Graphene Oxide
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Fundamentals and Applications

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About the Editors

**Dr. Ayrat M. Dimiev**

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Ayrat M. Dimiev received his PhD degree in physical chemistry from Kazan University, Kazan, Russian Federation. After three years of holding an assistant professorship at Kazan Agricultural University, he emigrated to the USA to teach the International Baccalaureate chemistry course. In 2008 he joined the group of Professor James M. Tour at Rice University, where he started his studies in the field of carbon. His research spreads over the areas of unzipping carbon nanotubes, carbon-based dielectric composite materials, graphite intercalation compounds, and graphene oxide chemistry. His most important contributions to the field were revealing the mechanism of the stage transitions in graphite intercalation compounds, and developing the dynamic structural model of graphene oxide. In 2013, Dr. Dimiev accepted a personal invitation from AZ Electronic Materials (presently EMD Performance Materials Corp., USA, a business of Merck KGaA, Darmstadt, Germany) to help in developing their newly started carbon program. During his time at EMD Performance Materials Corp, he employed his expertise in the field to develop and commercialize new products comprising graphene oxide and other carbon nanostructures. In May 2016, Dr Dimiev returned to his alma mater in Kazan as a head of the Laboratory of Advanced Carbon Nanostructures, Kazan Federal University. Dr. Dimiev is the author of 18 recent publications in the carbon field, with an overall total number of citations exceeding 2000; he also has five recent patent applications.

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Siegfried Eigler received his PhD in organic chemistry from the Friedrich-Alexander-Universität Erlangen-Nürnberg in 2006 under the guidance of apl. Prof. Dr. Norbert Jux. Subsequently he conducted industrial research at DIC-Berlin GmbH, part of DIC Corporation, Japan. The research concentrated on electrically conductive polymers and the development of novel semiconducting monomers. In 2009 he started working on the synthesis and application of graphene oxide. Two years later he became a lecturer and research associate at the Friedrich-Alexander-Universität Erlangen-Nürnberg. There, he
conducted deep research on the synthesis of graphene oxide and he realized that defects in the carbon lattice could be avoided by controlling the synthesis. With this discovery he could investigate the controlled chemistry of graphene oxide and synthesized several new graphene derivatives and composites. Currently, his research focuses on advancing the controlled chemistry of graphene. Dr. Eigler has authored 27 papers in the field of carbon research and applied for one patent related to the wet-chemical synthesis of graphene that allows the control of the defect density. He accepted an offer from Chalmers University of Technology, Gothenburg, Sweden, as Associate Professor which started in 2016.
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Foreword

This book presents a timely review of research on graphene oxide, which is a term representing the individual layers obtained by exfoliation of graphite oxide.

Although graphite oxide was first synthesized in the 1850s, it is a material that has attracted renewed and intense interest only in the past decade because it affords a product material, by relatively straightforward exfoliation in water, of individual layers of functionalized graphene. The functionalization of the graphene consists of hydroxyl and epoxide groups, among others, and the individual layers, for which the term “graphene oxide” has been used, are thus hydrophilic, such that they form stable dispersions in solvents like water. This has allowed stable dispersions of chemically modified graphene (of a particular type) to be readily prepared and then used in interesting ways.

It was fortunately possible that we could help with “early contributions” in this past decade, including use of graphene oxide or its modifications to make (i) electrically conducting polymer composites, (ii) thin “paper-like” material composed of stacked and overlapped platelets, and (iii) electrodes for supercapacitors. It has been gratifying to see the growth of a now relatively large body of literature about both fundamental aspects of the chemistry and properties of graphene oxide and its derivatives, and of applications or potential applications. Graphene oxide and its related product or derivative materials have been shown to be highly versatile and have been applied in a wide range of studies.

Fundamental aspects as well as applications are well covered herein, and the book should be useful for learning about graphene oxide and related materials, and thus for providing a basis for thinking about new possibilities as well.

