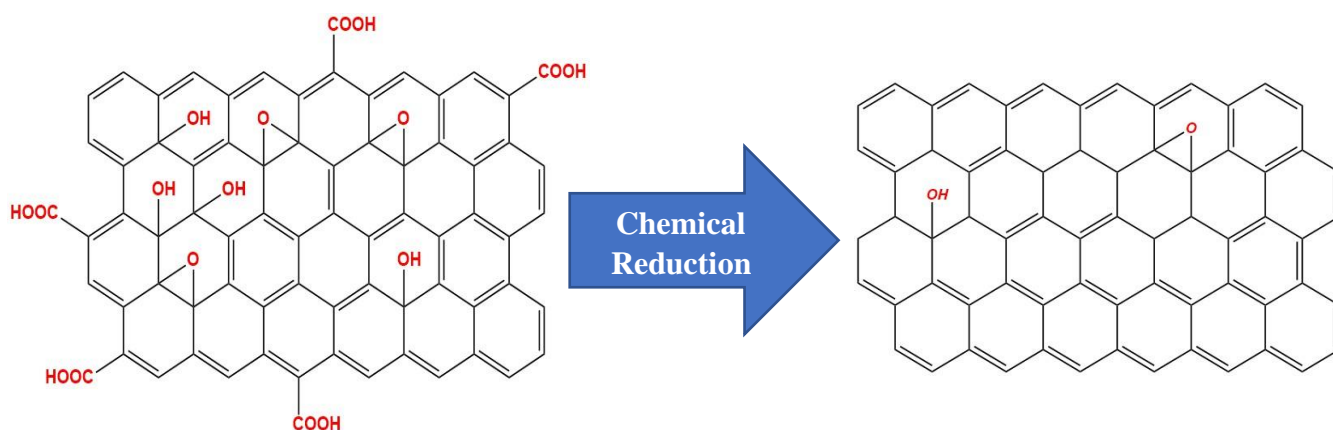# CHALMERS

Chemical reduction of graphene oxide using different reducing agents

A Bachelor's Thesis within Chemical Engineering 180 hp

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DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING

CHALMERS UNIVERSITY OF TECHNOLOGY

Gothenburg, Sweden 2020

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Cover: Graphene oxide, Reduced graphene oxide
Gothenburg, Sweden 2020

Sammanfattning

Grafen är ett tvådimensionellt material bestående av kolatomer ordnade i en hexagonal struktur. Det har uppvisat intressanta egenskaper och är därför av stort intresse för forskare. Grafenoxid (GO) består av ett grafenplan med funktionella syregrupper bundna till det. Genom att avlägsna syregrupperna kan man framställa så kallad reducerad grafenoxid (rGO). De funktionella grupperna är då mycket färre och den elektriska ledningsförmågan ökar. I detta projekt utfördes kemisk reducering där tre olika kemikalier prövades som reduktionsmedel: jodvätesyra, askorbinsyra och natriumhydroxid. Syftet var att undersöka huruvida dessa relativt säkra ämnen kunde användas till reducering, i vilken grad de kunde reducera GO och hur man kunde analysera materialet. Resultat från IR-spektroskopi visade med stor tydlighet att alla tre ämnen utförde reduktion av grafenoxiden. Detta bekräftades av UV/Vis-spektrofotometri i alla fall förutom i det med jodvätesyra. Analysmetoden XPS skulle ha kunnat visa förhållandet mellan kol och syreatomerna. Dock så utfördes ingen XPS-analys på grund av utbrottet av Covid-19 och därför kan ingen säker slutsats om den exakta reduktionsgraden dras.

Abstract

Graphene is a two-dimensional materiel consisting of carbon atoms ordered in a hexagonal structure. It has shown interesting properties and is therefore of big interest to scientists. Graphene oxide (GO) consists of a graphene sheet with oxygen functional groups attached to it. By removing the oxygen groups one can produce so called reduced graphene oxide (rGO). The oxygen functional groups are then much fewer, and the electrical conductivity is improved. In this project, chemical reduction was conducted with three different chemicals as reductants: hydroiodic acid, ascorbic acid, and sodium hydroxide. The purpose was to investigate whether these relatively safe substances could be used for reduction, to which degree it could reduce GO and how to characterize the materials. Results from IR spectroscopy shows very clearly that all the three substances did reduce graphene oxide. This was confirmed by UV/Vis-spectrophotometry in all cases except the one with hydroiodic acid. The analytical method XPS could have shown the ratio between carbon and oxygen atoms. However, an XPS analysis was not performed due to the Covid-19 outbreak and therefore no conclusion can be made about the exact degree of reduction.

LIST OF ABBREVIATIONS

GO – Graphene Oxide

rGO – Reduced Graphene Oxide

AA – Ascorbic Acid

DMF – N,N-Dimethylformamide

<u>Acknowledgement</u>

Contents

1. Introduction

1.1 Electron configuration and hybridization of carbon

Carbon has the atomic number six. The electron configuration is $1s^2 2s^2 2p^2$ meaning that the outer shell is filled up by one pair of electrons in the 2s, two unpaired electrons in the p subshell and one empty p orbital. One of the electrons in the 2s orbital can be promoted (raised) to the empty p orbital. That gives four unpaired electrons and thereby the ability to form four bonds. The interaction between the orbitals alters the shape and forms four equally shaped orbitals equally distant from each other. It creates a tetrahedron where all hybrid orbitals point in the direction of its corners. This is known as sp^3 hybridization. The angle between the bonds are approximately 109,5 degrees.

There are also other possibilities. One s orbital and two p orbitals can form three hybrid orbitals. This is called sp^2 hybridization. Unlike the sp^3 orbitals, the three hybrid orbitals are separated by 120 degrees in a flat plane. This leaves one unpaired electron in the p orbital perpendicular to the plane. Two of the hybrid orbitals overlap with each other to form a strong σ-bond. The unhybridized p orbital can create so called π-bonds with another unhybridized p orbital enabling double bonds between atoms. Sideways overlap is not as strong as head-to-head overlapping, so π-bonds are weaker than σ-bonds. A double bond, however, is considerably stronger than a single bond.

Electron in the unhybridized p orbital is named as π-electron. It has additional abilities to form double bonds. This is evident when looking at the properties of a benzene ring. The π-electrons do not form double bonds between two specific atoms. Instead they are spread equally over the ring contributing to all the bonds in the molecule. This is called resonance and the π-electrons are named to be delocalized electrons as they move freely across the molecule. [1]

1.2 Graphene

Carbon has always been one of the most common chemical elements due to its importance in living systems and industry. Carbon's unique electronic structure makes it possible for more stable carbon allotropes, more than any other element. Carbon allotropes are accomplished when the structure of carbon gets modified in different ways to give different forms of carbon in the same physical phase. One of the most common carbon allotropes is graphite. The carbon atoms in the plane are sp^2 hybridized and bonded to three other atoms in a hexagonal honeycomb structure. The π-electron move freely across the plane. It is these electrons that makes graphite electrically conductive. The movement of the delocalized π-electrons also has another function, they create van der Waals forces between the planes and this is what builds the structure of graphite as they hold the graphene sheets together. The van der Waals forces are weak compared to covalent bonds. That is why graphite is used in pencils as the layers are easily peeled off while the planes themselves remain intact. The interaction between the sheets differs from the hydrogen bonding between water molecules. This makes graphite insoluble in water. [2]

Canadian physicist Philip R. Wallace could demonstrate the existence of two-dimensional (2D) graphite while he was studying graphite's electronic behavior and presented his work in a pioneering paper in 1947. [3] German chemist Hanns-Peter Boehm could see the 2D graphite for the first time in 1961 under the electron microscope. [4] The 2D graphite was given the name 'Graphene' in 1986 by chemists Boehm, Setton and Stumpp. The word 'Graphene' is a combination of the word 'graphite' and the suffix -ene which represents the polycyclic aromatic hydrocarbons. [5] Graphene, an allotrope of carbon, is a single layer of graphite, just one atom thick. It has a two-dimensional structure due to the sp^2 bonding of the carbon atoms that gives it a honeycomb appearance (Figure 1). [6] Although graphene and its structure were known to scientists for several decades, no one could isolate it from

graphite until 2004 when two scientists from The University of Manchester succeeded. By using micromechanical cleavage, the scotch tape method, Professor Andre Geim and Professor Kostya Novoselov could peel the graphite and isolate a single layer of it on a silicon oxide substrate. They were awarded the Nobel Prize in Physics for their groundbreaking experimental work on graphene.[6]
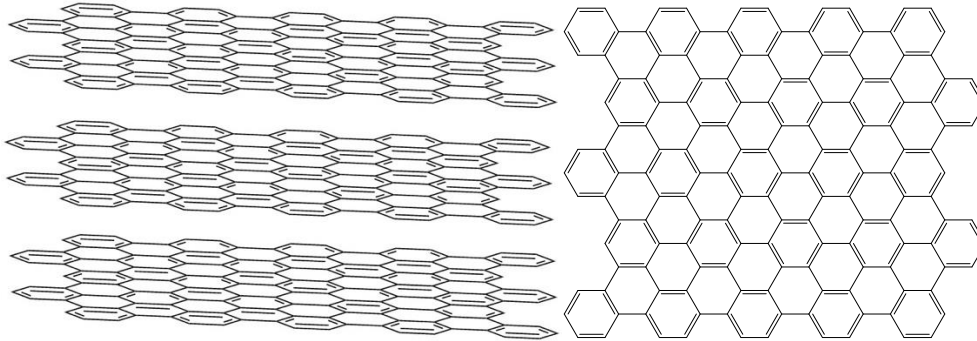
Figure 1. The chemical structure of graphite and graphene.

