity of the developed reactions.

The topics in this thesis is as follows. Chapter 2 outlines the experimental and computational evaluation of the edge selectivity of the addition (reagent: ozone) and substitution (reagent: deuterium chloride; DCl) reactions of several PAHs. The ozonation reaction was further investigated graphite and CVD-graphene which lead to proposed edge-oxidation under comparatively mild conditions. Chapter 3 discusses the hydrogenation and hydroxypropylation of CVD-graphene immersed in formic acid or iso-propanol upon irradiation with white-light.
1.6 Chemistry in this thesis

Ozonation

Using ozone as an oxidative reagent has many advantages: at ambient conditions it is a gas, it is considered an environmentally friendly reagent, and it has been well studied.\textsuperscript{82-85} As early as 1905, Harries published a paper on the investigation of oxidative cleavage of unsaturated compounds using ozone.\textsuperscript{86} Today, ozone is a commonly used reagent for oxidative cleavage (ozonolysis) of alkenes and PAHs. In synthetic organic chemistry, ozonolysis of PAHs can be performed to obtain functionalized PAHs.\textsuperscript{82, 87-96}

As proposed by Criegee,\textsuperscript{84} the mechanism of ozonolysis proceeds in three steps. Firstly, an intermediate primary ozonide forms by cycloaddition. Since primary ozonides are only stable at low temperatures (usually below -78 °C), the primary ozonide decomposes into carbonyl and carbonyl oxide. Lastly, the carbonyl oxide and the carbonyl react to form the final ozonide (Figure 9).

\textbf{Figure 9.} The three steps of ozonolysis. In the first step, a primary ozonide is formed via 1,3-cycloaddition; in the second step, a retro 1,3-cycloaddition forms a carbonyl oxide and a carbonyl; and, in step three, an ozonide forms after a 180° rotation (flip) of the carbonyl.

In the first two steps of the ozonolysis (steps 1 and 2 in Figure 9), the intermediates formed (primary ozonide and carbonyl oxide) can be trapped \textit{in situ}, yielding products other than the ozonide. It has been demonstrated that the carbonyl oxide formed during ozonolysis of both alkenes and PAHs may be trapped with a variety of nucleophiles.\textsuperscript{97-99} The carbonyl oxide can also be trapped by a second, more reactive carbonyl, forming a cross-ozonide.\textsuperscript{84, 100-103}

Over the last 30 years, several efficient methods for oxidative removal of PAHs from soil and water have been developed. The procedures employs ozone in combination with other reagents that promotes formation of hydroxy radicals.\textsuperscript{104-107}
**Electrophilic aromatic substitution (EAS) reaction**

An EAS is a reaction where a hydrogen (usually) bonded to an aromatic carbon is replaced by another entity. (Figure 10)

Here, $^2\text{HCl}$ (DCl) was selected as the reagent to study the selectivity of the reaction with PAHs 1-6, as deuterium incorporations can be observed by $^1\text{H}$ NMR spectroscopy. While reaction of alkenes with aqueous hydrochloric acid usually results in addition of water, a corresponding water addition to PAHs under the conditions explored herein is unlikely.

![Figure 10. Mechanism of electrophilic aromatic substitution (EAS).](image)

**Hydrogenation**

Hydrogenations, leading to reductions of, *e.g.* alkenes, arenes, alkynes or carbonyls are usually achieved either by dihydrogen or transfer hydrogenation reagents. (Figure 11) Dihydrogen, is flammable, explosive, and hazardous $^{108}$ thus using transfer hydrogenation reagents e.g., *iso*-propanol, methanol and formic acid are preferred. Transfer hydrogenation reagents provide hydrogen species (protons and hydrides) *in situ* and, the reaction usually require a metal catalyst (*e.g.* Pd or Rh).$^{109}$

![Figure 11. General hydrogenation of benzene with dihydrogen or formic acid.](image)
2 Ozone as reagent for edge-selective functionalization of graphene (Papers I - III)

Previous work has demonstrated that addition reactions and electrophilic aromatic substitution (EAS) reactions with graphene are edge-selective. In this chapter, the regioselectivity and versatility of ozone with PAHs, and several graphitic materials from work reported in Papers I-III and the appendix are discussed.