It is perhaps of interest to speculate about the future, and I do so here only briefly. For graphene oxide, and in general chemically modified graphenes, there are many exciting possibilities. Fine control of the chemical functionalization, including with oxygen-containing groups, remains an important challenge. As greater control of the specific location and distribution of functional groups is achieved, and, when desired, of the deliberate removal of carbon atoms from the “graphene lattice”, a wider range of applications, including for better sensors and in materials such as composites and filters, will emerge. There is also the fascinating possibility of control of folding or “crumpling” through thermodynamics and clever design of where functional groups are “placed” and how they interact: intra-sheet to “fix” certain morphologies, or perhaps inter-sheet and also with their surrounding environment. (This could be a type of origami but is not limited to specific types of folding.)

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Preface

Graphene oxide (GO) has become one of the most extensively studied materials of the last decade. It has facilitated massive interdisciplinary research in the fields of chemistry, physics, and materials science. Due to its unique properties, GO has been successfully tested for numerous applications. This fruitful research has resulted in an enormous number of publications. Several review articles have summarized the most recent advances. However, up to the present day, very little has been done to systematize all the published research, and to assist a non-expert audience interested in the field. This book is designed to fulfill this task. The content of each chapter and the book in general develops from basic to more complex. The material is presented in the categories typical for the classical fields of science. This makes this book unique and different from the other literature.

Today, keeping track of all the recent publications in the field is difficult even for experts. For non-experts, it is practically impossible to navigate this ocean of publications. This task is further complicated by confusion that is widespread in the modern GO field. This confusion is caused by the misuse of the main fundamental concepts, and by oversimplification and misinterpretation of GO chemistry. It is very difficult to identify trustable high-quality publications that correctly employ fundamental chemical terms, and correctly interpret experimental data. In this book, we intend to demonstrate the actual GO chemistry based on trustable publications, with correct usage of the main fundamental concepts, as they have been identified up to now.

Since the beginning of the graphene era in 2004, GO has been closely associated with graphene. At that time, GO was considered mainly as a precursor for graphene. The term “chemically converted graphene” (CCG) was introduced for reduced graphene oxide (RGO) to highlight the graphene-like nature of RGO. The misuse of the term “graphene” instead of RGO in the literature creates significant confusion among a non-expert readership. We aim to help readers to differentiate between the two by drawing a clear borderline between graphene and RGO, and by showing where they are similar, and where they are different. Additional confusion arises from the misuse of the term RGO for material obtained by annealing of GO. We highlight that those two are very different materials, and we introduce the term “thermally processed graphene oxide” (tpGO) for the latter.

Since the electrical properties of RGO are inferior of those of real graphene, GO is often considered as graphene’s “younger brother”, or as a low-grade graphene. This point of view was dominant up until about 2011. Later, it was demonstrated that GO is a unique and valuable material in itself, both from fundamental science perspectives and for practical applications. The main advantage of GO over the graphene counterpart is its solubility and processability in water and in several organic solvents. Another benefit of GO is due to its versatility of chemical modification to alter its properties. The ability for mass production on the scale of tonnes makes GO especially attractive for applications compared to its graphene counterpart. We intend to demonstrate all the advantages and uniqueness of GO in this book.
The book is divided into two parts. Part I focuses on the fundamentals of GO, and Part II on the applications of GO.

Part I starts with research on GO, which has a very long history. It did not start in 2006 with the work on GO reduction, as one might think by looking at the citation indexes of some publications from that period. Very serious and in-depth studies on GO chemistry were conducted throughout the entire twentieth century. Most of these studies, performed in the best old-school traditions, were in many ways advantageous when compared to some modern publications. The fundamentality of scientific thinking, the methodology of the research, and, importantly, the trustworthiness of reported data were on a level that is rather rare in the modern GO field. One could easily avoid misinterpretations of experimental results by studying those early works before even designing one’s own experiments. Because of the high importance of that early research, and in an attempt to make the connection between the two eras, we begin the book with a historical retrospective of GO research done in the twentieth century (Chapter 1). This is written by the long-term expert in the field, one of the developers of the famous Lerf–Klinowski structural model, Anton Lerf.

