

Graphene – Exciting Insights into the Synthesis and Chemistry of the Miracle Material of the 21st Century and Its Implementation in Chemistry Lessons for the First Time

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Abstract The two-dimensional modification of carbon which is also known as “graphene” is an extremely interesting material due to its physical properties, such as a very high electrical conductivity and an intrinsic mechanical strength that is even better than that of steel. For that reason, it has already been called the “miracle material“ of the 21st century. Up to now, the synthesis of graphene was too dangerous to implement it into the school curricula. The authors present a method of synthesizing graphene which can be put into practice at school without hesitation. Following experiments show the varying properties of graphene oxide and graphene during synthesis. In this way, different structure-property relationships, which appear to be one of the most important concepts in chemistry lessons, can be analyzed.

Keywords: electrical energy storage systems, supercapacitors, graphene, structure-property relationships

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1. Introduction

Graphene is another modification of carbon besides diamond, graphite and fullerenes and can most easily be described as a two-dimensional layer of hexagonally arranged and sp^2 -hybridized carbon atoms. Due to this two-dimensionality and its unique physical properties (high electron mobility [1], great intrinsic mechanical strength) graphene has become the focus of attention of

scientific research. Besides modern electronic devices such as flexible displays and ultra-thin touch screens [2,3], the use of two-dimensional graphene-based materials in electrochemical double-layer capacitors – also known as supercapacitors – is being discussed as a possible field of application at the moment [4,5]. Supercapacitors differ from batteries in that there is no electron transfer between electrolyte and electrode during charging process. The ions are physically absorbed on the surface of the electrodes where they form an electrical double-layer.

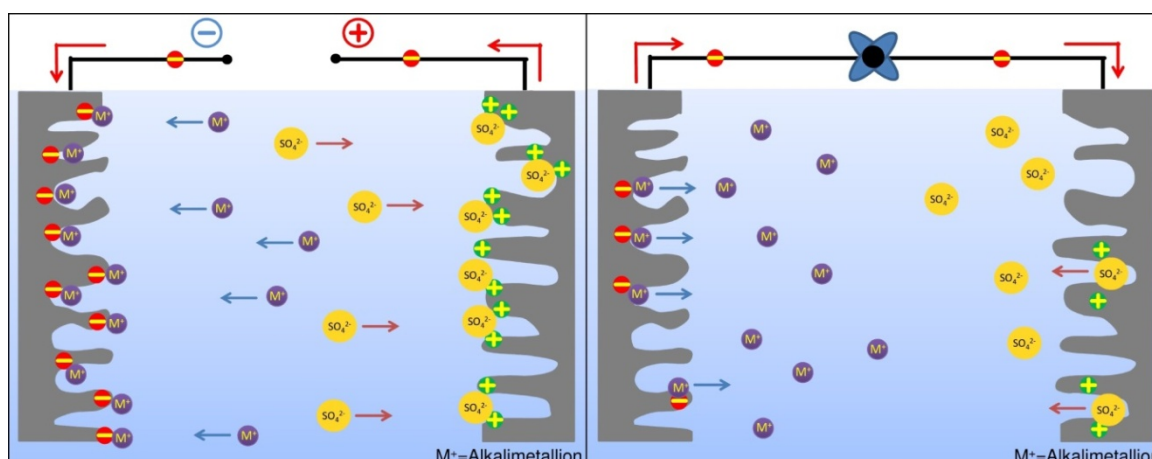


Figure 1. Left side: charging process of a supercapacitor; right side: discharging process of a supercapacitor in an aqueous solution of an alkali metal salt

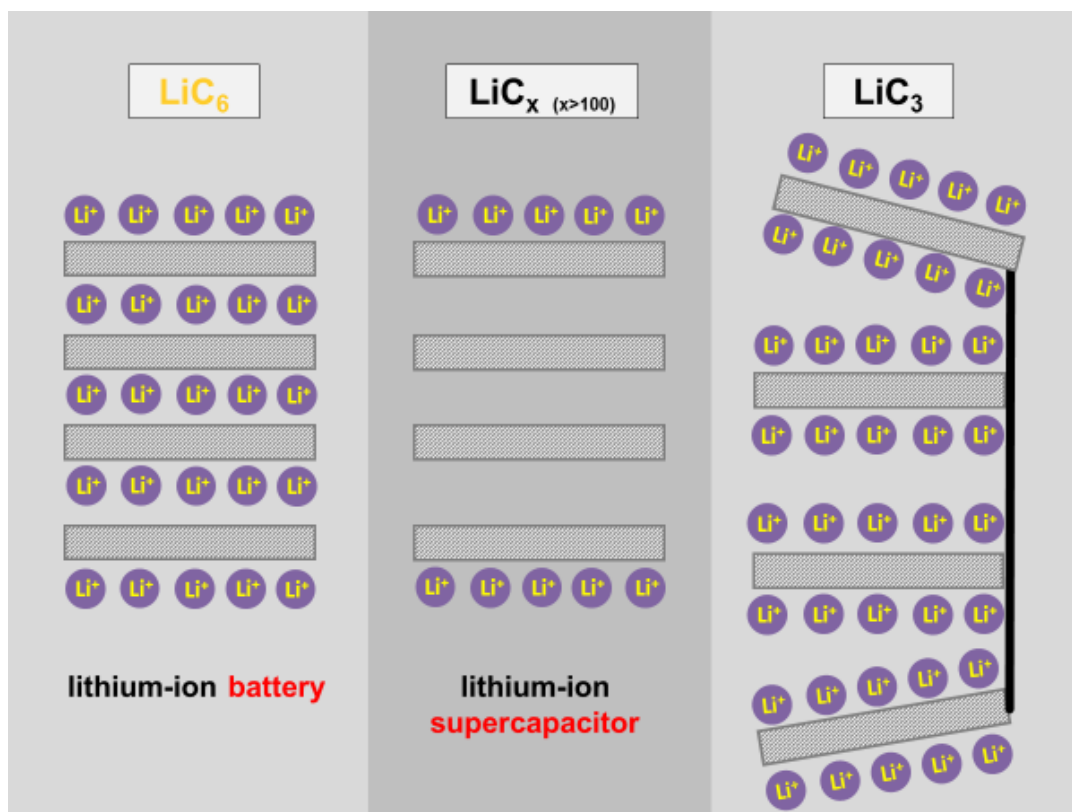


Figure 2. Schematic illustration of a lithium-ion battery's fully charged negative electrode (left); of a lithium-ion supercapacitor (middle); of a graphene-based lithium-ion supercapacitor (right)

The fast adsorption of ions on the surface of the electrodes makes it possible for a supercapacitor to be charged and discharged very quickly. However, the energy density of supercapacitors is low when compared to batteries, since only the surface of the electrodes is available to store electrical energy [6]. One possibility to maximize the energy density is to increase the active surface area of the electrodes, so that more ions can be adsorbed without adjusting the electrode mass ratio. By using two-dimensional graphene as electrode material, the "dead volume" of supercapacitors could be removed almost completely, and energy storage systems could be created which would significantly surpass the energy density of contemporary lithium-ion batteries.

