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Structural factors controlling size reduction of graphene oxide in liquid processing

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ABSTRACT

Graphene oxide materials can be prepared in manifold synthesis approaches and allow for further post-functionalization to adopt the properties of the desired application. Small sized sheets with lateral dimensions on the 100 nm scale are e.g. beneficial for cell applications. Breakage of sheets by liquid phase processing is an ideal way to generate such nano-sized sheets. However, until now it is unknown how functionalization influences the breakage behavior. We have chosen single layered oxo-functionalized graphene (oxo-G) derivatives with lattice defects < 1% to evaluate their size reduction rate upon ultra-sonication of flakes with respect to the type and degree of functionalization of the graphene sheets. Lateral dimensions of the processed sheets were quantitatively determined in solution by analytical ultracentrifugation. The highest size reduction rate is observed for pristine oxo-G, which bears the highest degree of functionalization of around 60% and the negatively charged organosulfate group. Partial hydrolysis of organosulfate, or conversion of surface-functional groups to hydroxyl-groups in majority or partial defunctionalization lead to size-reduction rates which are up to 25% lower in comparison with the initial oxo-G. Moreover, the size reduction rate can be correlated in first approximation also with UV–vis spectroscopy.

1. Introduction

Graphene is a one atom thick layered material built up from sp^2 hybridized carbon atoms aligned in a honeycomb structure. It is inheriting numerous superlative physical properties such as extreme high conductivity, transparency and flexibility making graphene a highly desired product for industrial scale production [1–5]. So far, however, the top-down production of high purity single-layer graphene suspensions with defined lateral dimensions is an open task.

A highly promising top-down processing route is exfoliation of chemically modified graphite, e.g. by use of strong oxidants and acids. The so called Hummers' and Offeman's method or Brodie's method convert graphite into graphite oxide (GrO) [6,7]. The thus obtained GrO readily yields mono-layered graphene oxide (GO) suspensions by short post-processing such as by ultrasonication in water [8,9]. After subsequent purification steps, highly oxidized single layers of graphene sheets decorated with different functional

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groups like hydroxyls, epoxides, ethers, carbonyls, carboxyls, endoperoxides and sulfates at the surface and edges are obtained [10–23]. The composition and the total number of functional groups change with respect to slight modifications of the synthesis protocol [24,25]. Furthermore, methods to convert sulfates to hydroxyls, or to partially remove oxo-groups attached to GO e.g. by addition of NaOH or NaBH$_4$ are well established [26–29]. Lately, a revised protocol at mild reaction conditions was established to synthesize single layer high quality oxo-functionalized graphene (oxo-G). Compared to typical GO synthesis routes performed under harsh conditions, less in-plane defects are identified in oxo-G. The density of in-plane defects, which requires C–C bond cleavage is generally below <0.8% and sometimes approaches as low as 0.05% [30]. The fundamentals of the chemistry and applications of graphene oxide are summarized in a recent book edited by Dimiev and Eigler [31].

In the view of future applications, controlled syntheses to produce chemically modified GO or oxo-G having defined lateral sizes are in the focus [32]. Lateral sizes of flakes in the range up to some tens of micrometers are desirable to produce materials for electronic devices, such as capacitors or conductive/transparent films. Sub-µm and nanoparticles of oxo-G are required in medical application for optimized uptake and fast impact in the body tissue and later removal by phagocytosis [23,33]. While the upper flake size is limited by the initial graphite flake size used for syntheses [16], smaller sizes can be either enriched by size classification or controlled size reduction of the obtained suspensions [34]. Recently we have demonstrated that processing of oxo-G suspensions by tip ultrasonication and stirred media milling leads to a controlled and homogeneous size reduction, which follows a power law function with respect to the energy uptake. The size reduction rate is related to the volume specific energy input independent of the applied processing method [35]. Thus, if power and process time are chosen properly, a defined lateral size of oxo-G can be reached by ultrasonication or stirredmedia milling much easier and with fewer mass loss than by density gradient centrifugation.

In contrast to native graphene, GO contains numerous defects yielding a much smaller Young's modulus and lower intrinsic material strength as described by theoretical considerations [36,37]. Furthermore, Feicht et al. [38] just demonstrated differences of in-plane moduli with respect to the synthesis method. Here, we report for the first time how the size reduction rate of micrometer sized and liquid phase processed oxo-G flakes is influenced by its chemical treatment after initial synthesis. This study offers insight into a key question of what contributes to the breakage leading to the lateral size reduction of modified oxo-G derivatives. We provide practical evidence for a decreased stability of flakes of oxo-functionalized graphene in dependence on the degree of functionalization and the type of functional groups.