In the modern literature, the structure of GO is greatly oversimplified. This leads to misinterpretation of the chemical reactions involving GO. Chapter 2, written by Ayrat Dimiev, aims to clarify some aspects of GO structure. In the form typical for textbooks, the mechanism of GO formation, its transformation during aqueous work-up, and the fine chemical structure of GO are methodologically described. The structure of GO is discussed with respect to its intrinsic chemical properties, such as the acidity of aqueous solutions. The methods used for GO characterization are reviewed in Chapter 3 in a tutorial manner. This chapter will be of particular importance for researchers entering the field. The advantages and disadvantages of different methods are highlighted. Several examples where different methods have helped to understand the structure of GO are discussed. This chapter is written jointly by the editors, Siegfried Eigler and Ayrat Dimiev.

In aqueous solutions, GO delaminates to single-layer sheets and forms colloidal solutions. From aqueous solutions, GO flakes can be transferred into the phase of low-molecular-weight alcohols; the alcoholic solutions are as stable against precipitation as aqueous ones. At certain concentrations, GO solutions form liquid crystals. The rheology of GO solutions is reviewed in Chapter 4 by Cristina Vallés. Colloid chemistry, surface science, rheology and liquid chemistry of GO are discussed in this chapter.

Due to its electronic configuration, GO possesses a number of remarkable optical properties. As opposed to pristine graphene, GO exhibits photoluminescence in the ultra-violet, visible and near-infrared regions, depending on its structure. The origins of this emission and other related questions are discussed in Chapter 5 by Anton Naumov.

The chemical properties of GO is the largest, most difficult and most controversial topic. In Chapter 6, written by Siegfried Eigler and Ayrat Dimiev, the following topics are discussed. The thermal and chemical stability of GO is reviewed first, followed by introducing wet-chemical non-covalent functionalization protocols. The covalent functionalization of GO, which is discussed next, is a very controversial topic. When well-known organic chemistry principles are applied to GO, it remains challenging to prove the successful accomplishment of reactions by analyzing the as-modified GO product. We provide an alternative interpretation for experimental results of some selected examples to demonstrate this challenge. The chemical reduction methods are summarized next, and special emphasis
is given to differentiating true chemical reduction from so-called “thermal reduction”. While discussing GO chemical properties, in parallel with typical GO, we discuss these properties for the oxo-functionalized graphene (oxo-G₁), a type of GO with very low density of structural defects. This sheds additional light on the role of defects in GO chemistry. Finally, additional properties of oxo-G₁ are introduced. Oxo-G₁ can act as a compound that enables the controlled chemistry for the design and synthesis of functional materials and devices.

In Part II, applications that use the reduced and non-reduced forms of GO are reviewed separately. A reduced form of GO is required where electrical conductivity is of importance. These applications exploit the graphene-like properties of RGO and tpGO.

Due to its two-dimensional character, real graphene is not available in bulk quantities by definition. It is obtained only as a substrate-supported material either by micromechanical cleavage of graphite, or by chemical vapor deposition (CVD) growth on the surface of a catalytically active metal. The electrical conductivities of RGO and tpGO are three or four orders of magnitude lower than that of real graphene due to the numerous defects or scattering centers in the former. Nevertheless, in applications where bulk forms of graphene are needed, GO derivatives are the only choice. Currently, about 90% of the studies performed with RGO and tpGO use the term “graphene” both in the title and in the abstract. We highlight that GO derivatives, and not real graphene, are used for the applications reviewed in Chapters 7 and 8.

Field-effect transistors and sensors are the two most promising applications that exploit the unique electronic properties of GO. RGO is also considered as one of the best candidates for fabricating transparent conductive films for many applications, due to its electrical and mechanical properties, reasonable carrier mobility, and optical transparency in the visible range. Chapter 7, written by Samuele Porro and Ignazio Roppolo summarizes the enormous potential for applications of GO in the above-mentioned fields.