1.2.1 Properties of graphene

Graphene possesses many outstanding properties which makes it a unique material including:

High surface area

Surface area is the total area covering the surface of an object. Graphene has a surface area of 2630 m^2/g. One can cover an entire soccer field with less than 3 grams of graphene. [7]

Strength, toughness and stretchability

Graphene is the strongest material ever tested. [8,9] The flat planes of carbon atoms can flex without breaking. [8] This feature makes it very flexible and can be stretched up to 25 percent of its original length without breaking,[9] a property which is of great importance for flexible electronics. [7] Defect-free monolayer graphene has a strength of 42N/m, which equals to an intrinsic strength of 130 GPa which is more than 100 times stronger than steel. [7, 8, 9] One of the most important mechanical properties of graphene is fracture toughness which is highly relevant in engineering. [10]

Stiffness

Graphene has shown a Young's modulus of approximately 1.0 TPa which is one of the highest materials. [7]

Atomic thickness

Graphene is a very light substance. [7, 8, 9,10,11] It is also one of the thinnest being only one carbon atom thick. [8,9,11] 1 square meter of copy paper is roughly 1000 times heavier than graphene. [10]

Electron mobility and resistivity

Graphene is a semimetal or zero-gap semiconductor. Carbon atoms are uniquely arranged in graphene electrons can travel easily at very high speeds without significant scattering. This saves energy that

gets lost in other semiconductors. It shows an electron mobility of 200000 cm^2/V*s, which is 10^7 times higher than copper. It has one of the lowest electrical resistivities of any known material at room temperature, 1 x 10^{-8} Ω·m, approximately 35% less than copper. [7]

Thermal conductivity

Graphene conducts heat remarkably well. [7] One of the features of graphene's strength is that the carbon to carbon bonds are very strong so that they can withstand destabilization from thermal fluctuations. [10] It shows thermal conductivity of 1500-2500 W/mK at room temperature, which is higher than that of carbon nanotubes, graphite and diamond. [7,9]

Transparency

Graphene can absorb approximately 2.3% of white light making it visible to human eye but remains very transparent. [9,10]

Impermeability

The closely connected carbon atoms in the graphene sheets work like nets, useful for trapping and detecting gases, but also holding gases, making it a highly impermeable material where even one atom of helium cannot pass through. [7,8]

1.2.2 Applications of graphene

Because of all of the above mentioned remarkably exceptional properties, graphene can be applied in numerous applications such as heat sensitive clothing, flexible, stretchable and foldable devices, next generation electronics, more efficient batteries, conductive paints, aerospace and automotive industries, ultrasensitive sensors, medicine and biotechnology for use in cancer treatment, bio-imaging tags and bioelectronics in living cells and nerve tissue. For example, graphene can be used for development of superfast, low-cost, high frequency electronics because the arrangement of carbon atoms in graphene allow electrons to easily travel at high velocities without significant scattering. Pores in graphene can allow transport of gas and water through the sheets allowing for selective permeability of gases. This can be applied in water purification, food packaging, for example. Graphene can be used in sensors for explosives detection, detect biomarkers for illness and bacteria, gas sensing, self-healable tattoos and environmental monitoring because every atom is exposed to its environment. [7]

1.2.3 Production methods of graphene

Graphene is a material that is highly sought after in various industries due to versatility in applications but is very difficult to produce in large amounts with high purity [12,13]. Therefore, a lot of research has been applied to synthesize it. [12] For graphene to become established on the market, an efficient production method is essential.

Mechanical Exfoliation

Mechanical exfoliation has a low yield and therefore is not suitable for mass production due to low yield and small-scale production. However, it does produce high quality graphene flakes, ranging of sizes 5 to 100 μm, which is great for basic research purposes.

Chemical vapor deposition

Chemical vapor deposition can produce in large sizes but normally requires very high temperatures for example, 1000 °C.

Liquid Phase Exfoliation

Liquid phase exfoliation of graphite in solvents can produce graphene nanosheets with sizes ranging from nm to a few μm. It does unfortunately have a low yield and the quality of graphene is not very high. However, the cost of production is low.

Epitaxial growth on SiC substrates

Heating silicon carbide (SiC) at high temperatures (1100 °C) under low pressures can also produce graphene. However, the cost of this method is high.

Carbon Nanotube Unzipping

Carbon nanotube unzipping produces high quality graphene nanoribbons. It can be a good method of produce graphene with a bandgap. [7]

Reduction of graphene oxide

Graphene oxide (GO) consists of graphene sheets with oxygen functional groups attached to its surface. The oxygen functional groups make graphene oxide dispersible in water with the help of ultrasonication.

1.3 Graphene oxide

One method applied is chemical oxidization of graphite using strong oxidizing agents. [14] It is considered a promising method of production on a large scale. [12]

Graphite oxide is a multi-layered structure with carbon atoms connected to oxygen-containing groups, such as hydroxyl and epoxy groups that bind to its edges as well as between individual layers of graphene (Figure 2). [12,13,14] This expands the layer of separation due to a change in the forces and makes the material hydrophilic. [13] This in turn disperses the material in water and enables the exfoliation of graphite oxide by the process of ultrasonication thereby producing single- or few-layer GO. [12,14] Graphene oxide can be dispersed in water and polar organic solvents by sonication due to the presence of oxygen functional groups. [14] During the oxidization process, the sp^2 bonds are disrupted and GO can therefore be regarded as an electrical insulator rather than a conductor [12,13]. Reduction of GO is therefore very important in order to recover its electrical conductivity. Reduced graphene oxide (rGO) creates aggregates once most of the oxygen functionalities are removed, making it difficult to get dispersed. [13]
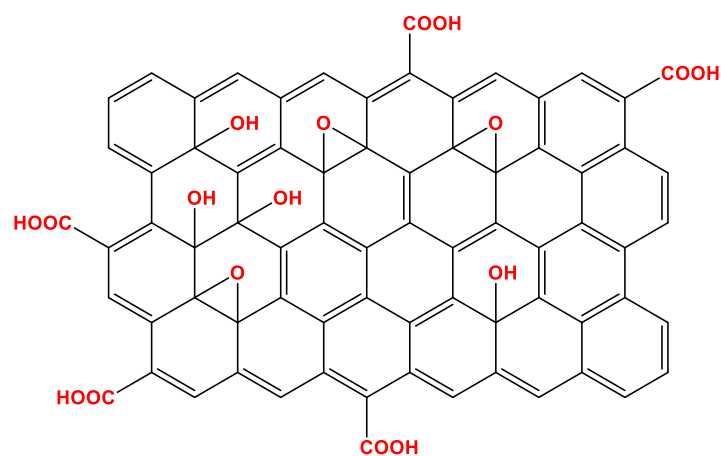
Figure 2. Chemical structure of GO.

For the production of GO, it uses inexpensive graphite and the chemical method of production is relatively cheap and gives a high yield. [13] There are mainly three methods to produce GO, namely, Hummer's, Staudenmaier's, and Brodie's. [12] Among the three approaches, the most common one is the Hummer's method, in which graphite is oxidized using potassium permanganate ($KMnO_4$) and 98 wt.% sulfuric acid. The process consists of 3 steps. In the first step, the temperature of the mixture was kept below 20 °C for 2 hours. Simultaneously the solution is continuously stirred. In the second step temperature is maintained for 30 minutes at 35 °C after $KMnO_4$ is dissolved. Deionized water is then added slowly into the mixture, due to a large amount of heat is released during this process. After 15 minutes, hot water and 30% H_2O_2 are added into the mixture under continuous stirring. The resulting solution is bright yellow and is filtered through filter paper. The solid mixture is washed with HCl and distilled water, and further dried in vacuum oven at 70 °C for 24 h. [7]

1.3.1 Dispersibility of GO

The dispersibility of GO comes from the ability of oxygen functional groups to form hydrogen bonds with the solvent molecules and also due to the changes in topology between graphene, flat, and GO that has oxygens pointing out from the flat surface. [15] Alcohols and water are both polar molecules and possess the ability to form hydrogen bonds with GO.