The wet-chemical oxidation and exfoliation of graphite,

which lead to the intermediate product graphite oxide, are one of the current strategies proposed to produce large quantities of graphene. The Van der Waals interactions between the individual graphite layers are already weaker in graphite oxide than in graphite. A subsequent ultrasonic treatment disrupts the Van der Waals interactions and separates the single one-atom-thick layers of graphene oxide. Oxygen-containing functional groups attach to the carbon structure of graphite due to its oxidation and disturb the conjugated π -electron system.

High oxidation leads to the complete loss of electrical conductivity and therefore, graphene oxide acts like an insulating material. By using appropriate methods, graphene oxide can then be reduced to graphene whereby electrical conductivity is restored.

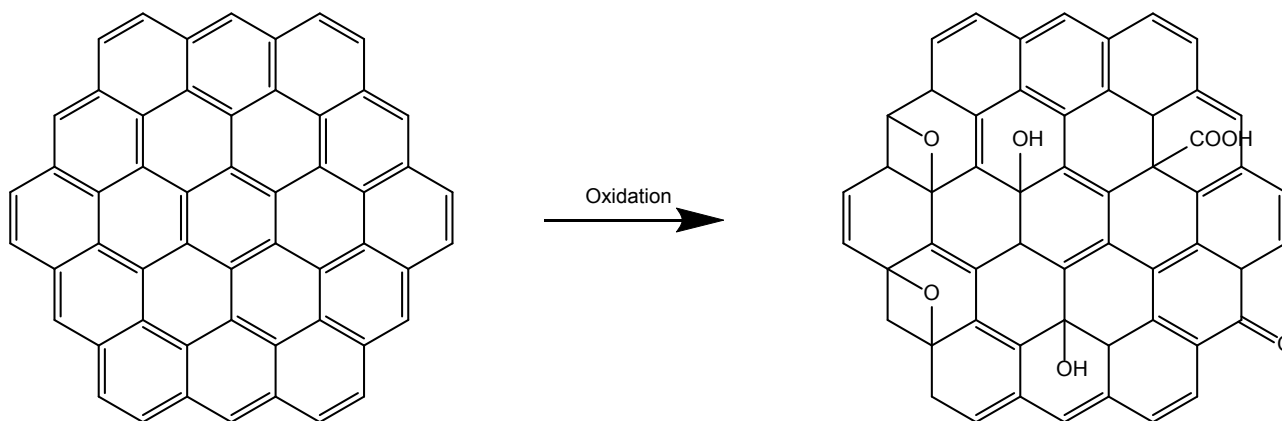


Figure 3. Oxygen-containing functional groups attached to grapheme

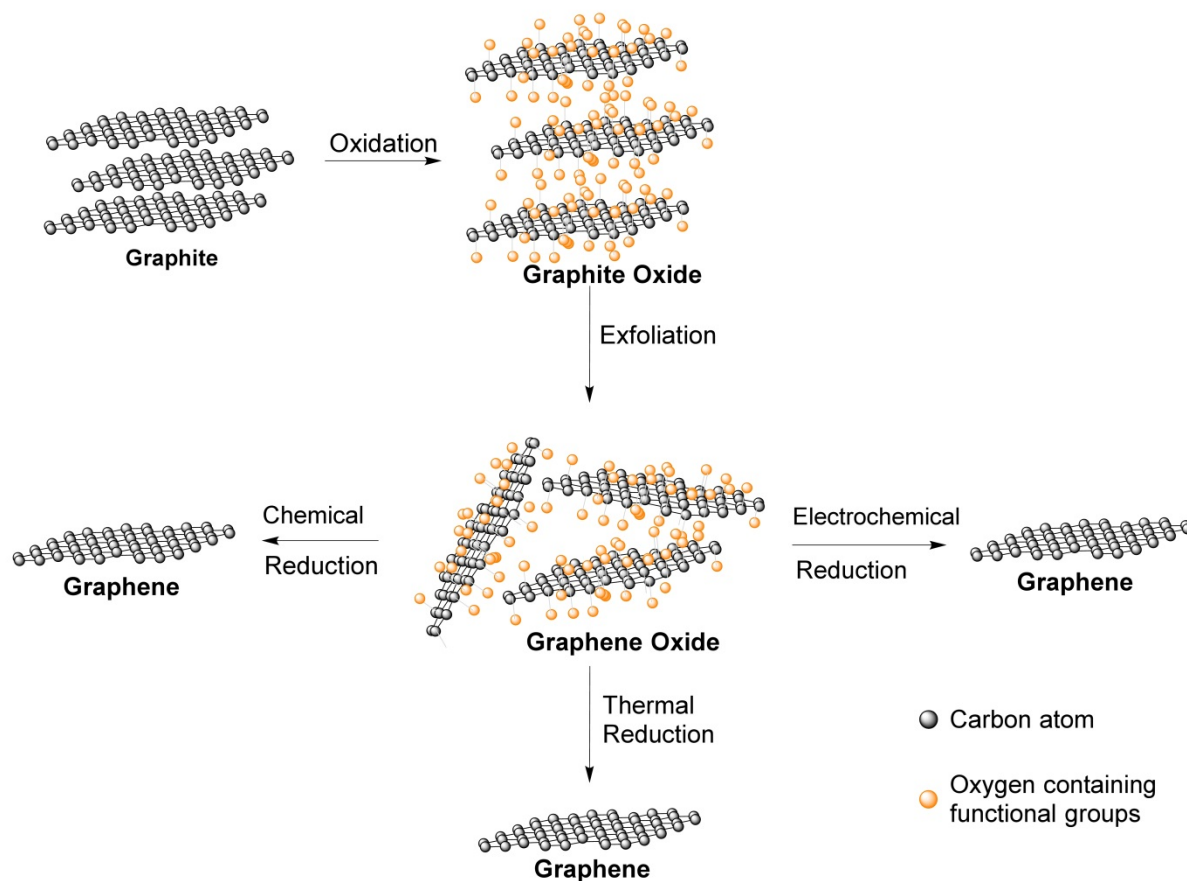


Figure 4. Schematic illustration of the synthetic pathway of graphene

In 1859, C.H. Brodie already examined the reactivity of graphite to gain information on the exact structure and molecular mass of graphite. For this purpose, he mixed graphite in a solution of potassium chlorate and fuming nitric acid and found out that the product of the reaction consisted of carbon-, oxygen- and hydrogen-atoms. The reaction product which is nowadays known as graphite oxide was called “graphitic acid” by Brodie [7]. Despite these findings, Brodie was unable to make exact statements on the structure of the molecule. Nearly 40 years after Brodie, Staudenmaier improved the process of synthesizing graphitic acid, because he felt Brodie’s method to be too complex and uncomfortable. He recorded as follows:

“The whole process has to be repeated four to six times, sometimes even more, until you finally succeed in synthesizing pure yellow graphitic acid, provided that the substance did not get lost earlier due to an explosion. As a result of the high number of operations, it is difficult to protect oneself against the large quantity of foul smelling and harmful gases which escape, making the synthesis of larger quantities of

graphitic acid almost unbearable in the long run.” [8].