The electrical conductivity and high surface area of tpGO have driven substantial efforts for its integration into advanced energy systems. In Chapter 8, the integration of GO into two major energy storage systems – lithium-ion batteries and supercapacitors – is discussed. Particular attention is given to understanding the important physicochemical properties that can be emphasized in order to achieve the greatest performance, as well as the synthetic processes used to derive these unique benefits. This chapter is written by Cary Hayner, CTO of SiNode Systems, a start-up company that develops a new generation of lithium-ion batteries based on the novel electrode material comprising GO.

Due to the two-dimensional character of GO flakes, and their solubility in water, GO can be cast into thin films by simple drop casting or filtration. The as-formed GO membranes exhibit unimpeded permeability to water molecules, being absolutely impermeable to other molecules and atoms. Applications of GO and RGO for selective membranes are reviewed in Chapter 9 by Ho Bum Park, Hee Wook Yoon and Young Hoon Cho.

Due to the processability of GO in water and organic solvents, GO has been tested as a component in numerous composite materials. The incorporation of GO into polymers modifies electrical and thermal conductivity, lowers permeability and improves mechanical properties. This topic is covered in Chapter 10 by Mohsen Moazzami Gudarzi, Seyed Hamed Aboutalebi and Farhad Sharif.

Biomedical applications and toxicity studies of GO are of utmost importance for using GO in real applications. Other materials, such as carbon nanotubes, are suspected to be
toxic or carcinogenic. Therefore, the current advances in analyzing the medical properties and biomedical applications of GO are covered by Larisa Kovbasyuk and Andriy Mokhir in Chapter 11.

GO and its derivatives possess unique properties that grant them interest as catalysts in oxidative reactions, Friedel–Crafts and Michael additions, polymerization reactions, oxygen reduction reactions and photocatalysis. This property is reviewed in Chapter 12 by Ioannis Pavlidis.

The scalable production of GO still holds the key to its commercialization. The most crucial factor for GO to be commercially viable is its cost-effectiveness. This is not a simple task to ascertain, since GO production involves lengthy purification procedures that produce significant quantities of acidic waste. The challenges facing commercial GO production are discussed in Chapter 13 by Sean Lowe and Yu Lin Zhong.

This book is written and edited by professionals in their respective fields, and it is intended to be helpful for a very broad community, including experts broadening their field of research.

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Part I
Fundamentals
1

Graphite Oxide Story – From the Beginning Till the Graphene Hype

Anton Lerf

1.1 Introduction

The formation of graphite oxide (GO) was described for the first time by Brodie in a short note that appeared in 1855 in Annales de Chimie in French [1]. Another preparation method – the reaction of graphite with potassium chlorate in fuming nitric acid, now known as the “Brodie method” – and a detailed description of the composition and the chemical properties of the new compound were published in 1859 in the Philosophical Transactions of the Royal Society of London [2]. One year later this paper was published in both French and German translations [3, 4]. The titles of all these papers [1–4] do not give any hint of a new carbon compound. The title of the English version is as follows: “On the atomic weight of graphite”. The new compound was called “oxyde de graphite” in the first publication, and “graphitic acid” in the later papers. It is also worth mentioning that Brodie himself did not cite his first work on the new compound.

The actual aim of Brodie’s scientific work presented in his publications was to differentiate by means of chemical methods various forms of carbon with dissimilar properties but all called graphite. Among the reactions described in the second paper, there was also the treatment of graphite with a mixture of concentrated nitric and sulfuric acids, leading to the graphite sulfate intercalation compound. The graphite intercalation compound was described for the first time by Schafhautl [5] (pp. 155–157) in 1840, but it was hidden in two other publications devoted almost exclusively to iron–carbon steels. This might be the reason why Brodie was not aware of this data, and did not cite it. On the other hand, the
content of the first paper had been presented before in the *London and Edinburgh Philosophical Magazine*. In the paper of 1859, Schafhäutl [6] (pp. 300–301) complained that nobody took notice of his result.