2.1 Ozonation of graphite and graphene

Full oxidation of graphene to GO is, among other things, useful from a processability perspective, even if most of the properties associated with the basal plane of graphene are lost and not fully recovered upon reduction to rGO. If only the edges of graphene are oxidized, the properties of graphene are retained while the groups on the edges can contribute to better solubility than that of non-oxidized graphene, even if it is not as good as that of GO.

Ozone reacts edge-selectively with graphene and it is important to know the identity of the functional groups that can be incorporated at the edges in order to understand how this type of edge functionalization can be used. Ozone normally undergo addition reactions, but it can also undergo substitution reaction with aromatic compounds. Ozone can also form radicals and ozonation under radical promoted conditions might result in graphene that is even more oxidized.

Here, the identity of functional groups that can be incorporated at the edges of graphene and GNRs by ozonation were investigated by studying PAHs with different edge configurations. Further, ozonation of triphenylene with various carbonyls lead to several new compounds. Also, the possibility to use ozone under conditions similar to those in Paper I and also ozone under radical promoted conditions to develop comparatively mild procedures to oxidize graphite and graphene were investigated. (Figure 12)
Figure 12. Illustrated here is the alkene as part of graphene edges and which functionalities to expect. These pathways are investigated in Papers I-III. In the first two steps of the ozonolysis, the intermediates formed (primary ozonide and carbonyl oxide) can be trapped in situ to yield different products. Ozone can also form hydroxyl radicals and undergo substitution reaction.

2.2 Addition and substitution reactivity of PAHs (I-II)

Ozonation of PAHs 1-7

When investigating the ozonation reactions with the PAHs, either the solvent system or the reagents were varied, keeping all other variables unchanged. Ozononation of PAHs 1-7 produced thirteen isolated products (Figure 13) whose structure were determined. The relative stability of PAHs 1, 2, 5 and 7 to ozone has previously been reported; PAH 5 was observed to be the most stable followed by 1, 2, lastly 7 being the most reactive PAH.\(^{117}\) The zigzag edges of acenes have been reported to be more reactive to oxidation than the armchair edges.\(^{26}\) This corresponds well with our observations, where both B[a]P 3 and anthracene 7 (zig zag) was observed to be more reactive towards ozone than pyrene 1 and B[e]P 4 (k region). Triphenylene 5 (bay region) is the least ozone reactive (Table 1).
Table 1. Ozonolysis of compounds 1-5 in dry DCM-d$_2$ at 20°C and their proposed regioselectivity with ozone.

<table>
<thead>
<tr>
<th>PAH</th>
<th>time, s</th>
<th>conversion of %</th>
<th>Proposed regioselectivity</th>
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<tr>
<td>1</td>
<td>5</td>
<td>40</td>
<td>K region</td>
</tr>
<tr>
<td>1</td>
<td>10</td>
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<td>4</td>
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<td>4</td>
<td>10</td>
<td>98</td>
<td>K region</td>
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<td>7</td>
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<td>90</td>
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For PAH 3, it was difficult to obtain substantial amounts of products as similar to previous reports by Fieser. However, the production of various quinones have been mentioned by others. Triphenylene 5 slowly degraded to a mixture of minor products, in amounts below the detection limit of $^1$H NMR spectroscopy, irrespectively of using dry conditions, water or methanol. However, ozonolysis of PAH 5 with acetone, resulted in its conversion to the cross-ozonide 5a. Also, pyrene ozonated in fomaldehyde have been reported to form the cross-ozonides at the k region.

See Figure 13 for all isolated products as well as PAHs 1-7 relative ozone reactivity.
Figure 13. The isolated products from ozonolysis of PAHs 1, 2, 4 and 6 using either water or methanol as solvent or under dry conditions in dichloromethane (DCM). The products 1d, 2a-d, 4a-c, 5a, 1f, and 2e have not previously been reported. Compounds 4a-c are not fully characterized.
From the results above, it is demonstrated that ozone is a versatile reagent, depending on solvent a variety of functional groups are accessible on the edges of graphene. Further we propose that for the zigzag edges, ketones or hydroxyl groups will be incorporated regardless of conditions and they will react faster than armchair edges. On the armchair edges, incorporation of aldehydes, ozonides, cross-ozonides, peroxides, hydroperoxy acetals, carboxylic acid groups are possible and can be controlled by the choice of solvent.