Staudenmaier improved Brodie’s method by adding sulfuric acid to the reaction mixture. Furthermore, he replaced the fuming nitric acid with diluted nitric acid and added potassium chlorate in small amounts to the reaction mixture. By introducing these small changes to the instructions of the synthesizing process, he was both able to produce graphitic acid in a single reaction vessel and to reduce the risk of explosion [8].

At present, the synthesis method according to Hummers [9] is the most common and efficient oxidation- and exfoliation process apart from those of Brodie [7] and Staudenmaier [8]. Hummers’ method requires a mixture of potassium permanganate (KMnO_4) and concentrated sulfuric acid (H_2SO_4) as oxidizing agents. Even though permanganate is a strong oxidizing agent, manganese heptoxide (Mn_2O_7) is the real active reagent which is built during the reaction of permanganate and sulfuric acid [10]. The temperature needs to be strictly controlled during synthesis, since manganese heptoxide tends to react explosively if exposed to temperatures at 55°C [11].

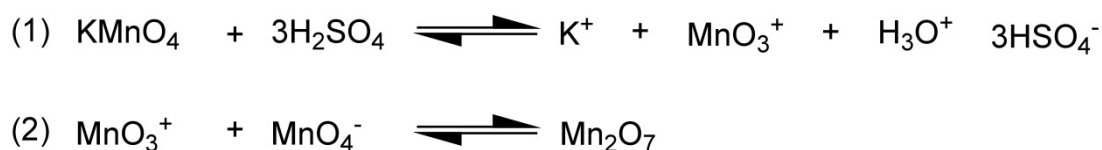


Figure 5. Formation of manganese heptoxide (Mn_2O_7) by reaction between KMnO_4 and sulfuric acid [11]

The synthesis of graphene oxide can be easily scaled with this method. However, the handling of explosive mixtures which contain concentrated acids is extremely dangerous. Aside from the synthesis' associated inherent risks, the inadequate equipment of schools and the insufficient experimental experience of pupils represent further reasons why it is impossible to use the techniques of Hummers, Brodie or Staudenmaier for the synthesis of graphene oxide at school.

In Freiburg (Germany), Oetken's working group pursued the goal of developing a harmless and easy electrochemical process to synthesize graphene oxide [12] which in consequence does not need dangerous chemicals and also leads to an impressive yield in a short time. During an anodic reaction progress in the presence of negatively charged ions, graphite can be exfoliated through intercalation of these anions along with their hydrate shell. The electrochemical oxidation caused by an applied voltage of 20 V as well as the presence of a suitable oxidizing agent (ClO_3^-) lead to the formation of oxygen-containing functional groups on the planar graphene surface [13].

This article describes the electrochemical synthesis of graphene oxide in detail and illustrates how graphene oxide can be reduced to graphene based on a simple photochemical reaction. Furthermore, the changing properties of the material caused by reduction of graphene oxide to graphene during synthesis are examined and the produced graphene is characterized more closely by fascinating analytical experiments.

2. Experimental Materials and Procedures

Chemicals were purchased from Sigma Aldrich. All selected materials are commercially available and can be obtained easily.

2.1. The Electrochemical Synthesis of Graphene Oxide

Materials and chemicals:

Crystallizing dish ($\varnothing = 95$ mm, height = 55 mm), graphite foil (5 cm x 2 cm), copper foil (5 cm x 2 cm), connecting cables, alligator clip, voltage supply, voltmeter, ammeter, mixer, vacuum pump & Büchner funnel, Büchner flask, vacuum hose, round filter ($\varnothing = 70$ mm), distilled water, potassium chlorate.

Graphene oxide is produced by electrochemical exfoliation and oxidation of graphite foil. For that purpose, a graphite foil (5 cm x 2 cm) is used as positive terminal (+) in a 0.5 M potassium chlorate solution (electrolyte solution) and electrolyzed for 20 minutes with an applied voltage of 20 V. (Caution: The electrolyte heats up during the procedure owing to the high electric current!)

As soon as the graphite foil is completely decomposed, the resulting solution is blended in a blender (e.g. SILVERCREST® Smoothie-Maker SSME 250 A1) for 45 seconds at maximum power, building a fine suspension. The suspension is then deposited on a filter paper by using a Büchner funnel and cleaned with 100 ml of distilled water.