The circumstances of the beginning of the GO story have been outlined in extenso because of their curiousness. In 1865 Gottschalk [7] reproduced and confirmed the results of Brodie. In his publication the term “graphitic acid” appeared for the first time in the title: “Beiträge zur Kenntnis der Graphitsäure” (‘Contributions to the knowledge of graphitic acid’). GO received greater attention only due to the publication of Berthelot [8] in 1870 in which he proclaimed Brodie’s procedure for the preparation of GO as a method to distinguish different forms of graphitic carbon, although Brodie had already described the different behavior of various graphite forms toward oxidation reactions earlier.

In 1898 Staudenmaier [9] discussed in detail the problems and disadvantages of the various preparation methods existing up to the end of the nineteenth century. He also described his trials to find more convenient and less dangerous preparation methods, and presented the new preparation method which is named after him to the present day.

Of utmost importance is the publication of Kohlschütter and Haenni in 1919 [10]. It marks the end of the classical research on GO, which was based on classical chemical analysis and a careful description of the reaction behavior. On the one hand, it carefully reviews and evaluates all the previous publications on the topic. Based on crystallographic considerations, reproducing the results of Brodie [2] and Weinschenk [11], the authors consider the close structural correlation between graphite and GO as evidence for a “topotactic” relation. This paper presents new data for the formation of GO, its thermal decomposition and chemical reduction, and the products of chemical reduction. Also, in this publication, the authors discarded their own previous pessimistic view that GO could be nothing other than an adsorption of CO and CO₂ at graphite surfaces.

A new period of GO research was opened by Hofmann in 1928 [12] and by Hofmann and Frenzel in 1930 [13] by applying for the first time powder X-ray diffraction (XRD) to GO. Based on these investigations and chemical considerations, Hofmann and his school of researchers gave the first structural model of GO to find general acceptance. This period of research started in 1928, continued through 1930 and 1934 with the first structural models by Thiele [14] and Hofmann *et al.* [15], and ended in 1969 with a new structural model proposed by Scholz and Boehm [16]. During this period, GO structural models were modified several times, mainly due to the debate between Hofmann and Thiele, and due to the application of new spectroscopy methods allowing the proof of assumptions about the functional groups playing a role in the chemistry of GO.

The third period of activity on GO was initiated by the first application of magic angle spinning nuclear magnetic resonance (MAS NMR) on ¹³C by Mermoux *et al.* in 1989–1991 [17, 18]. In the extended publication [18], the authors questioned the structural model of Scholz and Boehm [16] and credited the model of Ruess [19] as the one that best fitted their data. However, later this interpretation was questioned again [20]. The interpretation of the 60 ppm signal as originating from epoxide functions revitalized the first model of Hofmann *et al.* [15], with some modifications [20]. This model has been confirmed in various studies [21], but is now again questioned by a two-component model [22].

Graphite oxide was a laboratory curiosity [23] till the discovery of graphene by Geim and Novoselov [24]. Soon after this discovery, the easy reduction of graphite oxide was considered as a cheap method to obtain graphene layers. This idea started a hype of research
on GO, which has lasted up to now. Looking at many modern publications from a historical perspective, one cannot avoid the impression that many groups have fallen into traps, which previous generations of scientists have learned to circumvent. And, vice versa, reading the previous publications from the actual point of view, one discovers a lot of interesting aspects that have been described with scrutiny, later considered as unimportant, still later forgotten completely, but can now be re-evaluated on the basis of recent research.

