Graphite sulphate – a precursor to graphene†

Siegfried Eigler

Graphite sulphate is used as a precursor to graphene for the first time. The positively charged graphene layers react with water to yield a processable graphene derivative. The unprecedented low density of defects is determined to be 0.06% on average and may open the way for electronic applications.

Graphene is a nanomaterial of interdisciplinary interest and attracts attention of physicists as well as chemists or engineers. 1–3 Chemical vapour deposition is currently the method of choice to prepare large area graphene films and the quality is constantly increasing. 4 However, the wet-chemical synthesis of graphene is scalable and provides high potential for applications. 5,6

Recently, the direct exfoliation of graphite in organic solvents attracted a lot of attention. 7,8 Although flakes of graphite (G1) and few-layer graphene (Gfew-layer) were wet-chemically produced by non-covalent exfoliation, the size of flakes is < 1 μm and solvents with high boiling points are needed that limit the overall quality. 8 Graphene oxide (GO), an oxo-functionalised derivative of graphene, can be prepared on a large scale and mostly single layers with a reasonable size of flakes of several μm are obtained. 6 Furthermore, there is constant progress in improving functionalisation methods. 5,6,9 GO is also a potential precursor of graphene, however, with a variable amount of defects. 10,11 The quality of GO strongly depends on the synthetic protocol. Thus, GO can be amorphous, like humic acids, as a result of CO2 formation due to over-oxidation, or the carbon framework remains almost intact by avoiding CO2 formation during synthesis under certain reaction conditions. 8,10,12,13

Generally, the quality of G1 is limited by the density of defects within the carbon framework of GO. 11,14,15 Furthermore, defects in G1 limit its performance in applications, such as electronic devices. Consequently, novel synthetic protocols have to be developed to further limit the formation of defects. The lowest density of defects in GO, reported yet, is about 0.3% on average, as determined by statistical Raman microscopy (SRM). 5,11,16 The lowest density of defects of single flakes of GO is as low as 0.01%. Also the mobility of charge carriers depends on the density of defects of related G1 and values of about 250 cm2 V−1 s−1 are described for a density of defects of 0.3% and 1000 cm2 V−1 s−1 for a density of defects of 0.01%. 5,10 However, to enter the field of electronic applications, such as sensor materials or transparent electrodes, the average quality of wet-chemically prepared G1 must be enhanced. Also strong oxidants, such as potassium permanganate in sulfuric acid, commonly used to synthesise GO, bear some problems. 10,17,18 The reaction is exothermic and must be controlled by cooling and manganese salts are not environmentally friendly. Additionally, manganese impurities in graphene based materials should be avoided because they disturb their properties in applications. 19–21

Here, it is demonstrated for the first time that processable oxo-functionalised graphene is yielded from graphite sulphate (Scheme 1), which is a precursor to G1 and Gfew-layer with an unprecedented low density of defects of about 0.06% on average with a reasonable size of flakes of about 1–5 μm.

Recently, Dimiev et al. published the investigation of the formation of blue stage 1 graphite sulphate from natural graphite in sulphuric acid using persulphate as an oxidant (Scheme 1). 22,23 Although graphite sulphate is well known since decades, 24–27 it was not demonstrated to be a suitable precursor of oxo-functionalised graphene (oxo-G1) or G1 with a low density of defects. Rüdorff and Hofmann characterised graphite sulphate in depth, 25 and their analyses revealed an ideal structure of the stage 1 intercalation compound of C24H5O2·H2SO4 (Scheme 1). It can be assumed that the positively charged G1 layers in graphite sulphate can react with donors, such as water. However, up to now attempts failed to yield functionalised G1, with lateral dimensions of several μm, confirmed by Raman spectroscopy. 28,29

At first, graphite sulphate was prepared by the procedure described by Dimiev et al. from natural graphite in sulphuric acid by the addition of persulphate (Scheme 1). 22,23 The formation of graphite sulphate is confirmed by the colour change from black to blue (Fig. S1A, ESI†) and further confirmed by Raman spectroscopy.

