Graphene Research

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Graphene—How a Laboratory Curiosity Suddenly Became Extremely Interesting

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graphene · graphite · graphite oxide · history of science · thin films

Once again, an allotrope of elemental carbon is at the center of intensive research. After the flood of publications on intercalation compounds of graphite (triggered by a report in 1974 on its very high electrical conductance),[1] fullerenes (1985),[2] and carbon nanotubes (1991),[3] graphenes have been the subject of countless publications since 2004.[4,5]

By graphene, one understands single-carbon hexagonal networks within the structure of graphite. The term was recommended by the relevant IUPAC commission on the suggestion of Eberhard Stumpp (TU Clausthal) and a subcommittee of the Working Group Carbon of the German Ceramic Society to enable characterization of the properties of single two-dimensional layers which exist independently of neighboring carbon layers. The older expression "graphite layers" is unsuitable in this respect, because a three-dimensionally arranged structure with an ABAB… stacking sequence of the layers is identified in "graphite". According to *Recommended IUPAC Terminology for the Description of Carbon as a Solid*,[6] the term "graphene" should only be used when reactions, structural relationships, and other properties of individual layers are discussed. However, the term "graphene" is today frequently applied to stacks of a few graphene layers, which often adhere to one another and are only partially overlapping. Graphene layers also occur in disordered carbons with turbostratic stacking, that is, a random rotation and displacement of neighboring layers, for example, in active carbons.

Similar to carbon fibers and carbon nanotubes, graphene has a very high tensile strength in the layer direction, which, together with a high flexibility, makes sharp folds in the layer possible.[7] Their radius of curvature corresponds to that of carbon nanotubes. Interest in graphenes increased dramatically after Novoselov, Geim et al. reported on the unusual electronic properties of single layers of the graphite lattice, in other words graphene:[5,8,9] Graphene is a semiconductor with a zero band gap and is characterized by an exceptionally high mobility of the charge carrier, a very high electrical conductance, and an unusual quantum Hall effect. The charge carriers behave like relativistic particles of rest mass zero, to which the Dirac Equation can be applied.[5] This had previously been derived theoretically.[10] Narrow ribbons of graphene with a thickness of 1 to 2 nm are, however, semiconductors with a distinct band gap, and these can be used to produce transistors.[11–13] Many applications of graphene have been hoped for and promised.

The thickness of the air-stable graphene layers can be determined by atomic force microscopy (AFM). They are also visible under an optical microscope, however, if they are supported on a suitable carrier surface, for example, a 300 nm thick SiO_2 film on silicon. Depending on how many graphene layers are present, other interference colors appear because of the increased optical path length.[4] This greatly simplifies the localization of the graphenes. Such a microscopy image is shown as an example in Figure 1, where regions with one, two, and three graphene layers are easily recognized.[14]

Even before the studies of Novoselov and Geim, efforts had been carried out to prepare very thin graphite or graphene layers, since interesting properties were expected.[15–17] The most important preparative methods are described here briefly. Thin graphite layers suitable for investigation by electron microscopy have for a long time been prepared by "stripping off" highly ordered pyrographite (HOPG) or graphite crystals with cellophane-based adhesive tape.[18] Novoselov, Geim et al. found that the skillful and patient use of this method enabled extremely thin films with only one or just a small number of graphene layers to be obtained.[4,5] If the adhesive tape with a thin graphite layer is pressed onto a thin SiO_2 coating on a silicon wafer, the graphene layers remain attached to the SiO_2 surface after skillfully peeling away the tape. This method produces defect-free and smooth preparations, but has the disadvantage, however, that only small amounts can be produced. Preparative methods are, therefore, being sought that can provide graphene reproducibly in large amounts with little effort.

Graphite crystals or flakes may be dispersed in aqueous solutions of surfactants by ultrasound into graphene monolayers or layer packets (exfoliation).[19] This is also possible without additives in many organic solvents that have an affinity for graphite.[20]

It has long been known that defect-free graphene layers are formed by the thermal decomposition of SiC crystals at 1080–1320 °C.[21] Starting from the (111) surface of the cubic

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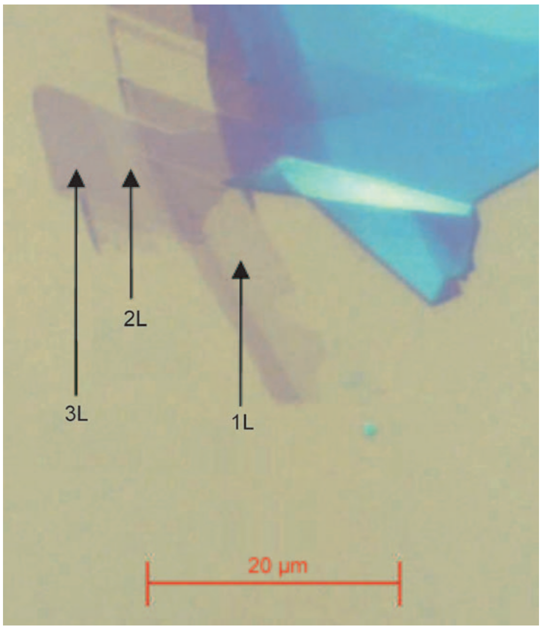

