



Systematic evaluation of different types of graphene oxide in respect to variations in their in-plane modulus



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ABSTRACT

Graphene oxide samples prepared in various laboratories following a diversity of synthesis protocols based on Brodie's (BGO) and Hummers/Offeman's (HGO) methods were compared in respect of their in-plane moduli. A simple wrinkling method allowed for a spatial resolution $<1.5 \mu\text{m}$ by converting the wrinkling frequency. Quite surprisingly, a drastic variation of the in-plane moduli was found spanning the range from 600 GPa for the best BGO types, which is in the region of chemically derived graphene, all the way down to less than 200 GPa for HGO types. This would suggest that there are no two equal GO samples and GO should not be regarded a compound but rather a class of materials with very variable physical properties. While large differences between Brodie's and Hummers/Offeman's types might have been expected, even within the group of Hummers/Offeman's types pronounced differences are observed that, based on ^{13}C solid-state NMR, were related to over-functionalization versus over-oxidation.

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1. Introduction

In the note of B. C. Brodie in 1855 [1] about the purification of graphite he described the first preparation of graphene oxide (GO). Since then, essentially two other preparation methods were established by Staudenmaier in 1899 [2] and Hummers/Offeman in 1958 [3], similarly described by Charpy in 1909 [4]. Nowadays, the Hummers/Offeman method is commonly used because it is faster and safer than the others. The structure of GO is still a big puzzle, as it is a heterogeneous and turbostratically disordered material with varying amounts and types of functional groups. Moreover, the proposed structure models are based on GO prepared by different

synthesis methods [5–9]. All synthesis protocols apply quite harsh conditions, such as concentrated acids and strong oxidizing agents, for the oxidation of graphite. Due to the heterogeneous character of the oxidation reaction and the fact that an electronic conductor (graphite) is converted into an insulator (GO) in the course of the reaction, gradients in the local concentration of the reactants are inherent to the process. Accordingly, the type, number and density of functional groups (hydroxyl, epoxy, carboxyl, organosulfates) [8,9] introduced by oxidation vary spatially within the material and, moreover, critically depend on the kinetics of the reaction and on the reactants used. As the oxidation starts at the rim of the platelets and concentrically proceeds to the geometric center, defects will be created by local over-oxidation to CO_2 . The size and therefore the size distribution of the type of graphite used also determines the degree of over-oxidation [10]. A degradation of the smaller platelets will commence while the larger ones are not yet completely

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converted to GO. Consequently, the properties of GO vary for every batch which was prepared by even the same synthesis protocol. Kunz et al. found that there are even variations within sub- μm domains of a single nanoplatelet [11].

The choice of reactants also changes the intracrystalline reactivity of GO. Strong differences of swelling behavior of different types of GO are well established. BGO typically exhibits crystalline swelling and phase transitions between one and two layered solvates, while HGO shows osmotic swelling in all so far studied solvents [12–14].

Typically, GO is characterized by X-ray diffraction, NMR and vibrational spectroscopy and local variations are consequently averaged in the bulk analysis [15]. Rare exceptions are X-ray photoelectron spectroscopy and μm -Raman spectroscopy that allow for determination of functional groups and defect densities of reduced GO in the μm range [16,17].

Recently, we presented a characterization of the mechanical properties of HGO and chemically reduced HGO sheets with high spatial resolution by applying a simple wrinkling procedure [11]. Herein, we apply this method to compare graphene oxide samples prepared in various laboratories following a diversity of synthesis protocols (supporting information) based on Brodie's (BGO) and Hummers/Offeman's (HGO) methods in respect of their in-plane moduli.

2. Experimental

Topographic AFM images were obtained using two different commercial AFM instruments, a Nanoscope Dimension V and ICON AFM from Bruker, USA, operated in TappingMode™. Aluminum-coated silicon cantilevers (OTESPA-R3, Bruker) with a spring constant of 26 N m^{-1} and typical resonance frequencies of 300 kHz were used. Image processing and analysis was conducted with NanoScope Analysis v1.40.

All ^{13}C MAS solid-state NMR experiments were acquired on Bruker Avance-III HD spectrometers operating at a B0 field of 9.4 T, corresponding to a ^{13}C and ^1H frequency of 100.6 MHz and 400.1 MHz, respectively. The samples were spun at 12.5 kHz in a 4 mm MAS double resonance probe (Bruker). The one-pulse MAS spectra were obtained after 160–440 scans using a 90° pulse of 3.5 μs and a recycle delay of 360 s. Proton broadband decoupling of 70 kHz with spinal-64 was applied during acquisition. All ^{13}C spectra are referenced with respect to tetramethylsilane using the secondary standard adamantane. Deconvolution of NMR spectra.