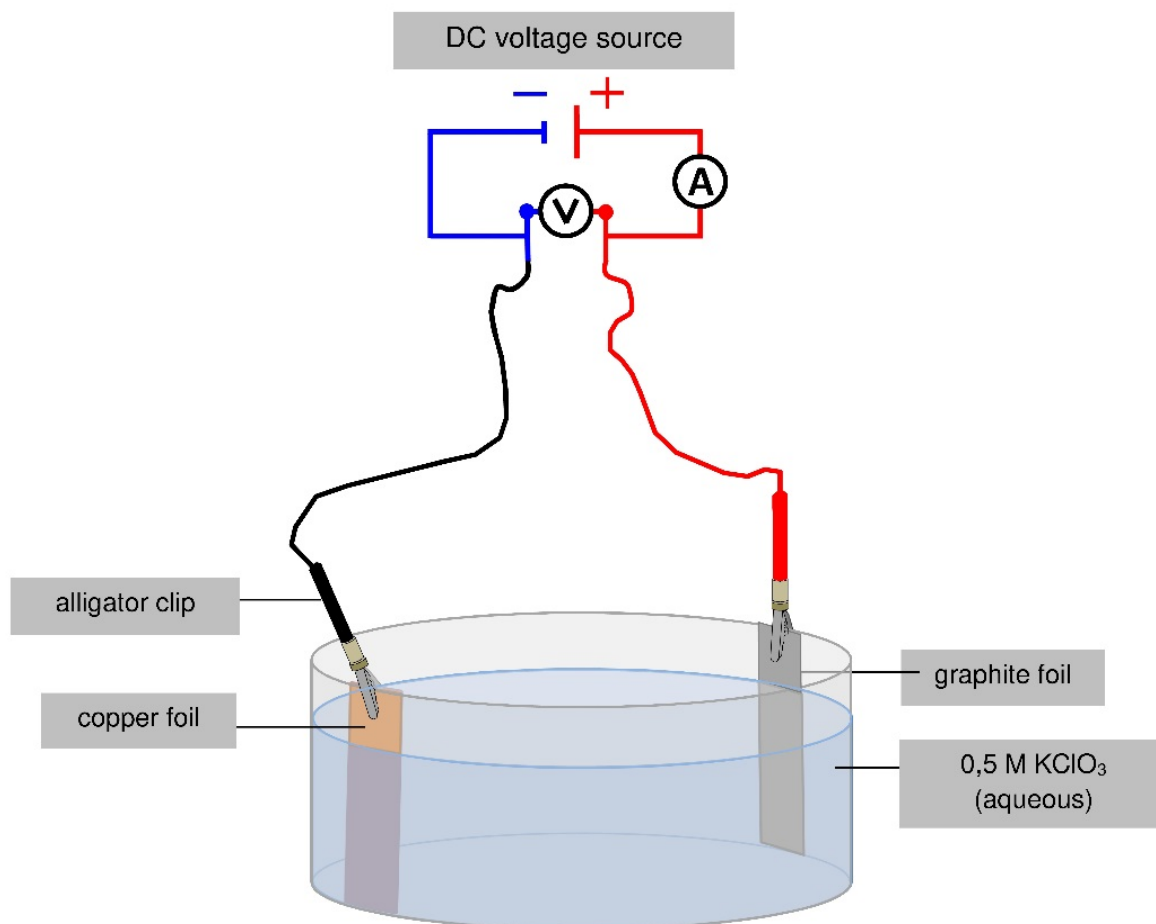


Figure 6. Experimental setup of the electrochemical synthesis of graphene oxide

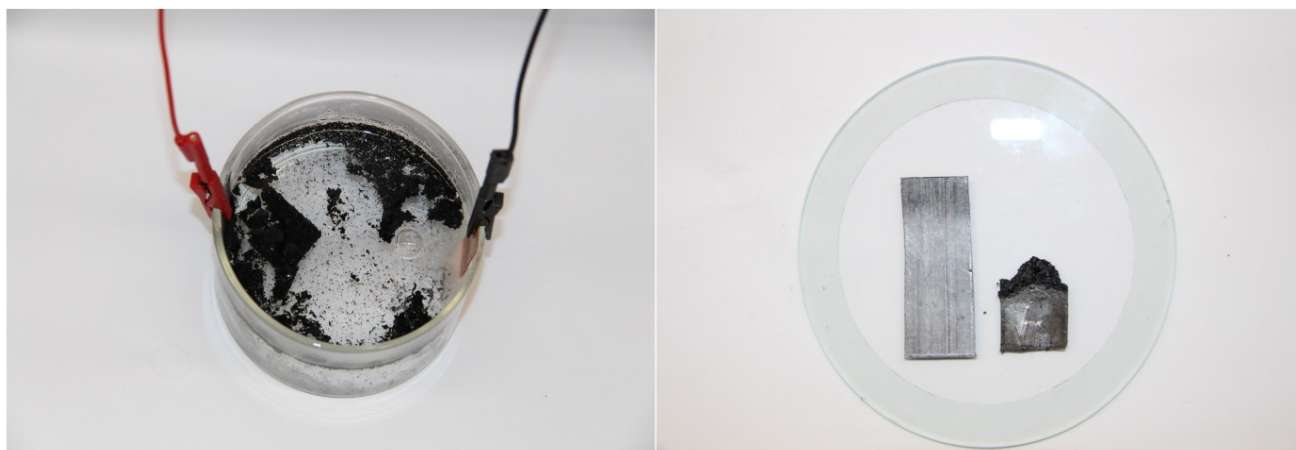


Figure 7. Left: decomposition products of the electrolytic process; right: comparison of the graphite foil before and after electrolysis

2.2. The Photochemical Reduction of Graphene Oxide to Graphene & the Ensuing Evidence of Graphene by Measuring Conductivity

Materials and chemicals:

Hair dryer, graphene oxide, flash unit (flash from the Xenon lamp equipped on a common digital camera), voltage supply, connecting cables, electrical device (e.g. propeller).

The electrochemically produced graphene oxide is dried on the filter paper with the help of a hair dryer. Afterwards, a common flash unit is placed on the graphene oxide and the flash is triggered. The emitted light energy reduces graphene oxide to graphene. To verify that the electrical conductivity is restored, the experimental setup (shown in Figure 9) is constructed. This is done by closing an electric circuit using both the synthesized graphene oxide and the photochemically reduced graphene. An electrical device is interposed to test electrical conductivity. The voltage supply is adjusted to 15 V.

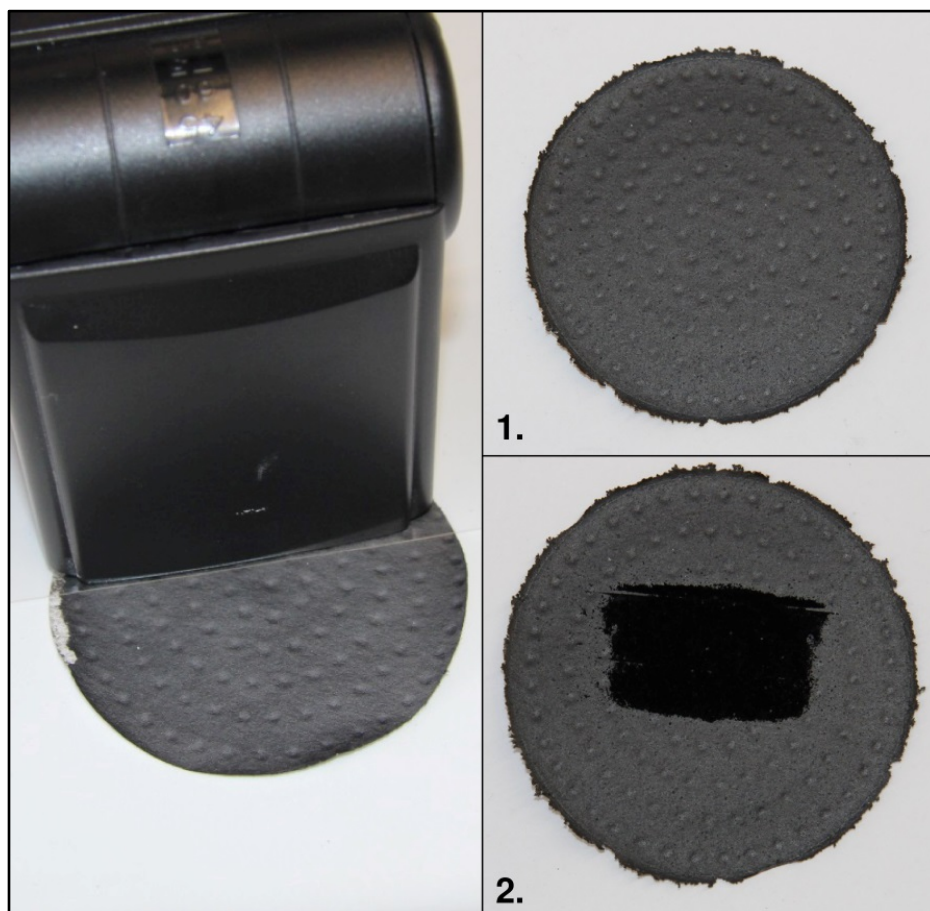


Figure 8. Reduction of graphene oxide through light emission. The camera flash converts the grey graphene oxide (1.) into black graphene (2.)