Figure 1. Optical image of graphene with 1, 2, and 3 layers (layers, L) on Si with a 300 nm layer of SiO_2. Reproduced from Ref. [14] with permission from Elsevier. I thank Prof. J. S. Park (Sendai, Japan) for supplying the original image.

modification, or (0001) in the case of hexagonal SiC, the layers form one after another by vaporization of surface-bound Si. The formation of monolayers had been observed even before the work of Novoselov, Geim et al.[22] The adjustment of the reaction conditions (primarily temperature and time) for the targeted formation of monolayers is, however, extremely difficult. Well-ordered graphene monolayers are also formed by the pyrolytic deposition of carbon from hydrocarbons (for example, methane) onto the surface of transition metals or transition-metal carbides.[17,23] This method has also been resurrected recently to obtain large graphene layers on surfaces by deposition onto a thin copper film.[24] The graphenes can be isolated by dissolution of the metal.

Larger amounts of extremely thin carbon films may be prepared from graphite oxide (GO) by flash heating or by the reduction of aqueous dispersions. GO was prepared for the first time by Brodie about 150 years ago by the oxidation of graphite with fuming nitric acid and potassium chlorate under cooling.[25] In the procedures of Staudenmaier[26] as well as of Hummers and Offeman[27] graphite is first oxidized with a mixture of concentrated H_2SO_4 and HNO_3 to the blue first stage of graphite hydrogen sulfate, with HSO_4^- ions and H_2SO_4 molecules intercalated in the interlayers, and in a second stage finally oxidized to GO with $KClO_3$ or $KMnO_4$. Colorless transparent flakes are formed on complete oxidation. Longer storage of the washed and dried preparations, especially on exposure to light, results in GO taking on a dark brown color via a brownish intermediate. Since the compound has acidic properties, it was at first called graphitic acid. My academic teacher, Ulrich Hofmann, showed by X-ray diffraction in 1932 that it had a turbostratic layer structure, whose layers of 0.6 nm are clearly thicker than those of graphite (0.3354 nm).[28] The layer distances of wet preparations are still larger and increase with an increasing water vapor partial pressure. Thus, the one-dimensional swelling of layered structures, which also plays an important role in many clay minerals, was described for the first time.

Hanns-Peter Boehm, born 1928 in Paris, studied chemistry at the Erweiterten Phil.-Theol. Hochschule Regensburg (1947–1951). He obtained his Diploma at Munich University in 1951. This was followed by a PhD (1953) and a Habilitation in inorganic chemistry (1959) at the Technical High School (now Technical University) Darmstadt. From 1960 to 1966 he was a lecturer at the University of Heidelberg, where he was appointed assistant professor in 1966. From 1970 to 1994 he was professor for Inorganic Chemistry at the Ludwig Maximilian University in Munich. He has been emeritus since 1994.

The composition of anhydrous GO is approximately $C_8O_2(OH)_2$. Almost none of the carbon of the graphite used is lost during the formation of GO.[29] In a later investigation, we confirmed this observation, which is important with respect to the formation of carbon layers from GO.[30] The yield of GO in the reaction of relatively coarse graphite flakes was 96 %.

Significant numbers of weakly acidic hydroxy groups have been detected in GO which can be neutralized with NaOH or sodium ethanolate.[31] It is speculated that these OH groups are parts of enol groups. In addition, carboxy groups form at the edges of the layers. Epoxide, aliphatic OH groups, and C=C bonds have been detected by solid-state ^{13}C NMR spectroscopy.[32] A structural model for GO has been developed based on these observations.[33] Other structural models have been described in a review article on "graphene oxide" (that is, single GO layers).[34]

GO deflagrates at 200–325 °C on rapid heating, with the formation of light, voluminous black flakes—the so-called graphite oxide soot.[35] Figure 2 shows an electron microscopy image of a particle of GO soot. Very thin flakes with numerous creases are recognizable, reminiscent of crumpled paper. The layers of GO are torn apart by the sudden development of gases during the exothermic deflagration. CO, CO_2, and H_2O are formed during the thermal decomposition, but no molecular oxygen.[36] It follows from this that the graphene layers in GO soot must have many defects, mainly vacancies in the hexagonal layers or aggregates of vacancies. As a consequence, the exceptional electronic properties of the graphene layers are greatly impaired. An investigation on the thickness of the flakes of the GO soot concluded that it consisted of a significant proportion of monolayers of graphene to which, however, considerable oxygen-containing functional groups were attached.[37] The C/O ratio was 10:1.