TopSpin 3.2 was used for the deconvolution of the NMR spectra. A range from 380 ppm to -110 ppm was used. The Gauss/Lorentz ratio was kept constant at 0.5 and 7000 iterations were made. Linebroadening for overlapping peakgroups were tried to be kept in the same range. The best overlaps were above 80%. The integrals of the peaks were normalized to the integral of the peak at 130 ppm.

The degree of functionalization was taken as the ratio of the sum of sp³ signals (60 ppm and 70 ppm) and the sum of all ^{13}C signals.

Raman spectroscopic studies were done on Horiba HR Evolution confocal Raman spectrometer equipped with a microscope (100 \times objective) and an automated XYZ table, at laser excitation of 532 nm.

3. Synthesis of graphene oxide (GO) samples

3.1. Hummers/Offeman method

3.1.1. HGO Eigler

Natural flake graphite (1 g, 300–425 μm , grade 3061, Asbury Carbon USA) was stirred in cold H_2SO_4 (24 mL, 98 vol%, Sigma Aldrich) for 1 h before KMnO_4 (2 g, Sigma Aldrich) were added over

4 h. The mixture was further stirred for 16 h. Then, diluted H_2SO_4 (20 mL, 20 vol%, Sigma Aldrich) was slowly added over 2 h and double distilled water (100 mL) over 16 h. Finally, the reaction was stopped by the addition of H_2O_2 solution over 40 min (40 mL, 5 vol %, Sigma Aldrich). The obtained HGO was purified by repetitive centrifugation and redispersion with pure water (10 min, 1500 RCF). As the pH was almost neutral, delamination was performed by pulsed tip sonication (2 min, 40 W). At last, non-monolayer and minor amounts of smallest particles were removed by repetitive centrifugation at low rpm and then high centrifugation parameters (3 times, 30 min, 1500 RCF, 1 time 45 min, 13000 RCF). We obtained a stable golden dispersion containing exclusively HGO monolayer.

3.1.2. HGO Talyzin

Natural graphite powder (1 g, 74 μm , Alfa Aesar) and NaNO_3 (1 g, Scharlau) were added in a flask (placed in an ice bath) to concentrated H_2SO_4 (40 mL, 95–97 vol%, Merck). Magnetic stirring of the mixture solution was maintained at each steps of the synthesis procedure. KMnO_4 (3 g, VWR) was added very slowly to the solution in order to avoid the increase of temperature above 20°C . The flask was removed from the ice bath after 2 h and it was then heated in an oil bath at 35°C for 2 h. After this first heating step, the solution was poured under vigorous stirring on deionized water H_2O (40 mL) in an ice-surrounded flask (instant temperature increase to 98°C). The solution was heated a second time in an oil bath at 90°C for 30 min. Subsequently, deionized water (100 mL) and H_2O_2 (6 mL, 30 vol%, Merck) were added under vigorous stirring in order to stop the synthesis reaction. The resulting material was washed 3 times with a HCl solution (20 mL, 10 vol%, Merck), stirred for 30 min and then centrifuged (4400 rpm, 15 min). The HGO sample was next repeatedly washed with deionized water and centrifuged (4400 rpm, 15 min). Once the pH was brought back to neutral, freeze-drying could be carried out on the HGO sample.

3.1.3. HGO Feicht

Natural flake graphite (1 g, 125–250 μm , Reinstflocke (RFL) 99.5, Kropfmühl AG) and NaNO_3 (1 g, Sigma Aldrich) were mixed with concentrated H_2SO_4 (30 mL, 98 vol%, Sigma Aldrich). Subsequently, KMnO_4 (3 g, Sigma Aldrich) was interspersed over a period of 3 h and the reaction was kept at room temperature for 12 h. Thereafter, the mixture was slowly poured into ice-cooled deionized water (30 mL) and H_2O_2 (30 vol%, Sigma Aldrich) was added until the solution turned golden. GO was purified by repeated washing/centrifugation (3 times, 10 min, 3800 rpm) followed by a dialysis to an ionic conductivity of $2 \mu\text{S cm}^{-1}$.

3.1.4. HGO Feicht extracted

A part of the suspension of HGO Feicht was mixed with the same volume of ethanol and 1-dodecylamine (1 g, Sigma-Aldrich). Afterwards, HGO modified with 1-dodecylamine was extracted into diethyl ether and washed with water. For the removal of the 1-dodecylamine the suspension was mixed with an aqueous NaOH/ethanol mixture (50:50, 700 mL, 4 times), stirred for 15 min and then centrifuged (15 min, 10000 rpm). Finally, HGO was washed with water and centrifuged (3 times, 30 min, 10000 rpm).

3.2. Brodie method

3.2.1. BGO Brand/Böhm 1962

This BGO was also used in the publication “Der ‘Verpuffungspunkt’ des Graphitoxids” of H.-P. Böhm in 1965 and was denoted as “GO-Bra.” in the table on page 78 [18]. The preparation was done following the instructions of B.C. Brodie. [19] We translated the original description quite freely without changing the content:

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