Department of Chemistry and Pharmacy and Institute of Advanced Materials and Processes (ZMP), Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU), Dr.-Mack Str. 81, 90762 Fürth, Germany. E-mail: siegfried.eigler@fau.de; Fax: +49 (0)911 6507865051; Tel: +49 (0)911 6507865005
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A single Raman band at 1624 cm\(^{-1}\) is observed as depicted in Fig. S1B (ESI†). After the formation of graphite sulphate, the reaction mixture was diluted with water, causing an increase in temperature to 60 °C. Excess of sulphuric acid and other salts were removed by repeated centrifugation and redispersion in water. The oxidation of graphite flakes was indicated by Raman spectroscopy by the defect induced broad D peak (Fig. S2, ESI†). Sonication of the oxidised particles in a mixture of water and methanol (1/1) caused exfoliation to oxo-G\(_{few-layer}\) and even delamination to oxo-G\(_1\). Larger particles were subsequently removed by centrifugation and the Langmuir–Blodgett technique was used to deposit flakes on a 300 nm SiO\(_2\)/Si wafer for analysis by atomic force microscopy (AFM) and SRM. In Fig. 1A the AFM image of oxo-G\(_1\) and oxo-G\(_{few-layer}\) is depicted (AFM overview shown in Fig. S3, ESI†). An area of 40.000 \(\mu m^2\) of the film of flakes was investigated by SRM. The analysis of the disorder induced D peak, the G peak and the 2D peak confirms the absence of any graphene or unoxidised graphitic material as illustrated by the plot of \(I_D/I_G\) against \(\Gamma_D\) (Fig. S4, ESI†). Due to the functionalization in oxo-G\(_1\) and oxo-G\(_{few-layer}\) \(\Gamma_D = 100 \pm 15\) cm\(^{-1}\). The degree of functionalization is roughly estimated to be about 4%, as outlined below and in Table S1 (ESI†). UV/Vis spectra reveal an absorption band at 318 nm beneath 253 nm, which indicates residual unoxidised domains in oxo-G\(_1\) and oxo-G\(_{few-layer}\) (Fig. 1B). Furthermore, a C-content of 86% is determined by elemental analysis (EA) and also the mass-loss determined by thermogravimetric analysis (TGA) of 13% indicates the low degree of oxidation (Fig. 1D). An m/z 64 is detected which relates to SO\(_2\) formation at a decomposition temperature with a maximum at 380 °C, which originates most likely from organosulphate, as identified before. The residual S-content determined by EA is 1.6% and thus, about 5% of the mass is related to organosulphate. This observation is in agreement with a recent study on the contamination of GO by chemical treatment. TGA data further reveal that water is the major species detected between 250 °C and 350 °C which contributes mostly to the main weight-loss. A structure containing hydroxyl groups is further supported by FTIR spectroscopy (Fig. S5, ESI†). Consequently, a plausible structure of hydroxylated graphene with trapped water molecules and some organosulphate is proposed (Scheme 1).

Subsequently, the quality of G\(_1\) was determined. Flakes of oxo-G\(_1\) and oxo-G\(_{few-layer}\) were deposited on a 300 nm SiO\(_2\)/Si wafer and exposed to vapour of hydroiodic acid and trifluoroacetic acid, a highly efficient reduction method suitable to generate G\(_1\). The flakes of G\(_1\) and G\(_{few-layer}\) were analyzed by AFM and the images reveal a height of G\(_1\) of about 1 nm (Fig. 2B) and a typical size of flakes of approximately 1–5 \(\mu m\) (Fig. S6, ESI†). The G\(_1\) nature of flakes was confirmed by Raman spectroscopy and the density of defects within the carbon framework of G\(_1\) was also evaluated. Raman spectra of G\(_1\) exhibit a G and 2D peak in addition to a defect induced D peak. The full-width at half-maximum (\(\Gamma\)) of the 2D peak is a criterion to identify single layers of G\(_1\) by a value < 40 cm\(^{-1}\). Furthermore, spectra of G\(_{few-layer}\) can be filtered by the intensity of the G peak. For the first time, the SRM analysis of data probed from an area of 250.000 \(\mu m^2\) reveals that 79% of Raman spectra of G\(_1\) (out of 2873 spectra) show a
some organosulphate groups are proposed. Although the yield of dispersed G₁ and G_{few-layer} is improvable, the size of flakes is 1–5 μm, suitable even for applications, such as sensor devices. For the first time, an unprecedented low average density of defects of 0.06% was determined for wet-chemically prepared flakes of G₁, and all Raman spectra of G₁ exhibit a sharp 2D peak. Although the potential of this type of oxo-G₁ is not yet explored, it can be assumed that it is a precursor to G₁ suitable for functionalization. Also the reactivity of G₁ and the influence of defects can be evaluated and the field of electronic applications is within reach.

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### Notes and references


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![Fig. 2](image-url) - (A) SRM analysis of a film of flakes of G₁ (plot of I_{D}/I_{G} against γ_{2D}, inset: histogram of γ_{2D} with the maximum of γ_{2D} = 33 cm⁻¹). (B) AFM image of G₁ derived from oxo-G₁; inset: height-profile along the grey line. (C) Raman spectrum of G₁, γ_{D,G,2D} in italics numbers.

γ_{2D} < 40 cm⁻¹ (Fig. 2A). The γ_{2D} values of analyzed spectra indicate a maximum in the histogram at 33 cm⁻¹ depicted in the inset of Fig. 2A. A typical Raman spectrum of G₁ is presented in Fig. 2C with a γ_{2D} = 27 cm⁻¹. The relation of Raman data and the density of defects was introduced by Lucchese and Cancado and allows estimating the density of defects to about 0.06% on average. In comparison, the best average quality of G₁ prepared by GO with an almost intact carbon framework (ai-GO) was 0.3%. The here presented data indicate the best average quality, with a density of defects of 0.06% with a μm size of flakes (1–5 μm, 0.06% G₁). The reaction of graphite sulphate with water was also conducted at <10 °C, conditions used for the preparation of ai-GO. SRM data reveal a slightly increased quality of G₁ with a density of defects of about 0.04% (Fig. S7, ESI†). Unfortunately, the yield of G₁ prepared here can only be estimated, because of contamination with G_{few-layer}. However, SRM data reveal that about 25% of flakes are G₁ and improvement of separation techniques will increase the part of G₁. Furthermore, the amount of G₁ isolated from 1 g of graphite is estimated to be approximately 4% and hydroxyl groups beneath material readily delaminates in water–methanol to oxo-G₁ and oxo-G_{few-layer}. The degree of functionalization is roughly estimated to be approximately 4% and hydroxyl groups beneath...