**A new compound from ozonolysis of triphenylene 5**

Functionalized PAHs are a group of compounds with properties relevant to many fields, including organic dyes, ligands for asymmetric catalysis, pharmaceuticals, and agrochemicals, and they have the potential to be used as organic conductors or semiconductors. The isolation of cross-ozonide 5a from triphenylene 5 was unexpected since no products from ozonolysis of triphenylene have previously been reported or been detected under other conditions. The isolated product 5a is potentially a useful compound and several sites for future functionalization have been introduced (Figure 14).

![Figure 14. Cross-ozonide 5a from ozonolysis of triphenylene 5 in acetone.](image)

Other carbonyls were investigated with PAH 5 forming other cross-ozonides, cross-ozonide 5a was also reduced to the corresponding aldehyde.

**Evaluation of experimental and calculated regioselectivity for addition and substitution of PAHs 1-7**

The regioselectivity for deuterium substitution in PAHs 1-6 was observed with 1H NMR spectroscopy. For acenaphthylene 6, deuterium oxide was added to the alkene. For PAHs 1-3 and 5, the selectivity observed was consistent with the results found by Dewar *et al.* in 1956 when they determined the selectivity for a nitration with PAHs.

The calculated and experimentally observed regioselectivity for addition and substitution reactions with PAHs 1-7 are summarized in Figure 15. Calculating the local IE surfaces has potential to be a good tool for predicting the regioselectivity for both addition and substitution reactions under kinetic control with graphene. The calculated regioselectivities were not completely consistent with our experimental results. It is possible that the main products from the ozonation reactions were not observed because of polymer forma-
tion (PAH 2) or subsequent oxidation leading to degradation (PAH 5). For the reaction with triphenylene, the observed product (cross-ozonide 5a) was only detected when thermodynamic conditions (high concentrations and temperatures) were used.

![Experimentally determined regioselectivity of ozonolysis and deuterium substitution of PAHs 1-7 and their calculated IE surfaces.](image)

Figure 15. The experimentally determined regioselectivity of ozonolysis and deuterium substitution of PAHs 1-7 and their calculated IE surfaces. The red arrows indicate ozonolysis and the blue arrows indicate deuterium substitution. For PAH 3, the location of the ozonolysis could not be determined.

The local IE surfaces for three hydrogen-terminated GRNs were calculated to demonstrate their reaction with ozone and to visualize how ozone can be used to introduce different functional groups depending on the edge configuration. (Figure 16) This type of chemical differentiation of the edges could potentially be used to connect GRNs with control of the edge alignment.
2.3 Ozonation of graphite and graphene (III)

In section 2.2, ozonation reactions of PAHs to introduce a variety of functional groups depending on edge type and solvent were discussed. This section presents ozonation reactions of graphite in water, ethanol or hydrogen peroxide solution under sonication.

Several graphitic materials were investigated: natural crystalline graphite flakes were chosen since they constitute the most abundant form of graphite; HOPG containing almost perfect graphite and very low levels of impurities, and graphite foil having a porous structure which is ideal for intercalation. Also CVD-graphene on SiO$_2$/Si was investigated. The foil, flakes and HOPG
were analyzed by Raman spectroscopy, and the flakes were also analyzed by TGA. The CVD-graphene was analyzed by XPS and SEM.

**Ozonation of graphite in water or hydrogen peroxide solution**

Graphite foil samples in water or aqueous hydrogen peroxide solution were treated with ozone with or without sonication. The foil swelled upon treatment (the amount of swelling increased during oxidation) and a cooperative effect between ozone, hydrogen peroxide and sonication was observed. Foil sonicated in hydrogen peroxide solution and ozone demonstrated 40-fold swelling (Figure 17). Under the same conditions, HOPG showed only moderate swelling and dissociated into multiple sheets, with the same smooth, shiny appearance as the initial foil.