1.3.1.1 Dispersibility of GO in alcohol

Alcohols are polar molecules and can form hydrogen bonds with the oxygen functional groups of GO. However, GO shows poor solubility in alcohols. Neklyodov et al. proposed a possible explanation: As the hydroxyl group on the alcohol forms hydrogen bonds with the oxygen functional groups in the GO, the hydrophobic tail of the alcohol is tuned outwards. The materials in the bulk solution are unable to form hydrogen bonds with the molecules attached to the surface.

1.3.1.2 Dispersibility of GO in water

GO is dispersible in water. The structure of GO depends on its water content. In the dry state, there are intralayer hydrogen bonds and interlayer hydrogen bonds, as shown in Figure 3a. The distance between the layers in this case is 5 Å. In the wet state, graphite oxide swells, the distance between the layers increases to 9 Å. The structure looks very different as the layers are not hold together by the functional groups themselves but by water molecules with hydrogen bonds to both layers (Figure 3a). Figure 3b shows the increase in the interlayer distance with humidity. [15,16]
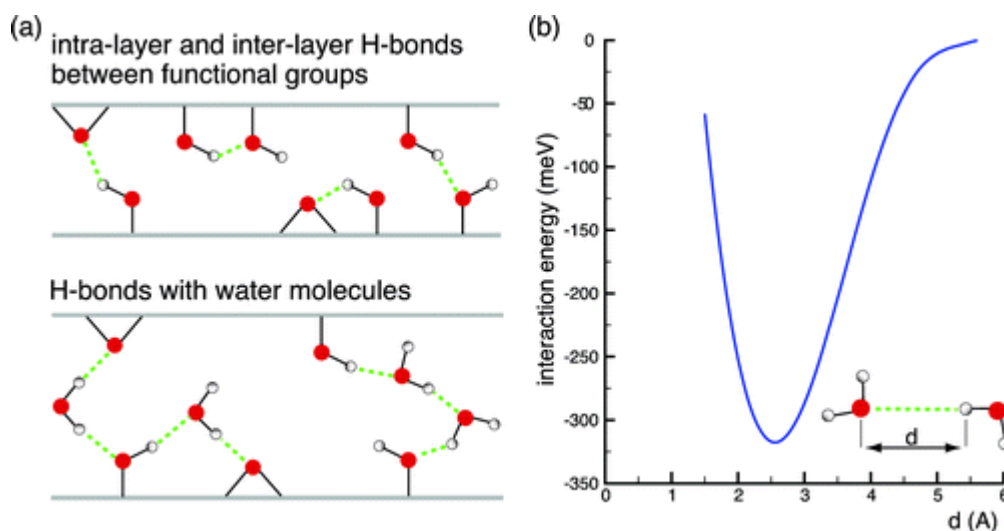
Figure 3. (a) Hydrogen bonds in the hydrated GO with different water content. (b) Change of the O· · ·H bond energy with bond distance d. Copyright @ ACS 2010.

1.4 Reduced graphene oxide (rGO)
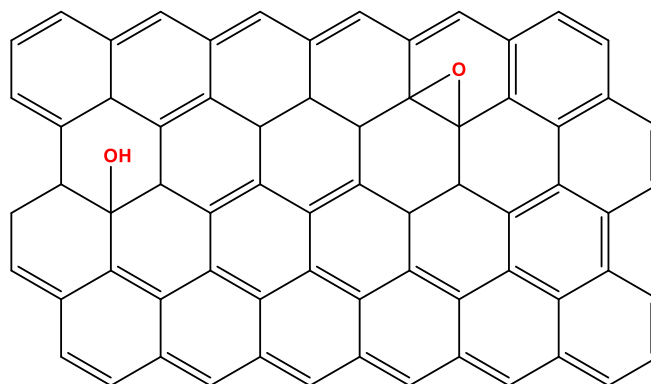
Figure 4. The possible chemical structure of rGO.

1.4.1 Methods for reduction of graphene oxide

Reduction of graphene oxide (GO) is a process to restore the structure of graphene by removing oxygen functional groups and restore the sp^2-hybridized carbon-carbon bonds (Figure 4). [12,13] Several methods have been developed, but there are two methods that are most commonly employed for reduction, i.e., chemical and thermal reduction. [13]

Thermal reduction

Thermal reduction means that graphite oxide is being heated to a high temperature that makes carbon dioxide and carbon monoxide evolve between the sheets. The gases create a pressure which eventually cracks the graphite oxide and liberate single layers. Although this method removes much of the oxygen, evolution of carbon dioxide and carbon monoxide also means that carbon atoms in the graphene plane are being removed. This has a negative impact on the carbon plane as it creates defects

and lowers the electrical conductivity. In addition, the mechanical strength of rGO is affected because the process also creates imperfections and vacancies due to a reduction in mass. [13]

Electrochemical reduction

Electrochemical reduction can produce very high quality rGO. This process involves a thin coating of GO either on a glass or an indium tin oxide (ITO) substrate. A circuit is created through the GO when an electrode is connected at the end of each substrate. The rGO created from this method shows a very high electrical conductivity and a very high carbon to oxygen ratio. There is also no toxic waste produced. One disadvantage with this method is that it is difficult to deposit GO on to the electrodes in bulk.

Solvothermal reduction

Solvothermal reduction is when reduction takes place in a sealed container in which the GO is dispersed in a liquid solvent, like water. The pressure in the container can be raised which allows for heating of the solvent to a temperature above its boiling point in atmospheric conditions. Supercritical water for example can then be a reducing agent for GO. To obtain a stable dispersion, alkaline conditions should be used. This method has many advantages, supercritical water both remove the oxygen functional groups and restores the aromatic structure in the carbon plane which is essential for the electrical conductivity. Although other solvents can be used for reduction, using water is good from an environmental point of view as no toxic substances are used.

Chemical reduction

Currently, chemical reduction is seen as the most suitable for mass production of graphene. [17] It is important that the process applied separates individual layers. [13] The quality produced is however not the same as, for instance mechanical exfoliation, but the scale of production is larger. [13] In chemical reduction, moderate temperatures are used which lowers the risk of damaging the graphene sheets. Hydrazine has been one of the most widely used and has shown promising results. However, hydrazine is very toxic and potentially explosive. Therefore, there is an interest in finding other non-hazardous chemicals to efficiently reduce GO. Substances that have been proved to be effective are hydroiodic acid (HI), ascorbic acid (Vitamin C) and sodium hydroxide (NaOH). In this project they will be used as the reducing agents. [18]

1.4.2 Ascorbic acid for chemical reduction of GO

L-ascorbic acid (LAA), commonly known as vitamin C, is a water-soluble molecule that is found in vegetables and citrus fruits. [19,20] It is an essential part of the human diet. [19] It plays a role in the immune system and aids in the formation of collagen, which is an important building block of various tissues, for example bone, teeth and fibrous tissue. [20] L-ascorbic acid plays a vital part in numerous biological functions. [21] It is a molecule with a high reducing potential and is therefore an important antioxidant. [12,22] Because it is non-toxic, high antioxidant and reducing properties, it can be used in chemical processing, such as chemical reduction of GO. [12]