The composition and properties of GO depend on the method of preparation. GO prepared by the method of Brodie has the lowest oxygen content and is the most stable. It

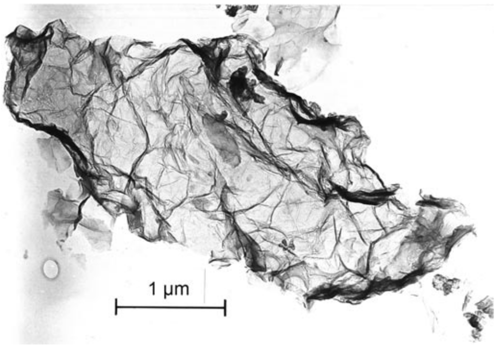

Figure 2. Electron microscopy image of a particle of graphite oxide soot. Image: K. Heideklang, 1960.

darkens much more slowly than the other preparations after oxidation.[38] Deflagration occurs at $> 300\,°C$, whereas it starts as low as about $200\,°C$ with GO prepared by the method of Hummers and Offeman.[39] GO prepared by the method of Staudenmaier lies in between.

GO in aqueous suspension is reduced back to black elemental carbon by strong reducing agents such as hydrazine, hydroxylamine, or iron(II) ions.[35,40] However, the carbon formed does not have the three-dimensional ordered structure of graphite, but shows turbostratic order only. Only the two-dimensional (10) and (11) interferences are seen together with a broad (002) line at about 0.36 nm in the X-ray diffractogram.[41,42]

What is now my association to graphene? Towards the end of the 1950s I worked, among other topics, on GO at the Eduard Zintl Institute of the Technical University Darmstadt. It was there that my friend Alex Clauss and I came to the idea that GO should indeed be reducible to carbon monolayers. We knew that GO flakes separated into single layers in highly diluted sodium hydroxide solution (ca. 0.01 M). The hydroxy groups of GO dissociate in alkaline media. The layers repel each other through the resulting negative charge and a colloidal sol is formed at low ion strengths. Reduction of GO in this state should allow single carbon layers to be obtained—in today's language graphene layers. We, therefore, prepared such solutions and reduced them with hydrazine or hydroxylamine. The brownish colloidal solution changed to dark brown and then to black, and after a short time a loose black precipitate separated. The exfoliation into single graphite oxide layers is today usually supported by ultrasound.

We were fortunate that a powerful electron microscope and a very capable operator, Mrs K. Heideklang, were available in the Eduard Zintl Institute. The electron microscopy images of the reduction product showed very thin films with far fewer folds than GO soot. Although we reduced the acceleration voltage to 60 kV to increase the contrast, the contours of the layers are hardly recognizable in the display, actually only the folds are visible. A reproduction of our image from our publications[41–43] would show even less contrast, and so one is not shown. The problem now was to determine how thick the films were with the lowest contrast. For comparison I needed thin films of known mass thickness. For this I took the contrast of the supporting film of collodion (nitrocellulose) used in the electron microscope. I had been made aware of work from the neighboring physical institute in which the mass loss of collodion from the electron radiation in the microscope was assessed at 75%.[44] A collodion film of known mass and area was prepared by spreading a solution of collodion in amyl acetate onto a known area of water saturated with amyl acetate. Its thickness was 10 nm. New images were prepared and the contrast of the film was determined on the basis of the numerous holes. The method is certainly not very accurate, but the results for the thinnest sites of the film of reduced GO at 0.3–0.6 nm (average: 0.46 nm) agreed well with the thickness of a graphene monolayer (0.354 nm). Regions with two, three, and four layers were also observed.

Whilst a lecturer at the University of Heidelberg (from 1960) I presented our results at the Carbon Conference in 1961 at Penn State University.[42] The results were also published in Germany,[41] but no one took any interest at that time. The preparation of isolated carbon layers by reduction of GO has only recently become of interest.[42,46]

Likewise, no carbon loss occurred in the reduction of GO; the network of carbon atoms remained intact. However, the carboxy groups formed on the edge of the layers remained, and also a considerable number of hydroxy groups bound to the C atoms of the layers remained.[45] The reduction product also contained nitrogen after reaction with hydrazine.[43,46] Our products contained about 76% C, 1.3% N, 1.3% H, and 8.0% ash; the rest must be oxygen.[43] Even if no empty C sites were present, the π-electron system of the carbon layers had considerable disturbances because of the bound foreign atoms, which impaired the electrical conductance. The electrical conductance is significantly lower than for graphene prepared by the adhesive tape method.[45,47,48] As a consequence of this detrement compared to graphene prepared directly from graphite, they are often referred to as merely "reduced graphene oxide" or "chemically modified graphene".[48] Lower contents of foreign elements and a higher conductance of the layers have been observed after reduction of GO with $NaBH_4$.[47]

It will certainly require more intensive research work before electronic components based on graphene find practical application. The preparation of graphene layers by chemical synthesis from organic molecules that already contain condensed aromatic rings (bottom-up method) promises to be an interesting development.[13] Narrow graphene nanoribbons of uniform width that contain no interfering foreign atoms such as bound oxygen can already be obtained.[13]

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