![Graphite foil samples](image)

**Figure 17.** Graphite foil samples after various procedures: sonication in water, sonication in water with ozone, sonication in hydrogen peroxide solution, and sonication in hydrogen peroxide solution with ozone. The pieces of foil initially measured ca 0.5×5×5 mm. All objects displayed at the same scale.

Graphite flakes in water, hydrogen peroxide solution, or ethanol were treated with ozone with or without sonication. Interestingly, when flakes in ethanol were treated with ozone and sonicated, the sample exploded during treatment. Therefore, no more experiments with ethanol were attempted. As shown in the study with PAHs in methanol treated with ozone (section 2.2), hydroperoxy acetal groups are incorporated under these conditions. The formation of the unstable reaction mixture from graphite in ethanol might be due to such groups and the formation of over-oxidized debris forming as ozone consumes the graphite.

TGA of flakes treated in water or hydrogen peroxide solution indicated a drop in sample mass at 150-200 °C (Figure 18). Mass loss in this range is commonly interpreted as loss of covalently bound oxygen containing functionalities (for example hydroxyl and epoxy groups). The weight loss of ~2 % observed for the graphite flakes treated in hydrogen peroxide solution during sonication, was still significantly lower than weight loss nor-
mally found for GO and rGO,\textsuperscript{135,136} which could indicate edge-selective oxidation.

Figure 18. TGA of graphite flakes after treatment with hydrogen peroxide solution, ozone under sonication for 0 h, 24 h and 72 h.

The oxidized graphitic materials were analyzed by Raman spectroscopy (bulk measurement) and $I_D/I_G$ ratios were calculated from the Raman spectra. Increasing the oxidative treatment and time resulted in increased $I_D/I_G$ ratios. The highest observed $I_D/I_G$ ratio of 0.3 is still considerably lower than ratios commonly obtained for GO and rGO.\textsuperscript{19} These results further support edge-selective oxidation.

**Ozonation of CVD-graphene on SiO$_2$/Si in hydrogen peroxide solution**

The SEM images in Figure 19 show that a short treatment time (10 minutes) in aqueous hydrogen peroxide solution saturated with ozone had little effect on the graphene sheet; however, after 24 h, the graphene sheet was extensively degraded. The circular pattern on the surface was probably caused by formation of reactive bubbles during the procedure. XPS analysis of the material left on the substrate showed it to be graphene.

Figure 19. SEM images of CVD-graphene treated with ozone and hydrogen peroxide solution for A) 10 min and B) 24 h.
2.4 Summary and conclusions

From the investigations of PAHs we conclude that substitution and addition reactions displayed complimentary regioselectivities. Substitution reactions preferred zigzag edges and addition reactions preferred armchair edges. The regioselectivity for both the ozonolysis and deuterium substitution reactions with PAHs was mostly predicted by local IE surface calculations.

The ozonation experiments with PAHs with different solvents demonstrated two things. Firstly, ozone is a versatile reagent that can result in the formation of many different functional groups, depending on solvent and edge type. Secondly, the zigzag edge is more reactive than the armchair edge.

Graphite in water, ethanol or hydrogen peroxide solution was treated with ozone under sonication. Full oxidation to GO was not achieved but it is reasonable to conclude that edge-oxidation occurred. The highest extent of oxidation was observed when the graphite were treated simultaneously with ozone and hydrogen peroxide solution, indicating a cooperative effect (Figure 17).

Purification of the material obtained from treating graphite flakes with ozone under the above conditions is straightforward, as all reagents are either gases or have good solubility in water, and drying or filtering and rinsing with water is sufficient. No metals or acids were used in the oxidation process described here and thus the methods are comparatively environmentally friendly.

Further studies are required to optimize and fully understand the reactions but also to study the properties, such as electrical conductivity and dispersibility, of the obtained materials.
3. Photoassisted basal plane functionalization of graphene using transfer hydrogenation reagents (Papers IV and V)

The methods discussed in chapter 2 are efficient for edge functionalization. This chapter discusses basal plane functionalization by increasing the reactivity of graphene by irradiation. We studied the photoreactions of CVD-graphene on SiO$_2$/Si (Papers IV and V) and kish graphite (Paper V) with several transfer hydrogenation reagents.