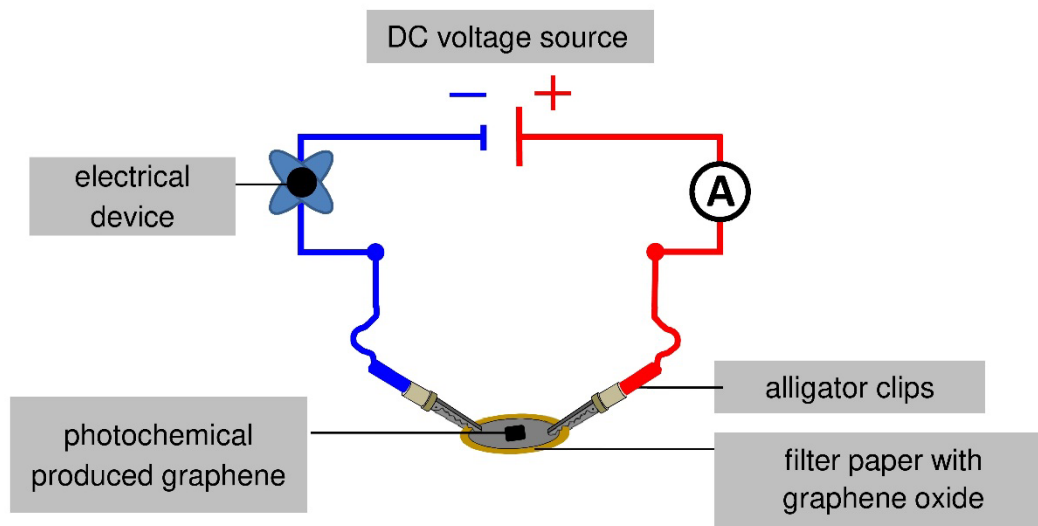


Figure 9. Experimental setup to proof electrical conductivity of both graphene oxide and graphene

2.3. Reduction of Graphene Oxide to Graphene – hydrophobic Behavior of Graphene

Materials and chemicals:

Beaker, wash bottle, magnetic stirrer with hotplate, thermometer, 2 snap cap vials, magnetic stir bar, distilled water, paraffin, sodium dithionite, sodium hydroxide

Graphene oxide is synthesized with the methods described in 2.1. and it is then separated from the filter paper with the help of a gentle jet of water and is

transferred to a snap cap vial. The graphene oxide suspension produced this way (about 50 ml) is then mixed with 0.9 g of sodium dithionite and 4 g of sodium hydroxide. The content of the snap cap vial is heated at approx. 80°C and stirred using a magnetic stir bar for about 10 minutes. After the magnetic stir bar has been removed from the beaker, the aqueous phase is covered with paraffin. Subsequently, the vial is capped and shaken vigorously. For comparison purposes, an additional graphene oxide sample can be prepared with the methods described in the first experiment and then covered with paraffin and shaken just as well.

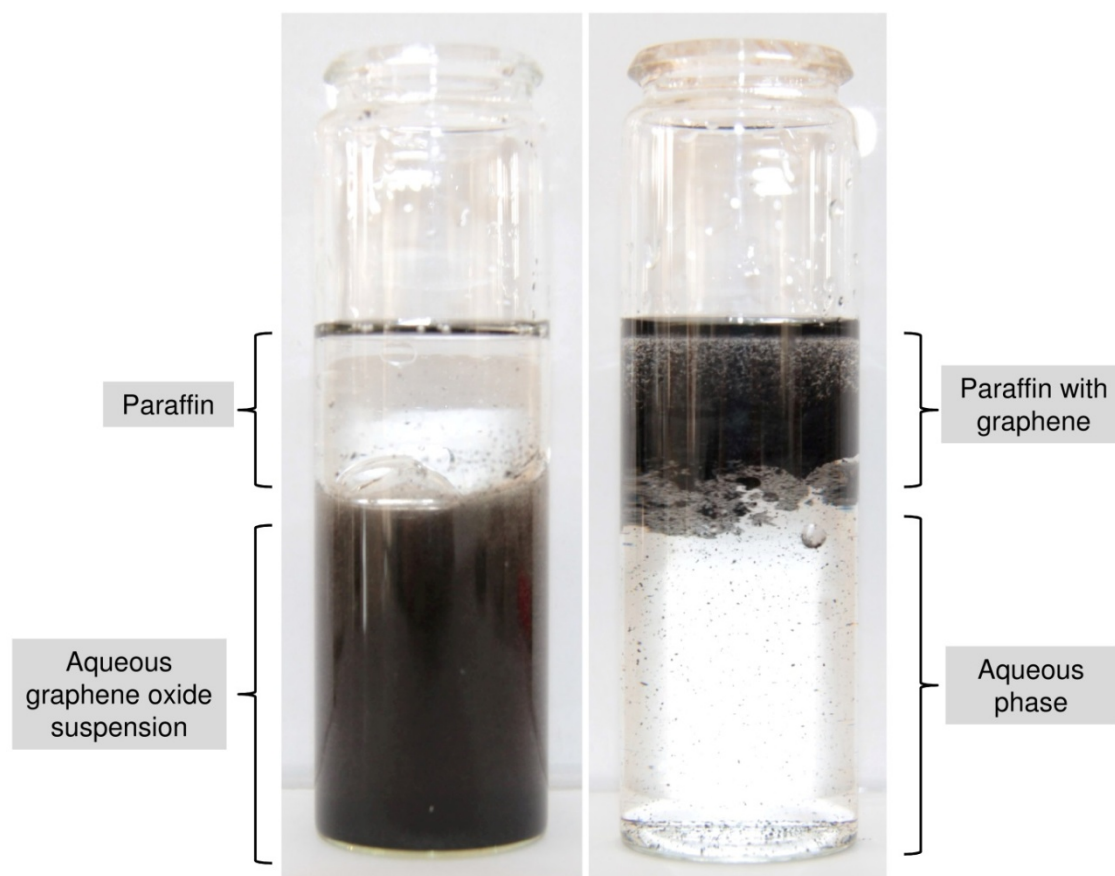


Figure 10. Left: graphene oxide has formed an aqueous suspension; right: graphene has formed a stable suspension within the paraffin

2.4. The Restacking Phenomenon – An Indication of the Presence of Individual Graphene Layers

Materials and chemicals:

Snap cap vial (50 ml), wash bottle, beaker (100 ml), vacuum pump & Büchner funnel, Büchner flask, vacuum-hose, round filter (pore diameter: $\varnothing = 0.2 \mu\text{m}$), beaker (25 ml), magnetic stirrer with hotplate, sodium dithionite, sodium hydroxide, graphene oxide (experiment no. 1)

Graphene oxide is first synthesized as described in 2.1, separated from the filter paper with the help of a gentle jet of water from a wash bottle and then transferred to a

beaker (100 ml). The aqueous demineralized graphene oxide suspension is deposited on a filter paper again, using a clean Büchner flask. Afterwards, approx. 25 ml of the liquid collected in the Büchner flask are transferred to a snap cap vial. The clear liquid is visually examined with a method utilizing the Tyndall effect which can be demonstrated with a laser pointer. The snap cap vial is then placed on a magnetic stirrer with hotplate and the content is heated at approx. 80°C . Following that, 0.45 g sodium dithionate and 1.8 g sodium hydroxide are dissolved in 10 ml of distilled water and added to the clear liquid in the snap cap vial. The content of the snap cap vial should be observed closely for the next 45 minutes.