The aim of this chapter is to sketch the storylines of various aspects of GO-related studies, which were important for understanding the peculiarities of GO. These topics include GO preparation and purification, the development of structural models, the problem of stability and decomposition, the swelling to a colloid, the acidity of GO, and the ability to intercalate very different chemical species. Some of these aspects have been on the agenda since the discovery of GO, and others came to attention triggered by progress in neighboring fields of research. This chapter is restricted mostly to the historical retrospective of GO studies. *My own thoughts and conclusions from the historical material, colored by my own experience in the field, are written in italic.*

### 1.2 Preparation of Graphite Oxide

#### 1.2.1 Trials for Improving and Simplifying GO Preparation

In his paper of 1855 Brodie achieved the oxidation of graphite by adding concentrated sulfuric acid to a mixture of graphite and KClO₃ [1]. The subsequent treatment with water led to disintegration of the solid and a strong extension of the volume. Calcination of the dry product resulted in graphite, which was contaminated with sulfates and chlorates. At the end of the short paper, Brodie mentioned as alternative oxidants nitric acid and bichromate.

In his publication of 1859 Brodie described first the treatment of graphite with a mixture of concentrated nitric and sulfuric acids [2]. The product obtained can be assigned in modern terms as the graphite intercalation compound of sulfuric acid, as one can conclude from the described properties of the sample, especially the exfoliation phenomena (observed earlier by Schafhäutl [5, 6]). Then Brodie stresses that replacing nitric acid by potassium chlorate or potassium bichromate leads to a different product that is bright yellow or brown and decomposes easily to a graphite-like material.

The procedure given in this paper for the new compound has been used to the present day and is called “Brodie’s method” [2]:

The details of this process are as follows:—A portion of graphite is intimately mixed with three times its weight of chlorate of potash, and the mixture placed in a retort. A sufficient quantity of the strongest fumic nitric acid is added, to render the whole fluid. The retort is placed in a water-bath, and kept for three or four days at a temperature of 60 °C until yellow vapours cease to be evolved. The substance is then thrown into a large quantity of water, and washed by decantation nearly free from acid and salts. It is dried in a water-bath, and the oxidizing operation repeated with the same proportion of nitric acid and of chlorate until no further change is observed: this is usually after the fourth time of oxidation. The substance is ultimately dried, first in vacuo, and then at 100 °C. A modification of the process which may be advantageously adopted, consist in placing the substance with the oxidizing mixture in flasks exposed to sunlight. Under these circumstances the change takes place more rapidly, and without the application of heat.
The note at the end of this paragraph, that sunlight can favor the formation of GO, sounds very interesting, but seems to have been overlooked up to now.

From that time there were many trials to replace the used reagents (fuming nitric acid, concentrated sulfuric acid and potassium chlorate) by less dangerous and more convenient oxidizing reagents. Staudenmaier [9] and Kohlschütter and Haenni [10] mention explicitly the dangerous reaction of chlorate with concentrated sulfuric acid leading to ClO₂, which decomposes at temperature above 45 °C in explosions. Is that fact the reason why Brodie did not mention this procedure in his second paper?

Luzi [25] and later Charpy [26] applied KMnO₄ and HCrO₄ (“acide chromique”) in sulfuric acid, both mentioning the tendency to decompose graphite (see section 1.1.2). Kohlschütter and Haenni [10] mentioned unsuccessful trials of oxidation with persulfuric acid, Caro’s acid and ozone. Boehm et al. [27] studied Ce(IV) nitrate, Co(III) sulfate, NaOCl, (NH₄)₂S₂O₈ and OsO₄. Hofmann and Frenzel [13] and later Boehm et al. [27] obtained GO by the reaction of graphite suspended in a mixture of concentrated nitric and sulfuric acids with gaseous ClO₂. Boehm et al. [27] also obtained GO by oxidation of graphite suspended in concentrated sulfuric acid with Mn₂O₇ and by reaction of a suspension of graphite in fuming nitric acid with an O₂/O₃ mixture for 10 days.

Despite these efforts, at the present day only two further methods are of importance, the procedures described by Staudenmaier [9] and Hummers and Offeman [28], respectively.