3.1 Basal plane functionalization of graphene

The key to basal plane functionalization is the ability of graphene to absorb visible light, which probably results in a photoexcited material. Thus, the use of light should allow for milder reactants (e.g. iso-propanol and formic acid) to react with graphene without adding metals or using high temperatures and pressures.

CVD-graphene on Si/SiO$_2$, kish graphite, and HOPG were used as substrates and methanol, ethanol, iso-propanol, tert-butanol, and formic acid were investigated as reagents. With CVD-graphene and the graphitic materials, white light emitting diode (LED) irradiation was used.

The CVD-graphene on Si/SiO$_2$ was analyzed by Raman spectroscopy, SEM, AFM and XPS, and the graphite was analyzed by Raman spectroscopy, LOM, AFM and WCA measurements.

White light irradiation of CVD-graphene with formic acid or iso-propanol

CVD-graphene immersed in formic acid or iso-propanol and irradiated with white light resulted in changes to the material. These changes varied with the conditions. SEM imaging revealed that, under conditions involving white light and formic acid, parts of the material were missing, while for conditions involving white light and iso-propanol, the surface was intact (Figure 20).
Analysis with XPS and Raman spectroscopy showed partially hydrogenated graphene on the SiO$_2$/Si surface after formic acid treatment. For the iso-propanol treated graphene, XPS analysis showed an increase in both oxygen content and sp$^3$ carbons atoms on the surface. AFM measurements of the same sample indicated increased adhesion between the SiO$_2$ tips. These observations are not consistent with hydrogenation of graphene nor were they observed for formic acid-treated graphene, and we suggest that graphene reacts differently with the two reagents, with formic acid leading to hydrogenation of the surface, and iso-propanol leading to addition of iso-propanol to the surface (Figure 21).

Both of these functionalization methods are photoassisted, and do not proceed without light, although the mechanism behind is so far unknown. The XPS analysis show that the extent of functionalization is too large to be limited to the edges, and therefore basal plane functionalization is proposed. However, if the photoexcitation is spread evenly over the graphene surface, no reaction would happen; the photoexcitation is likely localized – but how this occur and where it localized is not known.
Figure 21. Proposed functionalization of graphene under white light irradiation with A) formic acid and B) iso-propanol.

Time-dependence of basal plane functionalization of CVD-graphene treated with iso-propanol
XPS analysis indicated that reacting CVD-graphene with iso-propanol for different times (0h, 6h, 12h, 18h, 24h, and 48h) allowed the degree of functionalization to be controlled (Figure 22).

Figure 22. Plot of the integrated areas of sp², sp³ and C-O in XPS peaks after deconvolution for CVD-graphene after irradiation in iso-propanol for various reaction times.

Secondary functionalization of isohydroxypropylated CVD-graphene
Iso-propanol-treated graphene was chlorinated to investigate whether the material could be further functionalized and to confirm the incorporation of hydroxyl groups by iso-propanol (Figure 23). Substitution of a hydroxy group for a chloride using thionyl chloride is commonly used in organic synthetic procedures. XPS analysis revealed the reaction to be successful,
thus providing further support for iso-propanol fragments binding into the graphene.

![Figure 23. Proposed reaction of iso-propanol treated graphene with thionyl chloride.](image)

3.2 White light irradiation of graphite with iso-propanol

When kish graphite and HOPG were treated under our iso-propanol conditions, a clear change in morphology was observed by LOM (Figure 24). An increase of the D band in the Raman spectra was also observed.

![Figure 24. Light optical microscopy images of A) pristine HOPG (left) and iso-propanol-treated HOPG (right); and B) pristine kish graphite (left) and iso-propanol-treated kish graphite (right).](image)

WCA measurements were performed to measure the wettability of the samples before and after treatment. Before the reaction the WCA value was 89° and after the reaction the WCA values were 61° and 58° (Figure 25). Graphite oxidized with the well-established Hummers method or Brodie method give reported WCA values of 43.8°, 58° and 60.7°, respectively. Our WCA values around 60° indicate that our method introduces polarity, making graphite more hydrophilic.