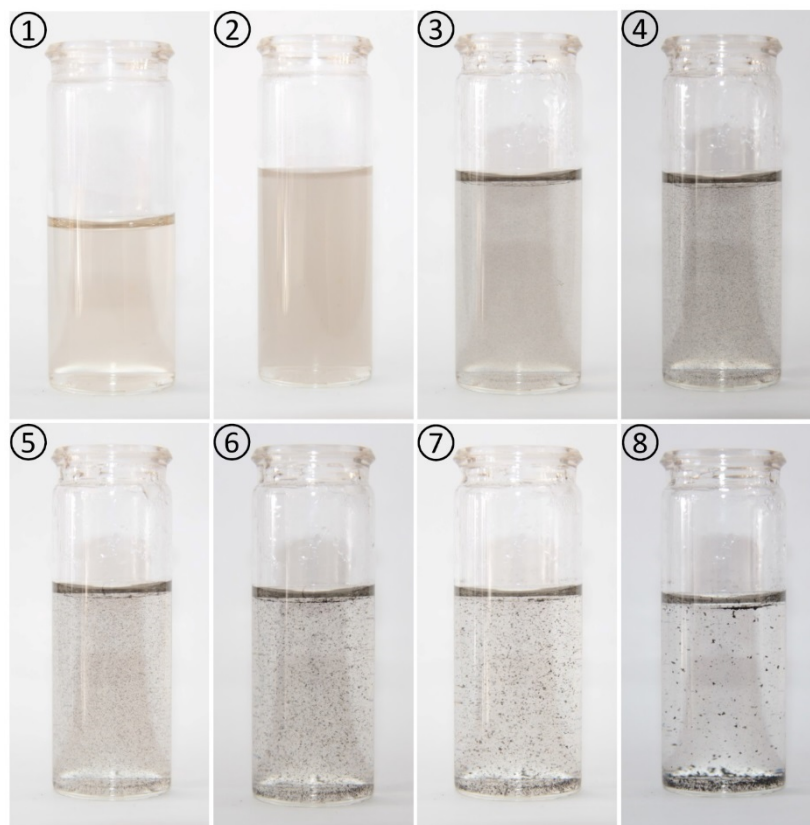


Figure 11. Reduction of a clear graphene oxide solution using sodium dithionite. Graphene flakes appear “out of nothing”. Observation in regular intervals for altogether 45 minutes

3. Results and Discussion

3.1. Graphene Synthesized with Materials Available at School

The electrochemical synthesis of graphene oxide is much more suitable for academic purposes than the other methods discussed in this article, as it is cheap, easy to perform and does not present any health risks. Potassium chlorate was chosen as conducting salt in these experiments, since it is a strong oxidizing agent and appropriate for use at school. Figure 7 indicates that the part of the graphite foil which is immersed in the electrolyte quickly decomposes. Using the graphite foil as positive pole results in the extraction of electrons if voltage is applied. The charge is balanced by hydrated chlorate ions diffusing towards the graphite foil where they are intercalated into the graphite lattice. The high voltage and the oxidizing

agent oxidize the graphite and the co-intercalated hydrate shell of the chlorate ions. The arising gaseous reaction products (cf. chemical equation 4 & 5) increase the electrode's partial pressure causing sheets of individual graphene oxide layers to flake off the graphite into the solution.

Blending the exfoliated and oxidized graphite converts it to a very fine suspension. Thus, the graphene oxide can be deposited on a filter paper in a very uniform layer. The product was then cleaned with distilled water to remove salty by-products.

After drying with a hair dryer, the authors received a grey graphene oxide layer on the filter paper. Graphene was synthesized by photochemical reduction of graphene oxide. We chose a photochemical method since it is easy to perform and allows a quick characterization of the chemical substances. The spot the flash was pointed at showed the typical black coloration of graphene. By radiation of light energy, oxygen-containing functional groups of graphene oxide are split into CO_2 and water [14].

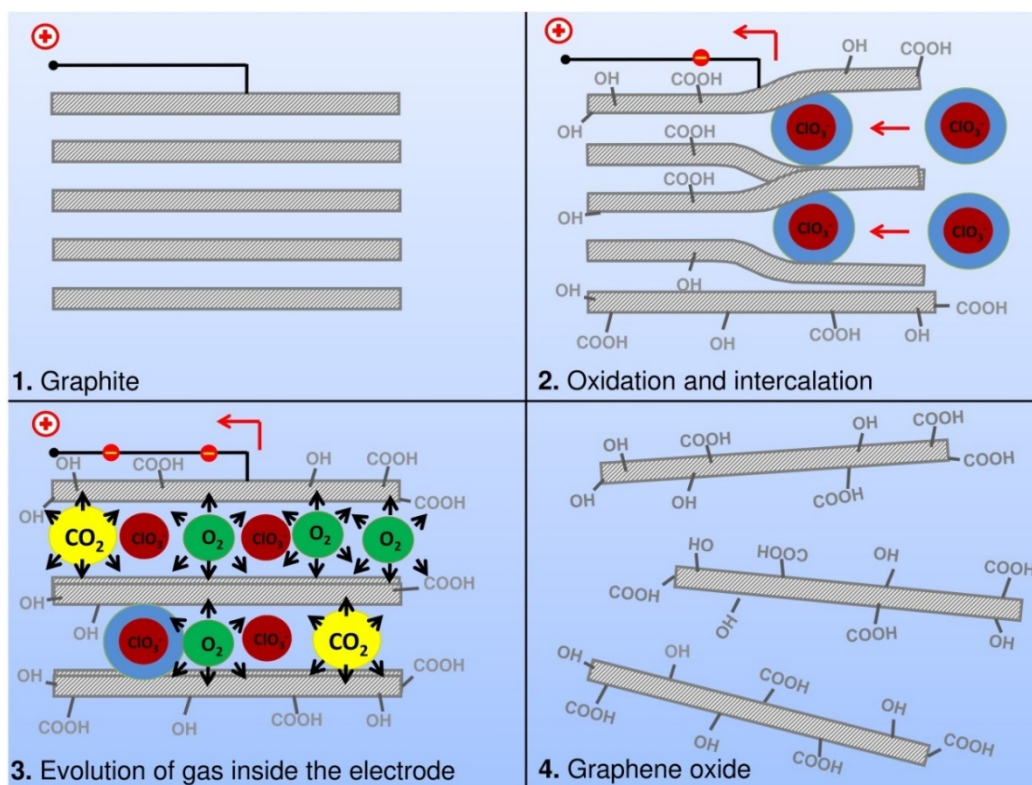


Figure 12. Synthesis of graphene oxide from graphite. 1st image: graphite; 2nd image: hydrated chlorate ions intercalate into the graphite lattice, oxidizing carbon; 3rd image: high voltage leads to decomposition of the hydrate shell. The arising gases exert pressure on the electrode, causing individual carbon layers to flake off. 4th image: single graphene layers in an aqueous solution