Staudenmaier [9] used (as Luzi [25] did) exfoliated (“aufgeblähten”) graphite, adding it to the mixture of concentrated nitric and sulfuric acids when the mixture was cooled to room temperature after mixing. He mentioned explicitly that the oxidation is faster the faster the KCIO₃ has been added, but more KCIO₃ is then necessary because of the temperature increase leading to stronger decomposition of the chlorate. Whereas he used up to 25 g of graphite for one procedure, he never observed an explosion. The green product obtained after washing and drying can then be transferred to the yellow product by a reaction with a solution of potassium permanganate in diluted sulfuric acid. Interestingly, Staudenmaier commented on the procedure used by Luzi, but did not mention Luzi’s trials with permanganate.

Kohlschütter and Haenni [10], Hofmann and Frenzel [13] and Hamdi [29] used the “Staudenmaier method”, but with some modifications, as follows. Instead of exfoliated graphite, they used powdered graphite; hence, the reaction afforded longer reaction times. At least three oxidation cycles were necessary to get a reasonable degree of oxidation. The oxidation with permanganate solution was dropped without giving an explicit reason. Hofmann and Frenzel [13] and Hamdi [29] also found the process hazardous.

Hummers and Offeman [28] for the first time successfully applied permanganate as an oxidant for the formation of GO: powdered graphite flakes and solid sodium nitrate were suspended in concentrated sulfuric acid and then the permanganate added in portions, so that the temperature can be kept below 20 °C. Then the temperature of the suspension was brought to 35 °C, and kept at that temperature for 30 minutes. The now pasty suspension was then diluted by adding water, causing a temperature increase up to 98 °C. After 15 minutes the mixture was diluted with more water and the residual permanganate reduced with hydrogen peroxide.

Boehm and Scholz [30] discussed for the first time the drawbacks and advantages of the three preparation methods for GO. (Almost no attention has been paid (only 11
The GO samples obtained via “Brodie’s method” are the purest and the most stable ones (see section 1.4.1).

The purification of GO samples prepared according to the “Staudenmaier method” and the “Hummers–Offeman method” is much more tedious; especially, the Hummers–Offeman samples are contaminated with a considerable amount of sulfur, probably bound to carbon as sulfonic acid or as esters of sulfuric acid.

Replacing KClO₃ by NaClO₃ prevents the formation of insoluble KClO₄, which is hard to remove by washing with water.

Warning is mentioned to allow temperature increase during pouring the sample into water at the end of the oxidation reaction because of decomposition.

The chemical composition of the various samples shows a great variation, but there is a trend in the degree of oxidations: the C/O ratio decreases in the order Brodie > Staudenmaier > Hummers–Offeman.

The principal routes of work-up have been established since the early days of GO research. It is a tedious process, which can lead to changes in samples exposed to light or to water for too long. The work-up always starts with a strong dilution of the acids. In the first step, it is recommended to pour the reaction mixture into a huge amount of excess water to keep the temperature as low as possible. Since the particles of GO are very small, the sedimentation takes some time. During the washing process, the sediment volume increases strongly and the time for sedimentation becomes longer. In order to shorten the process, the GO is precipitated after some dilution/sedimentation cycles by adding dilute HCl. The obtained precipitate can be separated from the solvent by filtration or centrifugation. For the cleaning steps, dialysis or electrodialysis [29] has also been applied.

A very strange purification was recommended by Thiele [14]: he removed the oxidation mixture (KClO₃/H₂SO₄/HNO₃) by repeated boiling with concentrated nitric acid; the nitric acid is then removed by washing with acetic acid/acetic acid anhydride, and at the end with alcohol or ether.

Obtaining dry GO is also a tricky business. It is almost impossible to remove the solvent water completely. The minimum water content (5–10%) can be achieved without decomposition at room temperature in vacuum and in the presence of P₂O₅. An alternative method is freeze-drying [30].