2. Experimental

2.1. Chemicals and general instrumentation

Graphite grade *3061* has been provided from Asbury Graphite Mills (USA). Potassium permanganate, concentrated sulfuric acid, hydrogen peroxide and sodium borohydride were purchased from Sigma Aldrich® (Germany). Double distilled water was obtained from Carl Roth® (Germany). All chemicals were used as obtained.

For the ultrasonication treatments of our samples an "UP-200S" tip sonotrode (working frequency 24 kHz, Dr. Hielscher, Germany) was used. We used a Sigma 4K15 centrifuge equipped with both 80 mL (21,000 RCF) and 200 mL plastic beakers (13,000 RCF). UV-vis-spectra of the GO-suspensions were recorded using a "Cary 100 Scan" spectrophotometer (Varian, United States). Measurements

were performed in the wavelength range from 200 nm to 800 nm using quartz cuvettes with an optical path length of 10 mm. The ζ-potential was determined using a Zetasizer Nano-ZS (Malvern Instruments, England). Thermogravimetric analyses (TGA and TGA-MS when coupled with mass spectroscopy (MS)) were performed on a PerkinElmer Pyris 1 TGA/Clarus SQ-8C and a Netzsch Skimmer STA 409 CD, respectively. Samples consisting of 0.3 mg–2.0 mg of freeze dried material were heated up to 650 °C (20 °C/minute). Freeze-drying was accomplished on an ALPHA 1-4 LDplus (Martin Christ, Germany). Elemental analysis (EA) was performed by combustion and gas chromatographic analysis with an EA 1110 CHNS analyzer (CE Instruments, Engalnd).

2.2. Preparation of oxo-G^0 and oxo-G^{ΔT}

The oxo-G^0 stock dispersion used for our experiments was produced as described previously [35]: Briefly, graphite (1 g; 83.33 mmol) was dispersed in 24 mL of cold (<10 °C) sulfuric acid (98%) and reacted over night with potassium permanganate (2 g, 12.66 mmol). The potassium permanganate was slowly added to the graphite dispersion over a total time of 4 h and the reaction temperature was kept below 10 °C. In the next step, 20 mL of diluted sulfuric acid (20%) were slowly and continuously added to the reaction mixture over 1 h. After that, pure water (100 mL, 16 h) and hydrogen peroxide solution (40 mL, 5%, 0.5 h) were added successively. The thus obtained dispersion was abundantly washed 6 times with cold water by repetitive centrifugation (10 min at 1500 RCF) and dispersing in water. The pH of the final supernatant was neutral. Delamination was performed by 4 min of pulsed tip sonication (20 W; 2 s on 2 s off). The obtained dispersion was centrifuged 3 times (5 min at 1500 RCF) to remove aggregated particles and then centrifuged at 13,000 RCF for 45 min to remove major amounts of nano-sized particles. The temperature was kept below 10 °C throughout the process. The final concentration was determined by freeze drying of a defined amount of the sample overnight. A second batch of oxo-G was synthesized with a single variation leading to oxo-G^{ΔT}. The steps after adding H$_2$O$_2$ were performed at ambient temperature to allow a slight hydrolysis of organosulfates leading to a similar material with, however, a lower amount of organosulfates. Elemental analysis (EA) of oxo-G^0: N: 0.00% C: 40.26% H: 2.95% S: 5.99%; EA of oxo-G^{ΔT}: N: 0.03% C: 48.44% H: 3.76% S: 4.60%. All values are given in weight percent.

2.3. Base treatment of oxo-G^0 (oxo-G^{base})

Equal volumes of 0.1 M aqueous cold (<10 °C) NaOH and of the initial dispersion of oxo-G^0 were mixed to yield a final suspension containing 0.05 M NaOH. The suspension was then stored for 20 h at 4 °C. Afterwards, the dispersion was centrifuged one time at 21,000 RCF over 30 min and the sediment was redispersed with 0.05 M NaOH. Subsequently, centrifugation and redispersing was repeated another 4 times with pure water. The color of the suspension changed from golden to dark brown. EA of oxo-G^{base}: N: 0.03% C: 49.74% H: 2.02% S*: 1.86% (* inorganic sulfur species).

2.4. Partial reduction of oxo-G derivatives (oxo-G^R, oxo-G$^{base/R}$, oxo-G$^{ΔT/R}$)

Defined volumes of oxo-G^0, oxo-G^{ΔT} and oxo-G^{base} derivatives were diluted to concentrations of 0.09 mg/mL. These suspensions were partially reduced with solid NaBH$_4$ (0.55 mg NaBH$_4$ per 1 mg oxo-G). The reducing agent was directly added and the dispersions were shaken. Then, the dispersions were finally stored overnight at 4 °C.