The hydroxyl groups of ascorbic acid are acidic enabling protonation and thereby making the AA nucleophilic. Jian et al. has suggested that a protonated hydroxyl group can open an epoxy ring. [22] Followed by the release of water, an intermediate is formed where the two carbon atoms previously bonded to the epoxy now bond to the AA. By thermal elimination, the AA is dissociated and released as its oxidized form dehydroascorbic acid (DHA). The mechanism for the reduction of hydroxyl groups is similar with the formation and dissociation of the same intermediate, as shown in Figure 5.
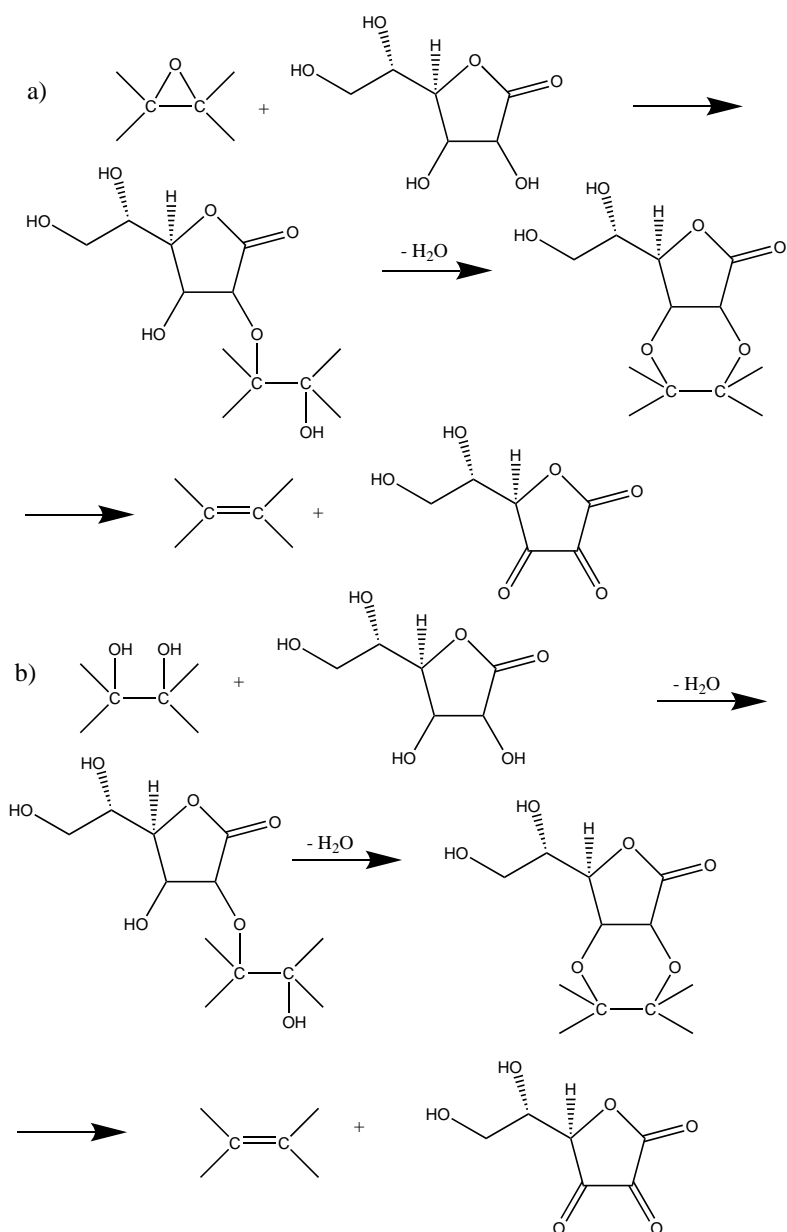
Figure 5. Possible reduction mechanism of GO by ascorbic acid (AA).

1.4.3 Hydroiodic acid used for chemical reduction of GO

HI is the strongest of the hydrohalic acids with a pKa of -10. Scientists have proposed a possible mechanism for the reduction of GO. Hydriodic acid catalyzes the opening of an epoxy group and convert it into a hydroxyl group. Protonation of the OH-group followed by release of H_2O and I_2, as shown in Figure 6a. [22,23,24] The reduction of hydroxyl groups follows a similar mechanism, as shown in Figure 6b.
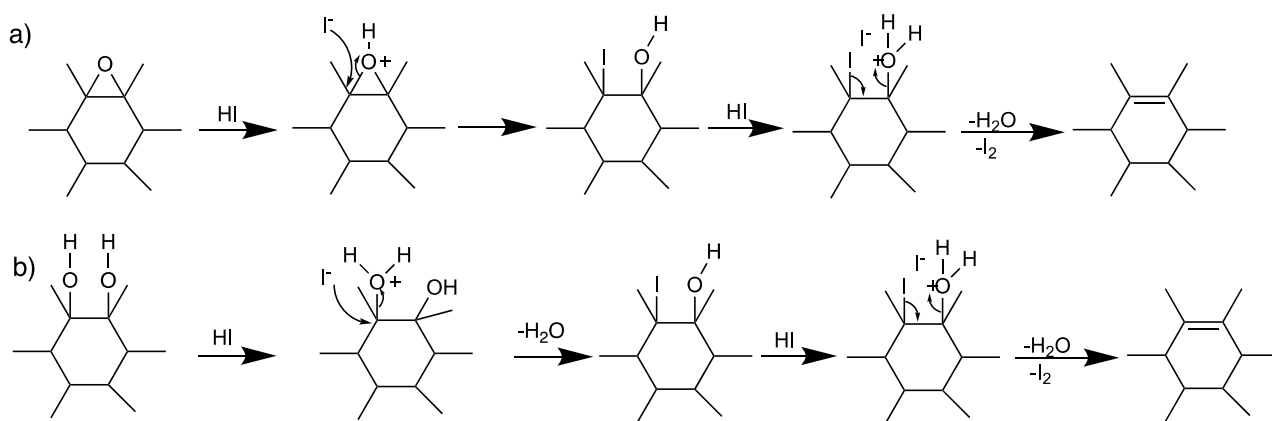
Figure 6. Possible reduction mechanism of GO using HI.

1.4.4 Reduction of Graphene Oxide by NaOH

NaOH is an alkaline, highly corrosive substance that can occur in solid or liquid form and is used in various industries for different manufacturing processes such as soaps, paper, explosives, dyes, metal cleaning and processing, oxide coating, electroplating, petroleum, commercial drain and oven cleaners. [25] It is odorless and when mixed with water or neutralized with acid it releases heat, which can ignite combustible materials. [26]

GO becomes negatively charged when the oxygen functional groups on the graphene sheet is deprotonated in an alkaline solution. This reaction can be made possible by interaction with Na^+ and GO with negative charge, as proposed by Wu et al. Based on a density functional theory (DFT) simulation GO was reduced in a sodium hydroxide (NaOH) solution which contained negatively charged OH^- anions, Na^+ cations and neutral H_2O molecules. The electrons released during deprotonation lowered the ring opening reaction of epoxy groups with a small barrier while simultaneously being reduced by Na^+ cation and water molecule (H_2O). Because Na^+ cations attracted GO which is negatively charged, the reaction was believed to be equivalent to the one between metallic Na and GO. In this reaction NaOH acted as a catalyst in the reduction of GO. This reduction process, however, resulted in many defects in rGO cutting the graphene sheet into pieces. This can further help our understanding of the nature of GO reduction. [27]

Ghorbani et. al. synthesized GO by modified Hummer's method. Reduced GO was prepared in pH value of 11 adjusted by NaOH at 140 °C for 6 h under continuous stirring. FTIR, Raman, SEM and XRD analyses revealed elimination of labile oxygen functional groups, thus partially restoring the π-conjugated network. Thermally stable carbonyl, carboxyl, ether, and phenolic groups hindered complete deoxygenation of GO and made their dispersion in water stable. Pressure can be controlled efficiently, and temperature is lower in modified hydrothermal method compared to that of simple hydrothermal method. [28]

1.5 Aim

The goal of this project is to investigate three possible chemical reduction routes to prepare reduced graphene oxide. The reducing agents are hydroiodic acid (HI), ascorbic acid (Vitamin C) and sodium

hydroxide. With analytical tools, the change in C/O ratios can be monitored before and after the reduction. By examining the results, an assessment can be made regarding the effectiveness of these methods.

1.6 Limitations

There are numerous methods on reducing graphene oxide both thermally and chemically, but this project will use three different reagents for chemical reduction. A comparison with the other existing and sometimes more established methods cannot be made. The properties of the product such as the electrical conductivity and tensile strength will not be tested.

1.7 Specification of issue under investigation

- The structure and properties of GO.
- How GO is reduced by ascorbic acid.
- To which degree the GO can be reduced by ascorbic acid.
- How GO is reduced by hydroiodic acid.
- To which degree the GO can be reduced by hydroiodic acid.
- How GO is reduced by sodium hydroxide.
- To which degree GO can be reduced by sodium hydroxide.
- What analytical methods can be used to monitor the experiment.

2. Methodology

2.1 Materials

Graphene oxide was obtained from a commercial source (Graphenea).

2.2 Chemicals

HI – Janssen Chimica – 57wt%
DMF – Sigma Aldrich
Sodium bicarbonate – Scharlau
Sodium hydroxide – Fisher Chemical
Ascorbic Acid – Amresc
Acetic acid– Sigma Aldrich

2.3 Instruments

- Sonicator – Elma, Elmasonic P

- UV/Vis-spectrophotometer – Varian, 50 Bio: Can analyse one cuvette each time. More about UV/Vis spectrophotometry is at section 2.2.

- Centrifuge – Eppendorf, Centrifuge 5417R: Centrifuge 5417R uses small tubes that can hold a total volume of 1,5 ml. It can hold a total of 30 tubes at one time.

- Centrifuge – Sigma, 4-16KS This centrifuge can hold 6 large tubes.