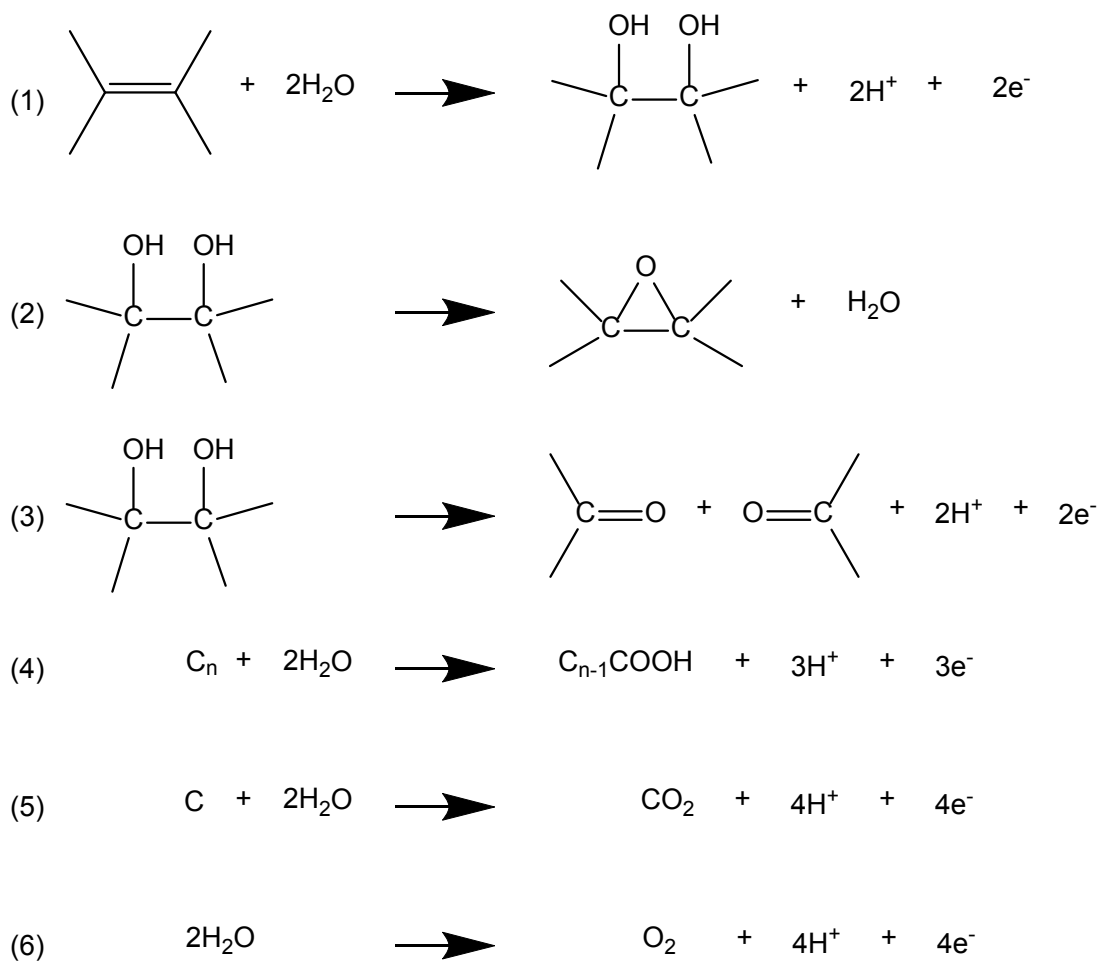


Figure 13. Possible processes during the anodic oxidation of graphite (1-5) and oxidation of water molecules from the hydrate shell according to [12,15]

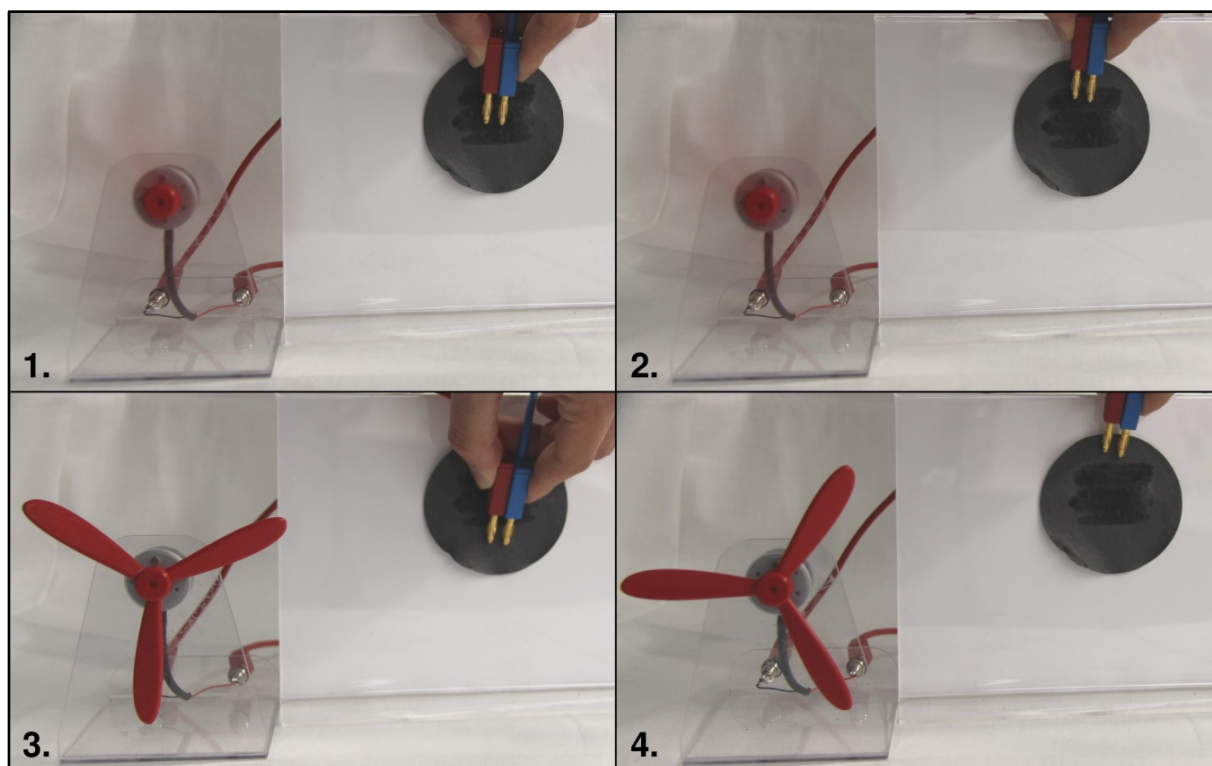


Figure 14. The electrical device only rotates if the electrical circuit is closed with the photochemically reduced graphene (3.-4.). Graphene oxide works as an electrical insulator (1.-2.)

As already mentioned, graphene oxide acts in contrast to graphene like an electrical insulator. By measuring the conductivity, it could clearly be proved that it is in fact possible to produce graphene oxide and graphene with the synthesis described in this article. For this purpose, an electrical circuit with an electrical device interposed for conductivity measurement was first closed with the synthesized graphene oxide and afterwards with the photochemically reduced graphene (Figure 14).