Apart from these chemical preparation methods, it is possible to obtain graphite oxide also by electrochemical oxidation. This was shown for the first time by Thiele [31] in 1934. He applied a very high current density and obtained in concentrated sulfuric acid first the blue phase, which is the sulfuric acid intercalation compound, and then a so-called primary oxide, graphite oxide and perhaps humic acid. Later Boehm et al. [27] and Besenhard and Fritz [32] obtained GO under controlled conditions in 70% perchloric acid. However, the degree of oxidation is considerably lower than for GO samples prepared via chemical oxidation. In the case of the concentrated sulfuric acid, beyond the first-stage phase C₄₈(HSO₄) (H₂SO₄)₂, there is a two-phase region in which there is a superposition of GO formation and O₂ evolution. The processes in this range depend strongly on the current density, indicating that the processes involved are much slower than the formation of the graphite sulfate intercalation [33].
1.2.2 Over-Oxidation of Graphite

Whereas graphite treated with boiling sulfuric acid loses only a small quantity of carbon as CO₂ [7, 34], most of it is lost when oxidizing agents such as nitric acid or K₂Cr₂O₇ are added to the boiling mixture [7]. Even Schafhäutl observed that repeated treatment of a piece of graphite with boiling sulfuric acid and the addition of nitric acid leads to a continuous loss of the material and finally to a complete disappearance [6].

Gottschalk [7] showed that the graphite-like carbon obtained by thermal decomposition of GO (prepared via the “Brodie method”) reacted faster during the Brodie reaction the more oxidation/decomposition cycles had been carried out: after the third oxidation, only traces of GO were found. In every oxidation cycle the quantity of graphite is reduced, and after the fourth oxidation step the graphite is gone completely.

Charpy [26] showed later that pristine graphite can be transferred to GO by bichromate or permanganate in sulfuric acid, but these reactions lead easily to over-oxidation: at room temperature one can get GO with nearly no loss of graphite. By oxidation with permanganate at 45 °C, a small part of the graphite is lost, whereas at 100 °C already 50% is oxidized to CO₂. In the case of chromate, 50% is lost at 45 °C and all graphite is transferred to CO₂ at 100 °C.

In their GO preparation experiments in which they used a modified “Staudenmaier method”, Kohlschütter and Haenni [10] described that the amount of GO obtained decreases with every step of oxidation (the yield of GO being 95% after the first oxidation and only 54% after the fifth repetition of oxidation) till nothing is left. The amount of GO obtained decreases also with the time that graphite or graphite oxide is in contact with the oxidizing medium.

Hofmann and Frenzel [13] found that the C/O ratio of the obtained GO decreases (thus the oxygen content increases) with decreasing size of the graphite crystallites. Very interesting are the results of Luzi [25]. He demonstrated that, besides the insoluble GO, some soluble by-products, especially mellitic acid, are formed, even in chlorate/nitric acid mixtures. The quantity of this by-product increases with subsequent oxidation steps. According to Thiele [14], up to 50% of mellitic acid is formed when GO is prepared via the procedure of Staudenmaier. To avoid it, the portions of chlorate should be small, the time intervals of additions longer, and the reaction temperature should be kept below 20 °C. Thiele [14] stated also that GO can be transformed to humic acid. In a later paper Thiele [35] mentioned that under special circumstances (not formulated) humic acids can be obtained as an intermediate state of the total oxidation of graphite to CO₂ by application of alkaline oxidation agents. In the same paper [35] he stated that humic acid is formed when an aqueous suspension of GO is left in air.

Ruess [19] remarked upon an increasing tendency to form mellitic acid or to destroy the graphite structure with decreasing particle size of the starting graphite. This tendency is confirmed by my own experience. We have obtained mostly mellitic acid with the Hummers–Offeman method, when we applied the optimal reaction conditions for getting GO from crystalline graphite (particle size 500 μm) to a graphite powder with particle diameters of <100 μm (unpublished results). And even Hummers and Offeman [28] recommended in their work-up process to filter the suspension while it is still warm to avoid precipitation of mellitic acid. In their GO preparation Hummers and Offeman used powdered graphite flakes with particle size 325 mesh (44 μm).

On the basis of these very early results in GO research, I have the feeling that Rourke et al. [22] do not really present a new structural model, but investigate intermediate states between the formation of GO and mellitic acid.