- **IR spectrometer – Bruker, Vertex 70v:** This spectrometer is used to analyze solid samples. More about IR spectroscopy is in section 2.2

2.4 Experimental procedure

2.4.1 Reduction of GO using ascorbic acid

2.4.1.1 Sonication and reduction

When reducing GO with ascorbic acid, 20 mg of graphite oxide was dispersed in 200 ml of water in a round bottom flask. The GO was not evenly distributed in water as some of the GO sheets were still attached to each other. In order to fully exfoliate the graphite oxide into GO, a certain amount of mechanical force needed to be applied. Sonication is a method used to apply a mechanical force on a substance by sound waves and making a dispersion more homogeneous. Sound waves are longitudinal waves with alternating compression and decompression. When run in water the decompression creates a vacuum which in turn create a bubble. The bubble expands to the point where it can no longer absorb energy and implodes. The implosion of a bubble is compared to a reaction at 5000 K at 2000 times atmospheric pressure. [29] It creates a liquid microjet which shoots out of the imploding bubble and applies a strain on the GO sheets, separating them from each other. [29,30,31]

The round bottom flask containing the dispersion was placed in a sonicator for 30 minutes at a frequency of 37 kHz. The result of the sonication was clearly visible as the dispersion became more homogenous. 200 mg of ascorbic acid was then added to the dispersion. A magnet was added to the flask that was sealed and the reaction mixture was stirred at a speed of 350 rpm. It is held under room temperature which can vary between 21-23 °C. The time is always noted to keep a clear record of the reduction time.
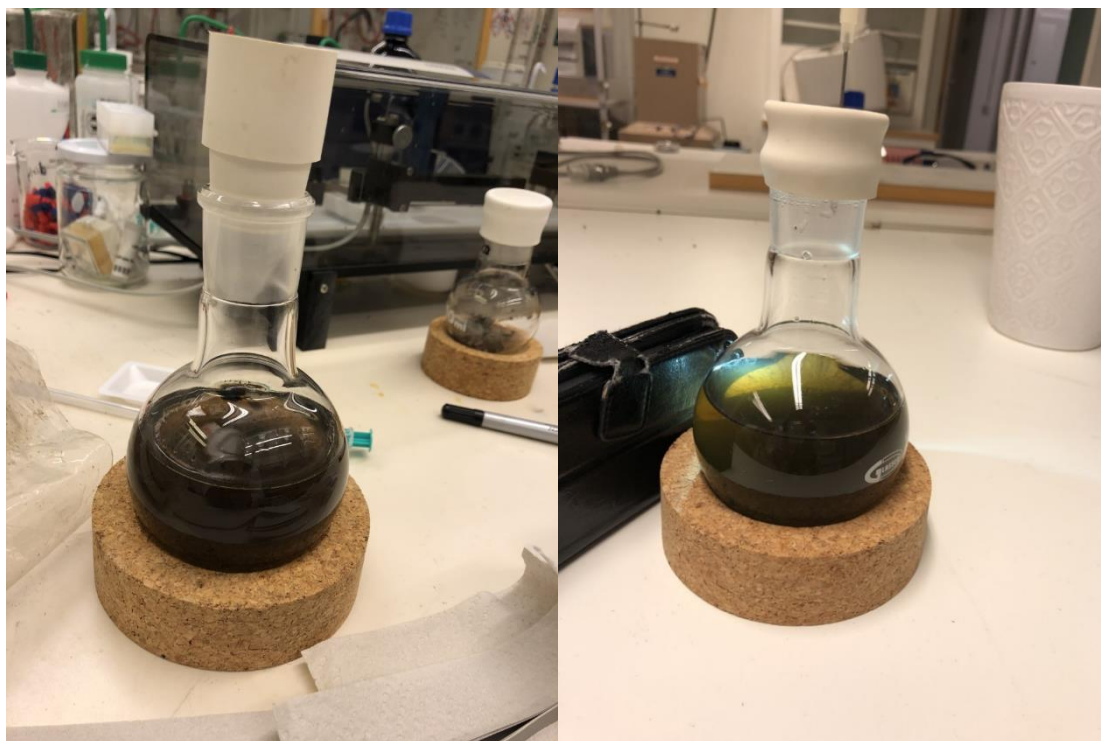
Figure 7. GO dispersion before and after sonication.

2.4.1.2 Cleaning and preparation for characterization

Ascorbic acid is very UV-active and will completely overshadow the absorption curve. As a consequence, the solid product must be separated from the solvent and be washed to remove the excess of ascorbic acid. There are various methods to achieve this. The product can be filtrated and washed with water or it can be centrifuged. To monitor the reaction a fast preparation is needed that enables the reaction to be monitored every day and allow us to see how far it had gone. In this section, it will be explained in detail why centrifugation was the method that proved most useful. After the first reaction with ascorbic acid, centrifugation was used for all the reactions.

The centrifuge used is Eppendorf 5417R where two small bottles were centrifuged at 12 000 rpm for ten minutes. The supernatant was then removed with a pipette and the product was diluted with double-distilled water. This process was then repeated to remove any remaining ascorbic acid, so the product is completely clean for analysis.

The first attempt to analyze the material was done after 24 hours. A small sample was taken from the flask and was used without further treatment. In the UV/Vis absorption spectrum, it showed a massive absorption. The ascorbic acid still remained in the solution and absorbed a large quantity of UV-light, making any analysis impossible. The first successful attempt for analysis was made after 48 hours. The product was centrifuged and diluted as described above.

Attempts to vacuum filtration were also made. However, the filtration was very slow. Especially when a large quantity of product dispersion was filtrated, it had to run for several days. The pump creating the vacuum could not be left overnight for safety reasons. Only one filtration equipment was available in the lab. Because of these reasons, filtration did not prove to be a good method for quickly obtaining product. Therefore, centrifugation was considered a better method.

As previously described, two types of centrifuges were available in the lab: 4-16KS by Sigma and 5417R using Eppendorf. The tubes used for 5417R fit perfectly into the holders. The holders in 4-

16KS is much larger and can hold tubes with much greater volume. However, at the lab there are no tubes available with the same shape of the holders. Therefore, one can't run the centrifuge at a too high speed with a risk of damaging the tubes. The tubes used for 4-16KS could contain 45 ml each. Four tubes, a total of 180 ml, were filled with the product. They were centrifuged for 20 minutes and because of the reason stated above the speed was only 6 000 rpm. The attempt was unsuccessful as only part of the solid product gathered at the bottom, there was still too much left in the supernatant.

In Eppendorf, the speed used was 12 000 rpm and it was usually run for 10 minutes. The separation was successful as all the product gathered at the bottom, and the supernatant could easily be removed with a pipette. Therefore, all the product in the 45 ml-tubes was transferred to 24 small 1.5 ml-tubes and separated in the Eppendorf centrifuge. The solid product was then successfully isolated. When pipetting out the supernatant from the tubes there was inevitably some solid product that unintentionally followed.

Because of these findings, we have noticed the separation of the product on a large scale in Eppendorf was a problem. The separation in Sigma was insufficient and all had to be done in Eppendorf. It required 24 small tubes. They all had to be filled, sonicated, and then separated by removing the supernatant by pipette. This was a time-consuming process. It shows that the right equipment is important as a centrifuge with fitting tubes could have facilitated the process considerably at a high speed. In this experiment, only small samples were needed for analysis.

Another reaction was carried out with the following measures: 10 mg GO, 100 ml double distilled water, 100 mg AA. Notice that the ratios are the same as in the first reaction. At different times some of the dispersion was taken out and centrifuged, following an analysis in the UV/Vis spectrophotometer.

In addition to analytical instruments one can visually inspect the reaction: getting darker and flocculation appeared. They both indicate that a reduction has taken place.

2.4.2 Reduction of GO using hydroiodic acid

The reduced graphene oxide can be achieved by dispersing 5 mg of GO in acetic acid with a volume of 5 ml. Sonication of the mixture was performed until the dispersion was homogenous, then 0,1 ml of HI was added. The mixing process took place in a round-bottom flask that was put on a magnetic stirrer with a speed of 350 rpm. The reaction was kept at room temperature.

In order to neutralize the dispersion a base has to be prepared. The base used is a concentrated solution of sodium bicarbonate ($NaHCO_3$). 400 mg of $NaHCO_3$ was dissolved in 5 ml of double distilled water.

When making an analysis, a 3 ml of the reacting dispersion was taken out with a pipette and put in two Eppendorf tubes which was centrifuged at 12 000 rpm for 10 minutes. The supernatant was decanted, and the product was re-dispersed in water. Neutralization was performed by applying several drops of the sodium bicarbonate solution and the pH was monitored with a pH-paper. Because of the dark color of hydroiodic acid a few rounds in the centrifuge was needed. The process of centrifugation and washing were repeated many times before UV/Vis analysis.