3.2. Insights into the Synthesis and Properties of Graphene Oxide and Graphene

Graphene oxide has different oxygen-containing functional groups such as carboxyl-, carbonyl- or epoxy-groups. Dipole-dipole-interactions occur between graphene oxide and solvent in the aqueous medium. Graphene oxide suspensions are therefore stable in polar solvents such as

H₂O. Graphene oxide could be reduced to graphene in the aqueous medium by adding sodium dithionite as chemical reducing agent. In contrast to other substances proposed in scientific literature, sodium dithionite is a strong reducing agent that is environmentally friendly and therefore perfectly suited to be used in school lessons. Adding sodium hydroxide lowers the electrode potential of the dithionite-anion, which increases the reducing power even further. (cf. Figure 15) [16].

The formerly polar graphene oxide molecules are thus transformed into nonpolar graphene molecules, which form a stable suspension in nonpolar solvents such as paraffin.

After the aqueous phase has been covered with nonpolar paraffin, the graphene included can be transferred into the nonpolar phase by shaking. Meanwhile, in parallel measurements, the graphene oxide remained in the aqueous phase despite repeated shaking (cf. Figure 10).



Figure 15. Increasing the reducing power of sodium dithionite by adding NaOH

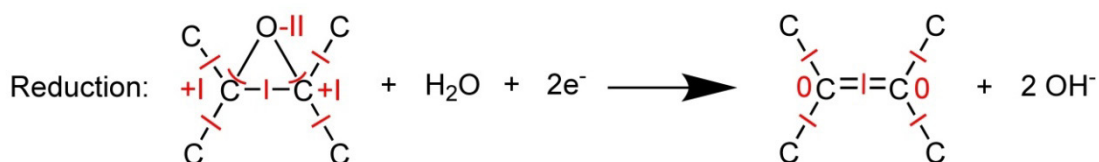
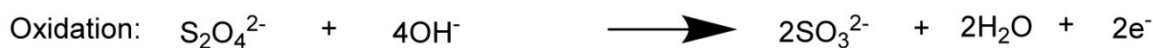


Figure 16. Reducing an epoxy group using sodium dithionite

3.3. The Restacking Phenomenon – An Indication of the Presence of Individual Graphene Layers

This experiment is meant to examine whether the electrochemical synthesis shown in the first experiment can form two-dimensional graphene (oxide) or at least graphene (oxide) containing a low number of graphene oxide sheets. The clear solution in the Büchner flask shows a positive Tyndall effect. Graphene oxide particles were sucked through the fine pores of the filter paper (pore-diameter \varnothing 0.2 μm) when it was filtered with the Büchner flask, which indicates that the described synthesis process forms aggregates of mono-, di- and trilayer graphene oxide. Parvez et al. already demonstrated that monolayer graphene (oxide) can be produced by electrochemical synthesis using both an scanning electron and an optical microscopy [12].

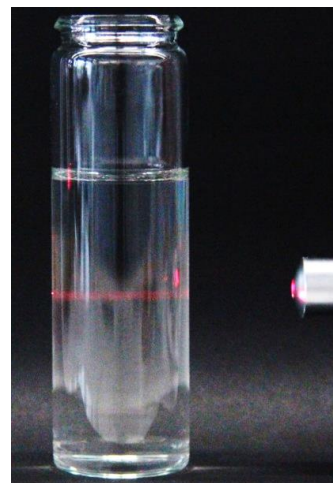


Figure 17. The beam is reflected by the smallest graphene oxide layers in the aqueous solution which are large enough to scatter light

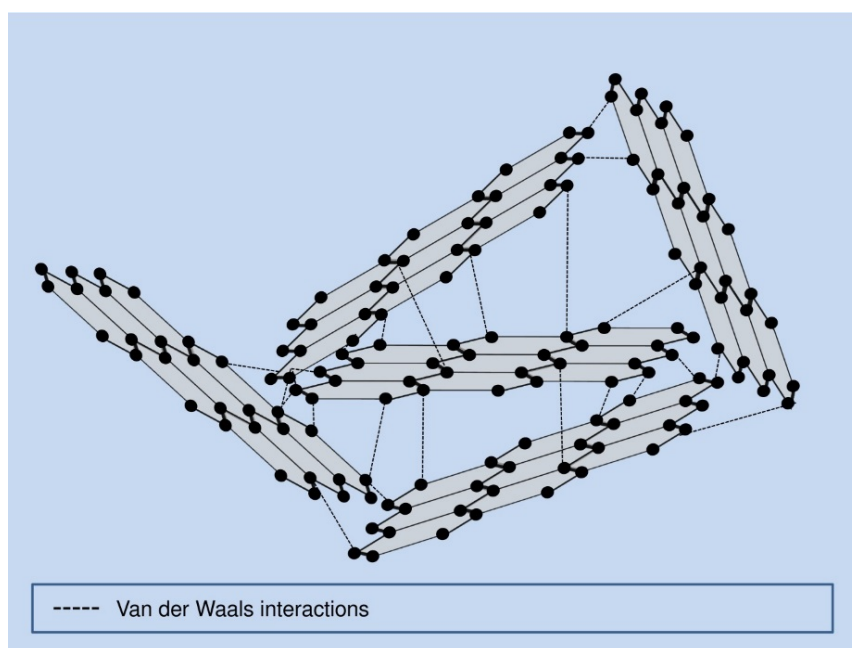


Figure 18. Individual graphene layers aggregate in a polar medium, forming a growing complex

By adding the reduction solution, the dissolved graphene oxide was reduced to graphene as described in 3.2. Whereas graphene oxide has a polar character due to its oxygen-containing groups, the graphene molecule behaves like a nonpolar substance. If individual graphene molecules floating in the solution collide, it is possible that Van der Waals interactions may arise as shown in Figure 18 causing the molecules to accumulate. Depending on the time, the microscopically small graphene molecules aggregate forming a growing complex which can be seen macroscopically [17,18,19,20]. This process can be observed in the experiment, first by the formation of a grey film then by flocculation (cf. Figure 11).

This process, which is known as restacking, is partially responsible for the fact that there have been no commercially available graphene-based energy storage systems yet. The graphene layers aggregate in graphene-based batteries after just a few charge and discharge cycles and form a complex like graphite. Many of graphene's unique properties such as an extraordinarily high active surface and good electrical conductivity are

thus significantly affected and get progressively lost over several charge and discharge cycles [19].

4. Conclusion

In this article, the authors explore that graphene oxide can be synthesized using an electrochemical process and that graphene can be produced by the subsequent chemical or photochemical reduction of graphene oxide. Important structure-property-relationships can be shown with simple experiments which can easily be implemented in school lessons. In contrast to graphene oxide, graphene has a hydrophobic character, which is why graphene only forms stable suspensions in nonpolar solvents whereas graphene oxide only forms stable suspensions in aqueous solvents. Additionally, the Tyndall effect indicates the presence of graphene particles with only a few layers. Finally, the restacking phenomenon which poses a huge problem for the design of graphene-based energy storage systems can be demonstrated in a simple way as well.

The experiments described in this article make it possible to synthesize and characterize graphene in school for the first time. In addition, further experiments need to be developed to demonstrate graphene's unique properties.

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