![Figure 25 Difference in the wettability of graphite before and after reaction with iso-propanol. A) Kish graphite and B) Kish graphite after reaction with iso-propanol for 7 days.](image)
3.4 Summary and conclusions

The methods presented in Papers IV and V are promising. Covalently functionalized graphene was obtained by irradiation of graphene on SiO$_2$/Si immersed in formic acid or iso-propanol. Formic acid treatment resulted in hydrogenation and iso-propanol treatment resulted in iso-propanol attachment to the graphene surface. The reactions are proposed to have led to basal plane functionalization.

The extent of functionalization is tuneable, as shown by changing the duration of the iso-propanol treatment of CVD-graphene. Further modifications of the material and the presence of hydroxyl groups were demonstrated using a chlorination reaction on iso-propanol-treated graphene.
4 Concluding remarks and future outlook

In this thesis comparatively mild reactions for edge or basal plane covalent functionalization of graphene are presented. Ozone gas or other water-soluble reagents (hydrogen peroxide, formic acid and iso-propanol) were investigated.

Ozone was used to functionalize PAHs in water or methanol resulting in a variety of functional groups, with several new compounds isolated. Ozonation of graphite in different solvents during sonication were proposed to introduce oxygen containing functional groups to the edges of graphite.

White light irradiation was used to mediate basal plane functionalizations, and these reactions proceeded slowly enough to enable control over the degree of functionalization.

As stated in chapter 1, the aims of the work presented were:

1. To develop reactions for covalent functionalization of graphene resulting in materials that require no subsequent processing and generate little waste.
2. To understand the selectivity of the developed reactions.

All methods developed in this work have potential to be used to produce new materials either by edge or basal plane covalent functionalization of graphene. The obtained materials can be used either directly or as precursors in other reactions. The properties of these new materials, which will vary according to edge-selective functionalization, basal plane functionalization, functional groups and extent of functionalization, are yet to be explored.
5 Grafen, modifierad grafen och polycykliska aromatiska kolväteföreningar

Med detta avhandlingsarbete har jag utvecklat metoder för att modifiera grafen samt ökat förståelsen för grafens reaktivitet.


Grafen kan ses som en enormt stor polycyklisk aromatisk kolväteförening (PAH) och har flera olika regioner som kan ha olika reaktivitet. Grafen har kanter, defekter samt ett inre plan. (Bild 1) För att förstå hur grafens kanter reagerar kan PAHer användas som små grafenkantmodeller och fördelarna med att studera grafens kanter på detta sätt är många. Analysmetoderna som blir möjliga, bland annat på grund av löslighet, leder till information på en högre detaljnivå än den nivå som är möjlig för grafit och grafen. Man kan i grafenkantmodellerna se var och vad som har hänt och få full inblick i hur olika reaktioner sker.

2 Grafen – den perfekta atomväven, nobelpriset i fysik 2010, Kungliga Vetenskapsakademien, 2010
Nuvarande metoder som finns för att kemiskt modifiera grafen innebär ofta kraftiga reaktionsförhållanden såsom användande av höga temperaturer, högt tryck, starka syror, radikaler, plasma eller metaller. Materialen som erhålls kan vara svåra att rena upp, och mycket avfall produceras.

I denna avhandling har grafenkanters reaktivitet med två olika reaktionstyper, additions- och substitutionsreaktioner, samt grafenytans fotoreaktivitet undersökt. Flera olika grafitmaterial samt grafen på kiseloxid har undersöpts och PAHer har använts som grafenkantmodeller. För kantoxidering av grafit och grafen har som reagens, ozon tillsammans med olika lösningsmedel använts. (Bild 2) Beroende på vilket lösningsmedel som används under ozoneringen kan olika funktionella grupper på kanterna erhållas. För graffenytmodifiering undersökt es ett flertal hydrogeneringsreagens, och av de undersökta reagensen resulterade myrsyra i hydrogenering av grafen och isopropanol i att isopropanol bands till ytan.

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Alla de nya metoderna beskrivna i denna avhandling har potential till att användas för att tillverka nya material under jämförbart milda förhållanden samt generera material som är lätt att rena upp, utan att producera mycket avfall. Alla egenskaper och potentiella användningsområden för dessa nya material är dock ännu i stort sett outforskade.
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7 References


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