2.4.3 Reduction of GO using sodium hydroxide

2 mg of GO is dispersed in 19,6 ml of double distilled water and 0,4 ml of 5 M sodium hydroxide solution were added in a round bottom flask and the mixture was sonicated for about 30-40 minutes until the dispersion was homogenous. The round bottom flask was put on a magnetic stirrer at a speed of 350 rpm and a temperature of 80°C. As the temperature is relatively high, cooling might be needed to prevent evaporation. Therefore, a condenser was placed on the round bottom flask. Water can be used as a coolant but in this case cooling by air was enough.
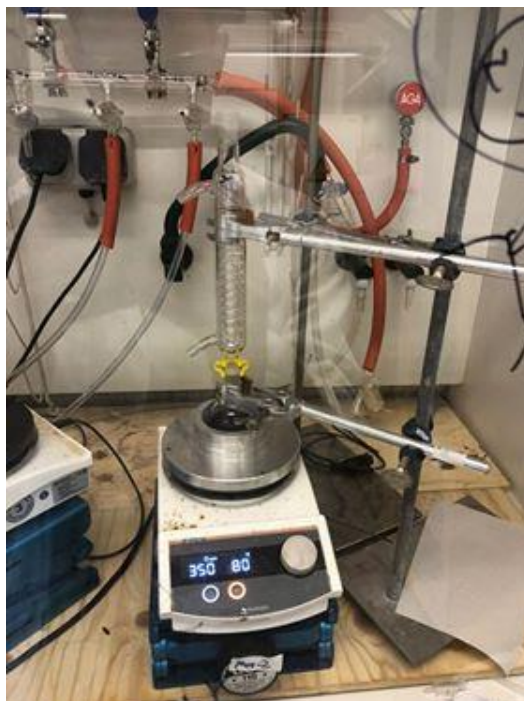

Figure 8. Condenser was used during reduction of GO using NaOH.

Sodium hydroxide is not believed to be UV-active in a way that would overshadow the results, so centrifugation is not necessary when tried in the UV/Vis-spectrophotometer.

2.4.4 Preparation for IR analysis

To make an IR-analysis the product has to be completely dry. All products that are to be analyzed had to go through the process of centrifugation and washing, this also included the one reacting with sodium hydroxide. When washing the product, the pH had to be monitored using a pH-paper. When it showed a pH of 7, the residues of hydroxide ions had been removed.

Eppendorf tubes containing the solid product was wrapped in aluminum foil with small holes in the opening. The tubes were put in a round bottom flask that was put on a hot plate and sealed with a rubber lid. A pump was connected to the flask through a needle and created a vacuum. The plate was heated to 60°C and the sample was left to dry overnight.

2.2 Characterization techniques

The analysis methods that can be used are UV/Vis absorption spectroscopy, IR spectroscopy, Raman spectroscopy, thermal gravimetric analysis (TGA) and X-ray photoelectron spectroscopy (XPS).

Fourier Transform Infrared Spectroscopy (FTIR) can be used for detecting graphene oxide (GO) and reduced graphene oxide (rGO). [32] It is an analytical tool for the detection of organic and inorganic compounds/materials. [32,33] FTIR can detect different functional groups according to their vibrations. [34] FTIR measures the absorption of infrared radiation of the sample versus the wavelength and the resulting bands identify molecular components and structure. [33] The FTIR spectrometer uses an interferometer to collect an interferogram of a sample signal. [35] It subsequently uses a mathematical algorithm called the Fourier Transform to obtain the spectrum. [33,35] The spectrum is presented as plots of intensity versus wavenumber (in cm^{-1}) where wavenumber is the reciprocal of the wavelength. [33]

UV/Vis spectroscopy measures the absorption at higher frequencies, in the ultraviolet and the visible spectrum. While IR radiation increases the vibrations in the molecule, UV causes the π-electrons to be raised to a higher energy level. If the molar absorptivity of the molecule is known, a calculation of the concentration can be made. [36]

Raman spectroscopy observes the scattering light of a sample when irradiated by a laser beam. By observing the scattered light, one obtains different peaks showing the intensities of the frequencies emitted. When sample molecules absorb light, the vibrational energy is raised to a so-called virtual state before it immediately drops again. There are several possible outcomes when the energy drops. In most cases it goes back to the initial state, thereby emitting a photon with the same frequency as the absorbed light. However, in some cases the energy drops to a higher state than the initial. The frequency emitted is then lower than the absorbed, these peaks are called stokes. The energy can also drop to a lower state emitting a higher frequency, so called anti-stoke shift. Using the specific energy difference between vibrational states in different molecules, the substance can be determined. [37]

X-ray Photoelectron spectroscopy (XPS) is based on the photoelectric effect. When a surface is exposed to electromagnetic radiation, electrons from the material are ripped off. To emit an electron, a specific amount of energy is required, this energy is called *binding energy*. The emitted electron carries a kinetic energy given by the radiation. This kinetic energy is measured and by subtracting the initial energy from the radiation with the kinetic energy, the binding energy is given. That tells which elements are present in the sample. [18,38]

Thermogravimetric analysis (TGA) is when the mass is measured against the temperature or time. [39] During heating of a substance there are numerous processes that can occur. These includes absorption, adsorption, vaporization, sublimation and thermal decomposition. They all have an impact on the substance's mass. This method can be used to determine a substance's thermal stability. [40,41]

3. Results and discussions
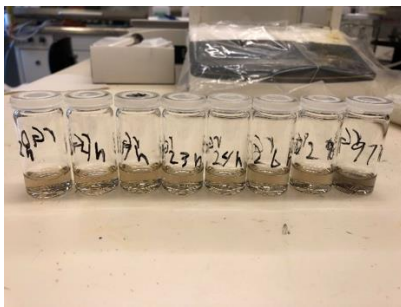
3.1 Reduction of GO by ascorbic acid

Figure 9. Reduction of GO with ascorbic acid at different time.

After 97 hours the yellow-brown colour had shifted to a darker colour, less transparent. The presence of small particles could also be spotted.

3.1.1 UV/Vis absorption spectra

The absorption spectrum of GO shows one peak and a shoulder. The peak at around 230 nm is due to π to π^* transition of C=C bonds. The shoulder peak comes from a n to π^*-transition in the C=O bond and is seen at around 300 nm.

When the GO is reduced, the absorption curve alters shape. The peaks at 300 nm disappears as the C=O groups are removed. The curve also experiences a so-called *redshift* as the peak for the aromatic C=C bonds shifts to a higher wavelength (red has a higher wavelength and thereby lower energy). This is also known as the bathochromic effect and indicates a restoration of the conjugated structure in graphene. The peak now appears at around 260 – 270 nm instead. [42,43,44,45]
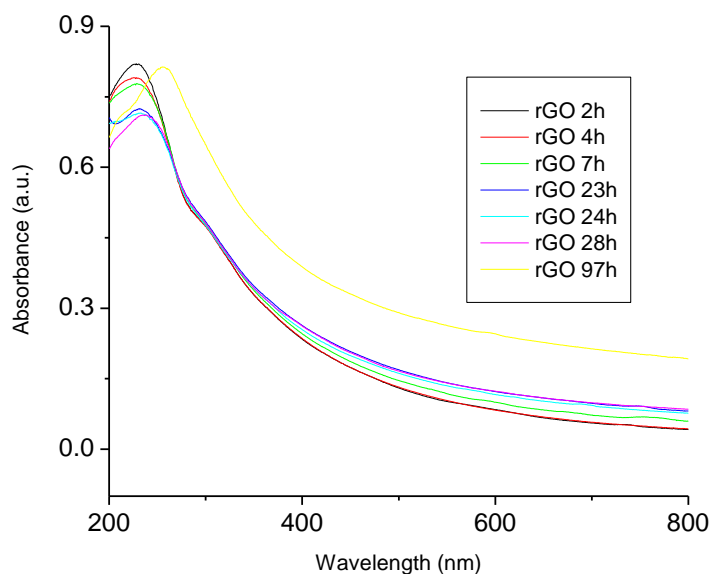

Figure 10. UV/Vis absorption spectra of rGO samples shown in Figure 10.

In the first day the characteristic shoulder at 300 nm can clearly be observed. After three days this shoulder peak is no longer visible. One can see the peaks more clearly in Figure 12 that zoomed in spectra are shown.
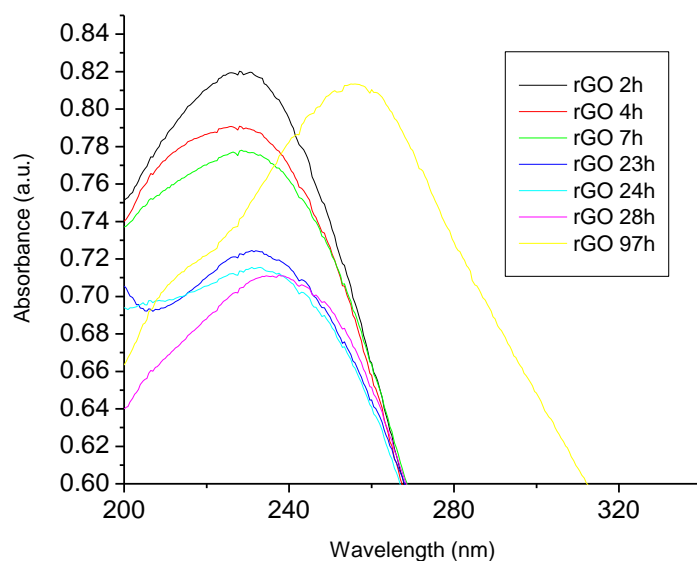
Figure 11. Zoomed in spectra of the UV/Vis absorption spectra shown in Figure 11.

During the first day the π-π* peak was around 230 nm and no clear shift can be observed yet. The next day a small but substantial shift was observed as the peak now appears somewhere between 235-240 instead. The last test was run after three days and the bathochromic shift was unmistakeably clear as the peak now has moved to around 260 nm. This corroborates with the visual observation and confirms that reduction has taken place.

3.1.2 IR spectra

Figure 12. IR spectra of GO and rGO.

The red curve shown the transmittance for GO, the characteristic peaks of GO can be seen very clearly (Figure 13): O−H (3400–3200 cm^{-1}), C=O (~1730 cm^{-1}), C=C (~1620 cm^{-1}), CO–H (~1410 cm^{-1}), C−O (~1220 cm^{-1}), and C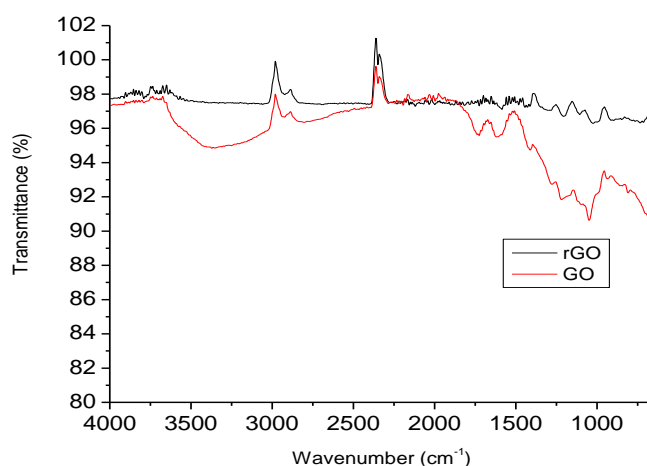−O−C (~1080 cm^{-1}).The black curve shows the GO after 97 hours of reduction where the intensity of the peaks has significantly reduced. This is another confirmation that reduction had taken place.

3.2 Reduction of GO using hydroiodic acid

When reduced with HI, flocculation could be observed after one day. Flocculation had gone so far that despite attempts to sonicate the samples, getting the product properly dispersed was not fully possible. The separation process followed the same procedure as with AA with the addition of neutralisation using sodium bicarbonate.

3.2.1 UV/Vis absorption spectra

When run in the UV/Vis-spectrophotometer, none of the characteristic peaks which were supposed to appear in GO or rGO were seen. Attempts were then made to clean the product more thoroughly by increasing the number of times of washing. Figure 14a shows two curves that is the UV/Vis analysis of the GO reduced by HI between a great time interval. They still look similar and no clear distinction can be observed.
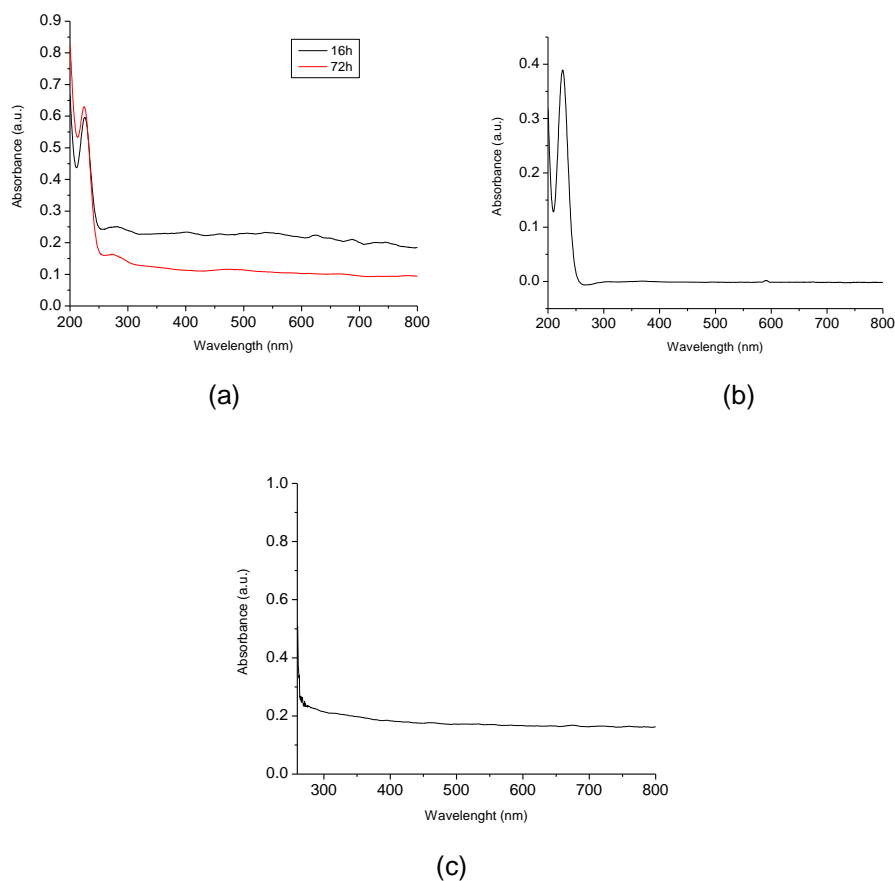

(a)

(b)

(c)

Figure 13. UV/Vis analysis of the GO reduced by HI with time (a), diluted HI solution (b) and rGO in DMF.

The peaks in figure 14a was believed to come from residues of HI. To confirm this, 2 μl of HI was added to a cuvette holding approximately 1,5 ml of double distilled water. When run in the UV/Vis-spectrophotometer the absorption surged. The sample was diluted several times to obtain a curve where the absorption was under 1. Figure 14b shown the curve of a diluted HI solution. The peaks appeared at approximately the same wavelengths as the rGO curves in Figure 14a.

The poor dispersibility of rGO was suspected to be a possible reason for the unconfirming curves. Therefore, solid product was instead dispersed in DMF where it appeared to show a better dispersibility. But when tested in the UV/Vis-spectrophotometer a similar curve appeared until 230 nm where the absorption skyrocketed. 268 nm is known to be a cut-off for DMF in UV/Vis absorption.

In our experiment we observed that while the rGO produced from HI did not disperse in water adequately, while it dispersed better in DMF. This indicates that DMF might be a better solvent to disperse rGO. However, the exact amount of rGO dispersed in DMF was not determined due to a very low concentration, making it difficult to accurately calculate the mass change on a filter paper.

The highly diluted sample with pure HI indicates that even the smallest amount of it can overshadow the UV/Vis curve. It might mean that the product wasn't cleaned properly despite that fact that is was run many times in the centrifuge. Another explanation already discussed was that the poor dispersibility. Due to the cutoff in DMF it could not be concluded if a better solvent could be a solution to the problem. It is difficult to make any firm conclusions because the concentration of rGO in DMF was not determined.

3.2.2 IR spectra

The IR spectra gave more interpretable results as the curve was not overshadowed and resembles the one of GO reduced by AA. The intensity of the peaks had dramatically decreased compared to the GO and indicated that a reduction actually had taken place. This is also in accordance with the flocculation of rGO in water.
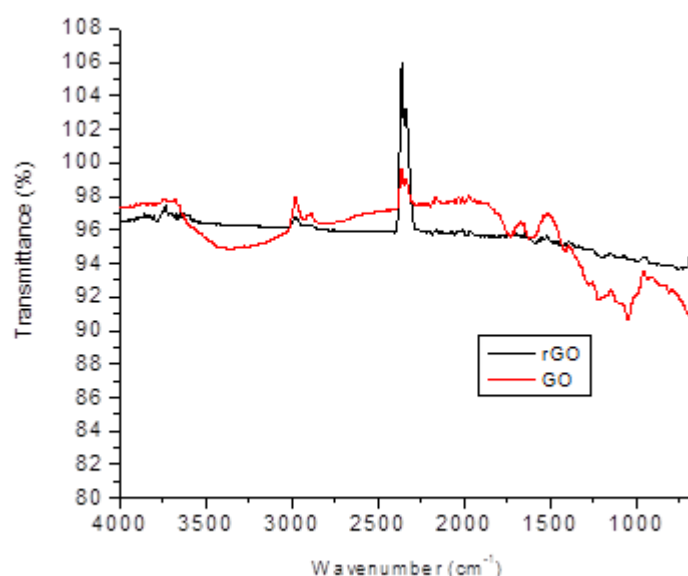

Figure 14. IR spectra of GO and rGO after HI reduction.

3.3 Reduction of GO with sodium hydroxide

Results from the reduction with NaOH were visible after a day when flocculation and darkening of the product could be seen. None of the sodium hydroxide was removed as it didn't disturb the UV/Vis analysis.

3.3.1 UV/Vis absorption spectra
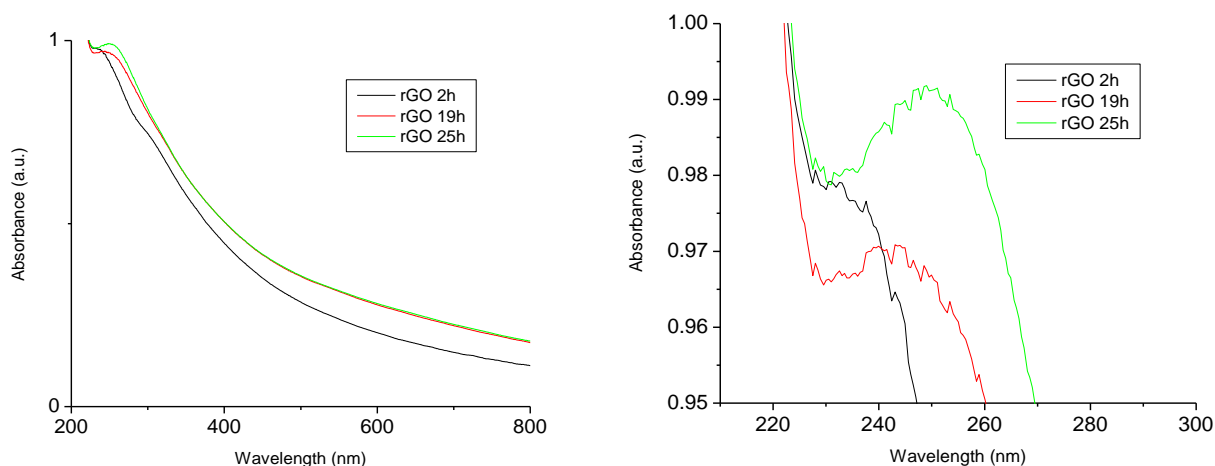
Figure 15. UV/Vis absorption spectra of GO reduction by NaOH.

100 µl of dispersion and 1400 µl water were mixed in a cuvette which was then directly run for UV/Vis measurement. Despite attempts to hold the samples at an even concentration, small differences still existed. They were however near enough to be easily compared to each other. After two hours not clear shift. After 19 hours, a shift has taken place as the peak now appeared at around 240 nm. The most shift is after 25 hours where it lies around 250 nm, indicating reduction indeed happened.

3.3.2 IR spectra

In the IR spectra the curve representing rGO also gave strong indication that reduction had taken place as the intensity of the peaks had significantly decreased.

Figure 16. IR spectra of Go and rGO after reduction with NaOH.

3.4 Further reflections

A comparison between the three methods can be somewhat tricky for several reasons. In the introduction one motive for reduction with new chemicals was safety, because hydrazine was hazardous. Both HI and NaOH are corrosive and should always be tre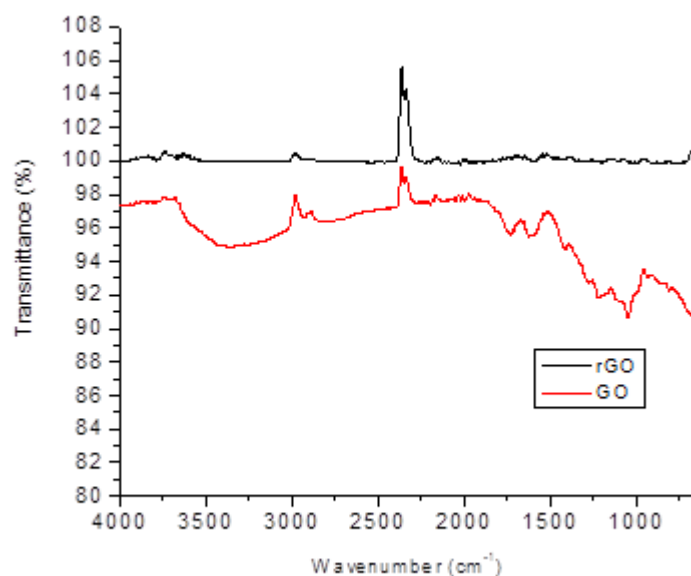ated with caution. Despite this, they are relatively safe and even gymnasium students use them during their lab training. Ascorbic acid is a nutrient and a very safe chemical and therefore one can conclude that it is the safest reaction in the present project.

The effectiveness is not obvious. The methods used in this project were adaptions from literature on previous studies leading to the usage of different chemicals and temperatures. GO reduced by sodium hydroxide showed an earlier bathochromic shift than AA. However, it must be remembered that the NaOH-reaction was – unlike others – heated to 80 °C. When transferring the results from laboratory to a large-scale production the energy demands from heating the reaction must be taken into account.

Heating the reaction with AA was not done here but it has been done in other studies including a master thesis from the Royal Institute of Technology where temperature was tried as a parameter. Making any conclusions on the time efficiency from the HI is not realized because of the low dispersibility of rGO in water, ethanol and DMF.

The most perspicuous quantity for determining the extent of a reduction would be the C/O-ratio. The instrument that could give the information is XPS. Making an XPS analysis would let us see how far the reduction has gone and make a comparison between different chemicals. Because of the situation with the spread of Covid-19, the department that housed XPS was restricted to individuals from other departments.

The purpose of this report was specified to investigate to what degree reduction of GO can be done with the used methods. We can conclude that reduction has been done to the degree that it is clearly observable by IR and UV (except for HI). Nevertheless, we can conclude that all methods used to reduce GO were successful.

4. Conclusions and outlook

The specific issues to be investigated was how GO was reduced by the applied chemicals, to which degree it could be reduced and what characterization methods could be used. This section will go through the conclusions that can be made based on the results in the experiments and the literature study. Ascorbic acid can be used as a reductant as shown by this experiment. The UV/Vis analysis showed clearly that reduction had taken place as it experienced a bathochromic shift. The preparation for characterization by UV/Vis spectrophotometry was fast, easy, and safe, which brings the advantage that one could easily monitor the reaction by this method. IR-spectroscopy was also used and showed good results. The mechanism for reduction is not fully determined but it has been suggested some possible reduction routes. Hydroiodic acid could also be used as a reductant as shown by the IR results which showed that reduction had occurred. This method however was not as easy to characterize as the previous one because the UV/Vis absorption did not show good spectra. Based on the observations and experimental results, the most probable reason was the poor dispersibility, contamination by very UV-active iodide ions or a combination of the two. Although the mechanism for reduction is under debate it has been proposed that the ability of the iodide ions to both substitute protonated hydroxyl groups, and to leave the carbon lattice without damaging which gives HI the ability to reduce GO. Sodium hydroxide is also effective for reducing GO. With moderate heating, reduction can be achieved after only a day as indicated by visual signs and confirmed by UV/Vis absorption analysis. UV/Vis can be used to monitor the reaction as the product requires no treatment to be analysed in the UV/Vis spectrophotometer. IR spectroscopy does also work as a method for characterization. The mechanism for reduction is not completely known but reaction routes has been proposed by scientists. The degree of reduction could not be determined. The characterization method required to decide that was XPS by the C/O-ratio. The instrument used for XPS was not available due to the spread of covid-19. Because of the reason described above and the fact that reduction with sodium hydroxide was carried out with moderate heating, a comparison between the different methods cannot be made. Nevertheless, it is safe to conclude that all reduction methods were successful and can be used for future proposes.

5. Ethics and safety

The laboratory experiments in this project did not involve any humans and animals' studies. This project however was conducted under special circumstances when there was a massive spread of the covid-19 (corona) virus. It was important for participants to keep a distance between them and other participants, especially to elderly individuals. Only a limited number of people could work in the same lab at the same time. Also, participants were suggested to avoid going by public transport to the extent which was possible.

Inside the lab, normal safety procedures were taken. Lab coat, protective glass, plastic gloves must always be worn inside the lab at any time when handling chemicals. The hydroiodic acid and sodium hydroxide used for reduction is corrosive, [46] and in case of contact with skin or eyes the affected part should be thoroughly rinsed with water.

The materials and chemicals used in the laboratories are written in section 2.1 and 2.2. These included vitamins, weak carboxylic acids, sodium ions, bicarbonate ions, iodide and acetone. Although these chemicals are relatively safe and can usually in small amounts be disposed in the sink, [47] they had been mixed with HI and NaOH during the reduction process, therefore they must be disposed in an acid or a base waste bottle, respectively. The sodium carbonate also had to be disposed in the base waste. The dispersions contained solid particles, they had to be filtrated before they could be disposed. The filters with the product could then either be saved or disposed in a dry waste.

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